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Spectroscopic properties and reactivity of a mononuclear oxomanganese(IV) complex†

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A non-porphyrinic, mononuclear oxomanganese(IV) complex was generated at room temperature and characterized by spectroscopic methods. The $Mn^{IV}{=}O$ adduct is capable of activating C–H bonds by a H-atom transfer mechanism and is more reactive in this regard than most $Mn^{IV}{=}O$ 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 H_2O_2 and oxygen evolution from water.[1] Oxomanganese(V) 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.[3a–c,4] In addition, few $Mn^{IV}{=}O$ complexes have been characterized by Mn K-edge X-ray absorption spectroscopy (XAS),[3b,5] a technique featuring prominently in the study of Mn enzymes[1b] and biominerals.[6] 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)-*N*-bis(2-pyridyl)methylamine). This $Mn^{IV}{=}O$ compound is more reactive than the majority of $Mn^{IV}{=}O$ 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 Mn^{II} 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 (*cf.* Tables S4 and S6; ESI†).

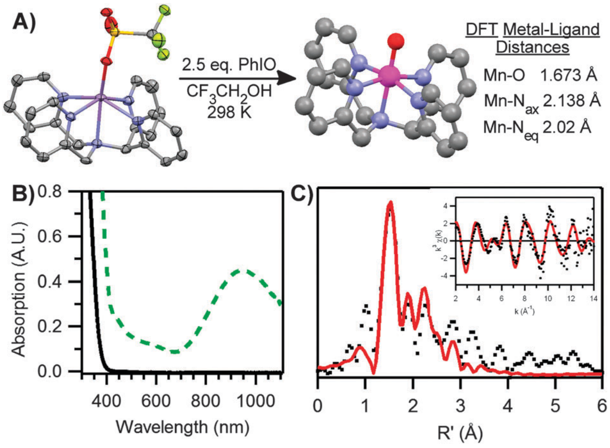

Fig. 1 (A) XRD structure of $[Mn^{II}(N4py)(OTf)]^+$ (**1**(OTf), left) and DFT (BP/TZVP) structure of $[Mn^{IV}(O)(N4py)]^{2+}$ (**2**, right). Hydrogen atoms are omitted for clarity. (B) 298 K electronic absorption spectra of **1** (black solid trace) and **2** (green dashed trace); both 2 mM in CF_3CH_2OH. (C) Fourier transform of the Mn K-edge EXAFS data and EXAFS spectrum (inset), experimental data (···) and fits (–), for **2** in CF_3CH_2OH.

The addition of excess PhIO (2.5 equiv.) to **1** in CF_3CH_2OH at 298 K led to the formation of a green species (**2**), with a broad electronic absorption band at 950 nm and weaker features at 600 and 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 $Mn^{IV}{=}O$ complexes in tetragonal, six-coordinate environments, which display broad near-infrared bands from ~1040–825 nm and weaker features at higher energies.[3a,b,7] The perpendicular mode X-band EPR spectrum of **2** is typical of a mononuclear, $S = 3/2$ Mn^{IV} ion (Fig. S4; ESI†).[3a,b,d,8] Hyperfine coupling for the $g_{eff} = 5.76$ feature is ~76 G, in good agreement with that observed for other $Mn^{IV}{=}O$ complexes.[3d] High-resolution electrospray-ionization mass spectral (ESI-MS) data of **2** reveal a major ion peak at *m*/*z* 219.0502, consistent with $[Mn^{IV}(O)(N4py)]^{2+}$ (*m*/*z* calc. 219.0563). When **2** is spiked with 10 μL $H_2{}^{18}O$ (97% ^{18}O-enriched), a new molecular ion peak is observed at *m*/*z* 220.0537, indicating incorporation of ^{18}O from $H_2{}^{18}O$ ($[Mn^{IV}(^{18}O)(N4py)]^{2+}$ *m*/*z* calc. 220.0585). These data together support the formulation of **2** as $[Mn^{IV}(O)(N4py)]^{2+}$.

As we have been unable to grow crystals of **2**, its molecular structure was investigated by Mn K-edge XAS. The edge energy

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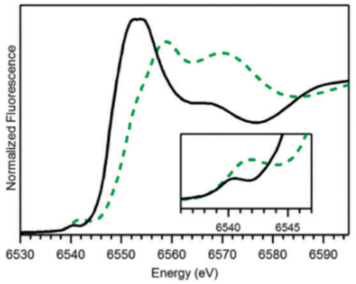

Fig. 2 20 K Mn K-edge XAS near-edge region of $\mathbf{1}(OTf)_2$ (black solid trace) and **2** (green dashed trace) in H_2O and CF_3CH_2OH, respectively.

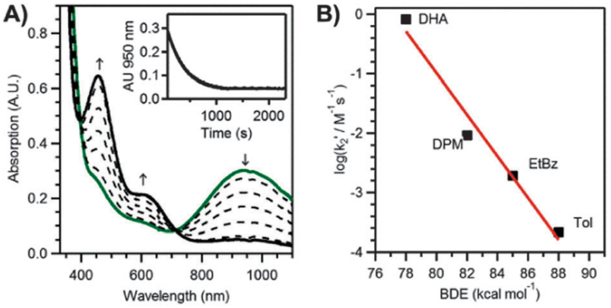

Fig. 3 (A) Electronic absorption spectra of **2** upon addition of 200 equiv. EtBz in CF_3CH_2OH at 298 K. Inset: decay of the 950 nm absorption signal. (B) Corrected second-order rate constant (k_2') *versus* bond dissociation enthalpies of organic substrates.

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 $Mn^{IV}{=}O$ complexes supported by salen and porphyrin ligands (6549.9–6551.2 eV; Table S3; ESI†).[5] 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 (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^{II}–O (solvent H_2O) 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–Waller 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 nitrogens 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 ~10 kcal mol^{-1} range of C–H bond strengths. For each substrate, the addition of an excess to **2** at 298 K under an Ar atmosphere led to (i) a disappearance in the optical bands of **2**, (ii) formation of a new species, **3**, with bands at 460 and 630 nm, and (iii) the appearance of an isosbestic point at 714 nm (Fig. 3A). The decay of **2** and the formation of **3** occurred with the same rate, both following pseudo-first order behaviour to at least four half-lives (see ESI†). Second-order rate constants (k_2', corrected for the number of reactive C–H bonds) determined for all substrates revealed a linear relationship between log(k_2') and substrate bond dissociation enthalpies (BDEs), with a slope of 0.35 (Fig. 3B). Such behaviour is highly suggestive of a rate-limiting H-atom transfer.[3a] In support, reactions of **2** with deuterated-DHA (d_4-DHA) reveal a kinetic isotope effect (KIE) of 11.2, which is larger than that observed for DHA oxidation by other $Mn^{IV}{=}O$ adducts (3.1–8).[2c,3a,4a,9] Activation energies (E) and Arrhenius prefactors (A) determined from the reaction of **2** with DHA and d_4-DHA from 35 to −5 °C in 1 : 1 $CF_3CH_2OH : CH_2Cl_2$ provide evidence for H-atom tunnelling (Table S10; ESI†). Specifically, the difference in activation energies for DHA and d_4-DHA ($E_D - E_H$) 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 Arrhenius prefactors (A_H/A_D = 0.02) is much less than 0.7, and comparable to that of $[Fe^{IV}(O)(N4py)]^{2+}$, where a H-atom tunnelling mechanism was also implicated.[10] The reaction of **2** with DHA proceeded with a second-order rate constant (k_2' = 3.6 M^{-1} s^{-1}) 2–3 orders of magnitude larger than those observed at similar temperatures for nearly all other non-porphyrinic $Mn^{IV}{=}O$ complexes (Table S8; ESI†).[3a,4a,9,11] 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 $[Mn^{IV}(O)(H_3buea)]^-$ but 2 kcal mol^{-1} smaller than those observed for other $Mn^{IV}{=}O$ complexes,[3a,4a,b] 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.[2c,3a,b,4c] 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.[12] To the best of our knowledge, two-electron oxidation of DHA by a $Mn^{IV}{=}O$ has only been observed for $[Mn^{IV}(O)_2(Me_2EBC)]^+$ and $[Mn^{IV}(O)(OH_2)(BQCN)]^{2+}$.[3c,4c]

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^{II} 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 Mn^{III} zero-field splitting parameters and high-quality glasses are often required to observe the weak six-line signals of mononuclear Mn^{III} centres in X-band experiments. The optical absorption features of product **3** are quite similar to those of $[Mn^{III}(OCH_2CF_3)(Bn\text{-}TPEN)]^{2+}$ (Bn-TPEN = *N*-benzyl-*N*,*N*′,*N*′-tris-(2-pyridylmethyl)-1,2-diaminoethane), which was the dominant Mn product when $[Mn^{IV}(O)(Bn\text{-}TPEN)]^{2+}$ was reacted with hydrocarbons.[3b] In addition, the dominant molecular ion peak in ESI-MS data of **3** is at m/z 620.1289, consistent with $[Mn^{III}(OCH_2CF_3)(N4py)](OCH_2CF_3)^+$ (m/z calc. 620.1293). Thus, we propose a mononuclear Mn^{III} 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 $[Mn^{IV}(O)(Bn\text{-}TPEN)]^{2+}$.[3b] Both N4py and Bn-TPEN are N5 aminopyridyl ligands that also support highly reactive $Fe^{IV}{=}O$ complexes.[10] For the $Mn^{IV}{=}O$ adducts, previous DFT computations predicted that **2** has a larger barrier for H-atom abstraction from cyclohexane than $[Mn^{IV}(O)(Bn\text{-}TPEN)]^{2+}$.[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, $[Mn^{IV}(O)(Bn\text{-}TPEN)]^{2+}$ reacts with cyclohexane at 25 °C. Thus, we are unable to determine a k_2 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 CF_3CH_2OH. In the reaction with EtBz, $[Mn^{IV}(O)(Bn\text{-}TPEN)]^{2+}$ (1 mM) shows a rate constant five-fold larger than that of **2** (2 mM): $k_2' = 2.7 \times 10^{-2}$ and 5.7×10^{-3} M^{-1} s^{-1}, respectively. Thus, while **2** is dramatically more reactive towards C–H bonds than most $Mn^{IV}{=}O$ adducts, it is less reactive than $[Mn^{IV}(O)(Bn\text{-}TPEN)]^{2+}$. This trend holds for the corresponding $Fe^{IV}{=}O$ adducts; *i.e.*, $[Fe^{IV}(O)(Bn\text{-}TPEN)]^{2+}$ 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 $Mn^{III/IV}$ reduction potential ($E_{1/2}$) ~700 mV higher than those of other $Mn^{IV}{=}O$ complexes (ESI†).[3a,4a,9] Thus, **2** is a significantly more effective one-electron oxidant. Notably the $E_{1/2}$ of **2** is similar to those of other dicationic Mn^{IV} complexes,[3a,9] suggesting that the increase in $E_{1/2}$ is attributed to the +2 total charge of **2** *versus* the +1 and −1 charges of other $Mn^{IV}{=}O$ adducts.[3a,4a] 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 $Mn^{III/IV}$ reduction potential and the pK_a of the Mn^{III}–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 $Mn^{IV}{=}O$ 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 $Mn^{IV}{=}O$ 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 Sc^{3+} on oxo and H-atom transfer reactions.[12b]

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