Inorg. Chem. **1982,** *21,* 4315–4317

Notes

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Reversible Binding of Dioxygen by Manganese Complexes of 3,5-Di-*tert*-butylcatechol: A Reappraisal

Stephen R. Cooper* and JudithAnn R. Hartman

Received November 30, 1981

Recently several reports have appeared in which the reversible binding of O_2 by manganese[1,2] and vanadium[3] complexes of 3,5-di-*tert*-butylcatechol has been claimed. Very recently we have shown[4] that reports of reversible binding of O_2 by vanadium–3,5-di-tert-butylcatechol complexes are in error, which has prompted us to study similar claims for reversible oxygen binding by $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ (throughout Cat = catecholate). From the results reported here it is clear that the observations described by the earlier workers are due to oxidation of the ligand and subsequent reactions of the oxidation products.

According to the previous reports[1,2] oxygenation of a solution of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ causes appearance in the optical spectrum of a shoulder at 450 nm, a spectral feature that was said to be characteristic of the red-brown "oxygen adduct". This spectral change reversed upon purging of the solution with Ar,[5] from which it was concluded that the interaction with oxygen was reversible.[1,2] We have reproduced the experiments described in ref 1 (a dimethyl sulfoxide solution containing 1 mM manganese(III) acetate, 3 mM 3,5-di-*tert*-butylcatechol, and 6 mM Me_4NOH was exposed for 3 min to pure, dry O_2 (in our experiments generated by thermal decomposition of $KMnO_4$)) and found that the spectral changes induced by oxygenation do indeed appear to reverse upon purging of the solution—*but the spectral changes reverse also upon sealing of the solution.* Furthermore, careful observation reveals that upon "reversal" of "oxygen binding" the solution scatters light and eventually deposits red-brown material,[6] which indicates that a significant degree of decomposition has occurred. (Separation of red-brown material is particularly obvious at higher concentrations of the complex). These observations are inconsistent with oxygen binding but *are* consistent with formation by oxidation of a species with a band near 450 nm, which undergoes subsequent decomposition.

We have found that the spectrum of the "O_2 adduct" (Figure 1) bears a striking resemblance to that exhibited by a solution of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ upon partial oxidization (under N_2) with a substoichiometric amount of Ag(I) or I_2 (Figure 2) (followed by addition of base). Thus the optical spectrum of the "O_2 adduct" can be reproduced *in the absence of O_2*.

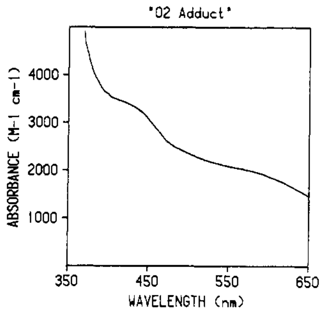

Figure 1. Optical spectrum of the "O_2 adduct" of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ in CH_3CN, redrawn from ref 2.

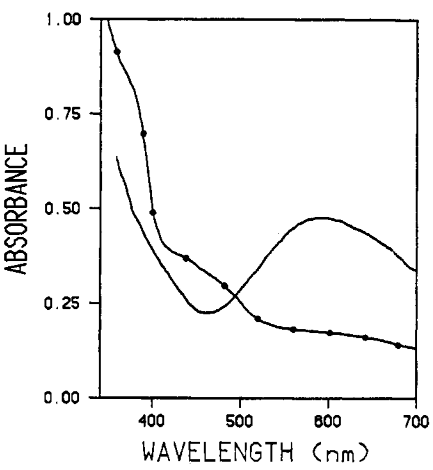

Figure 2. Optical spectrum of a solution of 2×10^{-4} M $K_2[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]\cdot 6CH_3CN$ in CH_3CN (1-cm path length) (solid line) and spectrum after addition by microliter syringe of 5 μL of 0.01 M $AgNO_3$ and 1 μL of 2.2 M Me_4NOH in MeOH to the solution above (3 mL) (circles). All solutions were under N_2.

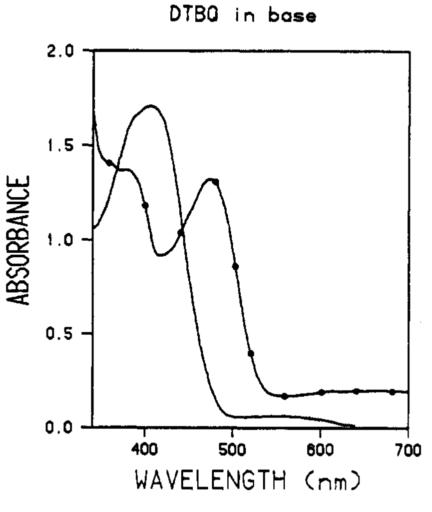

Figure 3. Optical spectrum of 1.1 mM 3,5-di-*tert*-butyl-*o*-benzoquinone in dimethyl sulfoxide (solid line) and spectrum after addition of 1 μL of 2.2 M Me_4NOH to the solution above (3 mL) (circles). Both solutions were under N_2.

One candidate for oxidation is the ligand itself. In alkaline solution 3,5-di-*tert*-butylcatechol is readily oxidized by air to

---

(1) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978,** *100,* 989–91.

(2) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1980,** *19,* 492–6.

(3) Wilshire, J. P.; Sawyer, D. T. *J. Am. Chem. Soc.* **1978,** *100,* 3972–3. In a subsequent paper some of these claims have been modified: Bosserman, P. J.; Sawyer, D. T. *Inorg. Chem.* **1982,** *21,* 1545–51.

(4) Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982,** *104,* 5092–102.

(5) Similar observations have been made for $Cr(Cat)_3^{3-}$: Isied, S. S.; Borgias, B.; Raymond, K. N., personal communication.

(6) The earlier workers mentioned the facility with which the "oxygen adduct" decomposes, the failure of the optical spectrum to return completely, and that irreversible chemical oxidation of the ligands is an intrinsic feature of the system.

0020-1669/82/1321-4315$01.25/0 © 1982 American Chemical Society

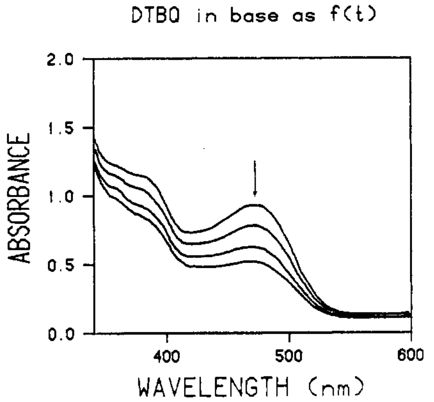

Figure 4. Optical spectra (at 2-min intervals) of 1.1 mM 3,5-di-*tert*-butyl-*o*-benzoquinone in dimethyl sulfoxide after addition of 1 μL of 2.2 M Me_4NOH to 3 mL of solution. All solutions were under N_2.

the corresponding semiquinone and quinone. Moreover, a number of transition metal ions have been shown to catalyze the oxidation of 3,5-di-*tert*-butylcatechol by air, and those of manganese have been shown to be particularly effective catalysts.[7,8] Although neither the semiquinone nor the quinone exhibits an optical band near the characteristic 450-nm shoulder of the putative O_2 adduct, *basic* solutions of the quinone exhibit a band maximum at 470 nm. Addition of Me_4NOH to a dilute solution of 3,5-di-*tert*-butyl-*o*-benzoquinone in dimethyl sulfoxide causes the initially yellow solution (λ_{max} 400, ϵ 1560) to become deep red-brown (λ_{max} 470, ϵ ~1200) (Figure 3). In addition, the absorbance at the 470-nm maximum rapidly decreases from its initial value (the absorbance is halved in 10 min) (Figure 4). For partially oxidized $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ (Figure 2) overlap of the absorbance of the unreacted complex with the band at 470 nm from alkaline 3,5-di-*tert*-butyl-*o*-benzoquinone gives rise to the characteristic spectral feature of the "O_2 adduct"—a shoulder at 450 nm.

The facts above offer a facile explanation of the spectral observations reported by the previous workers and the apparent reversibility of those changes. Quinones in basic solution are well-known[9-16] to undergo Michael addition by hydroxide ion to yield hydroxyquinones. Hydroxyquinones, in turn, are readily converted by disproportionation or oxidation (by air or unreacted quinone) to the corresponding semiquinones,[9,11,13-16] which rapidly couple to yield polymers. (Such systems have been studied for many years as models for the naturally occurring humic acids.[17-19]) Furthermore, as stated in a recent review,[20] such polymers are "easily soluble in (aqueous) alkali, giving green or brown solutions which readily absorb(ed) oxygen from the air to form deep brown solutions".

Exposure of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ to O_2 generates a steady-state concentration of the red-brown semiquinone of the Michael addition product, which is formed continuously by oxidation and is removed by precipitation of polymerized semiquinone (and probably also ring cleavage). Purging (or sealing) the solution causes generation of the red-brown semiquinone to cease, and when the semiquinone remaining in solution precipitates, the solution exhibits the spectrum of any unreacted $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$—in this respect the system superficially resembles one that binds oxygen reversibly. This suggestion explains why the system is more "reversible" in dilute solution[1,2] (polymerization is less obvious), why base concentration is critical[1] (base is necessary to generate the quinone and hydroxyquinone), why the "reversibility" is optimal in CH_3CN[2] (the oxidation products are less soluble in CH_3CN than many other solvents (e.g., methanol, water[21])), and why the higher and lower oxidation states of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ also appear to bind oxygen reversibly[1] (the initial oxidation state of the manganese is immaterial, since the observed phenomena involve only the catechol).

That oxidation of the catechol had in fact occurred in the experiments of the previous workers is apparent from the EPR spectrum reported for the "O_2 adduct",[2,23] which reflects the presence of free semiquinone radicals. The EPR spectrum reported for $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ (in CH_3CN at 4 K) consisted of a very broad signal (line width ≈500 G) at g = 3.67 and two superimposed signals at g = 2, a very sharp signal (line width ≈2 G), and a broader one (line width ≈500 G).[2] As mentioned by the authors, the sharp signal is due to free semiquinone, a signal which upon oxygenation increased "significantly".[2] (We find[28] the EPR spectrum of pure $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ to exhibit the two broad features but not the sharp signal from free semiquinone.) These results demonstrate that oxidation of the catechol certainly occurred in the earlier experiments; we have shown above that such oxidation leads to an optical spectrum that very closely resembles that of the putative "O_2 adduct".

A line of evidence which was taken[1,2] to indicate reversible oxygen binding by $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ is the reported

---

(7) Grinstead, R. R. *Biochemistry* **1964**, *3*, 1308-14.

(8) Tyson, C. A.; Martell, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 939-45.

(9) Venkataraman, B.; Frankel, G. K. *J. Am. Chem. Soc.* **1955**, *77*, 2707-13.

(10) Flaig, W.; Salfeld, J. C. *Naturwissenschaften* **1960**, *47*, 516.

(11) Eigen, M.; Matthies, P. *Chem. Ber.* **1961**, *94*, 3309-17.

(12) Reitz, D. C.; Hollahan, J. R.; Dravnieks, F.; Wertz, J. E. *J. Chem. Phys.* **1961**, *34*, 1457-8.

(13) Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1965**, 1488-94.

(14) Hewgill, F. R.; Mullings, L. R. *J. Chem. Soc. B* **1969**, 1155-61.

(15) Fitzpatrick, J. D.; Steelink, C. *J. Org. Chem.* **1972**, *37*, 762-7.

(16) Ashworth, P.; Dixon, W. T. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1130-3.

(17) Schulze, H.; Flaig, W. *Justus Liebigs Ann. Chem.* **1952**, *575*, 231-41.

(18) Erdtman, H.; Granath, M. *Acta Chem. Scand.* **1954**, *8*, 811-6.

(19) Flaig, W.; Ploetz, T.; Biergans, H. *Justus Liebigs Ann. Chem.* **1955**, *597*, 196-213.

(20) Lindsey, A. S. In "The Chemistry of Quinonoid Compounds"; Patai, S., Ed.; Wiley: New York, 1974; pp 793-855.

(21) Previously[22] the earlier workers oxidized 3,5-di-*tert*-butylcatechol in aqueous, alkaline solution to a red-brown solution (λ_{max} = 480 nm), which they attributed to a 3,5-di-*tert*-butyl-*o*-benzosemiquinone decomposition product.

(22) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 515-23.

(23) In their original communication,[1] these workers reported that the EPR spectrum of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ consists of a doublet with the separation characteristic of 3,5-di-*tert*-butyl-*o*-benzosemiquinone (2,4 G), each component of which was further "split by at least 11 hyperfine lines from coupling with coordinated manganese(III) ions". The manganese hyperfine coupling (not reported, along with solvent and temperature) must be smaller than that of the semiquinone doublet to appear as structure on it. The value implied (<2.4 G), although possible,[24] is unlikely because hyperfine coupling to ^{55}Mn is typically ≈100 G. We have found that similar spectra (a doublet, each component of which is split into 13 lines, the outermost of which are quite weak) can be obtained in the absence of manganese by treatment of solutions of 3,5-di-*tert*-butyl-*o*-benzoquinone (or 3,5-di-*tert*-butylcatechol in air) with base. Similar results have been reported for 3,5-di-*tert*-butyl-*o*-benzosemiquinone by Trapp, Tyson, and Giacometti,[25] who reported that the splitting from the protons of only the 5-*tert*-butyl group is resolved. The resulting spectrum has 11 obvious lines (couplings to the 3-*tert*-butyl and the 6-position ring proton are small) and several more partially resolved ones. Müller et al.[26] have also reported observation of 3,5-di-*tert*-butyl-*o*-benzosemiquinone spectra with 11-13 components at -40 °C. Observation of additional lines in semiquinone spectra has been attributed variously to coupling of semiquinones[27] and resolution of proton hyperfine structure from an alkoxide group that had attacked the ring.[12] These observations are a much more plausible source of the spectrum described earlier.

(24) Buchanan, R. M.; Downs, H. H.; Shorthill, W. B.; Pierpont, C. G.; Kessel, S. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 4318-20.

(25) Trapp, C.; Tyson, C. A.; Giacometti, G. *J. Am. Chem. Soc.* **1968**, *90*, 1394-1400.

(26) Müller, E.; Günter, F.; Scheffler, K.; Ziemek, P.; Rieker, A. *Justus Liebigs Amn. Chem.* **1965**, *688*, 134-49.

(27) Anderson, D. H.; Frank, P. J.; Gutowsky, H. S. *J. Chem. Phys.* **1960**, *32*, 196-204.

(28) Hartman, J. R.; Cooper, S. R., manuscript in preparation.

"reversibility" of the optical changes on oxygenation. Apparently reversible color changes on oxygenation of polyhydroxy aromatic compounds have been observed previously. In an early report Campbell[29] reported that oxygenation in alkaline solution of di-*tert*-butylpyrogallol (which is closely related to 3,5-di-*tert*-butylcatechol) causes transient generation of a deep purple color, which fades upon standing to yield a colorless solution. Similarly, Nanni, Stallings, and Sawyer[30] have recently reported reversible color changes on purging and reoxygenation of O_2^-–3,5-di-*tert*-butylcatechol solutions in the absence of any metal ions. In neither of these cases is there any question of reversible oxygen binding—rather it is apparent that transient coloration on oxygenation is due to formation and decay of a colored intermediate in the oxidation of the catechol (or catechol-like compound). Thus it is clear that observation of apparently reversible color changes on oxygenation of catechol-containing solutions does not in itself necessarily indicate reversible oxygen binding by such solutions.

Other physical data previously adduced in support of formation of an O_2 adduct included electrochemical and magnetic measurements. The cyclic voltammogram of the "O_2 adduct" contained an anodic peak at -0.5 V (vs. SCE) that was said[1] to be characteristic of the reduction product of the reversible O_2 adduct in dimethyl sulfoxide solution. This value is quite close to that recently reported[31,32] for the 3,5-di-*tert*-butyl-*o*-benzoquinone/semiquinone couple ($E_f = -0.47$ V) and could well be due to the presence of free semiquinone, consistent with the hypothesis and observations above. The earlier workers also reported that oxygenation of $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ caused a decrease in magnetic moment which reversed upon deoxygenation. We have not attempted to reproduce the magnetic measurements, since from the reported electrochemical data[1,2] it is apparent that the solutions were complex mixtures.[33] While we are unable to account for the apparent reversibility of the changes in magnetic moment, the decrease in solution moment on oxygenation can be explained by the work of Sealy and co-workers,[34] who have shown that synthetic melanin (a polymer formed by air oxidation of 3,4-dihydroxyphenylalanine in alkaline solution) readily binds tri- and even dipositive metal ions. Binding of manganese to precipitated polymer (generated upon oxygenation) necessarily decreases the solution magnetic moment, just as reported for the "O_2 adduct", since some of the paramagnetic ions are removed from solution.

In the following paper it is suggested that $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ cannot be oxidized by O_2 because O_2 is reduced to O_2^- at -1.0 V vs. SCE, i.e., below the potential at which $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ is oxidized. This argument predicts that no compound oxidized above -1.0 V should be air sensitive—a conclusion at variance with observation. It is well-known that compounds oxidized below 0 V vs. SCE are generally sensitive to oxidation by O_2.[35] As a concrete example, in CH_3CN $Ni(S_2C_2(CF_3)_2)_2^{2-}$ is reversibly oxidized at -0.12 V vs. SCE—and the compound is oxidized by air.[36] Since this compound is *more* difficult to oxidize than $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ (for which $E \approx -0.4$ V vs. SCE),[37] $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ must also be subject to oxidation by O_2. Thus the redox thermodynamics of the $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$–$O_2$ system do not in any way preclude oxidation of the former by the latter.

In fact, O_2/O_2^- is not the appropriate couple to use in media that contain water. Even carefully dried solvents contain sufficient water that the relevant potential is not that of the weakly oxidizing O_2/O_2^- couple but rather that of the more strongly oxidizing O_2/HO_2 couple. This is why there are compounds oxidized above the potential of the O_2/O_2^- couple that nevertheless are oxidized by O_2. In the original experiments on the "O_2 adduct"[1,2] Me_4NOH was used to deprotonate the catechol—a reaction which generates water. Furthermore, no mention was made[1,2] of an attempt to dry either the solvent or the Me_4NOH.

It is clear from the above results that the data presented by the earlier workers as indirect evidence for formation of an O_2 adduct are inadequate to sustain this hypothesis and are more reasonably ascribed to hydroxide attack on 3,5-di-*tert*-butyl-*o*-benzoquinone (previously generated by air oxidation of the ligand). It is also clear that, in the absence of *direct* manometric evidence for reversible oxygen uptake and release, reversible binding of dioxygen by manganese complexes of 3,5-di-*tert*-butylcatechol must be regarded with skepticism. In light of the present results and our previous studies of the vanadium–3,5-di-*tert*-butylcatechol system and its "O_2 adduct",[4] it is also clear that facile oxidation of the catechol (to either bound or free semiquinone), rather than dioxygen coordination,[38] is emerging as a general property of catechol complexes. For such complexes dioxygen coordination remains to be demonstrated.

Acknowledgment. We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to thank Professor E. J. Corey of this department for use of his spectrophotometer.

Registry No. $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$, 72268-94-1; 3,5-di-*tert*-butyl-*o*-benzoquinone, 3383-21-9.

---

(29) Campbell, T. W. *J. Am. Chem. Soc.* **1951**, *73*, 4190–5.

(30) Nanni, E. J., Jr.; Stallings, M. D.; Sawyer, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 4481–5.

(31) Stallings, M. D.; Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2655–60.

(32) Note that the chemistry discussed here could explain other results reported in ref 31: that electrogenerated 3,5-di-*tert*-butyl-*o*-benzosemiquinone is rapidly destroyed in a reaction that is accelerated by the presence of water and that addition of hydroxide to a solution of 3,5-di-*tert*-butyl-*o*-benzoquinone causes it to turn green, as discussed above.

(33) The earlier report[2] contains the statement that "the manganese(IV) complex probably is in equilibrium with catechol monoanion, semiquinone anion, quinone, and manganese(III) complexes". We suggest that rather than being in equilibrium, for which there is no evidence (e.g., our EPR results for $[Mn(3,5\text{-}(t\text{-}Bu)_2Cat)_3]^{2-}$ show no semiquinone[28]), these species are the components of a mixture.

(34) Felix, C. C.; Hyde, J. S.; Sarna, T.; Sealy, R. C. *J. Am. Chem. Soc.* **1978**, *100*, 3922–6.

(35) Headridge, J. B. "Electrochemical Techniques for Inorganic Chemists"; Academic Press: New York, 1969; pp 93–94.

(36) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1963**, *2*, 1227–32.

(37) Chin, D.-H.; Sawyer, D. T. *Inorg. Chem.*, following paper in this issue.

(38) Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1981**, *103*, 3961–3.

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521

Rebuttal to a Reappraisal of "Reversible Binding of Dioxygen by Manganese Complexes of 3,5-Di-*tert*-butylcatechol"

Der-Hang Chin and Donald T. Sawyer*

Received May 11, 1982

The proposition of the preceding paper[1] is that Magers, Smith, and Sawyer[2,3] erred when they attributed the spectroscopic changes that result from the oxygenation and argon deaeration of the tris(3,3-di-*tert*-butylcatecholato)manga-

---

(1) Cooper, S. R.; Hartman, J. R. *Inorg. Chem.*, preceding paper in this issue.

(2) Magers, K. D.; Smith, C. G.; Sawyers, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 989.

(3) Magers, K. D.; Smith, C. G.; Sawyer, D. T. *Inorg. Chem.* **1980**, *19*, 492.