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Hydrogen Bonding in Metal Oxo Complexes: Synthesis and Structure of a Monomeric Manganese(III)−Oxo Complex and Its Hydroxo Analogue

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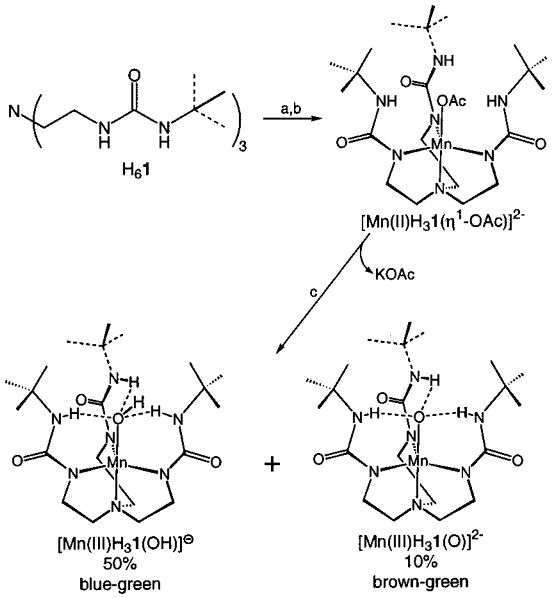
Manganese−oxo complexes have been widely studied because of their importance in biological processes and their utility as synthetic reagents.[1] In biological systems, these species are proposed as intermediates in certain catalases[2] and peroxidases,[3] and in the oxidation of water to O_2 in the oxygen-evolving complex of photosynthesis.[4] Synthetic manganese−oxo complexes, such as those with imines[5] and porphyrin ligands,[6] have been postulated to be the reactive species in catalytic oxidations of various organic compounds. These oxo complexes are believed to have high-valent manganese centers in either 4+ or 5+ oxidation states. The isolation and structural analysis of high-valent, mononuclear manganese−oxo complexes is limited to only Mn(V)=O complexes of tetraanionic chelating ligands.[7] In contrast, low-valent manganese complexes (e.g., 3+ valence) with terminal oxo ligands are not known. Low-valent manganese complexes contain μ-oxo bridges, where Mn(III)−(O)$_n$−Mn(III) dimers (n = 1, 2) are the norm.[8] This report describes the preparation and properties of a monomeric Mn(III)−oxo complex and its Mn(III)−hydroxo analogue. The isolation of these complexes is accomplished by using the chelating ligand $[H_3\mathbf{1}]^{3-}$, which forms a protective hydrogen-bonding cavity around the Mn(III)−O(H) units.

The importance of H-bonding in regulating metal ion reactivity is exemplified by metalloproteins. Several metalloproteins have active sites that contain either H-bond donors or acceptors that interact with external ligands that are covalently bonded to a metal center.[9,10] Efforts to mimic this multimode binding in synthetic complexes have involved both heme and non-heme systems.[11] However, duplicating these desirable effects in synthetic systems has proven difficult, in part because of the inability of synthetic complexes to correctly position H-bonding groups near the metal center. We have recently developed a urea-based tripodal ligand $[H_3\mathbf{1}]^{3-}$ that, when bonded to a metal ion, creates a H-bonding cavity around vacant coordination sites.[12] This cavity is formed by the planar urea groups of each tripodal arm and is large enough to accommodate external ligands. Intramolecular H-bonding between the cavity N−H groups and the atom coordinating to the metal center is probable because thermodynamically favored six-membered rings are formed when these interactions occur. Thus, the cavity motif in complexes of $[H_3\mathbf{1}]^{3-}$ provides up to three intramolecular H-bonds that can influence chemical reactivity.

Scheme 1[a]



[a] Conditions: (a) KH, DMA, Ar; (b) Mn(OAc)$_2$; (c) O_2, DMA, room temperature.

Scheme 1 outlines the synthesis of the Mn(II) and Mn(III) complexes.[13] The trigonal bipyramidal Mn(II) starting complex, $[\mathrm{Mn^{II}H_3}\mathbf{1}(\eta^1\text{-OAc})]^{2-}$, contains a monodentate acetate ligand whose coordination was confirmed by FTIR and X-ray diffraction measurements. $[\mathrm{Mn^{II}H_3}\mathbf{1}(\eta^1\text{-OAc})]^{2-}$ reacts with 1 equiv of O_2

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(1) (a) Groves, J. T.; Han, Y.-Z. In *Cytochrome P-450. Structure, Mechanism and Biochemistry*; Ortiz de Montellano, R. R., Ed.; Plenum Press: New York, 1995; pp 3−48. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401−1449. (c) Gardner, K. A.; Kuehnert, L. L.; Mayer, J. M. *Inorg. Chem.* **1997**, *36*, 2069−2078.

(2) (a) Pecoraro, V. L.; Baldwin, M. J.; Gelasco, A. *Chem. Rev.* **1994**, *94*, 807 and references therein. (b) Dismukes, G. C. *Chem. Rev.* **1996**, *96*, 2909−2926.

(3) Nicks, R. J.; Ray, G. B.; Fish, K. M.; Spiro, T. G.; Groves, J. T. *J. Am. Chem. Soc.* **1991**, *113*, 1838−1840.

(4) (a) Yachandra, V. K.; Sauer, K.; Klein, M. P. *Chem. Rev.* **1996**, *96*, 2927−2950 (b) Tommos, C.; Babcock, G. T. *Acc. Chem. Res.* **1998**, *31*, 18−25.

(5) Selected examples: (a) Srinvasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309−2390. (b) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, R. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801−2803. (c) Paluki, M.; Finney, N. S.; Pospisil, P. J.; Güler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948−954.

(6) Selected examples: (a) *Metallo-porphyrins in Catalytic Oxidations*; Sheldon, R. A., Ed.; M. Dekker: New York, 1994. (b) Nam, W.; Valentine, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 1772−1778. (c) Groves, J. T.; Lee, J.; Marla, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 6269−6273. (d) Jin, N.; Groves, J. T. *J. Am. Chem. Soc.* **1999**, *121*, 2923−2924.

(7) Collins, T. J.; Gordon-Wylie, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 4511−4512. (b) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899−901. (c) MacDonnell, F. M.; Fackler, N. L. P.; Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 7431−7432. (d) Miller, C. G.; Gordon-Wylie, S. W.; Horwitz, C. P.; Strazisar, S. A.; Periano, D. K.; Clark, G. R.; Weintraub, S. T.; Collins, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 2923−2924.

(8) (a) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153−1172 and references therein. (b) Kitajima, N.; Singh, U. P.; Amagai, H.; Osawa, M.; Moro-oko, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7757−7758.

(9) (a) Lu, Y.; Valentine, J. S. *Curr. Opin. Struct. Biol.* **1997**, *7*, 495−500. (b) Regan, L. *Trends Biochem. Sci.* **1995**, *20*, 280−285. (c) Holm. R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239−2314.

(10) For examples, see the following. Hemoglobin: (a) Perutz, M. F.; Fermi, G.; Luisi, B.; Shaanan, B.; Liddington, R. C. *Acc. Chem. Res.* **1987**, *20*, 309. (b) Springer, B. A.; Sligar, S. G.; Olsen, J. S.; Philips, G. N., Jr. *Chem. Rev.* **1994**, *94*, 699−714. Horseradish peroxidase: Mukai, M.; Nagano, S.; Tanaka, M.; Ishimori, K.; Morishima, I.; Ogura, T.; Wantanabe, Y.; Kitagawa, T. *J. Am. Chem. Soc.* **1997**, *119*, 1758−1766. Hydroylases: Lipscomb, W. N.; Sträter, N. *Chem. Rev.* **1996**, *96*, 2375−2433 and references therein.

(11) Representative examples: (a) Wuenshell, G. E.; Tetreau, C.; Lavalette, D.; Reed, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 3346−3355. (b) Momenteau, M.; Reed, C. A. *Chem. Rev.* **1994**, *94*, 659−698. (c) Chang, C. K.; Liang, Y.; Avilés, G.; Peng, S.-M. *J. Am. Chem. Soc.* **1995**, *117*, 4191−4192. (d) Collman, J. P.; Fu, L. *Acc. Chem. Res.* **1999**, *32*, 455−463. (e) Kickham, J. E.; Loeb, S. J.; Murphy, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 7031−7032. (f) Kitajima, N.; Komatsuzaki, H.; Hikichi, S.; Osawa, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1994**, *116*, 11596−11597. (g) Walton, P. H.; Raymond, K. N. *Inorg. Chim. Acta* **1995**, *240*, 593−601. (h) Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1996**, *35*, 3007−3011. (i) Berreau, L. M.; Mahapatra, S.; Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **1996**, *35*, 6339−6342. (j) Wada, A.; Harata, M.; Hasegawa, K.; Jitsukawa, K.; Masuda, H.; Mukai, M.; Kitagawa, T.; Einaga, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 798−799.

(12) Hammes, B. S.; Young, V. G., Jr.; Borovik, A. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 666−669.

(13) Synthetic details and characterization of all new compounds are given in the Supporting Information.

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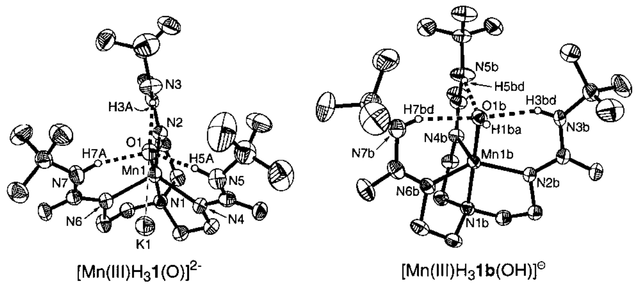

Figure 1. Thermal ellipsoid diagrams of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ (left) and $[Mn^{III}H_3\mathbf{1b}(OH)]^-$ (right).[16] The ellipsoids are drawn at the 50% probability level, and only the urea and hydroxide hydrogens are shown. Also shown for $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ is one of the potassium ions which weakly interacts with the cavity (O1- - -K1, 2.837(3) Å). Selected bond lengths (Å) and angles (deg) for $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ $\{[Mn^{III}H_3\mathbf{1}(OH)]^-\}$: Mn1−O1, 1.801(4) {1.872(2)}; Mn1−N1, 2.133(4) {2.033(2)}; Mn1−N2, 2.071(3) {2.031(2)}; Mn1−N4, 2.103(3) {2.076(2)}; Mn1−N6, 2.107(3) {2.015(2)}; O1−Mn1−N1, 176.27(14) {177.13(8)}; N2−Mn1−N4, 119.72(14) {134.76(8)}; N2−Mn1−N6, 115.84(14) {111.66(8)}; N4−Mn1−N6, 117.17(14){108.16(8)}.

to form two mononuclear Mn(III) complexes, $[Mn^{III}H_3\mathbf{1}(OH)]^-$ and $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$, that were isolated after removal of all volatile species. Separation of these two complexes was achieved by taking advantage of their different solubilities in acetonitrile. The brown-green, extremely water sensitive $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ complex was insoluble and was obtained in 10% yield. The blue-green, acetonitrile-soluble $[Mn^{III}H_3\mathbf{1}(OH)]^-$ complex was isolated in 50% yield. $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ and $[Mn^{III}H_3\mathbf{1}(OH)]^-$ are high spin with effective magnetic moments of 4.92 and 4.90 μ_{BM}, respectively.

The assignment of a terminal hydroxo ligand in $[Mn^{III}H_3\mathbf{1}(OH)]^-$ is supported by its spectroscopic properties being similar to those of $[Mn^{III}\mathbf{2}(OH)]^-$ (**2**, tris(cyclopentylcarbamoymethyl)amine), a trigonal bipyramidal complex with a known Mn(III)−OH unit.[14] For example, the FTIR spectrum of $[Mn^{III}H_3\mathbf{1}(OH)]^-$ has a band at 3613 cm^{-1} which corresponds to the ν(OH) of a terminal hydroxo ligand.[14] This band is absent in the FTIR spectrum of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$, as expected for a manganese oxo complex. The oxo and hydroxo oxygen atoms in $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ and $[Mn^{III}H_3\mathbf{1}(OH)]^-$ are derived from dioxygen. This was confirmed by $^{18}O_2$ labeling experiments in DMA: $[Mn^{III}H_3\mathbf{1}(^{18}OH)]^-$ has a $\nu(^{18}OH) = 3603\ cm^{-1}$ $[\nu(^{16}OH)/\nu(^{18}OH) = 1.004$; calcd 1.004)]. In $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$, the $\nu(Mn^{16}O)$ band appears at 617 cm^{-1} and is shifted to 582 cm^{-1} in $[Mn^{III}H_3\mathbf{1}(^{18}O)]^{2-}$ $[\nu(Mn^{16}O)/\nu(Mn^{18}O) = 1.06$; calcd 1.05].[15]

The overall solid-state structures of $[Mn^{III}H_3\mathbf{1}(OH)]^-$ and $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ are similar, with each Mn(III) center exhibiting a trigonal bipyramidal coordination geometry (Figure 1).[13,16] The three deprotonated urea nitrogens define the trigonal planes with average $Mn1-N_{urea}$ bond distances of 2.092(2) and 2.036(3) Å for $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ and $[Mn^{III}H_3\mathbf{1}(OH)]^-$. The remaining two axial coordination sites are occupied by the amine nitrogen N1 of $[H_3\mathbf{1}]^{3-}$ and oxygen atom O1 of either the oxo or hydroxo ligands: the O1−Mn1−N1 angle in the two complexes is similar at 176.26(14)° ($[Mn^{III}H_3\mathbf{1}(O)]^{2-}$) and 177.13(8)° ($[Mn^{III}H_3\mathbf{1}(OH)]^-$).

In $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$, the Mn1−O1 bond distance is 1.801(4) Å. This bond length is comparable to Mn−O distances found in complexes containing Mn(III)−O−Mn(III) cores[8] but is longer than the ~1.60 Å manganese−oxo distances reported for nonheme Mn(V)=O complexes.[7] As expected, the Mn1−O1 distance in $[Mn^{III}H_3\mathbf{1}(OH)]^-$ is significantly longer: 1.872(2) Å. In addition, the Mn1−N1 bond length in $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ is 0.100 Å *longer* than the corresponding bond in $[Mn^{III}H_3\mathbf{1}(OH)]^-$. The longer Mn1−N1 distance in $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ is consistent with oxo ligands having a stronger trans influence than hydroxides.[17]

The molecular structure of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ also reveals the presence of three intramolecular H-bonds between the oxo oxygen and NH groups of the surrounding urea cavity. The observed O···N distances are all indicative of strong hydrogen bonds: O1···N3, 2.848(5) Å; O1···N5, 2.721(5) Å; and O1···N7, 2.740(5) Å. The protonation of urea nitrogens N3, N5, and N7 was unambiguously established by location and refinement of the hydrogen atoms H3a, H5a, and H7a in the X-ray structural analysis. The average N−H and O···H bond distances are 0.87(2) and 1.92(4) Å, and the average O1−H−N angle is 163°. Moreover, all three urea N−H vectors are directed toward O1, which further supports the existence of intramolecular H-bonding in $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$. For $[Mn^{III}H_3\mathbf{1}(OH)]^-$ an overall cavity structure and a H-bonding pattern similar to those of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ is observed (Figure 1).[18] The hydroxo O−H vector in $[Mn^{III}H_3\mathbf{1}(OH)]^-$ is located between the urea arms containing N2 and N6, which results in a more asymmetric cavity compared to that in $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$. For example, the N2−Mn1−N6 angle of 134.76(8)° in $[Mn^{III}H_3\mathbf{1}(OH)]^-$ is increased significantly from the other two trigonal angles (see legend in Figure 1). A similar asymmetric disposition of cavity arms was observed in the structure of $[Co^{III}H_3\mathbf{1}(OH)]^-$.[12]

$[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ represents the first structurally characterized monomeric d^4 metal oxo complex for a first-row transition metal ion. There are few other well-characterized d^4 metal species with terminal oxo ligands,[19,20] However, monomeric d^4 metal oxo species have been proposed to be reactive intermediates in a number of biological and related synthetic systems.[21,22] The relative stability of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ compared to these reactive species is attributed to the trigonal symmetry of the complex[23] and the H-bonding cavity that surrounds the Mn(III) oxo unit. This rigid H-bonding cavity is also instrumental in preventing other reaction pathways that commonly lead to products with μ-oxo cores. Finally, terminal Mn−O(H) units are proposed to be present in intermediates generated during O_2 production in photosynthesis. With the isolation of $[Mn^{III}H_3\mathbf{1}(O)]^{2-}$ and $[Mn^{III}H_3\mathbf{1}(OH)]^-$, the role of these unique manganese−oxygen units in biological dioxygen formation may be more easily evaluated.[24]

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Supporting Information Available: Synthetic procedures for all new compounds and tables, figures, and X-ray structural data for $K_2[Mn^{II}H_3\mathbf{1}(OAc)]\cdot 2DMF$, $K_2[Mn^{III}H_3\mathbf{1}(O)]\cdot DMF\cdot CH_3CN$, and $K[Mn^{III}H_3\mathbf{1}(OH)]\cdot 0.5CH_3CN$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Shirin, Z.; Young, V. G., Jr.; Borovik, A. S. *Chem. Commun.* **1997**, 1967−1968.

(15) (a) For $[Mn^{III}H_3\mathbf{1}(OH)]^-$, $\nu(Mn^{16}O) = 586\ cm^{-1}$ and $\nu(Mn^{18}O) = 576\ cm^{-1}$. (b) The $\nu(Mn^{16}O)$ bands for monomeric Mn(V) oxo and Mn(IV) oxo complexes are reported at 979 and 754 cm^{-1}, respectively. Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899−890. 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.

(16) The crystal of $K[Mn^{III}H_3\mathbf{1}(OH)]\cdot 0.5CH_3CN$ has two independent, yet nearly identical, anions in the asymmetric unit, $[Mn^{III}H_3\mathbf{1a}(OH)]^-$ and $[Mn^{III}H_3\mathbf{1b}(OH)]^-$. Average metrical values of the two molecules are reported.

(17) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; p 465.

(18) The O···N distances in $[Mn^{III}H_3\mathbf{1a}(OH)]^-$ and $[Mn^{III}H_3\mathbf{1b}(OH)]^-$ are <2.900 Å.

(19) (a) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454−7462. (b) Wilkinson, G.; Hay-Motherwell, R.; Hussian-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, *12*, 2009−2012. (c) Cheng, W.-C.; Yu, W.-Y.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 57−62. (d) Welch, T. W.; Ciftan, S. A.; White, P. S.; Thorp, H. H. *Inorg. Chem.* **1997**, *36*, 4812−4821.

(20) An example of a monomeric d^6 metal oxo complex has also been reported: Spaltenstein, E.; Conry, R. R.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8741−8742.

(21) Sono, M.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, *96*, 2841−2887.

(22) (a) Collman, J. P.; Zhang, X.; Lee, V. J.; Uffelman, E. S.; Brauman, J. I. *Science* **1993**, *261*, 1404−1411. (b) Que, L., Jr. *J. Chem. Soc., Dalton Trans.* **1997**, 3933−3940.

(23) For discussions on the stability of trigonal monomeric metal oxo complexes, see ref 19a and the following: Fackler, N. L. P.; Zhang, S.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1996**, *118*, 481−482.

(24) A recent report of synthetic manganese complexes relevant to photosynthesis: Caudle, M. T.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1997**, *119*, 3415−3416.