"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.

0020-1669/82/1321-4317$01.25/0 © 1982 American Chemical Society

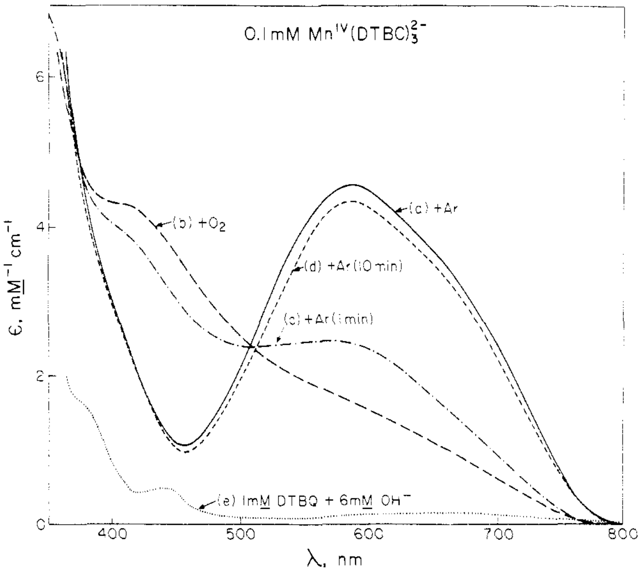


Figure 1. Absorption spectra in acetonitrile for $Mn^{IV}(DTBC)_3^{2-}$ [prepared in situ by the combination of $Mn^{II}(DMU)_6(ClO_4)_2$ (DMU = dimethylurea), 3,5-di-*tert*-butylcatechol ($DTBCH_2$), tetraethylammonium hydroxide ((TEA)OH), and 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) in a mole ratio of 1:2:4.6:1][2,6] under a purified N_2 (1 atm) atmosphere (spectrum a), after the solution is bubbled with O_2 (1 atm) for 1 min at 0 °C (spectrum b), after the preceding solution is purged with Ar for 1 min at 0 °C (spectrum c), and after the preceding solution is purged with Ar for 10 min at 0 °C (spectrum d). The spectrum for the product solution that results (10 min after preparation) from the combination of 1 mM DTBQ and 6 mM (TEA)OH in acetonitrile (Ar, 1 atm) is presented for comparison (spectrum e). The apparent molar absorptivities (ε) represent the observed absorbances divided by the initial concentrations of $Mn^{IV}(dTBC)_3^{2-}$ (0.1 mM) for curves a–d and by the initial concentration of DTBQ (1 mM) for curve e.

nate(IV) complex, $Mn^{IV}(DTBC)_3^{2-}$ in acetonitrile (CH_3CN) to reversible binding of dioxygen by the complex. Cooper and Hartman[1] conclude that the dominant process is an irreversible oxidation by oxygen of bound DTBC to give the *o*-quinone (DTBQ), which subsequently undergoes a Michael addition under alkaline conditions to give a brown, insoluble polymer. In support of this interpretation they present a spectrum (Figure 3)[1] for the product from the degradation of 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBQ) in an alkaline Me_2SO solution.

To give the reader quantitative perspective, we have repeated the spectrophotometric experiments of Magers, Smith, and Sawyer.[2,3] The resultant spectra for $Mn^{IV}(DTBC)_3^{2-}$ (a) in slightly basic acetonitrile (1 atm of Ar), (b) after oxygenation (1 atm of O_2) for 1 min, (c) after the preceding solution is purged for 1 min with argon, and (d) after the preceding solution is purged for 10 min with argon are compared in Figure 1. The presence of isosbestic points at 370 and 510 nm is consistent with an equilibrium process rather than with irreversible degradation (there is no evidence for any precipitate). For direct quantitative comparison, the spectrum for an alkaline solution of DTBQ (recorded 10 min after its preparation) is included in Figure 1. The spectrum for the latter solution (i) does not compare qualitatively or quantitatively with that for the O_2 adduct of $Mn^{IV}(DTBC)_3^{2-}$, (ii) is not reversible, and (iii) does not undergo a significant increase in absorbance at 440 nm for a period up to 50 h.

As observed previously,[2,3] the oxygenation–deaeration cycle for $Mn^{IV}(DTBC)_3^{2-}$ in acetonitrile is reversible; the respective absorption spectra diminish less than 5% per cycle. In contrast to the observation of the preceding note,[1] we do not observe a change from green to red-brown during the first 10 h after preparation of the alkaline DTBQ solution of Figure 1.

In response to the suggestion that the apparent reversibility is actually due to decomposition of the oxygenated complex,[1] we find that the spectrum for the solution of Figue 1b (the oxygen adduct) remains virtually unchanged for at least 2 h in a sealed cell at 0 °C.

The primary thesis of the reappraisal[1] (i.e., oxidation by molecular oxygen of the bound DTBC ligands of $Mn^{IV}(DTBC)_3^{2-}$ to give DTBQ) is not supported by the redox thermodynamics. A recent paper[4] demonstrates that the reversible redox potential for oxidation of $Mn^{IV}(DTBC)_3^{2-}$ in CH_3CN is approximately −0.4 V vs. SCE (between −0.1 and −0.6 V vs. SCE); the redox potential for reduction of O_2 is −1.0 V vs. SCE in acetonitrile.[5] The cyclic voltammetric oxidation potential for the $Mn^{IV}(DTBC)_3^{2-}$ complex under the solution conditions of Figure 1a is −0.2 V vs. SCE at 0 °C. Thus, the purported primary reaction [$O_2 + Mn^{IV}(DTBC)_3^{2-} \rightleftarrows Mn^{IV}(DTBC)_2(DTBSQ)^- + O_2^-$] is disfavored by −0.6 V. To have a net reaction requires stabilization of the product species by *adduct formation*, which can be a reversible process (Figure 1).

Conclusion

The reinterpretations and conclusins of Cooper and Hartman[1] are not supported by the experimental results. Recent studies[6] provide additional support for the conclusion that dioxygen is reversibly bound by dilute concentrations (~0.1 mM) of $Mn^{IV}(DTBC)_3^{2-}$ in slightly alkaline acetonitrile:

$$\begin{aligned} &Mn^{IV}(DTBC)_3^{2-} + O_2 + OH^- \rightleftarrows \\ &\qquad Mn^{III}(DTBSQ)_2(DTBC)(O_2^-)(OH)^{3-} \rightarrow \\ &\qquad\qquad Mn^{III}(DTBC)_2(O_2^-)(OH)^{3-} + DTBQ \end{aligned}$$

The fragile nature of the adduct and its instability at high temperatures, high concentrations, and in the presence of moist air or excess base were noted in the previous paper,[3] as was the limitation for the reversible process to the conditions of Figure 1. The new data of the preceding note (Figures 3 and 4)[1] constitute a confirmation of these irreversible degradation processes (especially in Me_2SO solutions) but are not the basis for a rational *reappraisal* of the reversible oxygenation reaction.

Acknowledgment. This work was supported by the National Institutes of Health—USPHS under Grant No. GM-22761.

Registry No. $Mn^{IV}(DTBC)_3^{2-}$, 72268-94-1; O_2, 7782-44-7.

---

(4) Jones, S. E.; Chin, D.-H.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 4257.
(5) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.
(6) Chin, D.-H.; Sawyer, D. T.; Schaefer, W. P.; Simmons, C. J., submitted for publication in *Inorg. Chem.*

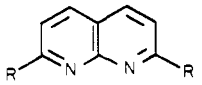
Contribution from the Department of Chemistry,
University of Victoria, British Columbia, Canada V8W 2Y2

Site Exchange of Octahedral Metal Centers between Equivalent Nitrogen Atoms in Complexes of 1,8-Naphthyridine or Phthalazine: A ^1H NMR Study of Pentacarbonylchromium and -tungsten Derivatives

Keith R. Dixon,* Donald T. Eadie, and Stephen R. Stobart*

Received March 19, 1982

The coordination chemistry of 1,8-naphthyridines (I), es-



I, R = H or Me

pecially the parent molecule (R = H, naph) and its 2,7-di-