A non-porphyrinic, mononuclear oxomanganese(IV) complex was generated at room temperature and characterized by spectroscopic methods. The MnIV=O adduct is capable of activating C–H bonds by a H-atom transfer mechanism and is more reactive in this regard than most MnIV=O complexes.

High-valent oxomanganese adducts are suggested as active oxidants for synthetic and biological manganese catalysts, including those involved in textile and paper bleaching with H2O2 and oxygen evolution from water.1 Oxomanganese(IV) adducts with S = 0 and 1 spin states have been reported, and these invariably feature strongly electron-donating, anionic ligands.2 Oxomanganese(IV) complexes with neutral, non-porphyrinic ligands are comparatively less common.3 Detailed studies of substrate oxidation exist for a limited number of complexes.3d,e,f In addition, few MnIV=O complexes have been characterized by Mn K-edge X-ray absorption spectroscopy [XAS],4a,d a technique featuring prominently in the study of Mn enzymes1b and biomimetics.6 In this report, we describe the spectroscopic properties and oxidative reactivity of an oxomanganese(IV) complex supported by the neutral, pentadentate N4py ligand (N4py = N,N,N′,N″-tetraakis(2-pyridylmethyl)pyridine). This MnIV=O compound is more reactive than the majority of MnIV=O complexes for C–H bond oxidation.

The manganese(II) complex [MnII(N4py)]2+ ([Mn(II)(N4py)]2+) was generated as the triflate salt. The X-ray diffraction (XRD) structure exhibits a distorted octahedral MnIII center with pentadentate N4py and monodentate triflate ligands (Fig. 1A). The Mn–ligand bond lengths are 2.1 to 2.3 Å. The Mn K-edge XAS spectrum of a frozen aqueous sample of 1(OTf)2 displays a pre-edge feature at 6540.6 eV and an edge at 6547.3 eV. The EXAFS data are best fit with 1 O at 2.09 Å, 5 N at 2.26 Å, and 3 C at 3.00 Å, in excellent agreement with the XRD structure (Fig. S4; ESI†). This MnIII=O species is calculated to have a $g_{\text{eff}} = 5.76$ feature at 76 G, in good agreement with that observed for other MnIV=O complexes.3d High-resolution electron spray-ionization mass spectral (ESI-MS) data of 1 reveal a major ion peak at m/z 219.0502, consistent with [MnIV(O)(N4py)]2+ (m/z calc. 219.0563). When 1 is spiked with 10 µL H218O (97% $^{18}$O-enriched), a new molecular ion peak is observed at m/z 220.0537, indicating incorporation of $^{18}$O from H218O ([MnIV(O)(18O)(N4py)]2+; m/z calc. 220.0586). These data together support the formulation of 2 as [MnIV(O)(N4py)]2+.

As we have been unable to grow crystals of 2, its molecular structure was investigated by Mn K-edge XAS. The edge energy
of 2 (6550.8 eV) is blue-shifted over 3 eV relative to that of 1, as expected for the higher oxidation state of Mn (Fig. 2). The edge energy of 2 is within 1 eV of those reported for MnIV=O complexes supported by salen and porphyrin ligands (6549.9–6551.2 eV; Table S3; ESI†). The pre-edge peak of 2 at 6541.9 eV is significantly more intense than that of 1 (Fig. 2, inset), consistent with a large deviation from centrosymmetry.

The Fourier transform (R’ space) of the EXAFS data of 2 exhibits a prominent, sharp peak at \( R’ \approx 1.5 \) Å with less prominent peaks at \( R’ \approx 1.9, 2.2, \) and 2.8 Å (Fig. 1C). The first coordination sphere of 2 is fit well with two or three shells of N/O atoms at distances \( \{7\} \) of 1.69, 2.00, and 2.24 Å (Table S4; ESI†). The shell at 1.69 Å, which corresponds to the oxo ligand, is much shorter than the MnII–O (solvent H2O) distance of 2.09 Å observed for 1. The remaining first coordination sphere can be fit with either a single shell of 5 nitrogen scatterers at 1.99 Å or two shells of nitrogen scatterers at 2.00 Å (4 N atoms) and 2.24 Å (1 N atom), representing the nitrogen atoms of the pentadentate N4py ligand. The fit with two shells of N scatterers affords lower GOF and Debye–Wallr values than the fit with just one shell of five N scatterers. Fits including outer-sphere features reveal two Mn···C shells at 2.82 and 2.97 Å (3 and 5 C atoms, respectively).

Metric parameters from the EXAFS data of 2 are in good agreement with a DFT-computed structure (Fig. 1A, right). This structure has a Mn=O bond of 1.673 Å (cf. the EXAFS distance of 1.69 Å). The equatorial nitrogen atoms in the DFT-optimized structure have an average Mn···N distance of 2.024 Å, while the trans amine has a longer distance of 2.138 Å, consistent with the two shells of Mn···N scatterers at 2.00 and 2.24 Å.

The ability of 2 to activate C–H bonds was investigated using dihydroanthracene (DHA), diphenylmethane (DPM), ethylbenzene (EtBz), and toluene (Tol), which span a dihydroanthracene (DHA), diphenylmethane (DPM), ethylbenzene (EtBz), and toluene (Tol) range and a sharp multiline signal at 714 nm (Fig. 3A). The decay of 2 with deuterated-DHA (d4-DHA) reveals a kinetic isotope effect (KIE) of 11.2, which is larger than that observed for DHA oxidation by other MnIV=O adducts (3.1–8). Activation energies (\( E \) and Arhenius prefactors (A) determined from the reaction of 2 with DHA and d4-DHA from 35 to −5 °C in 1:1 CF3CH2OH : CH2Cl2 provides evidence for H-atom tunnelling (Table S10; ESI†). Specifically, the difference in activation energies for DHA and d4-DHA (\( E_0 – E_D \)) is greater than the difference in zero-point energies of the C–H and C–D bonds (3.6 and 1.26 kcal mol\(^{-1}\), respectively); and the ratio of Arhenius prefactors (\( A_H / A_D = 0.02 \)) is much less than 0.7, and comparable to that of [FeIV(O)(N4py)]\(^2+\), where a H-atom tunnelling mechanism was also implicated. The reaction of 2 with DHA proceeded with a second-order rate constant (k2 = 3.6 M\(^{-1}\) s\(^{-1}\)) 2–3 orders of magnitude larger than those observed at similar temperatures for nearly all other non-porphyrinic MnIV=O complexes (Table S8; ESI†). An Eyring analysis of DHA activation from 35 to −5 °C, reveal \( \Delta H^\circ \) and \( \Delta S^\circ \) of 9 ± 0.8 kcal mol\(^{-1}\) and −35 ± 3 cal mol\(^{-1}\) K, respectively (Table S9; ESI†). These parameters yield a \( \Delta G^\circ \) (at 25 °C) comparable to that of [MnIV(O)(H2bpea)]\(^2+\) but 2 kcal mol\(^{-1}\) smaller than those observed for other MnIV=O compounds,\(^{3,9a,b,c,d} \) consistent with the greater reactivity of 2.

The reaction of 2 with DHA yielded 0.56(8) equiv. of anthracene per equiv. of 2. A final Mn oxidation state of 2.7(15) was determined by isometric titration. This product distribution is consistent with the generation of anthracene by reaction of 1 equiv. DHA with 2 equiv. MnIV=O rather than two successive H-atom transfers with a single MnIV=O centre. Thus, 2 acts as a one-electron oxidant, which has been observed for other MnIV=O compounds.\(^{3,9a,b,c,d} \) Such reactivity is consistent with DFT studies by Shaik and Nam that have shown a second H-atom transfer between the nascent organic radical and MnIII=OH centre to be less favorable than diffusion of the organic radical from the MnIII=OH adduct.\(^{12} \) To the best of our knowledge, two-electron oxidation of DHA by a MnIV=O has only been observed for [MnIV(O)3(Me2EBC)]\(^2+\) and [MnIV(O)(OH2)(BQCN)]\(^2+\).\(^{3,4c} \)

While the isometric product analysis gives an average Mn oxidation state following the reaction of 2 with DHA, the nature of the Mn-based products can be better defined on the basis of EPR, electronic absorption, and ESI-MS data. Perpendicular-mode EPR spectra of the product solution showed the strong MnIV=O signals replaced by very weak signals. Broad features over a large field range and a sharp multline signal at \( g \approx 2 \) are respectively attributed to mononuclear MnIII and binuclear species (Fig. S5; ESI†). Corresponding parallel-mode EPR spectra are silent. This does not preclude the presence of mononuclear MnIII species,
as favourable MnIII zero-field splitting parameters and high-quality glasses are often required to observe the weak six-line signals of mononuclear MnIII centres in X-band experiments. The optical absorption features of product 3 are quite similar to those of [MnIII(OCH2CF3)(Br-TPEN)]2+. In addition, the dominant molecular ion peak in ESI-MS data of 3 is at m/z 620.1289, consistent with [MnIII(OCH2CF3)[N4py]](OCH2CF3)+ (m/z calc. 620.1293). Thus, we propose a mononuclear MnIV species as the dominant Mn-based product when 2 reacts with DHA.13

The chemical reactivity of 2 is similar to that of [MnIV(O)- (Br-TPEN)]2+. Both N4py and Br-TPEN are NS aminopyridyl ligands that also support highly reactive FeIV=O complexes.10 For the MnIV=O adducts, previous DFT computations predicted that 2 has a larger barrier for H-atom abstraction from cyclohexane than [MnIV(O)(Br-TPEN)]2+;12 Although the addition of a large excess (400-600 equiv.) of cyclohexane increases the decay rate of 2, the reaction does not show pseudo-first order behaviour. In contrast, [MnIV(O)(Br-TPEN)]2+ reacts with cyclohexane at 25 °C. Thus, we are unable to determine a k2 value to provide a quantitative comparison of reactivity using cyclohexane. However, a comparison can be made using EtBz, with both which compounds react at 25 °C in CF3CHOH. In the reaction with EtBz, [MnIV(O)(Br-TPEN)]2+ (1 mM) shows a rate constant five-fold larger than that of 2 (2 mM): k2 = 2.7 × 10−2 and 5.7 × 10−3 M−1 s−1, respectively. Thus, while 2 is dramatically more reactive towards C–H bonds than most MnIV=O adducts, it is less reactive than [MnIV(O)(Br-TPEN)]2+. This trend holds for the corresponding FeIV=O adducts; i.e., [FeIV(O)(Br-TPEN)]2+ is more reactive towards C–H bonds.10

The origin of the high reactivity of 2 towards C–H bonds is currently unclear. Cyclic voltammetry studies of 2 show a MnIV reduction potential (E1/2) ~ 700 mV higher than those of other MnIV=O complexes (ESI).34,44,9 Thus, 2 is a significantly more effective one-electron oxidant. Notably the E1/2 of 2 is similar to those of other dicatonic MnIV complexes,34,9 suggesting that the increase in E1/2 is attributed to the +2 total charge of 2 versus the +1 and −1 charges of other MnIV=O adducts.34,44 However, rates of H-atom transfer reactions, which are strongly correlated to thermodynamic driving force, depend not only on the reduction potential of the oxidant, but also on the basicity of the metal–hydroxo product.14 Both the MnIV=O reduction potential and the pKa of the MnIII–OH complex, which for this system is unknown, are necessary for a thermodynamic analysis. While we cannot comment at present on the driving force for C–H bond activation by 2, we note that many other MnIV=O adducts have sterically demanding supporting ligands that shield the oxo. In contrast, the oxo ligand in 2 is well-exposed to substrate (Fig. 1A). Reduced steric clash with substrate could contribute to the relatively high reactivity of 2. Future work is needed to determine the role ligand sterics, solvent effects, and thermodynamic driving force play in influencing the H-atom transfer reactivity of 2, and to explore further why MnIV=O adducts such as 2 may eschew standard rebound or desaturation mechanisms for C–H activation.

This work was supported by the US NSF (CHE-1056470 to T.A.J.; CHE-1004897 for R.I.; CHE-0946883 and CHE-0079282 supported instrument purchases). XAS experiments were supported by the Center for Synchrotron Biosciences grant, P30-EB-009998, from the National Institute of Biomedical Imaging and Bioengineering (NIBIB). We thank Dr Erik Farquhar at NSLS for outstanding support of our XAS experiments.

Most recently Chen et al. reported the formation and characterization of 2 and described the effects of Sc0+ on oxo and H-atom transfer reactions.12

Notes and references


11 A potential complication for this rate comparison is the difference in solvents (Table S8; ESI†). 2 reacts with DHA at essentially the same rate in 1:1 CF3OH:CH2Cl2 (ESI†), though the KIE drops to 8.7. In other solvents 2 has limited stability or does not form.


13 In the absence of any substrate, the thermal decay of 2 yields a similar product, as judged by electronic absorption spectroscopy.


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