Insensitivity of Vanadyl−Oxygen Bond Strengths to Radical Type ($^2A_{1u}$ vs $^2A_{2u}$) in Vanadyl Porphyrin Cation Radicals

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Resonance Raman (RR) spectra are reported for vanadyl octaethylporphyrin, OV(OEP), tetramesityltetramethylporphyrin, OV(TMTMP), and tetramesitylporphyrin, OV(TMP), and their corresponding π-cation radicals obtained by chemical and electrochemical oxidation. The behavior of the ν_2 RR porphyrin "marker band", which moves to higher frequency upon oxidation of the OV(OEP) and OV(TMTMP) and to lower frequency for OV(TMP), shows that the resultant cation radicals have predominantly $^2A_{1u}$ and $^2A_{2u}$ ground states, respectively. In contrast to earlier work (Macor, K. A.; Czernuszewicz, R. S.; Spiro, T. G. *Inorg. Chem.* **1990**, *29*, 1996), it is demonstrated here that the shift of the $\nu(V=O)$ *is insensitive to radical type*, behavior which is in agreement with similar studies of the ferryl analogues (Czarnecki, K.; et al. *J. Am. Chem. Soc.* **1996**, *116*, 2929 and 4680). It is suggested that the observed downshifts of the $\nu(V=O)$ previously reported for RR spectra of vanadyl porphyrin π-cation radicals, relative to their neutral parents, are most reasonably ascribed to trans oxo ligand coordination (most probably a water molecule) during low-temperature electrochemical oxidation of the neutral species.

Introduction

A key intermediate in the enzymatic cycles of many oxidative heme enzymes such as peroxidases, catalases, and the cytochromes P450 is a highly oxidized, ferryl heme.[1] In addition, there is considerable interest in utilizing metal−oxo porphyrin catalysts in oxidaton reactions, including water splitting and hydrocarbon oxidation.[2] There is now much evidence accumulated to suggest that certain of these enzymatic and catalytic intermediates are most accurately formulated as metal−oxo porphyrin π-cation radicals in which one of the oxidizing equivalents is centered on the macrocycle ring system.[1−3]

Depending on relative energies of the two (nearly degenerate) highest occupied molecular orbitals (HOMO), the ground electronic state of the radical can be approximately described as $^2A_{1u}$ or $^2A_{2u}$, the energies being dictated by such factors as position and type of peripheral substituents, the nature of the trans-axial ligand and the identity of the central metal ion.[2−4] An issue of importance for understanding the diverse chemical reactivity of various heme enzyme intermediates, as well as for rational design of specific oxidative catalysts, is the extent to which the radical type ($^2A_{1u}$ or $^2A_{2u}$) can affect the inherent reactivity of the metal−oxo fragment.

Resonance Raman (RR) spectroscopy is potentially an ideal technique for addressing such issues in that it not only can provide direct documentation of the strength of the metal−oxo bond via strong enhancement of the $\nu(M-O)$ stretching frequencies, but also is effective in characterizing the nature of the electronic ground state of the radicals based on the frequencies observed for the so-called "marker modes" which are, in some cases, quite sensitive to structure and π-electron density.[4] These Raman studies of ferryl porphyrins and ferryl porphyrin π-cation radicals were facilitated by carefully conducted resonance Raman studies of neutral metalloporphyrins[5] and their corresponding π-cation radicals.[6]

Following early studies by Nakamoto and co-workers,[7] which first documented the frequencies (852−861 cm^{-1}) of the $\nu(Fe=O)$ modes of ferryl porphyrins in low-temperature inert matrixes, several other groups succeeded in observing frequen-

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cies ranging between 800 and 846 cm^{-1}, depending on the solvent and axial ligation.[4]

Subsequent studies by several other groups reported the RR spectra of the more highly oxidized ferryl porphyrin π-cation radicals, though controversies arose regarding the effects of environment, axial ligation, and apparent photosensitivity of these species.[8] In an attempt to avoid complications associated with the inherently high reactivity (poor stability) of the ferryl porphyrin radical species, Spiro and co-workers[9] exploited the relatively greater stability of the vanadyl porphyrin radicals so as to facilitate systematic studies of the roles played by solvent and radical type in determining the frequencies of the $\nu(V=O)$ mode. One of the more interesting facts emerging from the studies of the vanadyl systems was the reported observation that the inherent frequency of the $\nu(V=O)$ mode is dependent on the nature of the electronic ground state of the radical; i.e., it was reported that $\nu(V=O)$ shifts to higher frequency (relative to the neutral vandyl porphyrin) for a $^2A_{1u}$ cation, such as OV-(OEP$^{\bullet+}$), but to lower frequency for a $^2A_{2u}$ cation, such as OV-(TMP$^{\bullet+}$).[9b]

In recent years similar systematic RR studies have been reported for the ferryl porphyrin radicals,[10] certain of the results being in apparent conflict with the earlier results for the vanadyl systems. Specifically, the $\nu(Fe=O)$ modes of both $^2A_{1u}$ and $^2A_{2u}$ radical species were observed to occur at virtually identical frequencies; i.e., the frequency shift of the $\nu(Fe=O)$ mode upon oxidation was found to be insensitive to radical type. Inasmuch as the presence and nature of a (sixth) trans-axial ligand can have a substantial effect on the frequency of the $\nu(M=O)$ mode,[9a,10a] a plausible explanation for the apparent discrepancy between the ferryl and vanadyl systems is the possibility of uncontrolled differences in axial ligation between the different types of vanadyl poprhyrin radicals studied in the earlier works.[9b] Consequently, the present work was undertaken in an attempt to clarify these apparent discrepancies by conducting studies of both $^2A_{1u}$ and $^2A_{2u}$ vanadyl poprhyrin radicals under carefully controlled conditions so as to ensure identical axial ligation effects. In contrast to the earlier work, the data acquired in the present work clearly demonstrate that, as in the case of the ferryl analogues,[10] oxidation-induced frequency shifts of the $\nu(V=O)$ in the vanadyl porphyrin systems, $\Delta\nu_{ox}$, is rather insensitive to radical type, thus resolving the apparent controversy.

Experimental Section

Materials and Methods. Vanadyloctaethylporphyrin, OV(OEP), was purchased from MidCentury Chemicals (Posen, IL) and purified on a thin-layer silica column developed with benzene. 5,10,15,20-Tetramesitylporphyrin (H$_2$TMP) was synthesized by the literature method.[11] Its vanadyl compound [^{16}OV(TMP)] was synthesized by the method of Buchler et al.[12] with some modifications. H$_2$TMP (250 mg) was placed in a 25 mL round-bottom flask together with oxovanadium(IV) acetylacetonate, [OV(acac)$_2$] (600 mg), and phenol (5 g) and heated at 200 °C. After 5 h, the hot mixture was poured into water and OV-(TMP) was extracted with chloroform. The organic layer was separated, washed with 0.1 M HCl and then with 0.1 M NaOH followed by washing with distilled water, and dried over sodium sulfate. The chloroform solvent was evaporated on a rotary evaporator, following which the crude OV(TMP) was dissolved in methylene chloride, purified on silica gel column, and recrystalized from methylene chloride/methanol; yield: 206 mg. ^{18}OV(TMP) was prepared under a nitrogen atmosphere by a modification of a previously published procedure;[13] i.e., OV(TMP) (90 mg) was dissolved in dry toluene (8 mL), and thionyl chloride (1 mL) was added to the solution which gradually turned from red to brown. The reaction mixture was stirred for 12 h at room temperature and then placed in a freezer (−28 °C) for 12 h. The resulting precipitate [i.e., VCl$_2$(TMP)] was filtered off, washed with hexane, and dried in a vacuum desiccator. The porphyrin was then dissolved in 10 mL of dry toluene, 200 μL of H$_2$^{18}O (Isotec Inc., 98.8% ^{18}O atom) was added, and the reaction mixture was stirred for 3 h and then neutralized with solid NaHCO$_3$. After filtration, the resultant product was dissolved in methylene chloride, purified on a silica gel column and recrystallized from methylene chloride/methanol; yield: 67 mg. 2,7,12,17-Tetramethyl-3,8,13,18-tetramesitylporphyrin (H$_2$-TMTMP) and its *meso*-carbon deuterated analogue (H$_2$TMTMP-d_4) were synthesized according to the literature methods.[14] VO(TMTMP) and its deuterated analogue were obtained by using the procedure described above.[12] Phenoxathiinylium hexachloroantimonate (Phx-SbCl$_6$), used as an oxidant, was prepared by the previously published procedure.[15] Methylene chloride used as a solvent in OV(OEP) and OV(TMTMP) experiments was purchased from Aldrich (spectrophotometric grade) and purified as described previously.[10b,16] Methylene chloride used for OV(TMP) experiments was distilled over calcium hydride, CaH$_2$, prior to use.

Oxidation Reaction. Chemical oxidation of oxovanadylporphyrins was carried out using the following procedure. The π-cation radicals of OV(OEP), OV(TMTMP), and its *meso*-deuterated analogue were obtained at room temperature by dissolving the neutral vanadyl porphyrin in dry, freshly distilled methylene chloride to a final concentration of approximately 10^{-3} M. A 0.5 mL amount of this solution was then transferred into a standard NMR tube, and an approximately 5-fold excess of Phx-SbCl$_6$, dissolved in dry CH$_2$Cl$_2$, was added to the porphyrin solution by using a gastight syringe. The sealed tube was quickly shaken to form the cation radical. The experiment in which OV(OEP) was oxidized at room temperature with "wet" Phx-SbCl$_6$ was performed in a similar way using methylene chloride which contained traces of water. In contrast to OV(OEP$^{\bullet+}$) and OV(TMTMP$^{\bullet+}$), the π-cation radical of OV(TMP) is not stable at room temperature. Thus, a small portion of OV(TMP) was placed in a Dewar cell, air was evacuated from it, dry, freshly distilled, methylene chloride was transferred into the cell, and the contents were stirred

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until the vanadyl porphyrin was completely dissolved. Then the solution was cooled to -80 °C and approximately a 4-fold excess of Phx-SbCl$_6$, dissolved in cold methylene chloride, was added using a gastight syringe while stirring was continued.

The electrochemical oxidation of OV(OEP) at room temperature and OV(TMP) at -70 °C were performed with a specially design three-electrode Raman spectroelectrochemical cell[17] using the procedure described previously.[9]

Spectroscopic Measurements. Room-temperature RR measurements were performed using a spinning standard NMR tube with a cylindrical lens set up to minimize possible thermal or photodecomposition of the sample. RR spectra of OV(OEP), OV(TMTMP), OV(TMTMP-d_4) and their radicals were obtained with the 406.7 nm line of a Coherent model Innova 100-K3 krypton ion laser as an excitation source with a power of $5-10$ mW at the sample. RR spectra were acquired with a SPEX model 1269 single monochromator fitted with an UV-enhanced CCD detector (Princeton Instrumets, Princeton, NJ) and notch filter (Kaiser Optical, Ann Arbor, MI). The frequencies were calibrated with known frequencies of toluene and fenchone (Spectra Calc program, Galactic, Galactic Industries Corporation). RR spectra of π-cation radicals were collected sequentially and then summed. Those files which exhibited new features ascribable to thermal or photodecomposition were not included in the summation. RR spectra of ^{16}OV(TMP), ^{18}OV(TMP), and their cation radicals were recorded in a low-temperature Dewar cell (-80 °C). Excitation at 406.7 nm from a Coherent model Innova 100-K2 krypton ion laser was used with the power of 15 mW at the sample. The scattered photons were collected with a SPEX model 1403 double monochromator equipped with a Hamamatsu 928 photomultiplier tube. The accuracy of frequency readings for all presented RR spectra is ± 1 cm^{-1}.

Results

A. ^{2}A$_{1u}$ Systems. Vanadyl Octaethylporphyrin, OV(OEP). In Figure 1 are shown the observed RR spectra for OV(OEP) and its corresponding OV(OEP$^{\bullet+}$) cation radicals measured at room temperature. The relative intensities and frequencies observed here are quite similar to those previously published.[9b] The important issues to note are the fact that, upon oxidation, the ν_2 mode, occurring at 1584 cm^{-1} in the neutral parent (top spectrum), shifts up to 1602 cm^{-1} for the chemically oxidized species (middle and bottom spectra), behavior that is characteristic of an ^{2}A$_{1u}$ porphyrin cation radical.[4,6,10] It is also noted that the ν(V=O) mode observed at 991 cm^{-1} for OV(OEP) also shifts up to 1004 cm^{-1} upon oxidation, i.e., $\Delta\nu_{ox} = 13$ cm^{-1}, when dry, freshly distilled, methylene chloride is used as a solvent (middle spectrum). However, when the oxidation reaction was done in wet methylene chloride, i.e., traces of water were present in the reaction solution, a new band emerged at 978 cm^{-1} (bottom spectrum) that is assigned to the ν(V=O) of a six coordinate species discussed later.

Vanadyl Tetramesityltetramethylporphyrin, OV(TMT-MP). As we have shown previously, metal complexes of the TMTMP macrocycle, upon oxidation, yield ^{2}A$_{1u}$ type cation radicals.[10b,18] The RR spectra depicted in Figure 2 are consistent with this expectation. Thus, the ν_2 mode occurs at 1587 cm^{-1} for the neutral parent and shifts to higher frequency by $\sim$16 cm^{-1} upon oxidation, being observed at 1603 cm^{-1} in the case of OV(TMTMP$^{\bullet+}$). It is noted that the assignment of the ν_2 is supported by the expected[5,6] lack of sensitivity to methine bridge deuteration, as is evident from the virtually identical frequencies observed for the d_4 analogues. As in the case of the OV(OEP)/OV(OEP$^{\bullet+}$) pair, the ν(V=O) of the OV(TMTMP)/OV(T-

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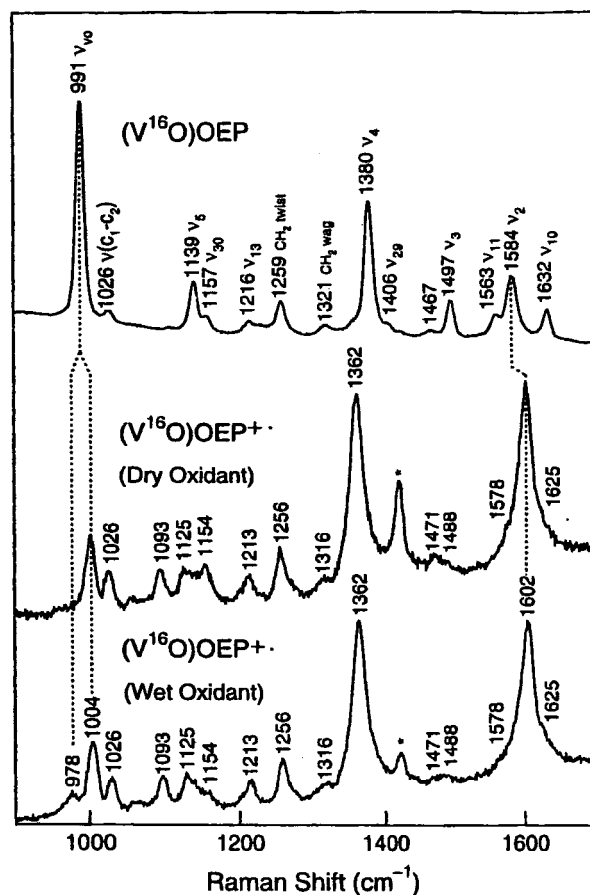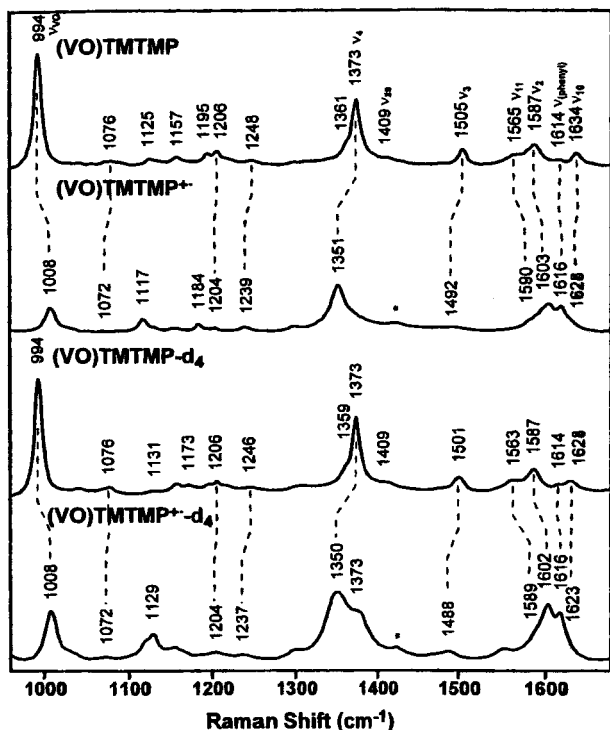

Figure 1. Resonance Raman spectra of OV(OEP) and its π-cation radicals formed by oxidation with Phx-SbCl$_6$ in dry (middle trace) and wet (bottom trace) methylene chloride measured at room temperature. Asterisks indicate CH$_2$Cl$_2$ solvent band.

MTMP$^{\bullet+}$) pair experiences a shift to higher frequency by 14 cm^{-1}, i.e., $\Delta\nu_{ox} = 1008-994 = 14$ cm^{-1}. Thus, the ν_{VO} for both ^{2}A$_{1u}$ cation radicals shifts to higher frequencies by a comparable amount upon oxidation (by $12-14$ cm^{-1}).

B. ^{2}A$_{2u}$ Systems. Vandyl Tetramesitylporphyrin, OV-(TMP). Shown in Figure 3 are the spectra, acquired at low temperature, for OVTMP and OV(TMP$^{\bullet+}$). The ν_2 mode appears as a very strong feature located at 1559 cm^{-1} for the neutral parent. Upon oxidation, there is a general loss of intensity which is characteristic for metalloporphyrin cation radicals and the ν_2 appears at 1512 cm^{-1}, assignments for *meso*-aryl porphryins having been established previously.[4,6,8,10] Thus, in this case, the RR spectra document the ^{2}A$_{2u}$ formulation for OV(TMP$^{\bullet+}$), yielding a substantial shift to lower frequency for ν_2. However, in contrast to the previous study,[9b] which yielded a shift to lower frequency for ν(V=O) of OV(TMP$^{\bullet+}$), compared to its value for OV(TMP), the present results clearly document a shift to higher frequency for ν(V=O) upon oxidation; i.e., from 997 cm^{-1} for OV(TMP) to 1012 cm^{-1} for OV(TMP$^{\bullet+}$). While some ambiguity arises for the assignment of ν(V=O) for the ^{16}OV-(TMP$^{\bullet+}$) owing, to the close overlap with porphyrin mode ν_6, the results for the ^{18}O-labeled analogue are not compromised by this overlap, the isolated ν(V=O) shifting from 953 to 970 cm^{-1} upon oxidation, i.e., $\Delta\nu_{ox} = 17$ cm^{-1}.

Discussion

Bond Polarization Effects. In the absence of complicating factors, an increase in the ν_{VO} stretching frequency is expected upon oxidation to the cation radical, simply on the basis of bond

Figure 2. Resonance Raman spectra of OV(TMTMP), its π-cation radical, its meso-deuterated analogue, OV(TMTMP-d_4), and its π-cation radical in dry, freshly distilled, methylene chloride measured at room temperature. The π-cation radicals were obtained by chemical oxidation of the parent complexes with Phx-SbCl$_6$. Asterisks indicate CH$_2$Cl$_2$ solvent band.
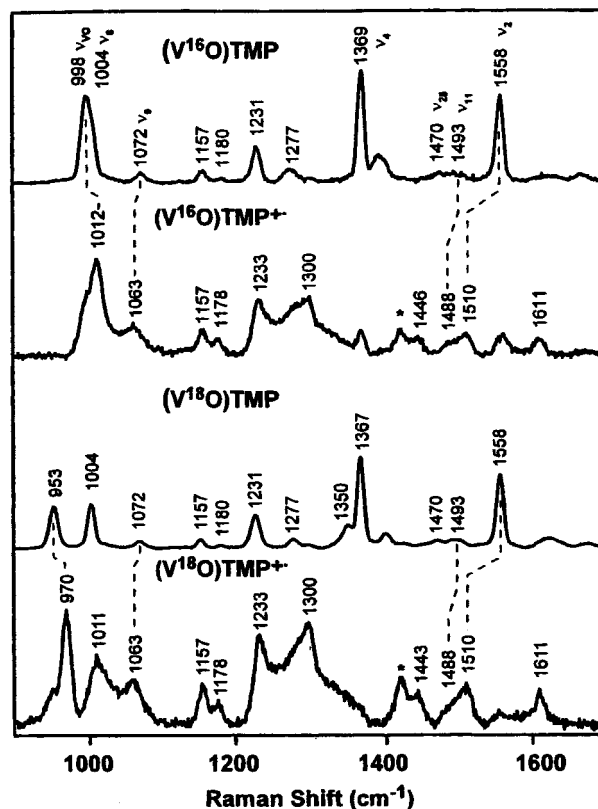

Figure 3. Resonance Raman spectra of ^{16}OV(TMP), ^{18}OV(TMP), and their π-cation radicals, respectively, in dry, freshly distilled, methylene chloride measured at -80 °C. The π-cation radicals were obtained by chemical oxidation of the parent complexes with Phx-SbCl$_6$. Asterisks indicate CH$_2$Cl$_2$ solvent band.

polarization effects.[9b,19] In the vanadyl fragment, the O^{2-} ligand acts as a σ and π electron donor to the V^{4+} ion, the p$_\pi$ orbitals (p$_x$ and p$_y$) on the oxygen interacting with the d$_\pi$ orbitals (d$_{xz}$ and d$_{yz}$). The nonbonding d$_{xy}$ orbital accommodates the single d electron of the V^{4+} and the d$_{z^2}$ and d$_{x^2-y^2}$ antibonding orbitals (with respect to the V$-$O and V$-$N pyrrole bonds) are of high energy. Removal of a porphyrin π orbital electron occurs upon oxidation.[20,21] The oxidized porphyrin donates less electron density to the V^{4+} ion, increasing the O$\rightarrow$V donation, resulting in a stronger V$-$O bond and correspondingly higher ν(V$=$O) stretching frequency.

To the extent that the a$_{2u}$ orbital concentrates charge on the N pyrrole atoms, while the a$_{1u}$ orbital has nodes at these positions,[3,6] this inductive effect of oxidation on the ν(V$=$O) is expected to be larger for ^{2}A$_{2u}$ compared to the ^{2}A$_{1u}$ systems. That this expectation is realized in the present results is confirmed by the observation of the slightly larger $\Delta\nu_{ox}$ observed for the OV(TMP)/OV(TMP$^{\bullet+}$) pair (17 cm^{-1}) compared to that observed for both ^{2}A$_{1u}$ systems [OV(OEP)/OV(OEP$^{\bullet+}$) and OV-(TMTMP)/OV(TMTMP$^{\bullet+}$)], where $\Delta\nu_{ox} = 12-14$ cm^{-1}.

Axial Ligand Effects. In the previous study of the RR spectra of vanadyl porphyrin π-cation radicals, wherein the radicals were generated electrochemically, the ^{2}A$_{2u}$ systems such as OV-(TMP$^{\bullet+}$) were observed to yield a decreased ν(V$=$O) frequency ($\nu = 982$ cm^{-1}) relative to the value for the neutral parent ($\nu = 998$ cm^{-1}); i.e., $\Delta\nu_{ox} = -16$ cm^{-1}.[9b] While rather convincing

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arguments, invoking symmetry lowering and orbital mixing effects, were made to satisfactorily account for the observed downshifts, the results presented in the present work, employing a chemical oxidant, document the shifts to higher frequency expected on the basis of bond polarization effects alone and thus eliminate the need to postulate lowered symmetry.

What remains to be addressed is the reason for the apparent discrepancy between the present results for the chemically generated OV(TMP)/OV(TMP$^{\bullet+\bullet}$) system and the previously reported results for the electrochemically generated OV(TMP)/OV(TMP$^{\bullet+}$) and OV(TPP)/OV(TPP$^{\bullet+\bullet}$) systems.[9b] As noted in the Results section, we emphasize the fact that the observations previously reported for the electrochemically generated radicals have been reproduced in the present work (data not shown) and the ν(V$=$O) is indeed observed to shift to lower frequency, appearing at 982 cm^{-1}, a value which is $\sim$30 cm^{-1} lower than that observed for the chemically oxidized species. Significantly, this difference of $\sim$30 cm^{-1} is, in fact, precisely the same magnitude of the difference observed for the ν(Fe$=$O) frequencies of ferryl π-cation radicals bearing different axial ligands.[10a] Thus, for OFe(TMP$^{\bullet+}$)(Cl$^-$) the ν_{FeO} appears at $\sim$801 cm^{-1}, whereas the ν(Fe$=$O) of the perchlorate analogue, OFe(TMP$^{\bullet+}$)-(ClO$_4^-$), is observed at $\sim$835 cm^{-1}.

The most reasonable explanation for the differences observed for the chemically generated OV(TMP$^{\bullet+}$) (this work) and the electrochemically generated OV(TMP$^{\bullet+}$) (this work and ref 9b) is that, in the latter case, the generated radical contains a relatively strong sixth axial ligand, whereas in the former case only the (weakly ligating) counteranion, SbCl$_6^-$, is associated with the radical. While it is true that vanadyl complexes show a strong preference for five-coordination, it is also known that

metalloporphyrin π-cations have a greater tendency to coordinate axial ligands relative to their neutral parents (to balance overall positive charge). In fact, it is a six-coordinate aquovanadyl porphyrin π-cation radical that is isolated from solution upon crystallization.[20]

Temperature effects alone cannot account for the discrepancy since the chemical oxidation of OV(TMP) and the electrochemical generation of the OV(TMP$^{\bullet+}$), both conducted at the same (low) temperature, yielded different frequencies. Interestingly, contamination by (strong) donor ligands did not occur in the case of the electrochemically generated OV(OEP$^{\bullet+}$) complex; i.e., chemical and electrochemical oxidation yielded identical spectra. Significantly, in this case, both oxidations were conducted at room temperature. Thus, the most likely explanation for the apparent discrepancy in the $^2A_{2u}$ case is that the electrochemical cell used for the oxidation produced contaminating donor ligand only at low temperature, perhaps by condensation of atmospheric H_2O. In support of this view, it is noted that when a small amount of water is added to the solution used for chemical oxidation of OV(OEP), the resulting OV-(OEP$^{\bullet+}$) exhibited an additional RR band at 978 cm^{-1} (Figure 1). This is the same frequency as the ν(V=O) of π-cation radicals of OV(TPP) and OV(TMP) generated by electrochemical oxidation of the parent complexes at low temperature.[9b] Thus, it seems likely that the apparent differences observed for the $^2A_{1u}$ and $^2A_{2u}$ systems in the previous study, wherein the radicals were generated electrochemically at the two different temperatures, arose because of contamination by a relatively strong axial ligand, such as H_2O or Cl^-, in the low-temperature experiments. The results of the present work, wherein such contaminating ligands are eliminated, is consistent with similar studies of the corresponding ferryl π-cation radicals,[10] which demonstrated the lack of sensitivity of $\nu_{Fe=O}$ to porphyrin ground-state configuration (i.e., $^2A_{1u}$ or $^2A_{2u}$).