



International Journal of ChemTech Research CODEN(USA): IJCRGG ISSN : 0974-4290 Vol.5, No.4, pp 1646-1654, April-June 2013

Synthesis And Electrochemical Studies On Oxidative Products Of Vanadyl Meso-5,10,15,20-Tetrakis(P-Hydroxyphenyl)Porphyrin

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Abstract: Vanadyl *meso*-5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin VO[T(*p*-OH)PP] was synthesized and characterized using UV-vis and NMR spectroscopy. The cyclic voltammetry (CV) results of VO[T(*p*-OH)PP] showed that the voltammogram is successive one electron transfer process and the second oxidation involves a process is irreversible due to the formation of secondary oxidation states involving the phenolic hydroxyl groups predominantly of oxidative electro-polymerizations. On subsequent scanning, the peak current decreases leading to film formation at the electrode. Oxidation was carried out between VO[T(*p*-OH)PP] and SbCl₅. The preliminary oxidation product was confirmed by UV-Visible spectroscopy. The VO[T(*p*-OH)PP] may undergo polymerization through mono cation during the oxidation. It was confirmed by CV and Electron Spin Resonance (ESR) spectra.

Keywords: vanadyl porphyrin, SbCl₅, cyclic voltametry, oxidative product, ESR.

Introduction

The oxidation products of transition metal porphyrins are characterized by using magnetic resonance techniques such as Nuclear Magnetic Resonance (NMR), Electron Spin Resonance (ESR) and Mossbauer spectroscopy and magnetic susceptibility measurements [1]. ESR spectra of vanadyl tetraphenyl porphyrin (VOTPP) and its oxidation products are reported [2-4]. Oxidation of VOTPP with $Br_2 / SbCl_5 / SnCl_4 / TiCl_4$ gave the oxidized product along with parent compound [3]. The biradical / triplet state generated by $SbCl_5$ could not be VOTPP in tetachlorethane with -radiation [4].

The CV results of oxidation product of VOTPP are well documented in the literature [5,6]. Reduction product of substituted VOTPP systems are also reported with limited information on the oxidation product; the porphyrin ring substituents and pyridyl electron-withdrawing substituent in the *meso* position of porphyrin ring makes the reduction process easier and the oxidation becomes more difficult [7].

Tetraethylporphyrinate -cation radicals [Fe(TEtP')(Cl)]SbCl₆] provide compelling evidence that oxidation had occurred at the porphyrin ring. The inter-ring geometry changes more dramatically upon oxidation for tetrapropylporphyrinate -cation radicals [Fe(TPrP)(Cl)] relative to that of [Fe(TEtP)(Cl)] [8]. The addition of iodine-silver perchlorate with Fe(III) porphyrins generates singly oxidized product and the UV–vis spectroscopy is particularly useful to determine the geometry of the metal-bisporphyrin complex in solution [9]. The ring distortions of 1,3-dioxopyrrolo[3,4-*b*]porphyrin, the central Ni(II) cation has an almost regular (NiN₄) square planar coordination geometry [10,11].

The d-orbitals of the metal and $a_{1u} \setminus a_{2u}$ orbitals of porphyrin ligand can have interactions in ruffle and saddle distortions [12-17]. The existence of such interactions is reported in vanadyl complexes of octaphenyl porphyrin [VO(OPP)] and vanadyl dodecaphenyl porphyrin [VO(DPP)] [18,19] and observed that porphyrin with saddle distortion undergoes disproportionation on oxidation. So far, the electrochemical studies of oxidation product of vanadyl *meso* 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin VO[T(*p*-OH)PP] have not been reported in the literature.

Here we describe the synthesis of novel vanadylporphyrin VO[T(p-OH)PP] and characterized by UVvis and NMR spectroscopy. The formation of oxidation product of VO[T(p-OH)PP] is confirmed by ESR spectra at low temperature. We have observed from ESR data that this system has generated the monomeric radical cation. Further the same complex was analyzed by cyclic voltammetry as well as UV-Vis spectra and their results were discussed in detail.

Experimental

Chemicals and instruments

meso 5,10,15,20-tetrakis (*p*-hydroxyphenyl) porphyrin [T(p-OH)PP], tetra-*n*-butylammonium iodide and antimony pentachloride were purchased from Aldrich and were used without further purification. Dichloromethane was refluxed over phosphorous pentoxide and distilled just before use.

Vanadyl *meso*-5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrinVO[T(*p*-OH)PP]was synthesized by the same method of preparation of vanadyl *meso* 5,10,15,20-tetrakis phenyl porphyrin (VOTPP) as reported in the literature [20,21]. Tetra-*n*-butylammonium perchlorate was prepared by treating tetra-*n*-butylammonium iodide with sodium perchlorate and the product was recrystallized from methanol.

¹H-NMR characterization

Nuclear magnetic resonance spectra were recorded on a Brüker DSX 300 MHz spectrometer in CD_2Cl_2 using TMS as internal standard. The chemical shifts are expressed in (ppm).

UV-Visible measurement

Absorption spectra were measured by Beckman 650DU spectrophotometer. Visible spectra were measured between the range 350-750 nm. Oxidations of VO[T(p-OH)PP] were carried out by adding a drop of 10⁻³ M SbCl₅ in quartz cuvette.

Cyclic voltammetric studies

Oxidation potentials were determined using CHI 620B Electrochemical Analyzer. The electrolytic cell comprised of the following: A platinum electrode [CHI (102)] and platinum wire were used as working electrode and auxiliary electrode, respectively. The Ag/AgCl₂ electrode was employed as a reference electrode. Dry dichloromethane was used as the solvent and *tetra-n*-butylammonium perchlorate (TBAP) (0.1 M) as a supporting electrolyte. The solvent in the electrolyte cell was deaerated by purging dry nitrogen gas before measurement and maintained inert atmosphere. Calibration of $E_{1/2}$ values and diffusion current were made by using a known concentration of pure zinc *meso* 5,10,15,20-tetrakis phenyl porphyrin in dichloromethane/0.1M TBAP medium.

ESR measurement

JEOL JES TE 100 ESR spectrometer operating at X-band was used for low temperature measurements at 77K. A cold finger Dewar was employed to lower the temperature during ESR measurements. Oxidation was carried



out in ESR tube by adding drops.

Scheme 1 Synthesis of vanadyl *meso*-5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin VO[T(*p*-OH)PP] (2) from *meso*- 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin [T(*p*-OH)PP] (1).

Reagents and condition: (i) Vanadyl sulphate, glacial acetic acid, dichloromethane, reflux.



Fig. 1 Spectrum (a) shows UV-Visible absorption spectrum of VO[T(p-OH)PP] in CH₂Cl₂, Spectrum (b) shows UV-Visible absorption spectrum of VO[T(p-OH)PP] in CH₂Cl₂ reduced with diethyl amine. Spectra (c) and (d) show UV-Visible absorption spectrum of VO[T(p-OH)PP] in CH₂Cl₂ oxidized with SbCl₅ at room temperature.

Table 1 Absorption band of VO[T(p-OH)PP] and after addition of 10⁻³ M SbCl₅

Complex	Soret band(in nm)	Q band (in nm)		
VO[T(<i>p</i> -OH)PP] in Fig 1a	435	480	568	
VO[T(p-OH)PP] + diethyl amine in Fig 1b	434	481	567	
VO[T(p-OH)PP] + one drop of SbCl ₅ in Fig 1c	442	486	569	682
$VO[T(p-OH)PP] + five drops of SbCl_5 in Fig 1d$	437	488	569	687

Table 2 ESR	data for VO	[T(p-OH)]	PP1 at 77	K and after	addition of	of 10^{-3}	M SbCl ₅
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Complex	A _{II}	Α	g _{II}	g
VO[T(p-OH)PP]	156.47	54.86	2.17	2.25
$VO[T(p-OH)PP]^+$ Addition of 0.02 ml of 10^{-3} M SbCl ₅	188.86	75.53	2.29	2.31
$VO[T(p-OH)PP]^+$ Addition of 0.06 ml of 10^{-3} M SbCl ₅	157.74	55.31	2.04	2.11

Results And Discussion

Synthesis and characterization of vanadyl porphyrin

¹H-NMR spectra

The vanadyl porphyrin **2** was obtained in one step as shown in Scheme 1. Porphyrin **1** was refluxed with vanadyl sulphate in the presence of glacial acetic acid under methanol medium. ¹H-NMR (CD_2Cl_2 , 300 MHz): ppm 5.2 (s, 4H, -OH protons), 6.6 - 7.1 (d, 16H, phenyl ring protons), 6.18 (s, 8H, olefinic protons of pyrrole ring), -2.80 (s, 2H, -NH protons pyrrole ring). As expected, the complete disappearance of the signal of –NH protons at –2.80 in vanadyl porphyrin confirms the complex formation between the porphyrin and vanadyl metal (VO) [22,23].

UV - Vis spectra

Fig. 1a has shown absorption spectrum of VO[T(p-OH)PP] in dichloromethane. Prior to ESR measurement, oxidation of VO[T(p-OH)PP] was carried out in quartz cuvette by the careful addition of 1M SbCl₅. A dirty green precipitate was formed. Addition of SbCl₅ to VO[T(p-OH)PP] in 10⁻³ M chloroform solution caused a shifting of soret band ($_{max}$ 442, 437 nm) with a decrease in intensity of VO[T(p-OH)PP] soret band (Fig. 1c and 1d) and the data is presented in Table 1. This results indicate that VO[T(p-OH)PP] binds to SbCl₅ much more strongly. These results suggest that hydroxyl substituented porphyrin may help to promote higher aggregation (or mixtures of monomeric and dimeric species). This effect can be reorganized by intermolecular axial coordination by hydroxyl groups and metal-metal axial bridging interactions induced by SbCl₅. Thus, the aggregation is either weakened or broken by adding a drop of diethyl amine which is shown in Fig. 1b. These spectroscopic findings indicates a change in geometry of VO[T(p-OH)PP] [24].



Fig. 2 Cyclic voltammogram of VO[T(p-OH)PP] in CH₂Cl₂ containing 0.1M TBAP at room temperature, Scan rate 0.05 V/s.



Fig. 3 Continues scanning of cyclic voltammogram of VO[T(p-OH)PP] in CH_2Cl_2 containing 0.1M TBAP at room temperature, Scan rate 0.05 V/s.



Fig.4 Difference pulse voltammeter of VO[T(p-OH)PP] in CH₂Cl₂ containing 0.1M TBAP at room temperature, Scan rate 0.05 V/s.

Cyclic voltammetry

The cyclic voltammogram of VO[T(p-OH)PP] exhibits the first oxidation at 0.6372V with its corresponding reduction at 0.4745V (Fig. 2). Its E value is 0.1627V, $E_{1/2} = 0.5559V$ and Ia / Ic 1. The second oxidation occurs at 1.2852V while its corresponding reduction occurs at 0.9482V. The $E_{1/2}$ Value is 1.1167V, E=0.3370V and its Ia /Ic>1. The voltammogram of the VO[T(p-OH)PP] is not a straight forward successive one electron transfer process. The first oxidation potential and its corresponding reduction potential are lower than that of VOTPP. While the second oxidation shows a very strong oxidation peak current. The peak current corresponds to more than one electron transfer. Similar trends were observed in the case of zinc(II) tetrakis(3,5di-tert-butyl-4-hydroxyphenyl)porphyrin [25]. The second oxidation involved in this process is irreversible due to formation of secondary oxidation states involving the phenolic hydroxyl groups [26]. The UV-Spectrophotometer data indicates that aggregation (or mixtures of monomeric and dimeric species) can be formed by intermolecular axial coordination by hydroxyl groups and metal-metal axial bridging interactions induced by SbCl₅ Aggregation may also lead to polymerization at electrode surface. Murray et al [27] attributed it to oxidative electro-polymerizations. On subsequent scanning, the peak current decreases leading to film formation at the electrode (Fig. 2). The electron donating group (-OH) increases the electron density of the macrocyle. This makes the removal of electron easier. Thus, the oxidation potential decreases. The electrondonating hydroxyl group would have decreased the electron density of the -ring system and the energy of both the HOMO and the LUMO, which makes them harder to oxidize and easier to reduce of the corresponding monomeric species [25]. After polymerization at electrode surface, on scanning, the voltammetry of VO[T(p-OH)PP] exhibits the first oxidation along with its corresponding reduction peak but when the second oxidation occurs the corresponding reduction peak disappears as shown in Figure 3. The oxidation process is confirmed by differential pulse voltammeter (Fig. 4) and the process is represented as:



ESR Spectra

Oxidations of VO[T(p-OH)PP] were carried out in dry dichloromethane using few drops of a solution of antimony pentachloride (10⁻³ M) at low temperature. The ESR spectra of VO[T(p-OH)PP] are shown in Figure 5a and with addition of SbCl₅ are shown in Figure 5b and 5c. The data is represented in Table 2. The oxidation product of VO[T(p-OH)PP] has an unusual ESR behavior compared to vanadyl octaethylporphyrin or vanadyl *meso* porphyrin [28]. In 10⁻³ M concentration, the ESR spectrum shows fifteen lines. It is not well-resolved spectrum in this case. Extensive broadening of the ESR lines in VO[T(p-OH)PP] and the presence of more than one species at liquid nitrogen temperature, have prevented a detailed analysis of the ESR spectra of the oxidized form of VO[T(p-OH)PP]. ESR spectra (a) and (c) show that values of A and g much closer but spectrum (c) is fifteen line spectra. This effect can be reorganized by intermolecular axial coordination by hydroxyl groups and metal-metal axial bridging interactions induced by SbCl₅. It appears that oxidation occurred through monomeric cation. During the oxidation, the values of A and g are high (spectrum b). This may be geometry of metalloporphyrin changed in dichloromethane medium upon the addition of axially coordinating SbCl₅.

Further addition of $SbCl_5$ remitted in the formation of solid product. This is due to polymerization which is also observed by some earlier works [20]. This is also evident from the CV study. The cations of these vanadyl porphyrins indicate that the ligand field possesses an axial symmetry. Hence the polymerization occurred through the monocation.



Fig. 5 Spectrum (a) shows X-band ESR spectrum of VO[T(p-OH)PP] in CH₂Cl₂ at 77 K. Spectra (b) and (c) show X-band ESR spectrum of VO[T(p-OH)PP] in CH₂Cl₂ oxidized with SbCl₅ at 77 K. **References**

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