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Reactions of Tetrabromocatecholatomanganese(III) Complexes with Dioxygen

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New five- and six-coordinate complexes containing the $[\mathrm{Mn^{III}(Br_4cat)_2}]^-$ core ($\mathrm{Br_4cat^{2-}}$ = tetrabromo-1,2-catecholate) have been prepared. Homoleptic $[\mathrm{Mn^{III}(Br_4cat)_3}]^{3-}$ reacts rapidly with O_2 to produce tetrabromo-1,2-benzoquinone ($\mathrm{Br_4bq}$). The $[\mathrm{Mn^{III}(Br_4cat)_2}]^-$ fragment is a robust catalytic platform for the aerobic conversion of catechols to quinones. The oxidase activity apparently derives from the coupling of metal- and ligand-centered redox events.

Significant recent attention has been directed toward the development of new redox catalysts that functionally mimic enzymes that mediate selective aerobic oxidation reactions.[1–3] These may act as oxygenases, by incorporating one or both oxygen atoms from O_2 into organic substrates, or oxidases, which couple substrate oxidation with the reduction of O_2 to water or hydrogen peroxide.[1,3] Catalysts that couple selective bond activation and functionalization to O_2 reduction must incorporate a multielectron capacity to avoid the loss of specificity that typically accompanies odd-electron autoxidation.[3,4] Traditional inorganic and organometallic catalysts for such reactions often utilize second- and third-row transition-metal ions with redox-inert ancillary ligands.[1,3] In these systems, the multielectron redox activity is entirely metal-derived. In contrast, redox-active "noninnocent" ligands may impart a multielectron redox capacity to mononuclear first-row metal complexes, which typically prefer only single-electron redox changes.[2] Aside from metalloporphyrin complexes, such ligand-derived multielectron reaction chemistry has been largely unexplored for redox transformations of small-molecule substrates but is receiving increased interest.[2,5]

We are developing new multielectron redox cycles based on the ability of quinoid (*o*-dioxolene) ligands[6a] and their derivatives[6b] to store and deliver charge in reactions with small-molecule substrates. In this regard, we were intrigued by reported reactions of O_2 with complexes containing the anionic bis(catecholato)manganese(III) core,[7] particularly the catalytic production of hydrogen peroxide from O_2 by $[\mathrm{Mn^{III}(Cl_4cat)_2(EtOH)(H_2O)}]^-$ ($\mathrm{Cl_4cat^{2-}}$ = tetrachloro-1,2-catecholate) with hydroxylamine as a sacrificial reductant.[8] It had been postulated that a vacant coordination site at the manganese center was a prerequisite to reaction with O_2.[7,8b] However, there was ambiguity regarding the mechanism of the reaction, particularly the speciation of the O_2-sensitive complexes and the possibility of ligand-based redox events during catalytic turnover.[8a] Presented herein are the syntheses of new five- and six-coordinate complexes based on the $[\mathrm{Mn^{III}(Br_4cat)_2}]^-$ fragment ($\mathrm{Br_4cat^{2-}}$ = tetrabromo-1,2-catecholate) and studies of their reaction with O_2.

Heating acetone solutions of $\mathrm{Mn^{II}(ClO_4)_2 \cdot 6H_2O}$ with 2 equiv of $\mathrm{Br_4catH_2}$ and $\mathrm{{}^nBuN_4OH}$ to reflux in air generates

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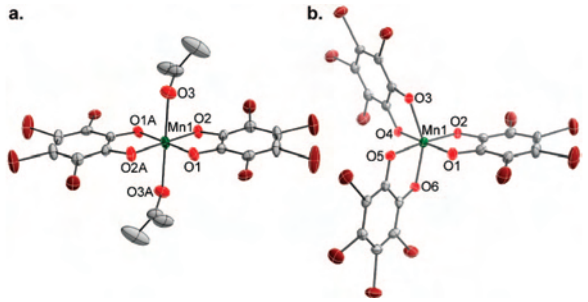

Figure 1. Solid-state structures of the anions in (a) (^{n}Bu$_4$N)-[Mn^{III}(Br$_4$cat)$_2$(Me$_2$C=O)$_2$] (**1**) and (b) (PPN)Li$_2$[Mn^{III}(Br$_4$cat)$_3$]·5THF (**4**) shown with 50% probability ellipsoids. Hydrogen atoms, THF solvate molecules, and countercations are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. For **1**: Mn1−O1 1.905(4), Mn1−O2 1.897(4), Mn1−O3 2.403(4), O1−Mn1−O2 86.17(15), O1−Mn1−O3 93.41(16), O2−Mn1−O3 95.27(17). For **4**: Mn1−O1 1.898(3), Mn1−O2 1.917(3), Mn1−O3 2.161(3), Mn1−O4 1.959(3), Mn1−O5 1.970(3), Mn1−O6 2.154(3), O1−Mn1−O2 85.05(13), O3−Mn1−O4 79.96(11), O5−Mn1−O6 79.84(11), O1−Mn1−O3 102.28(12), O1−Mn1−O6 96.79(11).

an olive-green solution, which upon cooling to −20 °C deposits (^{n}Bu$_4$N)[Mn^{III}(Br$_4$cat)$_2$(Me$_2$C=O)$_2$] (**1**) as an analytically pure, dark-green solid in ca. 60% yield. Recrystallization from acetone gave crystals suitable for X-ray diffraction (Figure 1a). The crystal structure of **1** contains a six-coordinate manganese anion located on a crystallographically defined inversion center and bound to two coplanar *o*-dioxolene ligands and two acetone molecules. The quinoid chelates have C−C and C−O bond lengths indicative of fully reduced catecholate ligands.[9] The axial Mn−O$_{acetone}$ bond distance of 2.403(4) Å is elongated relative to the 1.901(6) Å averaged Mn−O$_{Br_4cat}$ bond lengths, consistent with a high-spin 3d^4 electron configuration.[10] Recrystallization of **1** from MeOH affords the five-coordinate alcohol adduct (^{n}Bu$_4$N)[Mn^{III}(Br$_4$cat)$_2$(MeOH)] (**2**) with distorted square-pyramidal geometry (Figure S1 in the Supporting Information). The UV–vis spectra of both **1** and **2** are identical in either acetone or MeCN, suggesting that the axial ligands are substitution labile while the [Mn^{III}(Br$_4$cat)$_2$]$^-$ core is preserved in solution. However, contrary to the previous reports,[7b,8] this fragment reacts sluggishly with O$_2$. Exposure of green **1** or **2** to 1 atm of O$_2$ in acetone or MeCN affords conversion to a dark-blue species over weeks at ambient temperature. Likewise, the triphenylphosphine oxide complex (^{n}Bu$_4$N)[Mn^{III}(Br$_4$cat)$_2$(OPPh$_3$)] (**3**) is indefinitely stable under air in MeCN.[11] In light of these observations, the reported facile reactions of closely related species with O$_2$ merited reexamination.[7b,8,12]

A clue toward the identity of the true air-sensitive species came from observation of a second red-orange product in the reaction to prepare **1**. Independent synthesis confirmed that this material is hexabromo-2,3-oxanthrenequinone,[13] which arises from coupling of tetrabromo-1,2-benzoquinone (Br$_4$bq) with Br$_4$cat^{2-}.[14] The yield of the coupled product varies and is inversely proportional to the yield of **1**. Accordingly, reaction of Br$_4$bq with isolated **1** in MeCN under N$_2$ leads to the slow formation of hexabromo-2,3-oxanthrenequinone and decomposition of **1**.

The apparent intermediacy of free Br$_4$bq under the aerobic conditions employed for the preparation of **1** and the isolated yields of ∼60% for **1** suggest that 1 equiv of Br$_4$catH$_2$ is consumed as a sacrificial reductant for each equivalent of **1** produced.[15] Consistent with this hypothesis, anaerobic addition of Br$_4$cat^{2-} (generated in situ from Br$_4$catH$_2$ and LiOMe) to **1** in MeCN gives immediate conversion to a dark-green, air-sensitive material (**4**). Complex **4** is independently obtained from the reaction of Mn^{II}Cl$_2$·4H$_2$O with 3 equiv of Br$_4$catH$_2$ and 6 equiv of LiOMe in MeOH at ambient temperature, followed by air exposure and precipitation with PPNCl [PPN$^+$ = bis(triphenylphosphine)iminium]. Recrystallization from THF−pentane under N$_2$ afforded single crystals suitable for analysis by X-ray crystallography (Figure 1b). The structure reveals a manganese tris(tetrabromo-*o*-catecholato) trianion [Mn^{III}(Br$_4$cat)$_3$]$^{3-}$ in **4**. The complex has distorted octahedral geometry with three distinct sets of Mn−O bond lengths and an axial elongation typical of a Jahn–Teller distorted, high-spin manganese(III) ion.[10] Two Li(THF)$_2$$^+$ cations are in close contact with the axial oxygen atoms (Figure S2 in the Supporting Information). This successful isolation of **4** refutes earlier reports that suggested that homoleptic tris(catecholato)manganese(III) complexes are inaccessible because of geometric constraints imposed by the ligands.[8,16,17]

Exposure of **4** to O$_2$ in MeCN, acetone, or THF results in an immediate color change from green to dark blue/violet **5**. The UV–vis spectrum of **5** (Figure 2a) is nearly identical with the previously reported dianion [Mn^{IV}(Cl$_4$cat)$_3$]$^{2-}$[7b,8a,12] and is tentatively formulated as [Mn^{IV}(Br$_4$cat)$_3$]$^{2-}$. Consistent with this assignment, **5** is independently obtained from the addition of 1.0 equiv of AgPF$_6$ to **4** under N$_2$. The color of **5** in MeCN is temperature-dependent, reversibly converting from dark blue at −20 °C to green at +65 °C. This color change may reflect conversion to a [Mn^{III}(Br$_4$cat)$_2$(Br$_4$sq$^{\bullet}$)]$^{2-}$ (Br$_4$sq$^{\bullet-}$ = tetrabromo-1,2-semiquinonate) intravalence isomer. The electronic structure of **5** and related materials is a

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(11) (a) For O$_2$ sensitivity studies, **3** was generated in situ from the addition of excess OPPh$_3$ to **1**. The UV−vis spectrum of **3** in MeCN is unchanged with air exposure over weeks at ambient temperature. Isolated **3** was prepared by a modification of a literature procedure.[11b] An X-ray structure confirmed the five-coordinate monomeric nature of the anion in **3** with no close-cation contacts. (b) Larsen, S. K.; Pierpont, C. G.; DeMunno, G.; Dolcetti, G. *Inorg. Chem.* **1986**, *25*, 4828–4831.

(12) We have found chemical and physical properties of the Br$_4$cat^{2-} complexes to be very similar to those of their Cl$_4$cat^{2-} analogues (Figure S4 in the Supporting Information).

(13) Pure hexabromo-2,3-oxanthrenequinone was independently obtained from the addition of excess Br$_4$bq to **1** in MeCN under air (Figure S3 in the Supporting Information).

(14) (a) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439–3444. (b) Larsen, S. K.; Pierpont, C. G.; DeMunno, G.; Dolcetti, G. *Inorg. Chem.* **1986**, *25*, 4828–4831.

(15) Assuming Br$_4$catH$_2$ is a limiting reagent in the synthesis of **1**, the isolated yields of ∼60% for **1** are close to the theoretical yield of 66%. The discrepancy is likely due to the reaction of Br$_4$bq with **1**.

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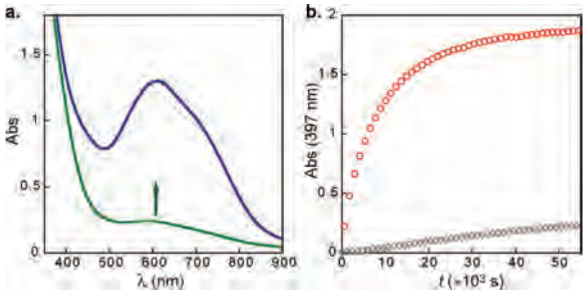
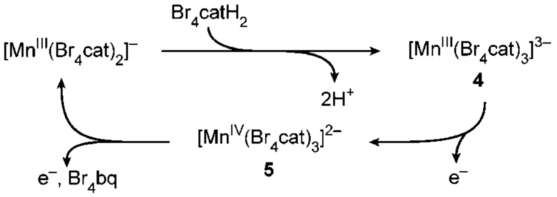


Figure 2. (a) UV–vis absorption spectra for a reaction of 2.9×10^{-4} M **4** (green line) with 1 atm of O_2 in MeCN to generate **5** (blue line) in 100 min at 25 °C. (b) Selected data for the oxidation of 1.0×10^{-3} M 3,5-$^{t}Bu_2catH_2$ to 3,5-$^{t}Bu_2bq$ ($\lambda_{max} = 397$ nm) under 1 atm of O_2 in acetone at 25 °C with 2.1×10^{-6} M **1** (red ○) and without manganese (gray ◊).

Scheme 1



subject of ongoing studies in our laboratory. Although **5** is indefinitely stable under N_2, it is unstable under O_2, affording **1** and Br_4bq-derived products over hours at 25 °C.[18] The fate of the reduced oxygen species is under investigation but is likely H_2O_2 based on literature precedent.[2b,7a,8]

The relative stabilities of **1**−**3** in oxygen suggest that their slow reaction with O_2 proceeds via an unfavorable pre-equilibrium comproportionation reaction between $[Mn^{III}(Br_4cat)_2]^-$ anions to generate trace amounts of air-sensitive **4**. However, the addition of 1 equiv of Cp^*_2Co to **1** in MeCN gives immediate conversion to a light-yellow product, which rapidly reacts with O_2 to generate green **4** and blue **5**, as evidenced by UV–vis spectroscopy. An identical yellow complex is obtained from the combination of $Mn^{II}Cl_2 \cdot 4H_2O$ with 3 equiv of Br_4catH_2 and 6 equiv of LiOMe in MeOH under N_2. These observations suggest that $[Mn^{II}(Br_4cat)_3]^{4-}$ is the initial product generated in the aerobic synthesis of **1** from manganese(II) salts and that Br_4cat^{2-} ligand redistribution on reduced $[Mn^{II}(Br_4cat)_2]^{2-}$ is facile.

The net conversion of Br_4catH_2 to Br_4bq by reaction with **1** and O_2 (via **4** and **5**; Scheme 1) comprises a complete catalytic cycle for aerobic catechol oxidation by the $[Mn^{III}(Br_4cat)_2]^-$ fragment. Indeed, heating **1** to reflux in air-saturated MeCN with >20 equiv of Br_4catH_2, and without base, results in high-yield formation of hexabromo-2,3-oxanthrenequinone. We postulated that the $[Mn^{III}(Br_4cat)_2]^-$ core could effect rapid catalytic quinone production from a more easily oxidized catechol substrate. Accordingly, quantitative conversion of 3,5-di-*tert*-butylcatechol (3,5-$^{t}Bu_2catH_2$) to 3,5-di-*tert*-butylquinone (3,5-$^{t}Bu_2bq$) is achieved with 0.2 mol % **1** in ca. 400 min under 1 atm of O_2 at 25 °C, without added base (Figures 2b and S5 in the Supporting Information). Analysis of the products by ^1H NMR spectroscopy and gas chromatography−mass spectrometry indicates that 3,5-$^{t}Bu_2bq$ is the only catechol-derived species formed, implying **1** is not active for intradiol or extradiol dioxygenase-type activity.[6a,19] Control experiments confirm that **1** is required for catalytic turnover (Figure 2b). If mixed-ligand $[Mn(Br_4cat)_2(3,5\text{-}^{t}Bu_2cat)]^{3-/2-}$ species analogous to **4** and **5** are intermediates during catalytic turnover, the reaction is >99% selective for internal oxidation of the $^{t}Bu_2cat^{2-}$ ligand over Br_4cat^{2-}. This redox selectivity reflects the >500 mV difference in the oxidation potentials of 3,5-$^{t}Bu_2catH_2$ versus Br_4catH_2,[20] which also contributes to the robust nature of the $[Mn^{III}(Br_4cat)_2]^-$ fragment in aerobic catechol oxidation catalysis.

In summary, whereas the $[Mn^{III}(Br_4cat)_2]^-$ fragment is itself surprisingly inert to O_2, in the presence of catechol substrates it reacts rapidly to produce quinone in an oxidase-type dehydrogenation reaction. Although such catecholase chemistry is not rare for metal−quinone complexes,[6a,21] our preliminary investigations of the title complex have already uncovered several salient features of these reactions. In particular, despite proceeding via a series of $1e^-$ steps, the reaction is selective for the $2e^-$ dehydrogenation of catechols. This multielectron capacity apparently derives from both metal- and ligand-centered redox events during catalytic turnover, a consequence of the close match in metal and ligand valence orbital energies. Additionally, the requirement for preassembly of a catalyst−substrate complex prior to reaction with O_2 facilitates intramolecular redox processes over competing intermolecular redox events. Our ongoing work in this field focuses on the development of new aerobic multielectron redox cycles, including amine and alcohol oxidations that derive specificity from the ability of a coordinatively unsaturated 3d metal ion to bind substrate prior to reaction with O_2. For instance, the affinity of the $[Mn^{III}(Br_4cat)_2]^-$ fragment for both alcohol and ketone substrates in solution (as in **1** and **2**, respectively) demonstrates the viability of this approach by modeling two key components in a cycle for catalytic aerobic alcohol oxidation.

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Supporting Information Available: Details of general experimental procedures; synthesis, spectroscopic, and analytical characterization of **1**, **2**, and **4**; a representative procedure for aerobic catechol oxidation; UV–vis absorption spectra for a catalytic oxidation of 3,5-$^{t}Bu_2catH_2$ to $^{t}Bu_2bq$; X-ray crystal structures of **2**, **4**, and hexabromo-2,3-oxanthrenequinone; and X-ray crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Complex **1** was isolated as an insoluble PPN^+ salt from the reaction of **4** with O_2 in THF. Its identity was confirmed by UV−vis spectroscopy in MeCN and by electrospray ionization mass spectrometry.

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