Communication

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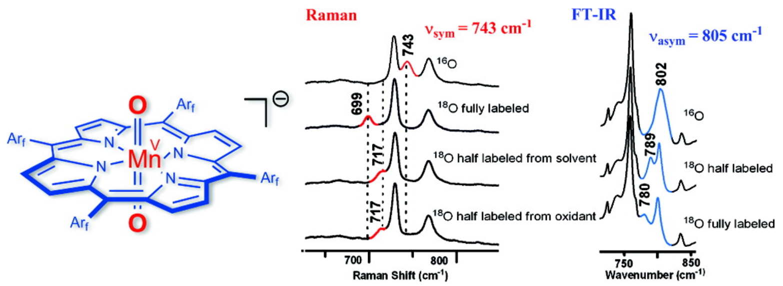
Ning Jin, Mohammed Ibrahim, Thomas G. Spiro, and John T. Groves

J. Am. Chem. Soc., **2007**, 129 (41), 12416-12417• DOI: 10.1021/ja0761737 • Publication Date (Web): 21 September 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Trans-dioxo Manganese(V) Porphyrins

Ning Jin, Mohammed Ibrahim,[§] Thomas G. Spiro,*,[§] and John T. Groves*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received August 15, 2007; E-mail: jtgroves@princeton.edu

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 d^2 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 H_2O_2 in CD_3CN/CD_2Cl_2 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^VTPFPP) generated by oxidation of Mn^{III}TPFPP with H_2O_2. Oxidation with $H_2{}^{18}O_2$ in $H_2{}^{18}O$ 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, $^{18}O{=}Mn{=}{}^{18}O$ (42 cm^{-1}).

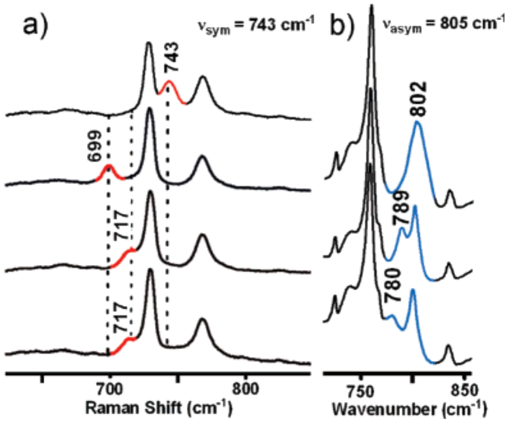
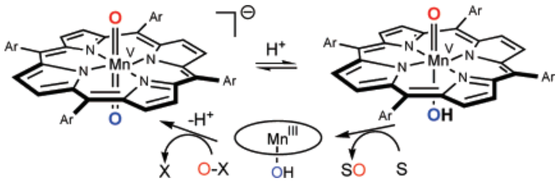


Figure 1. (a) RR spectra of $[Mn^V(O)_2TPFPP]^-$ generated with (from top to bottom) 1.2 equiv H_2O_2 in H_2O, $H_2{}^{18}O_2$ in $H_2{}^{18}O$, $H_2{}^{16}O_2$ in $H_2{}^{18}O$, and $H_2{}^{18}O_2$ in $H_2{}^{16}O$, respectively, in a 9:1 (v/v) CH_3CN/H_2O containing 10 mM TBAH. (b) IR spectra of solid $[Mn^V(O)_2TPFPP]^-$ $[NR_4]^+$ generated with (from top to bottom) H_2O_2 in H_2O, $H_2{}^{18}O_2$ in $H_2{}^{16}O$, and $H_2{}^{18}O_2$ in $H_2{}^{18}O$, respectively (see Supporting Information, Figures S3 and S8).

Scheme 1



Oxo-hydroxo tautomerism was introduced by Meunier to explain the pattern of ^{18}O-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 Mn^VTPFPP prepared using either $H_2{}^{16}O_2$ in $H_2{}^{18}O$ or $H_2{}^{18}O_2$ in $H_2{}^{16}O$ 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 $^{16}O{=}Mn{=}{}^{18}O$. 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 $\nu_{sym}(O{=}Mn^V{=}O)$ band is very sharp, with a half width of only 9 cm^{-1} that was unaffected by D_2O. By contrast, $[O{=}Mn^{IV}(OH)\text{-}TDMImP]^{3+}$ [12] has ν_{sym} at 731 cm^{-1} and a half width of 50 cm^{-1} that sharpened to 25 cm^{-1} in D_2O (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 $\nu_{sym}(O{=}Mn^V{=}O)$ values (741−744 cm^{-1}) are comparable to $\nu(Mn^{IV}{=}O)$ in oxoMn^{IV} porphyrins such as $O{=}Mn^{IV}TMP$ (754 cm^{-1}), $[O{=}Mn^{IV}(OH)TM\text{-}4\text{-}PyP]^{3+}$ (711 cm^{-1}),[13a] or $[O{=}Mn^{IV}(OH)TDMImP]^{3+}$ (731 cm^{-1}), but significantly lower than five-coordinate triple-bonded $O{\equiv}Mn^V$ 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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[§] Present address: Department of Chemistry, University of Washington, Seattle, Washington 98195.

10.1021/ja0761737 CCC: $37.00 © 2007 American Chemical Society

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

manganese porphyrins	$\nu(^{16}O)$/ cm^{-1}	$\Delta(^{16}O/^{18}O)/cm^{-1}$ half-labeled	fully-labeled	meso-substituents
MnTDCPP[a]	741	21	39	2,6-dichlorophenyl
MnTPFPP[a]	743	26	44	pentafluorophenyl
MnTMP[b]	741	25	44	2,4,6-mesityl
MnTDMImP[c]	744	24	40	*N*,*N*-dimethyl-imidazolium-2-yl
MnTM-2-PyP[c]	744	26	41	*N*-methyl pyridinium-2-yl

[a] Solvents: 9:1(v/v) CH_3CN/H_2O, 10 mM TBAH. [b] Solvents: CH_3CN, 10 mM TBAH. [c] Solvents: H_2O, 100 mM NaOH.

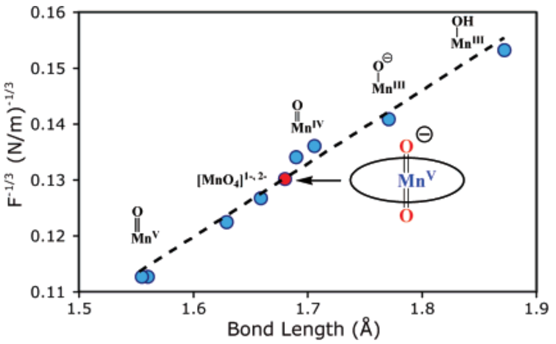

Figure 2. Mn−O bond length vs $1/F_{Mn-O}^{1/3}$ (see Supporting Information).

Ru^{VI} porphyrins,[15] while five-coordinate $O{=}Cr^{IV}$ porphyrins or $O{\equiv}Mn^{V}$ tetraamido complexes are more sensitive to ligand substituents.[14,15]

The IR spectrum of Mn^{V}TPFPP afforded strong confirmation of the Raman assignments (Figure 1b). The IR-active but Raman-inactive ν_{asym} for $^{16}O{=}Mn^{V}{=}^{16}O$ 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 Su[16] 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 $[Mn^{V}(O)_2TPFPP]^-$ 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-$Mn^{V}TPFPP^-$, 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 $[Mn^{V}(O)_2TPFPP]^-$ was half-labeled with $H_2{}^{18}O_2$ (in excess $H_2{}^{16}O$), the epoxide product contained 40 ± 3% ^{18}O, 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 $[Por\text{-}Mn^{V}\text{-}(O)_2]^-$ unit and, as with other manganates, 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 $[Por\text{-}Mn^{V}{=}O]^{+}$ [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*-dioxomanganese compounds of any type to be spectroscopically characterized. Trans-dioxo metal complexes are typically found for low-spin d^2 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]

Acknowledgment. Support of this research by the National Science Foundation (Grant CHE 0616633) is gratefully acknowledged.

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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JA0761737