Asian Journal of Chemistry; Vol. 33, No. 1 (2021), 26-30

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.22905

Electrochemical Studies on Vanadyl Complex with *meso*-5,10,15,20-*tetrakis*(2,5-Dimethoxyphenyl)porphyrin using Electron Paramagnetic Resonance and Cyclic Voltammetry

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Received: 16 July 2020; *Accepted*: 29 August 2020; *Published online*: 10 December 2020; AJC-20171

The oxidation products of transition metal complexes with porphyrin are being examined currently by many research groups. *meso*-5,10,15,20-*tetrakis*(2,5-Dimethoxyphenyl)porphyrin [T(2,5-$(OCH_3)_2$)PP] and its coordination compound with oxovanadium(IV) resulting in VO[T(2,5-$(OCH_3)_2$)PP] were prepared by the standard procedures. The resulting complex was characterized with or without the addition of antimony pentachloride by infrared (IR) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy and cyclic voltammetry (CV). The UV-visible absorption spectrum of porphyrin ligand-based oxidation of vanadyl porphyrin VO[T(2,5-$(OCH_3)_2$)PP] in the presence of 0.5 mM $SbCl_5$ has shown bands at 425, 540 and 650 nm. The final electro-oxidation product has a broad absorption band centered at 650 nm. It is characteristic of a porphyrin mono- cation which is seen due to oxidation at 0.0995V of ΔE value in the cyclic voltammogram of VO[T(2,5-$(OCH_3)_2$)PP]. These spectral features observed during the oxidation are in good agreement with the stepwise formation of mono-cation radical and di-cation. The EPR spectrum of VO[T(2,5-$(OCH_3)_2$)PP] suggests that it could be oxidized to the radical cation by oxidation with $SbCl_5$ in dichloromethane. A radical cation is observed at low temperature and this spectrum corresponds to monomeric π-cation radical. A spectrum of fifteen lines is observed on the further addition of $SbCl_5$ in dichloromethane. Thus, monomeric π-cation radical is recognized as $[VO(TPP)]^+$. It is confirmed by the appearance of a new band at 1275 cm^{-1} in the IR spectrum. Zero field splitting (ZFS) was calculated from the triplet state on the EPR spectrum. It is suggested that ZFS interaction occurs from the dipolar coupling between the two electrons.

Keywords: *meso*-Vanadyl porphyrin, Antimony pentachloride, Electron paramagnetic resonance, Cyclic voltammetry.

INTRODUCTION

The redox potentials of metalloporphyrins can be tuned to one's requirement by modifying the substituents in the periphery of the metalloporphyrin [1,2]. Substituents could be introduced in the *ortho- or para*-positions of the phenyl rings in the *meso* positions or α and β positions in the pyrrole ring. Many studies have been reported on the redox potentials of phenyl substituted *meso*-tetraphenyl porphyrin [3,4]. The redox potentials have been correlated with the Hammet constants of the substituents. The redox potential data are available for some metal complexes of porphyrins with more substituents in β-position and symmetric tetracynnotetraphenyl porphyrin [5,6]. At the room temperature, vanadyl octaethyporphyrin [VO(OEP)] was oxidized to the radical cation in solution [7,8]. The visible electronic spectrum of the species and the redox potential data indicate that oxidation occurs at the ligand π-orbital. The EPR spectrum recorded at room temperature indicates that the species are monomeric with S = 1 where one electron is in vanadium *d*-orbital and the additional one is in the π-molecular orbital of the porphyrin [8]. Subramanian *et al*. [9] had reported the EPR spectrum of the monomeric radical cation of vanadyl *meso*-porphyrin dimethyl ester at low temperature [10,11]. It was also observed the similar behaviour of the vanadyl *meso*-5,10,15,20-*tetrakis* (*m*-nitrophenyl)porphyrin oxidized by adding a drop of $SbCl_5$ at room temperature and low temperature. The EPR and cyclic voltammetric studies of the oxidation products to vanadyl *meso*-5,10,15,20-*tetrakis*(dimethoxy phenyl)-porphyrin, $VO[T(2,5-(OCH_3)_2)PP]$ have not been reported. Hence, the EPR, cyclic voltammetric and UV-visible analysis of an oxidation product of $VO[T(2,5-(OCH_3)_2)PP]$ were conducted. It is observed from the EPR data that this system has generated the monomeric radical cation at low temperatures.

EXPERIMENTAL

Synthesis: *meso*-5,10,15,20-*tetrakis*(2,5-dimethoxy phenyl)porphyrin $[T(2,5-(OCH_3)_2)PP]$ was synthesized using standard procedures [12,13], whereas oxovanadium(IV) complex $VO[T(2,5-(OCH_3)_2)PP]$ was also synthesized according to the previous report [14]. Tetra-*n*-butylammonium perchlorate was synthesized by sodium perchlorate which was used to treat tetra-*n*-butylammonium iodide (Aldrich Chemicals), then it was recrystallized from methanol, finally with dichloromethane, and then refluxed using phosphorous pentoxide and distilled before use. A solution of 1 M antimony pentachloride (Aldrich-Chemicals) in dichloromethane was utilized without cleaning.

Voltammetric analysis: Redox potentials were determined using CHI620B Electrochemical analyzer at North-Eastern Hill University, Shillong, India. The electrolytic cell comprises a CHI (102) platinum, platinum wire and Ag/AgCl electrodes were used as a working indicator and reference electrode. Dry dichloromethane was used as the solvent. Tetra-*n*-butylammonium perchlorate (TBAP, 0.1M) was used as the supporting electrolyte. The solvent in the electrolyte cell was deaerated with oxygen-free dry nitrogen gas before any measurement and the nitrogen blanket above the solution has been maintained. In the electrolyte cell, dry nitrogen gas was passed to the electrolyte (solvent) for making it oxygen-free, before any measurement and nitrogen blanket above the solution was maintained. Calibration of $E_{1/2}$ values and diffusion current were made using known concentration of pure zinc porphyrin (ZnTPP) in dichloromethane and 0.1M TBAP medium.

EPR measurements: EPR measurements at room temperature were performed at SAIF, IIT, Chennai, and at low temperature at Pondicherry University, Pondicherry, India. JEOL JES TE 100 EPR spectrometer working at X-band was employed for low measurements at 77 K. A cold finger Dewar was employed for the liquid nitrogen measurements. Oxidation was carried out in an EPR tube using 0.5 mM $SbCl_5$ at room temperature.

UV-Visible analysis: Absorption spectroscopy was measured by Beckman 650DU spectrophotometer at North-Eastern Hill University, Shillong, India. The visible spectra were measured between the ranges of 350-750 nm and the oxidation was carried out in a quartz cuvette by adding 0.5 mM $SbCl_5$.

RESULTS AND DISCUSSION

Cyclic voltammetric studies of $VO[T(2,5-(OCH_3)_2)PP]$: The cyclic voltammogram of $VO[T(2,5-(OCH_3)_2)PP]$ shows two redox couples (Fig. 1) with their $E_{1/2}$ values at 1.042 and 1.225 V, respectively. The first oxidation occurs at 1.085 V and its corresponding reduction occurs at 0.999V while the ΔE value is found to be 0.086 V. The second oxidation occurs at 1.2744V and its corresponding reduction occurs at 1.1749V and its ΔE value is 0.0995 V. The ratio of current I_a/I_c is equal to 1. In general, vanadyl porphyrin provided two oxidation peaks corresponding to the formation of the cation (~1.0 V *vs*. SCE) and the dication (~1.3 V *vs*. SCE). The $E_{1/2}$ values of two successive one-electron oxidations confirmed the oxidation process is ligand centered. The present study of the voltammogram of *meso*-vanadyl porphyrin indicates that a mono- and di-cation have been formed concerning two reversible oxidation peaks at the porphyrin ring [15]. The oxidation potentials have been assigned in the following scheme:

$$[VO(TPP)] \xrightleftharpoons[+e]{-e} [VO(TPP)]^{+} : E_{1/2} = 1.042\ V$$

Monomeric radical cation

$$[VO(TPP)]^{+} \xrightleftharpoons[+e]{-e} [VO(TPP)]^{2+} : E_{1/2} = 1.225\ V$$

Di-cation

$TPP = VO[T(2,5-(OCH_3)_2)]$

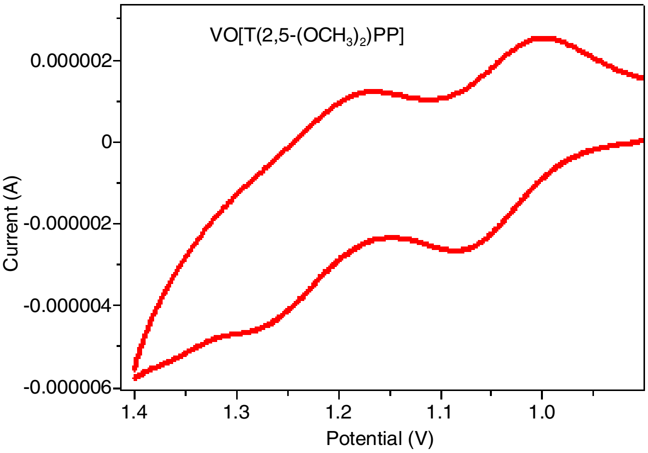


Fig. 1. Cyclic voltammogram of $VO[T(2,5-(OCH_3)_2)PP]$ at 0.06 V/s in CH_2Cl_2 containing 0.1 M TBAP at room temperature

The voltammogram of $VO[T(2,5-(OCH_3)_2)PP]$ indicates that oxidation potentials are slightly higher than that of the VOTPP about 0.024 V and 0.0095 V, respectively. But the oxidation potentials are slightly lower than that of $VO[T(m\text{-}NO_2)PP]$ [10] occurred at 0.012 V and 0.096 V. The reason for lowering the oxidation potentials in case of $VO[T(2,5-(OCH_3)_2)PP]$ may be attributed to symmetrical substitution of the phenyl ring, which is more or less similar geometry to that of VOTPP. Although the shifts in the potential either way are small and quite uniform, which suggest that there are some changes in the geometry of the molecules on substitution which affects the energy levels (HOMO) of the molecule and hence the shifts in the redox potentials occur. Perhaps, this is due to the interaction of *d*-orbital of metal and ligand orbital of porphyrin in a ruffle and saddle distortion as suggested by several researchers [15-18]. The voltammogram is indicative of reversible and successive one-electron transfer of the porphyrin ring.

UV-visible study of VO[T(2,5-(OCH$_3$)$_2$)PP]: The preliminary oxidation of VO[T(2,5-(OCH$_3$)$_2$)PP] has been carried out in quartz cuvette by adding 0.5 mM $SbCl_5$. The UV-visible absorption spectrum of VO[T(2,5-(OCH$_3$)$_2$)PP] exhibits peaks at 425, 540 and 650 nm as shown in Fig. 2. The soret band at 423 nm decreases its intensity and moves to 425 nm. The final electro-oxidation product has a broad absorption band centered at 650 nm, which is a characteristic of a porphyrin mono cation shown in the oxidation at 0.0995 V of ΔE value in cyclic voltammogram of VO[T(2,5-(OCH$_3$)$_2$)PP]. This spectral feature in the oxidation, which is in good agreement with the stepwise formation of mono-cation and di-cation radicals.

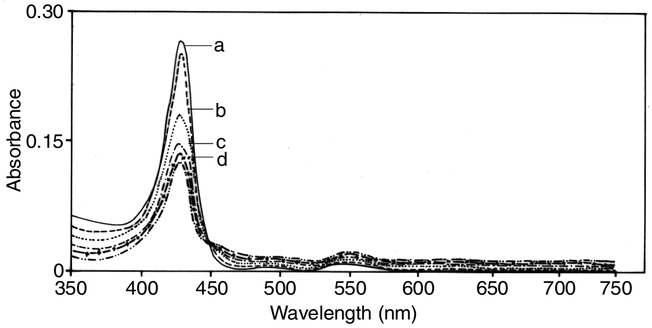


Fig. 2. UV-visible absorption spectrum of VO[T(2,5-(OCH$_3$)$_2$)PP] in CH_2Cl_2 oxidized with varying concentration of $SbCl_5$ (c, d) and reduced with diethylamine (b) at room temperature

After successive addition of 0.5 mM $SbCl_5$, a visible spectrum (Fig. 2b) shows peaks at 652 nm in VO[T(2,5-(OCH$_3$)$_2$)PP] indicating a axial coordination in a properly saddle-distorted porphyrin ring in which V-Np distances are drastically smaller, whereas in the porphyrin cores, it has been enlarged on the coordination of axial ligand [18]. Consequently, the Soret band is not significantly responsive to the coordination in metalloporphyrins, since the vanadyl ion is usually out of the plane of the porphyrin ring and the dπ-orbitals interact weakly with the p_π orbitals of the porphyrin ring [19]. The binding of $SbCl_5$ does not change the spin or metal oxidation states (V^{IV}, d^1-system) of the complexes [18].

These facts indicated that the addition of $SbCl_5$ in the system produces vanadyl(IV) porphyrin cations by one-electron oxidation representing the shift of oxidation peak showing from the porphyrin ligand to the central metal, corresponding with the replacement of one axial ligand $SbCl_4^-$ by the chloride ion in $SbCl_5$. Experimental results indicate that $SbCl_5$ coordinates to vanadyl porphyrin atom in the vanadyl porphyrin at the sixth position as the axial ligand. However, this axial position is weak. Finally, the addition of diethylamine to the solution of vanadyl porphyrin adduct of $SbCl_5$ (Fig. 2b) has shown that vanadyl porphyrin reappeared. It indicates that no demetallation occurs in the vanadyl porphyrin system.

EPR spectra of VO[T(2,5-(OCH$_3$)$_2$)PP]: Oxidation of VO[T(2,5-(OCH$_3$)$_2$)PP] is carried out with 0.5 mM $SbCl_5$ in dichloromethane at room and low temperatures. In Fig.4b, the radical cation is observed at low temperature and this spectrum corresponds to monomeric unoxidized *meso*-porphyrin [6]. The spectrum obtained after further addition of 0.5 mM $SbCl_5$ in dichloromethane exhibits fifteen lines. Thus, this pattern is recognized as $[VO(TPP)]^+$ and $[VO(TPP)]^{2+}$, the EPR spectrum indicates a mixture of an unoxidized monomeric vanadyl porphyrin and dimeric species. This type of spectrum indicates the presence of the species $[VO(MESO)VO(MESO)]^+$ with an effective spin S = 1/2 coupling with two equivalent ^{51}V nuclei. Change of the EPR spectrum in Fig.4c revealed that mono cation has been observed. This is characteristic of the species $[VO(TPP)]^+$ at low temperatures. It is similar to that of the dimeric species obtained for *meso*-porphyrin [14,20]. The anisotropy obtained in the EPR spectrum of Fig. 4b is very small.

A single line in the EPR spectrum (Fig. 3c) of the oxidized complex VO[T(2,5-(OCH$_3$)$_2$)PP] at room temperature corresponds to triplet state containing one ^{51}V coupling and arise only from a monomeric radical cation of vanadyl porphyrin, which has been hitherto detected by EPR only at room temperature [14,21]. The formation of a monomeric radical cation is confirmed with an additional absorption band at 1275 cm^{-1} in the IR spectrum [17].

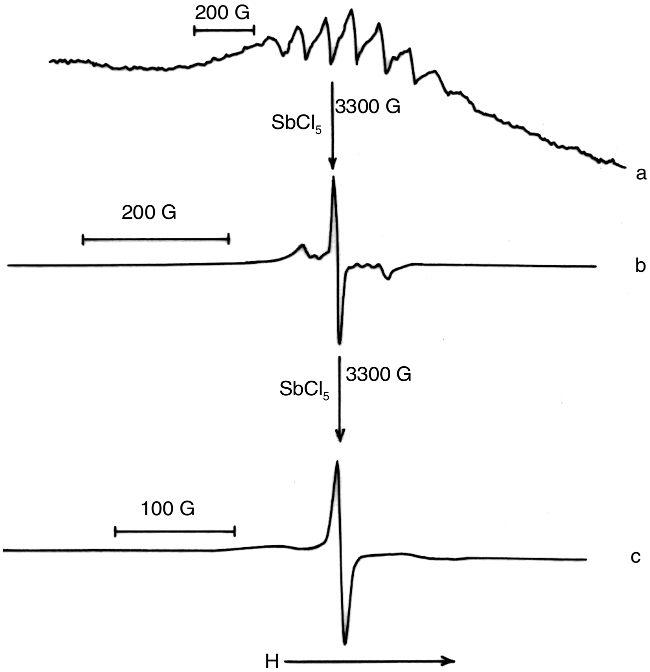


Fig. 3. EPR spectrum of VO[T(2,5-(OCH$_3$)$_2$)PP] in CH_2Cl_2 oxidized with $SbCl_5$ of varying concentration at room temperature

The parameters, D and $A_{\parallel}$ were estimated from the EPR spectrum (Fig. 4d) and specified that $A_{\parallel} < D/3$, which is due to the hyperfine interaction, as a perturbation above the sum of zero fields splitting (ZFS) and Zeeman interaction. The zero fields splitting including the Hamiltonian parameter was diagonalized for every angular orientation of the arrangement beneath axial symmetry. The powder spectrum was obtained by averaging all the angular orientations with the Gaussian quadrature method for mathematical interactions. The limitations A and

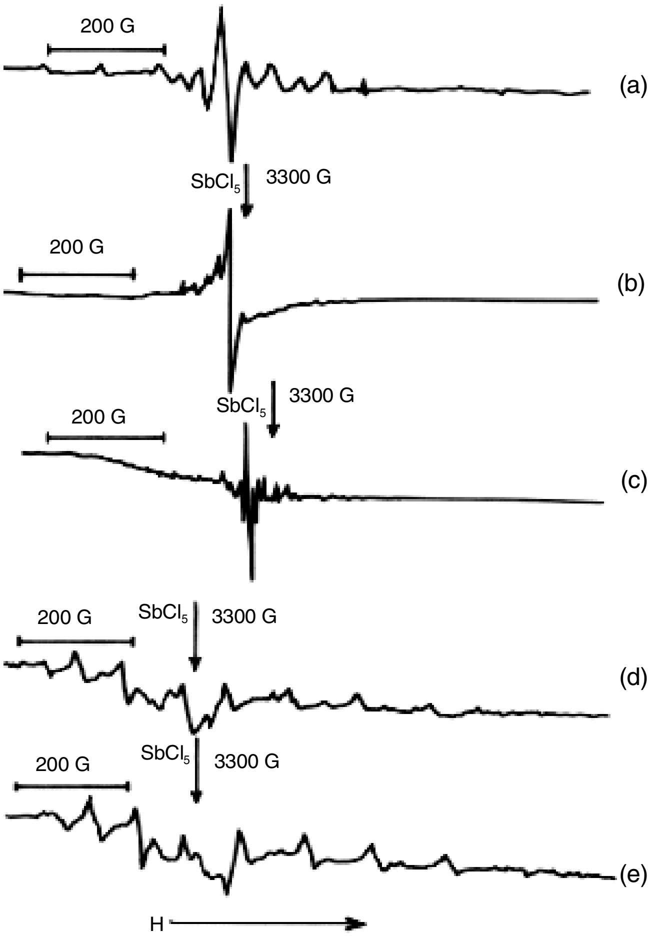


Fig. 4. EPR spectrum of VO[T(2,5-$(OCH_3)_2$)PP] in CH_2Cl_2 oxidized with $SbCl_5$ of varying concentration at low temperature

D were diverse to get the new spectrum, while this advance is quite rough; it provides a sensible correction to the new spectrum (Fig. 4d).

The spin Hamiltonian parameters attained are $g_\perp = 2.2236$ G, $g_\parallel = 2.2682$G.

$$A_\perp = 69.95\ \text{G},\ A_\parallel = 32.6355\ \text{G},\ D = 700\ \text{MHz}$$

where $D = 3/2\ D_\parallel$ or $D_\parallel = 2/3D = 466$ MHz. The value of D obtained from the spectrum is measured. The interelectron vector is equivalent to the plane of the ring and standard to the molecule with 4-fold axis. The D and g tensors are getting during the identical principal axis system with the *z*-axis parallel to the 4-fold symmetry axis. Thus the ZFS tensor is modified with the inter-electron axis on the *z*-axis

For an axially symmetric system, the ZFS tensors along the inter-electron axis (Z′) for Zeeman and zero field interaction are only considered.

$D_{x'x'} = -1/2\ D_{z'z'}$. The quantity $D_\parallel$ is along an axis perpendicular to the interelectron axis and hence,

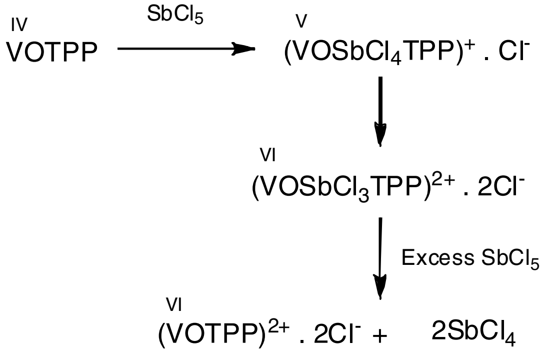
$$D_\parallel = D_{x'x'} = D_{y'y'} = -\frac{1}{2} D_{z'z'} \tag{1}$$

$$D_{z'z'}\ (\text{MHz}) = \frac{1.298g^2}{R^3} \tag{2}$$

where, $g^2 = g_\parallel^2 + 0.5g_\perp^2$.

The interelectron distance R is an inter-electron distance between the triplet state of two unpaired electrons using a value of $D_{z'z'} = 1280$ MHz, where we got a value for R as 4.73 Å; it is understood that the whole ZFS interaction was arise from dipolar coupling between two electrons. Unpaired π-electron density is a_{2u}. Nevertheless, the little inter-electron space obtained is in high-quality conformity through that of $VOTPP^+$. It undergoes oxidation fairly comparable to that of oxidation VOTPP. During oxidation, vanadyl porphyrin cores have been enlarged on axial ligand coordination. The binding of $SbCl_5$ does not alter the spin or metal oxidation states (V^{IV}, d^1-system) of the complexes [21].

Di-cation porphyrin was formed through monocation, which was confirmed by the peak at 1275 cm^{-1} in the IR spectrum (Fig. 5). At low concentration, VO[T(2,5-$(OCH_3)_2$)] directs to the arrangement of monomeric radical cation on oxidation at room temperature and a 15 line spectrum is obtained at low temperature similar to VO(OEP). It undergoes oxidation moderately comparable to that of the oxidation of VOTPP. Oxidation steps can be represented as [20]:



$$\begin{tikzcd} \overset{IV}{VOTPP} \arrow[r, "SbCl_5"] & \overset{V}{(VOSbCl_4TPP)^+ . Cl^-} \arrow[d] \\ & \overset{VI}{(VOSbCl_3TPP)^{2+} . 2Cl^-} \arrow[d, "Excess\ SbCl_5"] \\ & \overset{VI}{(VOTPP)^{2+} . 2Cl^-} + 2SbCl_4 \end{tikzcd}$$

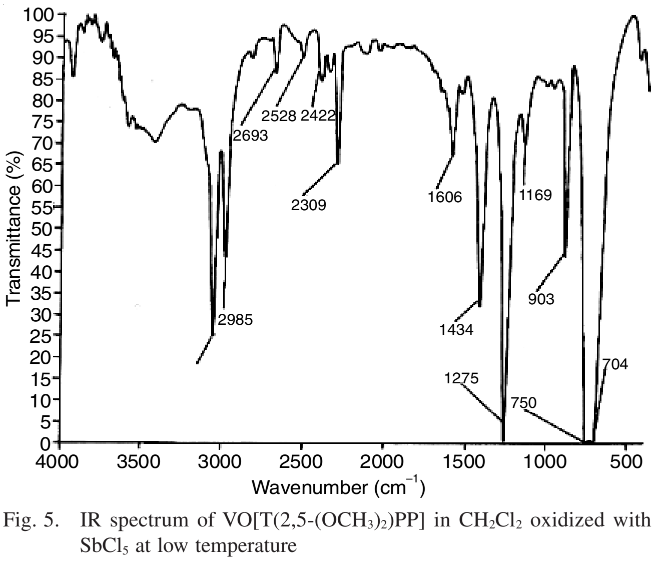


Fig. 5. IR spectrum of VO[T(2,5-$(OCH_3)_2$)PP] in CH_2Cl_2 oxidized with $SbCl_5$ at low temperature

Antimony tetrachloride has not been isolated yet. In the proposed mechanism, $SbCl_5$ oxidizes V^{4+} into V^{6+} and itself undergoes reduction into $SbCl_3$, and then $SbCl_3$ combines with excess $SbCl_5$ and degrades into $2SbCl_4$. At the end of the oxidation reaction, the reaction mixture becomes darker, indicating the formation of $SbCl_4$.

Conclusion

The UV-visible absorption spectrum of VO[T(2,5-$(OCH_3)_2$)-PP] exhibits a broad absorption band centered at 650 nm. It is characteristic of a porphyrin mono-cation, which shows oxidation at $\Delta E = 0.0995$ V in cyclic voltammogram of VO[T(2,5-$(OCH_3)_2$)PP]. These spectral features during the oxidation are in good agreement with the stepwise formation of mono-cation radical and di-cation. *meso*-VO[T(2,5-$(OCH_3)_2$)PP] generates a triplet state through monomeric cation and is confirmed by EPR spectra. The methoxy electron-donating substituent in meso position of the porphyrin ring leads to easier oxidations. Cyclic voltammetric data on this system has demonstrated a consecutive one electro-oxidation. The monomeric radical cation has also been obtained at low temperatures and confirmed by EPR spectral studies. The EPR result of VO[T(2,5-$(OCH_3)_2$)PP] is consistent with the cyclic voltammetric data of this system.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. F. Bedioui, S. Griveau, T. Nyokong, A.J. Appleby, CA. Caro, M. Gulppi, G. Ochoae and J.H. Zagal, *Phys. Chem. Chem. Phys*., **9**, 3383 (2007); https://doi.org/10.1039/B618767F
2. K.M. Kadish and E. Van Caemelbecke, *J. Solid State Electrochem.*, **7**, 254 (2003); https://doi.org/10.1007/s10008-002-0306-3
3. M. Sankar, P. Bhyrappa, B. Varghese, K.K. Praneeth and G. Vaijayanthimala, *J. Porphyr. Phthalocyan*., **9**, 413 (2005); https://doi.org/10.1142/S1088424605000514
4. P. Bhyrappa, M. Sankar and B. Varghese, *Inorg. Chem*., **45**, 4136 (2006); https://doi.org/10.1021/ic052035b
5. A. Giraudeau, H.J. Callot and M. Gross, *Inorg. Chem.*, **18**, 201 (1979); https://doi.org/10.1021/ic50191a042
6. A. Giraudeau, H.J. Callot, J. Jordan, I. Ezhar and M. Gross, *J. Am. Chem. Soc.*, **101**, 3857 (1979); https://doi.org/10.1021/ja00508a024
7. K.M. Smith, Porphyrins and Metalloporphyrins, Elsevier, p. 555 (1975).
8. G.R. Luckhurst, M. Setaka and J. Subramanian, *Mol. Phys.*, **32**, 1299 (1976); https://doi.org/10.1080/00268977600102691
9. J. Subramanian, V.P. Shedbalkar, A. Lemtur, R. Chakravorty and T.N. Saloi, *J. Phys. Chem.*, **100**, 4770 (1996); https://doi.org/10.1021/jp9511820
10. A.T. Singh and A. Lemtur, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **59**, 1549 (2003); https://doi.org/10.1016/S1386-1425(02)00333-5
11. O. Zhuang and X. Gao, *Sci. China B Chem.*, **40**, 215 (1997); https://doi.org/10.1007/BF02876414
12. I. Gupta and M. Ravikanth, *Tetrahedron*, **59**, 6131 (2003); https://doi.org/10.1016/S0040-4020(03)00950-5
13. I. Gupta and M. Ravikanth, *Tetrahedron Lett.*, **43**, 9453 (2002); https://doi.org/10.1016/S0040-4039(02)02258-X
14. J.G. Erdman, V.G. Ramsey, N.W. Kalenda and W.E. Hanson, *J. Am. Chem. Soc.*, **78**, 5844 (1956); https://doi.org/10.1021/ja01603a037
15. A. Lemtur, B.K. Chakravorty, T.K. Dhar and J. Subramanian, *J. Phys. Chem.*, **88**, 5603 (1984); https://doi.org/10.1021/j150667a029
16. A. Murugan, Ph.D. Thesis, Studies on Paramagnetic andRedox Properties of Some Metalloporphyrins, North Eastern Hill University, Shillong, India (2008).
17. E.T. Shimomura, M.A. Phillippi, H.M. Goff, W.F. Scholz and C.A. Reed, *J. Am. Chem. Soc.*, **103**, 6778 (1981); https://doi.org/10.1021/ja00412a055
18. A. Ghosh, I. Halvorsen, H.J. Nilsen, E. Steene, T. Wondimagegn, R. Lie, E. van Caemelbecke, N. Guo, Z. Ou and K.M. Kadish, *J. Phys. Chem. B*, **105**, 8120 (2001); https://doi.org/10.1021/jp011984x
19. S.K. Ghosh, R. Patra and S.P. Rath, *Inorg. Chem.*, **47**, 9848 (2008); https://doi.org/10.1021/ic800714w
20. A. Ali, S.K. Barman and R. Mukherjee, *Inorg. Chem.*, **54**, 5182 (2015); https://doi.org/10.1021/ic503103e
21. G.M. Ucoski, S. Nakagaki and F.S. Nunes, *J. Porphyr. Phthalocyan.*, **18**, 1093 (2014); https://doi.org/10.1142/S1088424614500473