Reactions of Tetrabromocatecholatomanganese(III) Complexes with Dioxygen

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New five- and six-coordinate complexes containing the $[Mn^{III}(Br_4cat)_2]^-$ core $(Br_4cat^{2-} = tetrabromo-1,2-catecholate)$ have been prepared. Homoleptic $[Mn^{III}(Br_4cat)_3]^{3-}$ reacts rapidly with O_2 to produce tetrabromo-1,2-benzoquinone (Br_4bq) . The $[Mn^{III}(Br_4cat)_2]^-$ 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 transitionmetal 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

- For example, see: (a) Advances in Catalytic Activation of Dioxygen by Metal Complexes; Simándi, L. I., Ed.; Springer: New York, 2003.
 (b) Biomimetic Oxidations Catalyzed by Transition Metal Complexes; Meunier, B., Ed.; Imperial College: London, 2000. (c) Borovik, A. S.; Zinn, P. J.; Zart, M. K. Dioxygen Binding and Activation: Reactive Intermediates. In Activation of Small Molecules: Organometallic and Bioinorganic Perspectives; Tolman, W. B., Ed.; Wiley-VCH: Weinheim, Germany, 2006; pp 187–234. (d) Acc. Chem. Res. 2007, 7, 465–634.
- (2) (a) Tolman, W. B. Metal-Radical Arrays. In Comprehensive Coordination Chemistry II; McCleverty, I. A., Meyer, T. J., Eds.; Elsevier Pergamon: Boston, 2004; Vol. 8, pp 715–737. (b) Chaudhuri, P.; Wieghardt, K.; Weyhermüller, T.; Paine, T. K.; Mukherjee, S.; Mukherjee, C. Biol. Chem. 2005, 386, 1023–1033. (c) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. Chem. Rev. 2004, 104, 013–1045.
- (3) (a) Stahl, S. S. Science 2005, 309, 1824–1826. (b) Stahl, S. S. Angew. Chem., Int. Ed. 2004, 43, 3400–3420.
- (4) Sheldon, R. A.; Kochi, J. K. Metal-Catalyzed Oxidations of Organic Compounds; Academic Press: New York, 1981.

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 sub-strates but is receiving increased interest.^{2,5}

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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 O2 by $[Mn^{III}(Cl_4cat)_2(EtOH)(H_2O)]^-$ (Cl_4cat^{2-} = tetrachloro-1,2catecholate) 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 O2.7,8b However, there was ambiguity regarding the mechanism of the reaction, particularly the speciation of the O2-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 $[Mn^{III}(Br_4cat)_2]^-$ fragment $(Br_4cat^{2-} = tetrabromo-1, 2-cate$ cholate) and studies of their reaction with O₂.

Heating acetone solutions of $Mn^{II}(ClO_4)_2 \cdot 6H_2O$ with 2 equiv of Br_4catH_2 and $^{n}BuN_4OH$ to reflux in air generates

- (7) (a) Tyson, C. A.; Martell, A. E. J. Am. Chem. Soc. 1972, 94, 939–945. (b) Ruiz, R.; Caneschi, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L.; Vazquez, M. Inorg. Chem. Commun. 2000, 3, 76–79.
- (8) (a) Sheriff, T. S.; Carr, P.; Coles, S. J.; Hursthouse, M. B.; Lesin, J.; Light, M. E. *Inorg. Chim. Acta* 2004, *357*, 2494–2505. (b) Sheriff, T. S. J. Chem. Soc., Dalton Trans. 1992, 1051–1058.

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^{(5) (}a) Blackmore, K. J.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* 2005, 44, 5559–5561. (b) Haneline, M. R.; Heyduk, A. F. *J. Am. Chem. Soc.* 2006, *128*, 8410–8411. (c) Bouwkamp, M. W.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* 2006, *128*, 13340–13341. (d) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* 2006, *128*, 13340–13341. (d) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* 2007, *129*, 7212–7213. (e) Edison, S. E.; Hotz, R. P.; Baldwin, M. J. *Chem. Commun.* 2004, 1212–1213. (f) Mukherjee, C.; Weyhermüller, T.; Bothe, E.; Chaulhuri, P. C. *R. Chemie* 2007, *10*, 313–325. (g) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* 2007, *129*, 12400–12401.

^{(6) (}a) Pierpont, C. G.; Lange, C. W. The Chemistry of Transition Metal Complexes Containing Catechol and Semiquinone Ligands. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1994; Vol. 41, pp 331–442. (b) Chaudhuri, P.; Wieghardt, K. Phenoxyl Radical Complexes. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 2001; Vol. 50, pp 151–216..



Figure 1. Solid-state structures of the anions in (a) (${}^{18}\text{Bu}_4\text{N}$)-[Mn^{III}(Br₄cat)₂(Me₂C=O)₂] (1) and (b) (PPN)Li₂[Mn^{III}(Br₄cat)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 (ⁿBu₄N)[Mn^{III}(Br₄cat)₂(Me₂C=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_{Br4cat} bond lengths, consistent with a highspin 3d⁴ electron configuration.¹⁰ Recrystallization of **1** from MeOH affords the five-coordinate alcohol adduct (ⁿBu₄N)[Mn^{III}(Br₄cat)₂(MeOH)] (2) with distorted squarepyramidal 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 $[Mn^{III}(Br_4cat)_2]^-$ core is preserved in solution. However, contrary to the previous reports,^{7b,8} this fragment reacts sluggishly with O₂. Exposure of green 1 or 2 to 1 atm of O₂ in acetone or MeCN affords conversion to a dark-blue species over weeks at ambient temperature. Likewise, the triphenylphosphine oxide complex (ⁿBu₄N)[Mn^{III}(Br₄cat)₂(OPPh₃)] (3) is indefinitely stable under air in MeCN.¹¹ In light of these observations, the reported facile reactions of closely related species with O2 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 (Br₄bq) with Br₄cat^{2–,14} The yield of the coupled product varies and is inversely proportional to the yield of **1**.

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Accordingly, reaction of Br_4bq with isolated 1 in MeCN under N_2 leads to the slow formation of hexabromo-2,3oxanthrenequinone and decomposition of 1.

The apparent intermediacy of free Br₄bq under the aerobic conditions employed for the preparation of 1 and the isolated yields of $\sim 60\%$ for 1 suggest that 1 equiv of Br₄catH₂ is consumed as a sacrificial reductant for each equivalent of 1 produced.¹⁵ Consistent with this hypothesis, anaerobic addition of Br₄cat²⁻ (generated in situ from Br₄catH₂ and LiOMe) to 1 in MeCN gives immediate conversion to a darkgreen, air-sensitive material (4). Complex 4 is independently obtained from the reaction of Mn^{II}Cl₂•4H₂O with 3 equiv of Br₄catH₂ 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 N₂ afforded single crystals suitable for analysis by X-ray crystallography (Figure 1b). The structure reveals a manganese tris(tetrabromo-ocatecholato) trianion $[Mn^{III}(Br_4cat)_3]^{3-}$ 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 O₂ 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 $[Mn^{IV}(Cl_4cat)_3]^{2-7b,8a,12}$ and is tentatively formulated as $[Mn^{IV}(Br_4cat)_3]^{2-}$. Consistent with this assignment, **5** is independently obtained from the addition of 1.0 equiv of AgPF₆ to **4** under N₂. 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 $[Mn^{III}(Br_4cat)_2(Br_4sq^*)]^{2-}$ (Br₄sq^{*-} = tetrabromo-1,2-semiquinonate) intravalence isomer. The electronic structure of **5** and related materials is a

- (12) We have found chemical and physical properties of the Br_4cat^{2-} complexes to be very similar to those of their Cl_4cat^{2-} analogues (Figure S4 in the Supporting Information).
- (13) Pure hexabromo-2,3-oxanthrenequinone was independently obtained from the addition of excess Br_4bq 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 Br₄catH₂ 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 Br₄bq with 1.
- (16) Hartman, J. R.; Foxman, B. M.; Cooper, S. R. *Inorg. Chem.* 1984, 23, 1381–1387.
- (17) A [Mn. (cat)₃]³⁻ ion was inferred from a spectrophotometric titration. See: Sever, M. J.; Wilker, J. J. Dalton Trans. 2004, 1061–1072.

⁽⁹⁾ Carugo, O.; Castellani, C. B.; Djinoviæ, K.; Rizzi, M. J. Chem. Soc., Dalton Trans. 1992, 837–841.

⁽¹⁰⁾ Krzystek, J.; Yeagle, G. J.; Park, J.-H.; Britt, R. D.; Meisel, M. W.; Brunel, L.-C.; Telser, J. Inorg. Chem. 2003, 42, 4610–4618.

^{(11) (}a) For O₂ sensitivity studies, **3** was generated in situ from the addition of excess OPPh₃ 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.



Figure 2. (a) UV–vis absorption spectra for a reaction of 2.9×10^{-4} M 4 (green line) with 1 atm of O₂ 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-'Bu₂catH₂ to 3,5-'Bu₂bq ($\lambda_{max} = 397$ nm) under 1 atm of O₂ in acetone at 25 °C with 2.1×10^{-6} M 1 (red \bigcirc) and without manganese (gray \diamondsuit).

Scheme 1



subject of ongoing studies in our laboratory. Although **5** is indefinitely stable under N₂, it is unstable under O₂, affording **1** and Br₄bq-derived products over hours at 25 °C.¹⁸ The fate of the reduced oxygen species is under investigation but is likely H₂O₂ based on literature precedent.^{2b,7a,8}

The relative stabilities of 1-3 in oxygen suggest that their slow reaction with O2 proceeds via an unfavorable preequilibrium comproportionation reaction between $[Mn^{III}(Br_4cat)_2]^-$ anions to generate trace amounts of airsensitive 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}Cl₂•4H₂O with 3 equiv of Br₄catH₂ and 6 equiv of LiOMe in MeOH under N₂. 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 Br₄cat²⁻ ligand redistribution on reduced [Mn^{II}(Br₄cat)₂]²⁻ is facile.

The net conversion of Br_4catH_2 to Br_4bq by reaction with **1** and O₂ (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 airsaturated 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-'Bu₂catH₂) to 3,5-di-*tert*-butylquinone (3,5-'Bu₂bq) is achieved with 0.2 mol % **1** in ca. 400 min under 1 atm of O₂ 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-'Bu₂bq is the only catechol-derived species formed, implying **1** is not active for intradiol or extradiol dioxy-genase-type activity.^{6a,19} Control experiments confirm that **1** is required for catalytic turnover (Figure 2b). If mixed-ligand [Mn(Br₄cat)₂(3,5-'Bu₂cat)]^{3-/2-} species analogous to **4** and **5** are intermediates during catalytic turnover, the reaction is >99% selective for internal oxidation of the 'Bu₂cat²⁻ ligand over Br₄cat²⁻. This redox selectivity reflects the >500 mV difference in the oxidation potentials of 3,5-'Bu₂catH₂ versus Br₄catH₂,²⁰ which also contributes to the robust nature of the [Mn^{III}(Br₄cat)₂]⁻ fragment in aerobic catechol oxidation catalysis.

In summary, whereas the $[Mn^{III}(Br_4cat)_2]^-$ fragment is itself surprisingly inert to O₂, 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 ligandcentered 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 O₂ 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 O₂. For instance, the affinity of the [Mn^{III}(Br₄cat)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-'Bu₂catH₂ to 'Bu₂bq; 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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- (20) Pascaly, M.; Duda, M.; Schweppe, F.; Zurlinden, K.; Müller, F. K.; Krebs, B. J. Chem. Soc., Dalton Trans. 2001, 828–837.
- (21) (a) For example, see: Triller, M. U.; Pursche, D.; Hsieh, W.-Y.; Percoraro, V. L.; Rompel, A.; Krebs, B. *Inorg. Chem.* **2003**, *42*, 6274– 6283. (b) Hitomi, Y.; Ando, A.; Matsui, H.; Ito, T.; Tanaka, T.; Ogo, S.; Funabiki, T. *Inorg. Chem.* **2005**, *44*, 3473–3478.

⁽¹⁸⁾ Complex 1 was isolated as an insoluble PPN⁺ salt from the reaction of 4 with O₂ in THF. Its identity was confirmed by UV-vis spectroscopy in MeCN and by electrospray ionization mass spectrometry.

⁽¹⁹⁾ Que, L., Jr.; Ho, R. Y. N Chem. Rev. 2006, 96, 2607-2624.