

Trans-dioxo Manganese(V) Porphyrins

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Transition metal oxo-species have been the focus of extensive studies because of their relevance to the redox biochemistry of dioxygen as well as myriads of oxidative catalytic processes. High valent oxo-manganese complexes have been described for porphyrin,¹ salen,² corrole,³ corrolazine,⁴ and non-heme systems.⁵ The O=Mn^V moiety has been suggested in the photosynthetic water oxidation process,⁶ and a bridged Mn^V porphyrin dimer has recently been demonstrated to oxidize water into dioxygen.⁷

We have previously described low-spin d² oxomanganese(V) porphyrin complexes that display an extraordinary range of reactivity toward oxo-transfer as a function of prototropic equilibria involving the axial ligand.⁸ A prediction of that work was that oxo-aqua and oxo-hydroxo-manganese(V) intermediates are reactive oxidants while the stable species observed at high pH are trans-dioxo complexes. Here we provide the first definitive spectroscopic evidence for *trans*-dioxomanganese(V) porphyrins [O=Mn^V=O]. Further, we show that protonation of these species affords the reactive intermediates usually associated with these catalytic systems (Scheme 1).

Oxidation of Mn^{III}-5,10,15,20-tetramesitylporphyrin (Mn^{III}TMP) with 1.2 equiv of H₂O₂ in CD₃CN/CD₂Cl₂ containing excess tetrabutylammonium hydroxide (TBAH), in a variation of the conditions reported previously by us^{8d} and recently by Nam et al.,⁹ yielded a solution with sharp, well-resolved ¹H NMR resonances typical of a diamagnetic oxoMn^V complex (Figure S1). Intriguingly, the ortho-methyl resonance of the mesityl substituent appeared as a sharp singlet at δ 1.87, in contrast to the *two*, well-resolved singlets observed for the isoelectronic oxoCr^{IV}TMP and nitridoMn^V-TMP.¹⁰ The equivalence of the ortho-methyl protons in Mn^VTMP could result from a compound of C_{4v} symmetry with rapid axial ligand interchange, such as by oxo-hydroxo tautomerism.¹¹ Alternatively, a D_{4h} symmetric compound with identical axial ligands, such as a *trans*-dioxo arrangement [O=Mn^V=O], would also display these features. Significantly, the ortho-methyl signal remained sharp with no evidence of exchange broadening even at -20 °C. This observation suggests either that oxo-hydroxo tautomerism is unusually fast, even at this low temperature in an aprotic medium, or that the *trans*-dioxo formulation is the correct one.

Confirmation of the D_{4h} symmetry of the oxidized Mn^V porphyrin species and assignment of the structure as a *trans*-dioxoMn^V complex were made on the basis of the Raman and IR spectra. Figure 1a shows Raman spectra of Mn^V tetrapentafluorophenylporphyrin (Mn^VTPFPF) generated by oxidation of Mn^{III}TPFPF with H₂O₂. Oxidation with H₂¹⁸O₂ in H₂¹⁸O caused the band at 743 cm⁻¹ to shift to 699 cm⁻¹. This isotopic shift (44 cm⁻¹) is considerably larger than expected for a simple, terminal Mn=O stretch (33 cm⁻¹) but is close to the calculated value for a *linear triatomic model*, ¹⁸O=Mn=¹⁸O (42 cm⁻¹).

Oxo-hydroxo tautomerism was introduced by Meunier to explain the pattern of ¹⁸O-exchange into oxidized substrates mediated by water-soluble manganese porphyrins.¹¹ We utilized this concept to generate *half-labeled* dioxo-Mn^V porphyrins. Raman spectra for

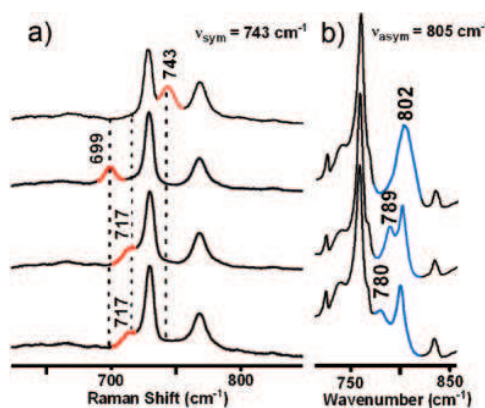
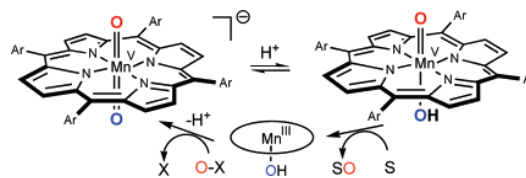


Figure 1. (a) RR spectra of [Mn^V(O)₂TPFPF]⁻ generated with (from top to bottom) 1.2 equiv H₂O₂ in H₂O, H₂¹⁸O₂ in H₂¹⁸O, H₂¹⁶O₂ in H₂¹⁸O, and H₂¹⁸O₂ in H₂¹⁶O, respectively, in a 9:1 (v/v) CH₃CN/H₂O containing 10 mM TBAH. (b) IR spectra of solid [Mn^V(O)₂TPFPF]⁻[NR₄]⁺ generated with (from top to bottom) H₂O₂ in H₂O, H₂¹⁸O₂ in H₂¹⁶O, and H₂¹⁸O₂ in H₂¹⁸O, respectively (see Supporting Information, Figures S3 and S8).

Scheme 1



Mn^VTPFPF prepared using either H₂¹⁶O₂ in H₂¹⁸O or H₂¹⁸O₂ in H₂¹⁶O showed identical features (Figure 1a): the 743 cm⁻¹ band shifted to 717 cm⁻¹, in good agreement with the 22 cm⁻¹ shift predicted for ¹⁶O=Mn=¹⁸O. The 717 cm⁻¹ band retained its intensity during the RR experiments (~10 min), indicating that oxygen exchange with bulk water is very slow. Moreover, the ν_{sym}(O=Mn^V=O) band is very sharp, with a half width of only 9 cm⁻¹ that was unaffected by D₂O. By contrast, [O=Mn^{IV}(OH)-TDMImp]³⁺¹² has ν_{sym} at 731 cm⁻¹ and a half width of 50 cm⁻¹ that sharpened to 25 cm⁻¹ in D₂O (Supporting Information, Figure S7). We have previously ascribed the broadening of HO-M=O Raman bands to a combination of M-OH hydrogen bonding and oxo-hydroxo tautomerism,¹³ features that are absent in [O=Mn^V=O].

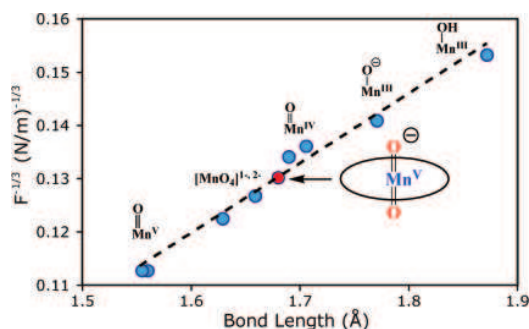
The symmetrical O=Mn^V=O stretching frequencies for four other Mn^V porphyrins were also assigned (Table 1). In each case we were able to prepare the respective half labeled and fully labeled dioxo complexes. The ν_{sym}(O=Mn^V=O) values (741–744 cm⁻¹) are comparable to ν(Mn^{IV}=O) in oxoMn^{IV} porphyrins such as O=Mn^{IV}TMP (754 cm⁻¹), [O=Mn^{IV}(OH)TM-4-PyP]³⁺ (711 cm⁻¹),^{13a} or [O=Mn^{IV}(OH)TDMImp]³⁺ (731 cm⁻¹), but significantly lower than five-coordinate triple-bonded O=Mn^V corrolazine or tetraamido complexes (970–981 cm⁻¹).^{4,14} As can be seen, ν_{sym} is insensitive to the nature of the meso substituent. Similar observations have been made for structurally related dioxo

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Table 1. Raman Data for Dioxo Manganese(V) Porphyrins

manganese porphyrins	$\Delta(\nu^{16}\text{O})/\text{cm}^{-1}$			meso-substituents
	$\nu^{16}\text{O}/\text{cm}^{-1}$	half-labeled	fully-labeled	
MnTDCPP ^a	741	21	39	2,6-dichlorophenyl
MnTPFP ^a	743	26	44	pentafluorophenyl
MnTMP ^b	741	25	44	2,4,6-mesityl
MnTDMImP ^c	744	24	40	<i>N,N</i> -dimethyl-imidazolium-2-yl
MnTM-2-PyP ^c	744	26	41	<i>N</i> -methyl pyridinium-2-yl

^a Solvents: 9:1 (v/v) CH₃CN/H₂O, 10 mM TBAH. ^b Solvents: CH₃CN, 10 mM TBAH. ^c Solvents: H₂O, 100 mM NaOH.

**Figure 2.** Mn–O bond length vs $1/F_{\text{Mn-O}}^{1/2}$ (see Supporting Information).

Ru^{VI} porphyrins,¹⁵ while five-coordinate O=C^{IV} porphyrins or O≡Mn^V tetraamido complexes are more sensitive to ligand substituents.^{14,15}

The IR spectrum of Mn^VTPFP afforded strong confirmation of the Raman assignments (Figure 1b). The IR-active but Raman-inactive ν_{asym} for $^{16}\text{O}=\text{Mn}^{\text{V}}=\text{O}$ was found by band-fitting to be at 805 cm⁻¹. For the half-labeled sample, a prominent new band appeared at 789 cm⁻¹ and an adjacent porphyrin band at 802 cm⁻¹ sharpened significantly (expected half-labeled shift is 15 cm⁻¹). The fully labeled sample displayed a new band at 780 cm⁻¹, also in good agreement with the calculated shift of 29 cm⁻¹.

Taken together, the Raman, IR, and NMR data provide unequivocal evidence for a *D*_{4h}-symmetric *trans*-dioxoMn^V bonding arrangement in these compounds. Such dioxo complexes have been previously proposed by Su¹⁶ and us^{8b,c} for water-soluble oxoMn^V porphyrins on the basis of the pH-dependence of oxo-transfer rates, DFT calculations, and electrochemical studies.

It is instructive to compare the Mn–O stretching frequencies observed here to those of terminal monooxo-manganese complexes. On the basis of ν_{sym} and ν_{asym} , the oxo-manganese bond force constant (*F*) and stretch–stretch constant (*k*) for [Mn^V(O)₂TPFP]⁻ were determined to be 454 and 67.2 N/m, respectively. Application of Badger's rule^{17a} to the available data produces a very good correlation between *F*(Mn–O) and the bond length, spanning five Mn oxidation states (Figure 2). Green has recently reported a similarly good correlation for oxoiron(IV) porphyrin complexes.^{17b} As can be seen, the O=Mn^V=O porphyrin appears on the fitted line in the middle of the known range, using the recently reported EXAFS bond length,^{9,18} consistent with two equivalent manganese–oxygen double bonds.

Dioxo-Mn^VTPFP⁻, as prepared, is unreactive toward olefins, as we have found for water-soluble Mn^V-porphyrins at high pH.^{8b} However, neutralization of the excess base with 1 equiv of trifluoroacetic acid caused an instantaneous reaction with added cyclooctene at -70 °C. Cyclooctene oxide was formed in 66 ± 5% yield. Control reactions in the absence of acid yielded no epoxide. When [Mn^V(O)₂TPFP]⁻ was half-labeled with H₂¹⁸O₂ (in excess H₂¹⁶O), the epoxide product contained 40 ± 3% ¹⁸O, showing that oxo exchange with bulk solvent is slow compared to the protonation-induced epoxidation reaction.

The low reactivity of dioxo-Mn^V porphyrins can be readily understood to result from the net *negative* charge on the [Por-Mn^V(O)₂]⁻ unit and, as with other manganese, the need to protonate an oxo-ligand to transfer the other oxygen to the substrate, as we have proposed.^{8c} Charge is a powerful mediator of electrophilic reactivity. MonooxoMn^V corroles, corrolazines, and tetraamides are known to be poor oxygen atom donors because of the tri- or tetraanionic nature of the ligand. Under typically neutral catalytic conditions, dioxo-Mn^V species would be in acid–base equilibrium with the oxo-hydroxo and oxo-aqua forms. OxoMn^V porphyrins bearing no axial ligand [Por-Mn^V=O]⁺¹⁹ or bearing weak-field ligands, such as hydroxo, are expected to be responsible for substrate oxygenation with high reactivity.

These Mn^V porphyrins appear to be the only *trans*-dioxo-manganese compounds of any type to be spectroscopically characterized. *Trans*-dioxo metal complexes are typically found for low-spin d² second or third row metals such as Ru^{VI} and Mo^{IV}. It is apparent that a full understanding of the electronic structure and reactivity of high-valent manganese must include consideration of the *trans*-dioxo bonding mode, thus extending the known π -bonding arrangements found in first-row transition metals that were first discussed by Ballhausen and Gray.²⁰

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Supporting Information Available: Experimental details, NMR Raman, and IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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