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Air Oxidation of a Five-Coordinate Mn(III) Dimer to a High-Valent Oxomanganese(V) Complex

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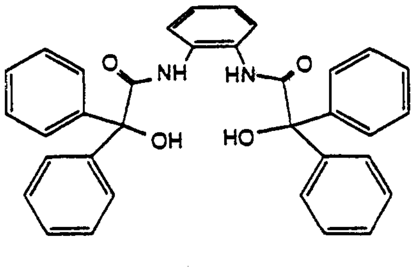
A variety of first row transition-metal complexes activate dioxygen or facilitate oxygen atom transfer to organic substrates.[1] In many cases the reactive species is assumed to be the terminal oxo group of a high-valent metal complex, but few such complexes have been isolated and structurally characterized.[1g,h,2] In order to assess the structure and reactivity of metal–oxo centers, we have developed the $\mathrm{PHAB^{4-}}$ ligand shown below [where $\mathrm{H_4PHAB}$ is 1,2-bis(2,2-diphenyl-2-hydroxyethanamido)benzene], incorporating design elements from the picket-fence porphyrins[1i] and oxidation-resistant tetradentate ligands synthesized by Collins and co-workers.[2] The latter workers have shown that bis-amido bis-alkoxo donor sets can stabilize high oxidation state metal–oxo complexes.[2] In addition to providing this electronic stabilization, the steric features of the PHAB ligand protect terminal metal–oxo centers and limit coordination numbers to less than six. We show here that the PHAB ligand forms a novel five-coordinate $\mathrm{Mn^{III}}$ dimer and describe a reaction with dioxygen that yields a $\mathrm{Mn^{V}}$–oxo complex. Dioxygen reactions with $\mathrm{M^{II}}$ complexes are well precedented,[1] but O_2 reactions with metal ions in the 3+ oxidation state are rare and, in the case of most $\mathrm{Mn^{III}}$ complexes, result in $\mathrm{Mn^{IV}}$–oxo– or –peroxo–bridged dimers or the $\mathrm{Mn^{IV}}$ one-electron oxidation product.[3] The air oxidation of the $\mathrm{Mn^{III}}$(PHAB) dimer proceeds in the absence of external reductants and results in the hydroxylation of the ether solvent through a proposed autocatalytic path. The surprising reactivity of these five-coordinate PHAB complexes stabilized in the higher oxidation states suggests new routes for selective oxidation of organic substrates.



The dimeric structure of $\mathrm{Li_2[Mn(PHAB)]_2}$ (**1**)·4MeCN is shown in Figure 1.[4] The alkoxo bridging motifs are similar to those found in other $\mathrm{Mn^{III}}$ dimers,[5] but the four phenyl groups restrict both $\mathrm{Mn^{III}}$ centers to a five-coordinate alkoxo-bridged geometry which is unprecedented in the rich chemistry of manganese dimers.[3c] A second distinct bridging interaction is formed by a lithium ion which is tightly bound between two terminal alkoxides.[6]

When lithium complexing agents are added, facile oxidation of **1** occurs in air or O_2-saturated, peroxide-free THF, yielding $\mathrm{[Mn^{V}(O)(PHAB)]^-}$ (**2**)[7] and 2-hydroxytetrahydrofuran (THF-OH). The oxomanganese(V) complex **2** has been isolated and structurally characterized[8] (Figure 1) as a square-pyramidal $\mathrm{Mn^{V}}$ with a terminal oxo bond distance of 1.558(4) Å, in good agreement with the values obtained for the two other structurally characterized oxomanganese(V) complexes.[2]

Conversion of **1** to **2**, monitored as a change in the visible spectrum at 410 nm (Figure 2), will not occur unless a lithium-specific chelator, such as excess 12-crown-4[9] or tetraalkylammonium chloride (R_4NCl), is added. Furthermore, the lithium-free dimer $\mathrm{(Bu^n{}_4N)_2[Mn(PHAB)]_2}$[10] (**3**) reacts with dioxygen to form **2** in the absence of R_4NCl or 12-crown-4. Apparently, loss of the $\mathrm{Li^+}$ bridge leads to formation of an O_2-reactive species. The latter could be a dimer in an altered conformation or a dissociation product of **1**, such as a four-coordinate $\mathrm{Mn^{III}}$ monomer.

The reaction of **1** with O_2 in the presence $\mathrm{Bu^n{}_4NCl}$ (Figure 2, inset) commences after an induction period of approximately 4–6 min, and complete conversion of **1** to **2** requires a total of ca. 10 min at 50 °C. A GC-MS analysis of the reaction mixture at this point revealed formation of 2–3 equiv of THF-OH per $\mathrm{Mn^{III}}$. The observation of an induction period and a decreasing half-life

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(4) Anal. Calcd for $\mathrm{Li_2[Mn^{III}(PHAB)]_2{\cdot}4MeCN}$, $\mathrm{C_{76}H_{60}N_8O_8Li_2Mn_2}$: Li, 1.04; Mn, 8.22. Found: Li, 0.99: Mn, 8.55 (Galbraith). Internally consistent C,H,N analyses were not obtained from eight determinations conducted by two laboratories (Oneida and Galbraith) on the same crystalline sample. Analysis of other crystalline samples of **1** gave similar results. UV–vis (THF): λ_{max} (nm) (ϵ (per Mn), $\mathrm{cm^{-1}\ M^{-1}}$) 390 (749), 410 (728), 467 (707). Synthetic procedures available as supplementary material. A diffraction quality crystal of **1**, taken directly from the mother liquor and coated with oil to prevent solvent loss, crystallized in the monoclinic space group $P2_1/c$, with a = 13.42(4) Å, b = 19.18(7) Å, c = 26.33(8) Å, β = 99.69(2)°, V = 6676 Å^3, ρ_{calc} = 1.318 g cm^{-3}, and Z = 4. Data collection at −120 °C for $2 \leq 2\theta \leq 46°$ provided 5381 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (SHELXS 86) and refined in TEXSAN 5.0 with anisotropic thermal parameters. Hydrogen atoms were calculated and fixed in the final refinements. The structure converged with a final R (R_w) value 0.061 (0.073) for 843 variables.

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(6) The lithium cation was not metathesized during the crystallization of **1** in the presence of 0.1 M KPF_6.

(7) Anal. Calcd for $\mathrm{Ph_4P[Mn^{V}(O)(PHAB)]}$, $\mathrm{C_{58}H_{44}N_2O_5P_1Mn_1}$: C, 74.51; H, 4.74; N, 3.00. Found: C, 73.61; H, 4.75; N, 3.07. UV–vis (MeCN): λ_{max} (nm) (ϵ, $\mathrm{cm^{-1}\ M^{-1}}$) 414 (4020), 552 (993), 730 (415). From $\mathrm{Bu^n{}_4N[Mn(O)(PHAB)]}$, UV–vis (THF): λ_{max} (nm) (ϵ, $\mathrm{cm^{-1}\ M^{-1}}$) 410 (3952), 558 (597), 730 (390). See supplementary material for synthetic procedures.

(8) Dark crystals of **2** are grown by layering diethyl ether onto a solution of **1** and Ph_4PCl in dichloromethane in the presences of air. **2** crystallizes in the monoclinic space group $P2_1/n$, with a = 19.156(3) Å, b = 11.842(4) Å, c = 20.025(3) Å, β = 92.48(1)°, V = 4538 Å^3, ρ_{calc} = 1.368 g cm^{-3}, and Z = 4. Data collection at −120 °C from $2 \leq 2\theta \leq 46°$ provided 3410 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods (SHELXS 86) and refined in TEXSAN 5.0 with 485 variables to final R (R_w) values 0.052 (0.052).

(9) The 12-crown-4 was distilled from NaH under nitrogen immediately prior to use to eliminate possible contaminating peroxides.

(10) Anal. Calcd for $\mathrm{(Bu^n{}_4N)_2[Mn(PHAB)]_2}$ (**3**), $\mathrm{C_{100}H_{120}N_6O_8Mn_2}$: C, 73.06; H, 7.36; N, 5.11. Found: C, 73.06; H, 6.94; N, 5.13.

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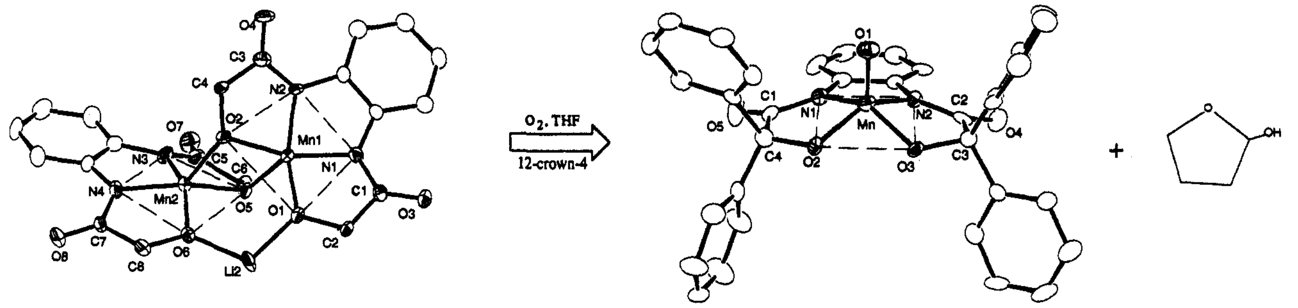

Figure 1. Reaction of **1** with O_2 in THF yields 2 equiv of $[Mn^V(O)(PHAB)]^-$ (**2**)[7] and 2-hydroxytetrahydrofuran (THF-OH). On the left is shown an ORTEP drawing of the core of $Li[Mn^{III}PHAB]_2^-$ for compound **1**, showing the 50% thermal probability ellipsoids. Solvate molecules, hydrogen atoms, and phenyl groups are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Mn1···Mn2, 3.052(9); Mn1–O1, 1.904(5); Mn1–O2, 1.927(5); Mn1–N1, 1.914(6); Mn1–N2, 1.900(5); Mn1–O5, 2.174(5); Mn2–O5, 1.926(5); Mn2–O6, 1.891(5); Mn2–O2, 2.115(5); Mn2–N3, 1.911(6); Mn2–N4, 1.925(6); Li2–O1, 1.87(1); Li2–O6, 1.87(1); Mn1–O2–Mn2, 97.0(2); Mn1–O5–Mn2, 96.0(2); O2–Mn1–O5, 80.3(2); O2–Mn2–O5, 81.9(2); O1–Li2–O6, 113.0(7). On the right side is shown an ORTEP drawing of $[Mn^V(O)(PHAB)]^-$ anion of **2**, showing the 50% thermal probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Mn–O1, 1.558(4); Mn–O2, 1.827(4); Mn–O3, 1.831(4); Mn–N1, 1.893(5); Mn–N2, 1.875(5); O1–Mn–O2, 110.0(2); O1–Mn–O3, 110.0(2); O1–Mn–N1, 109.2(2); O1–Mn–N2, 108.5(2).

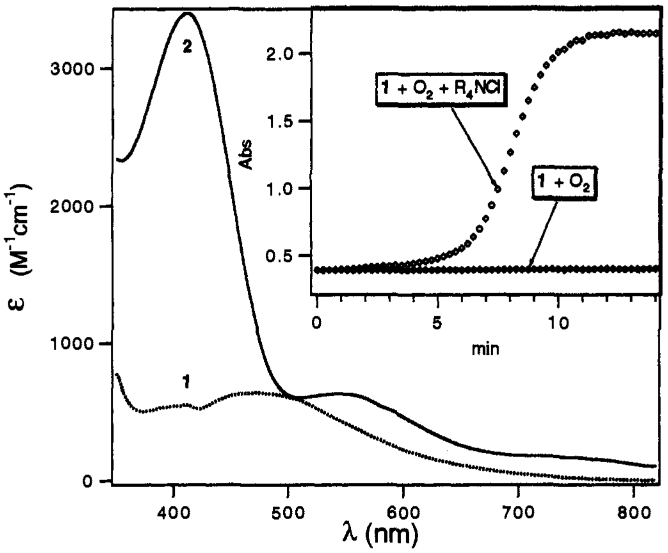

Figure 2. Absorbance spectra of the red $Li_2[Mn^{III}(PHAB)]_2 \cdot 4MeCN$ (**1**) in THF (freshly distilled from sodium/benzophenone) before and after admission of air to form 2 equiv of green $[Mn^V(O)L]^-$ (**2**) (ε values quoted per Mn). Inset: absorbance at 410 nm was recorded at 15-s intervals after addition of air to a THF solution of **1** (0.54 mM) in 10 mM Bu^n_4NCl, thermostated at 50 °C.

for formation of **2** are characteristic of an autocatalytic process.[11] We speculate that a $Mn^{III}(O_2)$ or $Mn^{IV}(O_2^-)$ intermediate initiates THF autoxidation by H atom abstraction. The resulting THF radicals could react with O_2 to ultimately give 2-tetrahydrofuran hydroperoxide (THF-OOH), which is expected to rapidly react with **1** to form **2** and THF-OH. The excess of THF-OH over Mn^{III} indicates that other reactions may yield THF-OH, such as the direct reaction of **2** with THF. In support of this model, we find that addition of exogeneous alkyl hydroperoxides causes an immediate conversion of **1** to **2** even without lithium complexing reagents at 50 °C. In addition, hydroperoxides are known to generate oxomanganese(V) complexes in related systems.[2a]

Other O_2 activation steps, such as initiation of THF autoxidation by trace contaminating Mn^{II} or Mn^{III} species or by residual THF-OOH in the neat solvent, are unlikely as neat solutions of **1** are stable in the presence of O_2 until R_4NCl or 12-crown-4 is added. Control experiments demonstrate that **2** does not require the presence of lithium complexing agents to initiate autoxidation of **1**. Thus contamination of solid samples of **1** by **2** cannot be responsible for initiating the overall reaction shown in Figure 1. Furthermore, when **1** is replaced by $Mn(acac)_2$, $MnCl_2$, $Mn(OAc)_2$, $Mn(OAc)_3$, or Mn^{II}(salophen),[13] no O_2 oxidation of the metal centers or THF is observed by GC at 50 °C over a 2-h period. While reduction of Mn^{III} complexes in other ligand fields can occur in THF,[12] an initiation step in which **1** is reduced to a Mn^{II} species is unlikely for these PHAB complexes. The extreme stability of the dimeric Mn^{III} centers of **1** and **3** with respect to reduction is clear in cyclic voltammetry experiments: neither **1** nor **3** is reduced electrochemically upon scanning to −2.0 V *vs* SCE in acetonitrile.[14]

Under anaerobic conditions, the oxygen atom of **2** can be transferred to a variety of substrates, including phosphines, ethers, and olefins.[15] For instance, the reaction of this Mn^V–oxo complex with norbornylene gave norbornylene epoxide in 11% yield.[16] We are evaluating these mechanisms with the intent of coupling the oxidation of **1** to **2** with oxo-transfer reactions in catalytic processes.

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Supplementary Material Available: Synthetic procedures, atomic positional parameters, thermal parameters, intramolecular bond distances and angles, and complete ORTEP drawings for **1** and **2** (28 pages); listing of observed and calculated structure factors for **1** and **2** (61 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) Salophen is an abbreviation for the Schiff base of *o*-phenylenediamine and salicylaldehyde.

(14) Cyclic voltammetry of **1** or **3** shows two reversible redox processes, consistent with one-electron oxidations of **1** to give the $Mn^{III}Mn^{IV}$ dimer (standard reduction potential (*vs* SCE), $E_{1/2} = 0.73$ V) and subsequently the $Mn^{IV}Mn^{IV}$ dimer ($E_{1/2} = 1.19$ V). Conditions: 2 mM **1** or **3** and 0.1 M $Bu^n_4NPF_6$ in MeCN; scan rate, 100 mV/s; glassy carbon electrode.

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(16) A solution of 0.060 mmol of $Bu^n_4N[Mn(O)(PHAB)]$, 0.060 mmol of bromobenzene (internal standard), and 0.545 mmol of norbornylene in 0.5 mL of 1,2-dichloroethane was degassed by three freeze–thaw cycles and placed under a N_2 atmosphere. This solution was heated to 50 °C for 2 h and then analyzed by GC. The only major product was identified as norbornylene epoxide by coinjection with the authentic material. A total of yield of 0.007 mmol of norbornylene epoxide (11%) was found.