J|A|C|S
COMMUNICATIONS

A Stable Manganese(V)-Oxo Corrolazine Complex

Beaven S. Mandimutsira,[†] Bobby Ramdhanie,[†] Ryan C. Todd,[†] Hailin Wang,[†] Adelajda A. Zareba,[‡]
Roman S. Czernuszewicz,[‡] and David P. Goldberg*[,†]

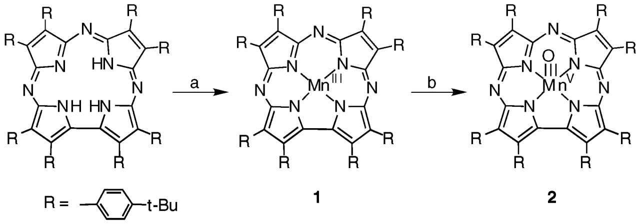
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, and
Department of Chemistry, University of Houston, Houston, Texas 77204-5003

Received September 23, 2002

High-valent metal-oxo species play important roles in a large number of synthetic and biological transformations.[1] In particular, manganese-oxo complexes of both porphyrin[2] and salen[3] catalysts are implicated in various oxygen atom transfer reactions of considerable synthetic importance and have also served as models for intermediates in heme protein-catalyzed oxidations and related reactions. Moreover, manganese-oxo species are postulated as important intermediates in the conversion of H_2O to O_2 during photosynthesis.[4] Thus, the direct spectroscopic observation and isolation of Mn(V)≡O complexes has been a highly desirable yet extremely difficult goal to accomplish because of the synthetic challenges involved in preparing ligands suitable for stabilizing such species. Spectroscopic characterization of an Mn(V)≡O porphyrin was not achieved until very recently,[5] and the three Mn(V)≡O complexes that are isolable at room temperature contain similar non-porphyrin, tetraanionic ligands with either bis-amido bis-alkoxo or tetraamido donors.[6] We have recently prepared a new type of porphyrinoid ligand called corrolazine that is a hybrid of a tetraazaporphyrin and corrole ring.[7] We report herein a remarkably stable Mn(V)≡O species, $(TBP)_8(Cz)Mn(V){\equiv}O$ (**2**) (TBP = 4-*tert*-butylphenyl), which was synthesized using a corrolazine ligand. This compound is, to our knowledge, the first oxomanganese(V)-porphyrinoid complex that can be purified by standard chromatographic methods and isolated at room temperature.[8] The extraordinary stability of **2** has allowed for complete characterization of the Mn(V)≡O moiety, including the first resonance Raman spectra of a (porphyrinoid)Mn(V)≡O complex. Interestingly, $(TBP)_8(Cz)Mn(V){\equiv}O$ is still thermodynamically competent to act as an oxygen atom transfer agent toward PPh_3.

The synthesis of the Mn(V)≡O complex **2** was accomplished as shown in Scheme 1. Insertion of manganese ion into the metal-free $(TBP)_8CzH_3$ went smoothly by reaction with 10 equiv of $Mn(acac)_3$ in refluxing pyridine. The product, $(TBP)_8(Cz)Mn(III)$ (**1**),[9] was purified by flash chromatography to give **1** as a dark brown solid in good yield (85%). Treatment of compound **1** with a stoichiometric amount of *m*-CPBA in CH_2Cl_2 resulted in an immediate color change from brown to the deep green of a new species, **2** (λ_{max} = 418, 634 nm). This new color persisted at room temperature for *several days*, and analysis of the reaction mixture by TLC showed that **2** migrated on silica gel as a well-behaved, green spot and was the only product in the reaction. Thus, we were encouraged to attempt to purify **2** by standard chromatographic methods. Remarkably, compound **2** was *easily isolated by flash chromatography under room-temperature, aerobic conditions*, giving **2** as a stable green solid in good yield (81%) after evaporation of the solvent. A microcrystalline solid of **2** can be obtained by dissolution in CH_2Cl_2 followed by the slow diffusion of MeOH at −20 °C.

Scheme 1 [a]



[a] Conditions: (a) 10 equiv of $Mn(acac)_3$, pyridine, 115 °C, 1 h; (b) 1.0 equiv of *m*-CPBA, CH_2Cl_2, room temperature, 1 min.

As expected for high-spin Mn(III), **1** exhibits a paramagnetic NMR spectrum. In contrast, the ^1H NMR spectrum of **2** in CD_2Cl_2 is *diamagnetic*, as is apparent from the sharp ^1H NMR resonances appearing in the normal aromatic (δ 7−9 ppm) and alkyl (δ 1−2 ppm) regions (Figure S1). There are a total of four inequivalent (4-*tert*-butyl)phenyl substituents in **2**, which give rise to the observed pattern of overlapping AB doublets in the aromatic region and the four, well-resolved singlets in the alkyl region. A diamagnetic ground state is expected on theoretical grounds for a Mn(V) (d^2) ion with a triply bonded, terminal oxo ligand. Moreover, the few examples of spectroscopically characterized (L)Mn(V)≡O compounds uniformly exhibit a diamagnetic NMR spectrum.[5,6,8] Results from high-resolution LDI-TOF mass spectroscopy confirm the characterization of **2** as an Mn complex with a terminal oxo ligand. The isotopic cluster centered at the molecular ion for **2** (*m*/*z* 1426.8) is in excellent agreement with the calculated pattern for $[(TBP)_8(Cz)Mn(O)]^+$ (Figure S2). Stirring a solution of **2** in CH_2Cl_2 with $H_2{}^{18}O$ (95%) under Ar for 12 h followed by evaporation of the solvent results in the facile exchange of the oxo ligand to give the ^{18}O-labeled product, as evidenced by a new LDI-TOFMS pattern consistent with 70% ^{18}O incorporation (Figure S2). Previous work on manganese porphyrin-mediated oxidations has shown that ^{18}O exchange with water is one of the hallmarks of an oxomanganese(V) porphyrin intermediate.[5,10] The NMR and mass spectral data provide compelling evidence that **2** is a bona fide Mn(V)≡O complex.

Finally, direct evidence for the oxomanganese(V) (permanganyl) species was obtained from resonance Raman (RR) spectroscopy. Excitation near the absorption maxima of the Soret band (418 nm) of **2** in CH_2Cl_2 results in the appearance of a strongly enhanced polarized Raman band at 979 cm^{-1} (Figure 1a). This new Raman band[11] is attributed to the stretching mode of the Mn−oxo bond, ν(MnO), because it shifts to 938 cm^{-1} with ^{18}O substitution; the expected shift for a Mn−O diatomic oscillator is 43 cm^{-1}. Solid **2** gives a similar ν(MnO) RR band at 997 cm^{-1}, which shifts to 954 cm^{-1} when the oxo group is exchanged with ^{18}O (Figure 1b). A

---

* To whom correspondence should be addressed. E-mail: dpg@jhu.edu.
[†] The John Hopkins University.
[‡] University of Houston.

10.1021/ja028651d CCC: $22.00

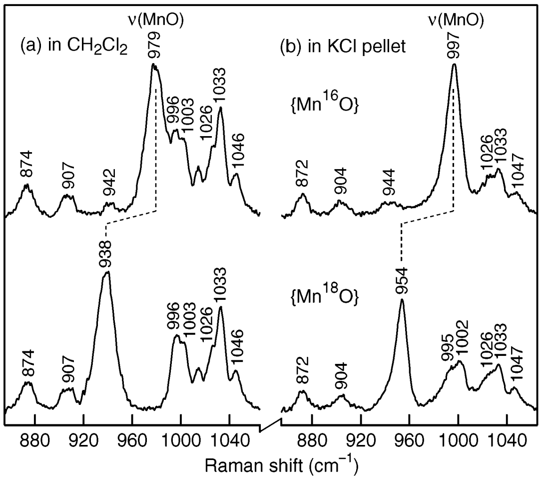


Figure 1. Resonance Raman spectra (855−1065 cm^{-1}) of **2**(^{16}O) (top) and its Mn^{18}O isotopomer (bottom) in (a) CH$_2$Cl$_2$ (~1 mM) and (b) solid state, excited at 413.1 nm (100 mW) and 7 cm^{-1} slit widths.

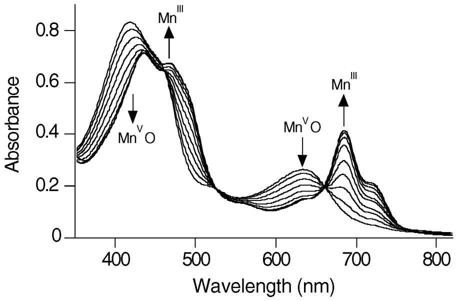
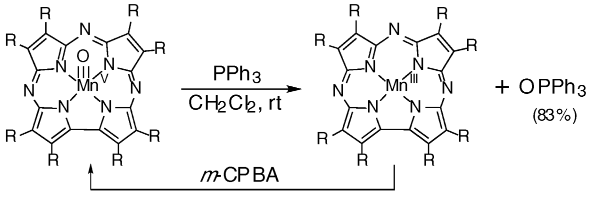


Figure 2. UV−vis titration of **2** (0.013 mM) and PPh$_3$ (0−1 equiv) in CH$_2$Cl$_2$ (5 mL) at 23 °C.

Scheme 2



diatomic oscillator calculation reproduces the 997 cm^{-1} frequency with a force constant of 7.25 mdyn/Å and predicts an ^{18}O shift of 44 cm^{-1}, in excellent agreement with experiment. To our knowledge, the only other Mn(V)≡O complexes that have been characterized by vibrational spectroscopy (RR, IR) are those containing a tetraamide macrocycle, for which ν(Mn^{16}O) = 981−970 cm^{-1} and ν(Mn^{18}O) = 942−933 cm^{-1}.[6c,d] Similar vibrational properties have been determined for the isoelectronic Mn(V)≡N and Cr(IV)≡O units in five-coordinate porphyrin complexes having a triply bonded axial nitrido or oxo ligand.[12] In contrast, five-coordinate oxomanganese(IV) (manganyl) porphyrins give the IR and RR bands of Mn(IV)=O at the characteristically low frequency of ~755 cm^{-1}.[13]

Complex **2** is capable of oxidizing PPh$_3$, as shown in Scheme 2. Reaction of **2** with increasing amounts of PPh$_3$ was monitored by UV−vis spectroscopy and revealed the spectral changes indicated in Figure 2, which are complete within the time of mixing and show good isosbestic behavior. The shoulder at 722 nm is indicative of weak coordination of OPPh$_3$ to the Mn(III) corrolazine complex, as determined by independent experiments (data not shown). Reverse titration with *m*-CPBA quantitatively regenerates **2**. The amount of phosphine oxide produced (83%) was measured by standard GC-FID techniques. The use of ^{18}O-labeled **2** in the same reaction gave (^{18}O)PPh$_3$ as shown by MALDI-MS, providing strong evidence for a direct oxygen atom transfer mechanism between **2** and PPh$_3$.

Complex **2** was also reduced by the substrate dimethyl sulfide (DMS), as observed by UV−vis spectroscopy. Oxidation of this thioether substrate is considerably more difficult than PPh$_3$ from a thermodynamic standpoint, and a complete reactivity profile (product analysis, reaction rates) of the Mn(V)≡O complex **2** toward thioethers as well as other substrates will form the basis of future reports.

Acknowledgment. We thank the NSF (CHE0094095 and CHE0089168 to D.P.G.) and the Robert A. Welch Foundation (E-1184 to R.S.C.) for financial support. R.C.T. acknowledges support from a Howard Hughes Summer Fellowship through the Johns Hopkins University. D.P.G. is also grateful for an Alfred P. Sloan Research Fellowship.

Supporting Information Available: Details of syntheses, mass spectroscopy, and resonance Raman spectroscopy (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Meunier, B., Ed.; Imperial College Press: London, 2000.
(2) *Metalloporphyrins in Catalytic Oxidations*; Sheldon, R. A., Ed.; Marcel Dekker: New York, 1994.
(3) Palucki, M.; Finney, N. S.; Pospisil, P. J.; Güler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948−954.
(4) Yagi, M.; Kaneko, M. *Chem. Rev.* **2001**, *101*, 21−35.
(5) (a) Jin, N.; Bourassa, J. L.; Tizio, S. C.; Groves, J. T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3849−3851. (b) Jin, N.; Groves, J. T. *J. Am. Chem. Soc.* **1999**, *121*, 2923−2924. (c) Groves, J. T.; Lee, J.; Marla, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 6269−6273.
(6) (a) Miller, C. G.; Gordon-Wylie, S. W.; Horwitz, C. P.; Strazisar, S. A.; Peraino, D. K.; Clark, G. R.; Weintraub, S. T.; Collins, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 11540−11541. (b) MacDonnell, F. M.; Fackler, N. L. P.; Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 7431−7432. (c) Workman, J. M.; Powell, R. D.; Procyk, A. D.; Collins, T. J.; Bocian, D. F. *Inorg. Chem.* **1992**, *31*, 1548−1550. (d) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899−901. (e) Collins, T. J.; Gordon-Wylie, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 4511−4513.
(7) (a) Ramdhanie, B.; Zakharov, L. N.; Rheingold, A. L.; Goldberg, D. P. *Inorg. Chem.* **2002**, *41*, 4105−4107. (b) Ramdhanie, B.; Stern, C. L.; Goldberg, D. P. *J. Am. Chem. Soc.* **2001**, *123*, 9447−9448.
(8) A recent report describes the characterization of a (corrole)Mn(V)O which is stable at room temperature for several hours if kept in dilute solution. See: Gross, Z.; Golubkov, G.; Simkhovich, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 4045−4047.
(9) The structure of this compound has been determined by X-ray crystallography and shows an axial MeOH coordinated to the Mn ion in the solid state. Details of the structure will be published elsewhere.
(10) (a) Bernadou, J.; Fabiano, A.-S.; Robert, A.; Meunier, B. *J. Am. Chem. Soc.* **1994**, *116*, 9375−9376. (b) Nam, W.; Kim, I.; Lim, M. H.; Choi, H. J.; Lee, J. S.; Jang, H. G. *Chem.-Eur. J.* **2002**, *8*, 2067−2071.
(11) The corresponding band is absent for the (TBP)$_8$(Cz)Mn(III) parent complex which has no axial oxo ligand (spectra not shown).
(12) (a) Campochiaro, C.; Hofmann, J. A., Jr.; Bocian, D. F. *Inorg. Chem.* **1985**, *24*, 449−450. (b) Czernuszewicz, R. S.; Spiro, T. G. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; Wiley-Interscience: New York, 1999; Vol. 1, pp 353−441.
(13) Czernuszewicz, R. S.; Su, Y. O.; Stern, M. K.; Macor, K. A.; Kim, D.; Groves, J. T.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4158−4165.

JA028651D