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 species.

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. Oxomanganese(V) adducts with neutral, non-porphyrinic ligands are comparatively less common. Detailed studies of substrate oxidation exist for a limited number of complexes. In addition, few MnIV=O complexes have been characterized by Mn K-edge X-ray absorption spectroscopy (XAS), a technique featuring prominently in the study of Mn enzymes and biomimetics. In this report, we describe the spectroscopic properties and oxidative reactivity of an oxomanganese(IV) complex supported by the neutral, pentadentate N4py ligand (N,N-bis(2-pyridylmethyl)-N4py). This MnIV=O compound is more reactive than the majority of MnIV=O complexes for C–H bond oxidation.

The manganese(II) complex [Mn II(N4py)]2+ (1) was generated as the triflate salt. The X-ray diffraction (XRD) structure exhibits a distorted octahedral Mn15 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 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 to two Mn–ligand bonded environments, which display broad near-edge features from 450 nm (Fig. 1B). At 298 K, the formation of 2 finished in ~10 minutes, and 2 showed a half-life of 30 minutes. The absorption features of 2 are very similar to those of other non-porphyrinic MnIV=O complexes in tetragonal, six-coordinate environments, which display broad near-infrared bands from ~1040–825 nm and weaker features at higher energies. The perpendicular mode X-band EPR spectrum of 2 is typical of a mononuclear, S = 3/2 Mn15 ion (Fig. S4; ESI†). Hyperfine coupling with the g_eff = 5.76 feature is ~26 G, in good agreement with that observed for other MnIV=O complexes. High-resolution electrospray-ionization mass spectral (ESI-MS) data of 2 reveal a major ion peak at m/z 219.0502, consistent with [MnIV(O)(N4py)]2+ (m/z calc. 219.0563). When 2 is spiked with 10 μL H218O (97% 18O-enriched), a new molecular ion peak is observed at m/z 220.0537, indicating incorporation of 18O from H218O ([MnIV(O18)(N4py)])2+ (m/z calc. 220.0585). 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...
2.24 Å (Table S4; ESI†). The pre-edge peak of DHA at 2.00 eV is significantly more intense than that of 1 (Fig. 2, inset), consistent with a large deviation from centrosymmetry.

The Fourier transform ($R'_s$ 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 ($r$) 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 Mn$^{IV}$--O (solvent H$_2$O) 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 COF and Debye–Waller factors for nearly all other non-porphyrinic Mn IV complexes (Table S8; ESI†). An Eyring analysis of DHA activation from 35 to −5 °C, reveal $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 9 ± 0.8 kcal mol$^{-1}$ and −35 ± 3 cal mol$^{-1}$ K, respectively (Table S9; ESI†). These parameters yield a $\Delta G^\ddagger$ (at 25 °C) comparable to that of [Mn IV(O)(H$_3$buea)]$^+$ but 2 kcal mol$^{-1}$ smaller than those observed for other Mn$^{IV}$--O complexes, 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 iodometric titration. This product distribution is consistent with the generation of anthracene by reaction of 1 equiv. DHA with 2 equiv. Mn$^{IV}$--O rather than two successive H-atom transfers with a single Mn$^{IV}$--O centre. Thus, 2 acts as a one-electron oxidant, which has been observed for other Mn$^{IV}$--O compounds. 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 Mn$^{III}$--OH centre to be less favorable than diffusion of the organic radical from the Mn$^{III}$--OH adduct. To the best of our knowledge, two-electron oxidation of DHA by a Mn$^{IV}$--O has only been observed for [Mn$^{IV}$O$_2$(Me$_2$EBC)] and [Mn$^{III}$O(OH)$_2$(BQCN)]$^{2+}$.

While the iodometric 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 Mn$^{IV}$--O signals replaced by very weak signals. Broad features over a large field range and a sharp multiline signal at $g \approx 2$ are respectively attributed to mononuclear Mn$^{IV}$ and binuclear species (Fig. S5; ESI†). Corresponding parallel-mode EPR spectra are silent. This does not preclude the presence of mononuclear Mn$^{III}$ 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)(Bn-TPEN)]2+ (Bn-TPEN = N-benzyl-N',N',N'-tris-(2-pyridylmethyl)-1,2-diamoethane), which was the dominant Mn product when [MnIV(O)(Bn-TPEN)]2+ was reacted with hydrocarbons. 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 MnIII species as the dominant, but not sole, Mn-based product when 2 reacts with DHA.13

The chemical reactivity of 2 is similar to that of [MnIV(O)- (Bn-TPEN)]2+. Both N4py and Bn-TPEN are N5 aminopyridyl ligands that also support highly reactive FeIV═O complexes.10a For the MnIV═O adducts, previous DFT computations predicted that 2 has a larger barrier for H-atom abstraction from cyclohexane than [MnIV(O)(Bn-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)(Bn-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 which both compounds react at 25 °C in CF3CH2OH. In the reaction with EtBz, [MnIV(O)(Bn-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 MnIV═O adducts, it is less reactive than [MnIV(O)(Bn-TPEN)]2+. This trend holds for the corresponding FeIV═O adducts; i.e., [FeIV(O)(Bn-TPEN)]2+ is more reactive towards C–H bonds.10c

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).3a,4a,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,3a,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.3a,4d 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 pKb 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.

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

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