

# Cyclic Voltammetric and EPR Studies on the Oxidation Products of Vanadyl Mesoporphyrin

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The results of cyclic voltammetric studies on vanadyl mesoporphyrin dimethyl ester, VO(MESO), at various concentration ranges are reported. Redox peaks have been identified for the dimeric species in the cyclic voltammograms. The monomeric radical cation of VO(MESO) has been identified at low temperatures, and the triplet EPR spectrum of this species is reported. The zero-field splitting parameters have been obtained by computer simulation. A distance of 3.8 Å between the d electron in the vanadium orbital and the unpaired  $\pi$  electron in the porphyrin ring in the monomeric radical cation of VO(MESO) has been obtained. This result is interpreted as arising from  $a_{1u}$  ground state for the  $\pi$  electron in the porphyrin.

## Introduction

The oxidation products of transition-metal porphyrins have received considerable attention in recent years.<sup>2</sup> A large number of techniques such as NMR, EPR, Mössbauer, X-ray crystallography, magnetic measurements, resonance Raman, and EXAFS have been used to characterize the structural features of these systems.<sup>3–16</sup> Many of the studies on the oxidation products, especially those of iron porphyrins, have been useful in tracing the mechanistic aspects of the functioning of heme enzymes.<sup>17</sup> Some of the iron and manganese porphyrins have been used as catalysts in oxidation reactions.<sup>18,19</sup> We report in the present work some of our findings on the ESR and electrochemical behavior of the oxidation products of vanadyl mesoporphyrin dimethylester, VO(MESO). One-electron oxidation products of vanadyl porphyrins serve as simple models for ferryl heme moiety [Fe(IV)=O] in heme enzymes.

In our earlier studies on vanadyl porphyrins, the identification of monomeric one-electron oxidation product of VO(MESO) in solution at room temperature (a biradical) was reported.<sup>20</sup> This species dimerises at low temperature and hence the monomeric cation radical could not be studied at low temperatures. Two types of dimers have been identified by EPR spectroscopy: one with  $S = 1$  ground state and the other with  $S = 3/2$  ground state. We now present a reasonably complete picture on the conditions under which the monomer radical cation and the two types of dimers are formed. We have also been successful in generating the monomeric radical cation of vanadyl mesoporphyrin at low temperatures. The EPR spectrum of this biradical-type system has also been obtained around 10 K and analyzed with computer simulation, to obtain the zero-field splitting parameters. The resonance Raman spectra of some of the monomeric vanadyl porphyrin radical cations have been reported by others.<sup>21</sup>

One more type of VO porphyrin species, apparently dimeric, has been reported recently.<sup>22</sup> Very carefully conducted EPR and magnetic susceptibility measurements on single crystals of vanadyl octaethyl porphyrinate radical cation, [VO(OH<sub>2</sub>)OEP]-SbCl<sub>6</sub>, indicate the presence of both intramolecular and intermolecular spin exchange interaction. Combined with X-ray structural data, the authors have proposed a steplike orientation

of pairs of VO(OEP) radicals. The EPR behavior of this species in solution confirms our earlier results, i.e., the system is present as a monomer at room temperature and a dimer at low temperatures with the  $\pi$  electrons being antiferromagnetically coupled. The authors have also obtained  $J$  values for the intramolecular ferromagnetic coupling (63 cm<sup>-1</sup>) and intermolecular antiferromagnetic coupling of the two  $\pi$  electrons (–139 cm<sup>-1</sup>).

## Experimental Section

**Chemicals.** VO(MESO) was prepared from mesoporphyrin dimethyl ester as reported earlier.<sup>20</sup> Tetra-*n*-butylammonium perchlorate was prepared by treating tetra-*n*-butylammonium bromide (SISCO Research Chemicals, India) with sodium perchlorate. It was recrystallized from methanol. Dichloromethane was refluxed over phosphorous pentoxide and distilled just before use. Commercial sample of antimony pentachloride (FLUKA) was used without purification.

**Cyclic Voltammetric Measurements.** Cyclic voltammograms were obtained using a BAS (Bioanalytical Systems Inc., USA) CV-1B unit with BAS cell. BAS Pt electrode, Ag/AgCl, or calomel electrodes were used. A digigraphic 2000 XY recorder was used in the set up. Scan rates were in the range of 100 mv/s. Dichloromethane with 0.1 M *tert*-butylammonium perchlorate was taken as the medium for all the cyclic voltammetric experiments.

**EPR Measurements.** EPR measurements were done both at NEHU, Shillong, and at TIFR, Bombay. Varian E109 EPR spectrometer operating at X-band was used for measurements up to liquid nitrogen temperature. EPR measurements in the range of 10 K were done using a home-built version of the EPR spectrometer available in the Chemical Physics Division of Tata Institute of Fundamental Research, Bombay. A helium-flow variable-temperature dewar (Air-products, USA) was used for EPR measurements at low temperatures.

**Computer Simulation.** A computer program from the Quantum Chemistry Program Exchange (QCPE 134) for the simulation of EPR spectra of single crystals has been modified and adapted for a PC system. The program involves diagonalizing the spin Hamiltonian matrix for each angular orientation to obtain the field positions and intensities. A procedure for averaging over all the angular orientations to obtain a powder

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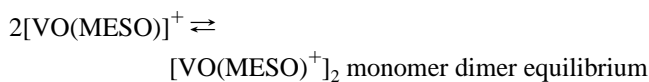
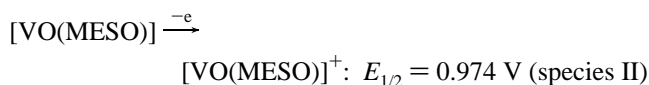
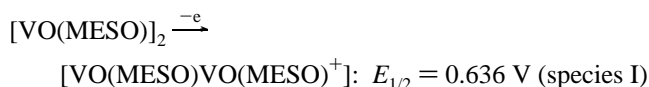
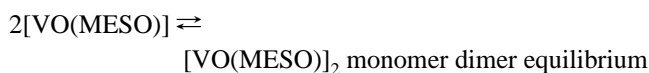
spectrum has been included and the program has been used in a PC-AT (HCL BUSYBEE, 80286, India). Simulations have been obtained on a dot-matrix printer.

## Results and Discussion

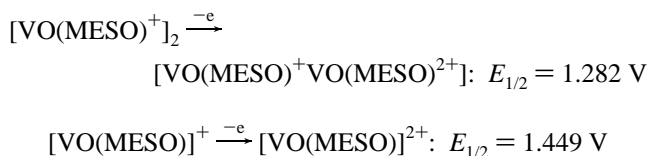
Aggregation is by no means unique in vanadyl porphyrins. It depends on the nature of the porphyrin rather than the metal. It is easier to identify the nature of the dimer through the EPR behavior of  $\text{VO}^{2+}$  than by any other approach. Proto- and mesoporphyrins tend to aggregate more extensively than octaethyl porphyrin. Tetramesityl porphyrins have very little tendency for aggregation.  $\text{VO}(\text{MESO})$  has been chosen as the best system in our studies since this system seems to exist only in monomeric and dimeric forms. Higher degree of aggregation if present, appears to be at a negligible level.

**Cyclic Voltammetric Studies.** Well-defined cyclic voltammograms have been obtained for  $\text{VO}(\text{MESO})$  in dichloromethane over a wide range of concentrations. In the concentration range 0.0005–0.001 M, two reversible oxidation peaks have been observed. These peaks are very similar to those observed for  $\text{VO}(\text{OEP})$  or  $\text{VO}(\text{TPP})$ . Thus one can easily assign the two oxidation steps respectively to the formation of a monocation radical and a dication. The  $E_{1/2}$  values for the first and second oxidation are very similar to those that have been observed for  $\text{VO}(\text{TPP})$  and  $\text{VO}(\text{OEP})$ . In the concentration range 0.004–0.008 M, each of these peaks splits into two with a separation of  $\sim 300$  mV (Figure 1b). The relative heights of the peaks I and II (or III and IV) depend on concentration. At high concentrations ( $\sim 0.01$  M), the peaks are very broad. These observations indicate that the splitting of the peaks arises probably due to aggregation effects. Similar splittings though not so well-resolved as in the present case have been reported for  $(\text{VO})^{2+}$  and  $\text{Zn}^{2+}$  protoporphyrin.<sup>20</sup> Maiya and Krishnan<sup>23</sup> report a study on dimeric crown ether porphyrins wherein the difference in the oxidation potential between the monomeric and dimeric systems is about 150–200 mV. That the aggregate is a dimer is borne out by EPR studies.

EPR studies have already been reported by us for the one-electron oxidation products of  $\text{VO}(\text{MESO})$  obtained by electrooxidation or oxidation with perchloric acid.<sup>20</sup> The species have been identified at room temperature, namely, the monomeric radical cation at low concentrations and a one-electron oxidation product of the dimer at higher concentration. These observations tie up nicely with the cyclic voltammetric studies reported in the present work. The oxidation potentials have been assigned in the following way. All the potentials are given with reference to  $\text{Ag}/\text{AgCl}$  electrode:



The dimer is labeled as species III:



Apart from the peaks corresponding to the monomeric radical cation,  $[\text{VO}(\text{MESO})]^+$  and the dication,  $[\text{VO}(\text{MESO})]^{2+}$ , additional peaks are obtained from the dimers  $[\text{VO}(\text{MESO})\text{VO}(\text{MESO})^+]^+$  and  $[\text{VO}(\text{MESO})^+\text{VO}(\text{MESO})^{2+}]^+$ .

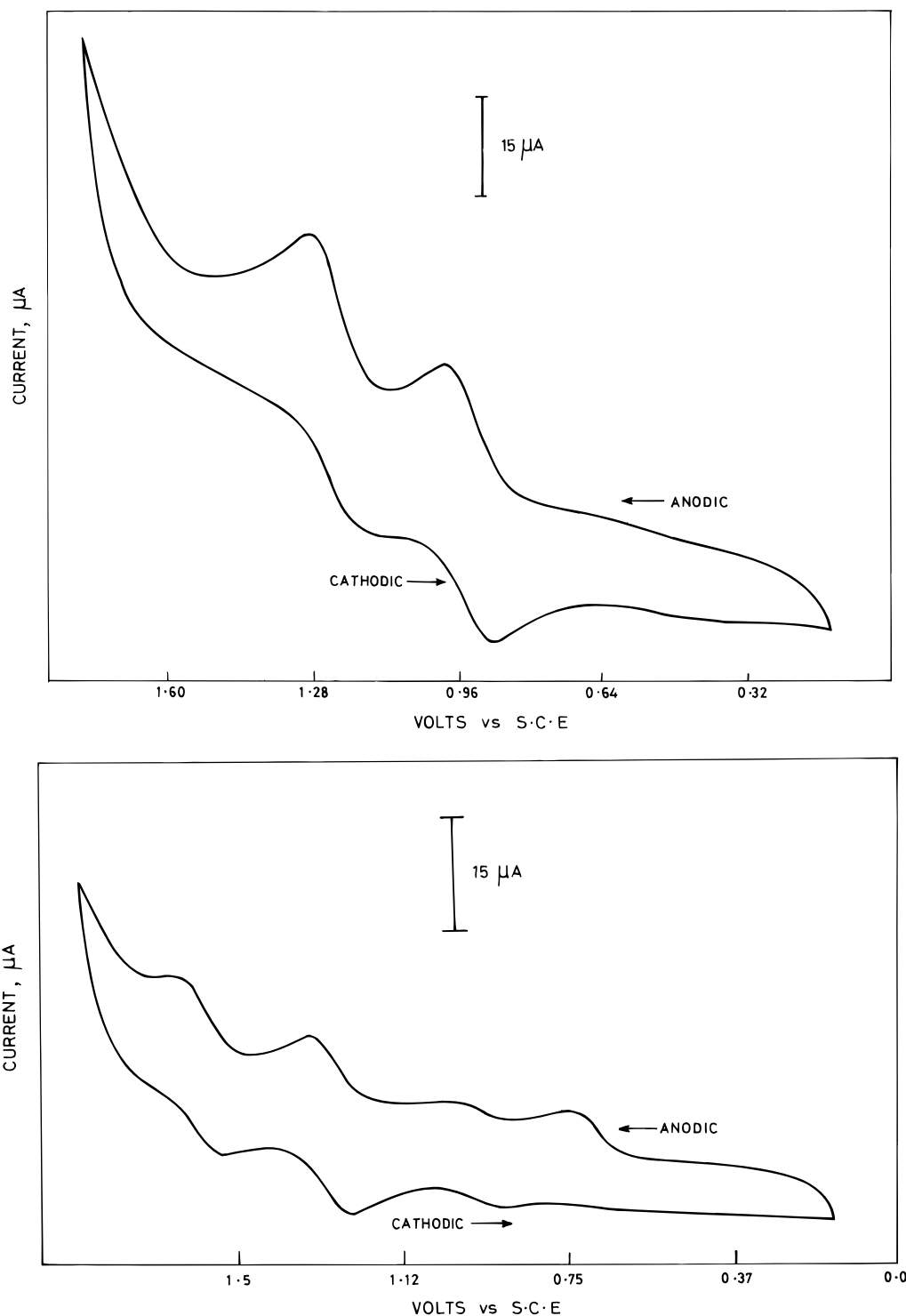
The above assignment of oxidation potentials has been done on the basis of structural data from EPR studies. Species I has been identified earlier in solution at room temperature and at 77 K.<sup>20</sup> This system has three unpaired electrons, one on each of the vanadium orbital and the third on the  $\pi$  molecular orbital of the porphyrin system. The EPR spectra obtained at room temperature and 77 K have been interpreted as arising from  $S = 3/2$  system. This species serves as a simple model for the radical cation obtained from the chlorophyll dimer.

Species II, namely, the monomeric radical cation of vanadyl porphyrin, has been identified in solution at room temperature.<sup>5,24</sup> This is an  $S = 1$  system behaving like a biradical at room temperature. The identification of this species by EPR at low temperatures had not been done before and is being reported in the present work.

Species III, again a dimer, corresponding to the  $S = 1$  state, has been identified by EPR only at low temperatures.<sup>24</sup> The other species corresponding to higher oxidation potentials, namely, 1.282 V and 1.449 V have not been identified by structural studies until now.

**EPR Studies.** In our earlier study we had reported the EPR spectrum of the monomeric radical cation (species II) at room temperature.<sup>20,24</sup> When this system is generated by electrooxidation or by oxidation with perchloric acid, it invariably dimerizes at low temperatures to give rise to the species  $[\text{VO}(\text{MESO})^+]_2$  (species III,  $S = 1$ ) the EPR spectrum of which has also been reported.<sup>20</sup> In the present work we have attempted to obtain the monomeric radical cation at low temperatures. Oxidation with antimony pentachloride with a 3–5-fold excess of the oxidizing agent also yields the radical cation which again dimerizes at low temperatures to yield the species  $[\text{VO}(\text{MESO})]_2^+$ , species III. When about a 10-fold excess of antimony pentachloride was used, a new type of EPR spectrum was obtained at liquid nitrogen temperature and with a considerable improvement in the resolution and signal-to-noise ratio at about 10 K. This spectrum appears like a typical triplet-state spectrum and contains hyperfine splitting arising only from one  $^{51}\text{V}$  nucleus. A good signal was also obtained at the half-field position corresponding to the presence of a single  $^{51}\text{V}$  nucleus (Figure 2a). The reversibility of the one-electron oxidation in the presence of a 10-fold excess of  $\text{SbCl}_5$  has been verified as follows. The contents of the EPR tube after recording the EPR spectra were transferred to a beaker containing 50 mL of water and traces of triethylamine. The vanadyl porphyrin was extracted with chloroform. The optical spectrum did not show any trace of free-base porphyrin. This spectrum is completely different from the EPR spectra obtained at low temperatures for I,  $[\text{VO}(\text{MESO})\text{VO}(\text{MESO})^+]^+$  ( $S = 3/2$ ) and for III,  $[\text{VO}(\text{MESO})^+]_2$  ( $S = 1$ ). A computer simulation of this spectrum (species II) was obtained as described below.

An EPR signal corresponding to a triplet state containing one  $^{51}\text{V}$  coupling could arise only from a monomeric radical cation of  $[\text{VO}(\text{MESO})]$  which has been hitherto detected by EPR only at room temperature. A spin Hamiltonian for this system could



**Figure 1.** (a, top) Cyclic voltammogram of VO(MESO) (0.001 M) in dichloromethane containing 0.1 M tetrabutylammonium perchlorate. Scan rate 50 mV/s. (b, bottom) Cyclic voltammogram of VO(MESO) (0.005 M) at the same scan rate.

be written as

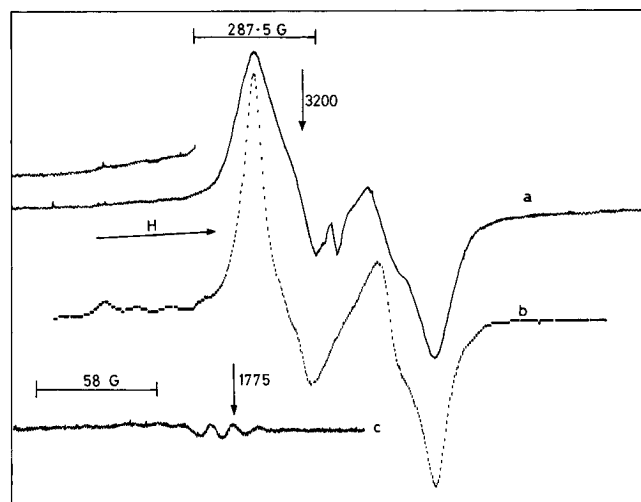
$$H = \beta[S_1 \cdot g_1 \cdot B + S_2 \cdot g_2 \cdot B] + S_1 \cdot A \cdot I + S_1 \cdot D \cdot S_2 + JS_1 \cdot S_2 \quad (1)$$

where the indexes 1 and 2 correspond to the unpaired electron on the vanadium atom and the unpaired  $\pi$  electron, respectively. The hyperfine interaction between the  $\pi$  electron and the vanadium nucleus is ignored. This spin Hamiltonian is similar to that adopted to interpret the metal-free radical interaction in spin-label bound metal complexes.<sup>25</sup> In these systems,  $J = 0$  or is of the order of  $10^{-4} \text{ cm}^{-1}$ . In the present situation, as

indicated by the EPR spectrum of VO(MESO)<sup>+</sup> at room temperature,  $J \gg h\nu$ , where  $\nu$  is the microwave frequency. The  $J$  value has been measured<sup>22</sup> for VO(OEP)<sup>+</sup>SbCl<sub>6</sub><sup>-</sup> as  $63 \text{ cm}^{-1}$ . In view of the strong exchange with respect to the microwave frequency, we can consider that the two electrons experience an average environment. An approximate Hamiltonian for the system can be written as

$$H = \beta S \cdot g \cdot B + S \cdot A \cdot I + S \cdot D \cdot S \quad \text{with } S = 1 \quad (2)$$

We shall consider only the dipolar interaction as the major contributing factor to the zero-field splitting (ZFS) interaction. Here  $S$  is the total spin angular momentum and  $g$  is the average



**Figure 2.** (a) X-band EPR spectrum of VO(MESO) in dichloromethane, oxidized with  $\text{SbCl}_6$  (10-fold excess) at 10 K. Microwave frequency: 9.203 GHz, magnetic field modulation frequency: 100 kHz. (b) Computer-simulated spectrum (see the text for parameters). (c) Half-field spectrum ( $g \approx 4$ ).

$g$  tensor for the d-electron and  $\pi$ -electron. Rough estimates of  $D$  and  $A_{\parallel}$  can be made directly from the spectrum, which indicates  $A_{\parallel} < D/3$ . Hence we have considered the hyperfine interaction as a perturbation over the sum of Zeeman and the ZFS interactions. The Hamiltonian including Zeeman and zero-field interactions was diagonalized for each angular orientation of the system under axial symmetry. The powder spectrum was obtained by averaging over all angular orientations, using Gaussian quadrature method for numerical integration. The hyperfine couplings were included as perturbation terms up to second order. The parameters  $D$  and  $A$  were varied to obtain the best fit with the experimental spectrum. Though this approach is rather crude, it gives a reasonable fitting to the experimental spectrum (Figure 2b). The spin Hamiltonian parameters obtained in this way are

$$\begin{aligned} g_{\perp} &= 1.995 & g_{\parallel} &= 1.940 \\ A_{\perp} (^{51}\text{V}) &= 0.04 \text{ MHz} & A_{\parallel} &= 0.17 \text{ MHz} \\ D &= 960 \text{ MHz} & E &= 0.08 \text{ MHz} \end{aligned}$$

The parameter  $D$  obtained from the experimental spectrum has to be rationalized in the following way: The interelectron vector is parallel to the plane of the ring and hence normal to the 4-fold axis of the molecule. The experimental  $D$  and  $g$  tensors are obtained in the same principal axis system with the  $Z$  axis being parallel to the 4-fold symmetry axis. Hence the ZFS tensor has to be recalculated with the interelectron axis on the  $Z$  axis.

Considering an axially symmetric Hamiltonian with Zeeman and zero-field interaction only, we have

$$H = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D_{\perp}(S_x^2 + S_y^2) + D_{\parallel}S_z^2 \quad (3)$$

In terms of  $D$  and  $E$  the Hamiltonian is

$$H = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) \quad (4)$$

where  $D = \frac{3}{2}D_{\parallel}$  or  $D_{\parallel} = 640 \text{ MHz}$ . Here the  $D$  and  $g$  terms are expressed in the same principal axis system with the 4-fold symmetry axis as the  $z$  axis. The interelectron axis is in the plane of the porphyrin ring. Hence if we express the ZFS tensor along the interelectron axis, ( $z'$ ):

$$D_{x'x'} = D_{y'y'} = -D_{z'z'}/2$$

Hence

$$D_{\parallel} = D_{x'x'} = D_{y'y'} = -D_{z'z'}/2$$

$$D_{z'z'} \text{ (in MHz)} = 1.298 \times 10^4 g^2/R^3 \quad (5)$$

where  $R$  is expressed in angstroms and  $g^2 = (g_{\parallel}^2 + 0.5g_{\perp}^2)$ . We have assumed here that the entire ZFS interaction arises from the dipolar coupling between the two electrons. This assumption is justified since for the exchange interaction  $J \ll KT$ . An interelectron distance of  $3.88 \pm 0.05 \text{ \AA}$  has been obtained in this way, which agrees very well with the earlier estimate of the same using relaxation matrix theory.<sup>24</sup> The interelectron distance can be interpreted in terms of one electron being in the center (d-electron) and the other ( $\pi$ -electron) in the periphery of the porphyrin ring. This corresponds to the  $\pi$ -electron having the spin densities mostly on the peripheral carbon atoms, which is possible for an  $a_{1u}$  ground state for the unpaired  $\pi$ -electron. This is a likely choice for the ground state of the unpaired electron, since the radical cations of a metallo-OEP type system all have an  $a_{1u}$  ground state for the unpaired  $\pi$ -electron while the meso-substituted metalloporphyrin radical cations (TPP) have an  $a_{2u}$  ground state. Additional confirmation of the above assignment comes from the EPR study of the radical species obtained on irradiation of VO(TPP).<sup>26</sup> A strong half-field line has been reported for this system, while the  $g = 2$  region is masked by the signal of the unoxidized species. In our system, only a weak half-field line has been obtained. Considering the fact that the intensity of the half-field line is proportional to the ZFS parameter, we can summarize that the interelectron distance in  $[\text{VO}(\text{MESO})]^+$  is larger than that in  $[\text{VO}(\text{TPP})]^+$ . The shorter interelectron distance in  $[\text{VO}(\text{TPP})]^+$  is consistent with the assignment of the unpaired  $\pi$ -electron to an  $a_{2u}$  orbital of the porphyrin, which has been shown to be the case for many other metallo-TPP radical cations. A similar conclusion has been reported from the resonance Raman studies on vanadyl OEP radical cation.

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## References and Notes

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