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

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 ^{1}H NMR resonances typical of a diamagnetic oxo Mn[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[V]TMP 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*-dioxo Mn[V] complex were made on the basis of the Raman and IR spectra. Figure 1a shows Raman spectra of Mn[V] tetrapentafluorophenylporphyrin (Mn[V]TPFPP) 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}).

jtgroves@princeton.edu.
§Present address: Department of Chemistry, University of Washington, Seattle, Washington 98195.

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^{V}TPFPP 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 ν_{sym}(O=Mn=O) band is very sharp, with a half width of only 9 cm^{-1} that was unaffected by D$_2$O. By contrast, [O=Mn^V(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 D$_2$O (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=M=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=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 Ru^{VI} porphyrins,[15] while five-coordinate O=Cr^{IV} porphyrins or O=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=^{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)$_2$TPFPP]$^-$ 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)$_2$TPFPP]$^-$ was half-labeled with H$_2$^{18}O$_2$ (in excess

H_2 ^{16}O), the epoxide product contained $40 \pm 3\%$ ^{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-$Mn^V(O)_2$]$^-$ 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-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$_V$ porphryins 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 transdioxo bonding mode, thus extending the known π-bonding arrangements found in first-row transition metals that were first discussed by Ballhausen and Gray.[20]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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18. It is clear from the data presented herein that the Mn(V) complexes reported in ref [9] are also anionic, D_{4h}-symmetric dioxo species. We suspect that the broad RR bands reported there with smaller isotopic shifts (34 cm^{-1}) are those of O=Mn^{IV}-OH complexes derived from photoreduction (cf. ref [13]).

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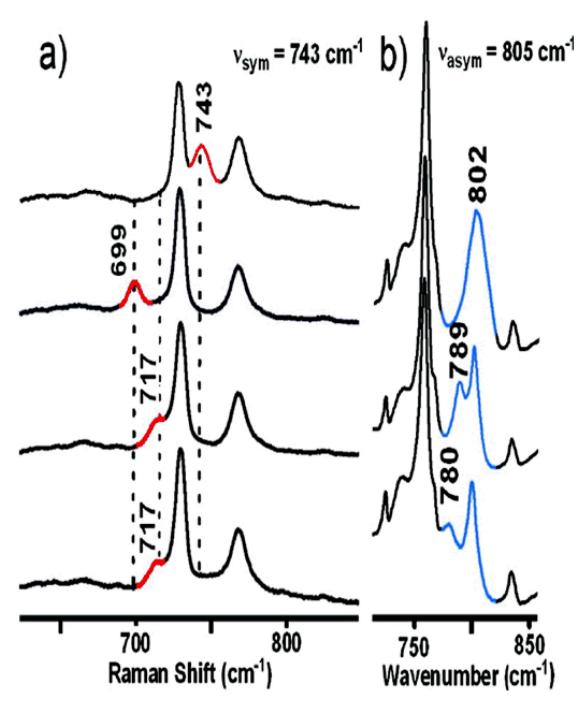
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Figure 1.
(a) RR spectra of $[Mn^V(O)_2TPFPP]^-$ generated with (from top to bottom) 1.2 equiv H_2O_2 in H_2O, $H_2\,^{18}O_2$ in $H_2\,^{18}O$, $H_2\,^{16}O_2$ in $H_2\,^{18}O$, and $H_2\,^{18}O_2$ in $H_2\,^{16}O$, respectively, in a 9:1 (v/v) CH_3CN/H_2O 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).
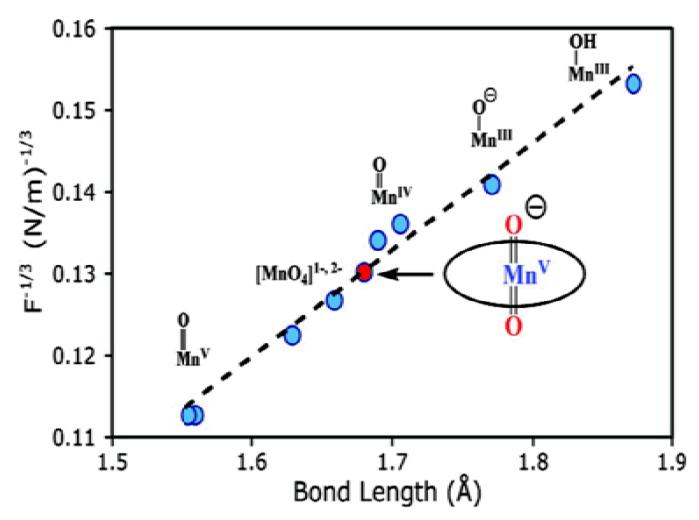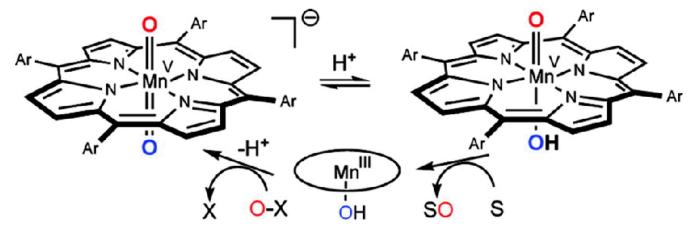
Figure 2.
MnO bond length vs $1/F_{Mn-O}^{1/3}$ (see Supporting Information).

Scheme 1.

Table 1

Raman Data for Dioxo Manganese(V) Porphyrins

manganese porphyrins	$\nu(^{16}O)/cm^{-1}$	$\Delta(^{16}O/^{18}O)/cm^{-1}$		meso-substituents
		half-labeled	fully-labeled	
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.