Inorg. Chem. **1990**, *29*, 2193–2194

Synthesis, Structure, and Magnetic Properties of a Reactive Complex Containing a Nearly Linear Mn^{III}–O–Mn^{III} Core, [Mn$_2$O(5-NO$_2$saldien)$_2$][1]

Oxo-bridged manganese complexes have attracted much attention recently,[2] principally because of their potential relevance to active sites in enzymes such as the *Lactobacillus plantarum* manganese catalase[3] and the oxygen-evolving complex in photosystem II (PSII OEC).[4] Among structurally characterized binuclear manganese oxo complexes, the $[\mathrm{Mn}(\mu\text{-O})_2\mathrm{Mn}]^{2+/3+/4+}$ core has become relatively common in the last several years.[5] There are also examples of the following oxo-bridged binuclear structural types: $[\mathrm{Mn}(\mu\text{-O})(\mu\text{-O}_2\mathrm{CR})_2\mathrm{Mn}]^{2+/3+}$,[6] $[\mathrm{Mn}(\mu\text{-O})_2(\mu\text{-O}_2\mathrm{CR})]^{+/2+}$,[7] and $[\mathrm{Mn}(\mu\text{-O})_3\mathrm{Mn}]^{2+}$.[8] On the other hand, binuclear complexes in which manganese(III) atoms are bridged by only a single oxo group are quite rare,[9-11] and in the known cases, the terminal ligands are not relevant to the biological systems mentioned above.[12] Reported herein are the notable structural, magnetic, and reactivity properties of a single oxo-bridged species with biologically relevant donors, [Mn$_2$O(5-NO$_2$saldien)$_2$] (**1**).

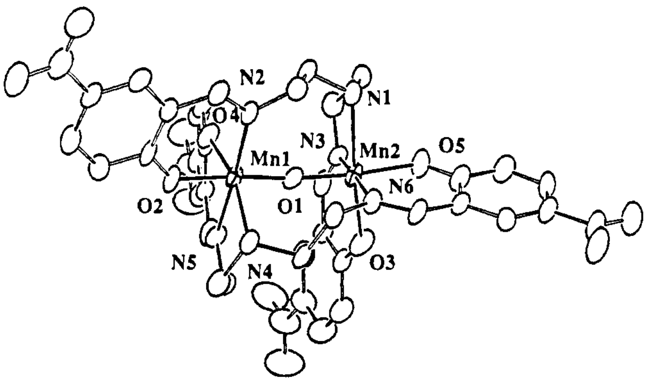

Figure 1. Molecular structure of [Mn$_2$O(5-NO$_2$saldien)$_2$] (**1**) showing anisotropic thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Mn(1)···Mn(2) = 3.490 (2), Mn(1)–O(1) = 1.757 (4), Mn(1)–O(2) = 1.914 (2), Mn(1)–O(4) = 2.040 (4), Mn(1)–N(2) = 2.140 (4), Mn(1)–N(4) = 2.223 (5), Mn(1)–N(5) = 2.182 (5), Mn(2)–O(1) = 1.751 (4), Mn(2)–O(3) = 2.088 (6), Mn(2)–O(5) = 1.917 (4), Mn(2)–N(1) = 2.253 (5), Mn(2)–N(3) 2.125 (6), Mn(2)–N(6) = 2.105 (7); Mn(1)–O(1)–Mn(2) = 168.4 (2).

Although the oxidation of Mn^{II} Schiff base complexes has been studied extensively,[13] including the system examined here,[13i] only in a few cases have oxo- or hydroxo-bridged products been structurally characterized.[14] The synthesis of compound **1** was achieved by oxidation of [Mn$_2$(5-NO$_2$saldien)$_2$] (**2**)[13i,15] with dioxygen. Dry O$_2$ was bubbled through a stirred solution of 1.0 g (1.08 mmol) of **2** in 3 L of CH$_3$CN for approximately 1 h. After storage of the resulting orange-brown solution at −14 °C for several days, 0.55 g (54% yield) of **1** as a brown crystalline solid was collected by filtration. A single crystal suitable for X-ray diffraction experiments[16] and bulk material for magnetic measurements were obtained directly from the reaction mixture.

The structure of **1**, shown in Figure 1, features two Mn^{III} atoms bridged by a single oxo group and an unusual binucleating binding mode for the pentadentate ligand 5-NO$_2$saldien. It is interesting to note that while the $\{\mathrm{M}(\mu\text{-O})\mathrm{M}\}^{4+}$ core is common for iron in a variety of ligand environments,[17] it is very rarely observed for

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(1) Abbreviations used: 5-NO$_2$saldien = *N,N'*-bis(5-nitrosalicylidene)-1,7-diamino-3-azapentane; PSII OEC = photosystem II oxygen-evolving complex; HB(pz)$_3$ = hydridotris(pyrazol-1-yl)borate; tacn = 1,4,7-triazacyclononane; bpy = 2,2′-bipyridine. phthal = phthalocyanine; tphpn = tetrakis(2-methylpyridyl)-2-hydroxypropane-1,3-diamine; py = pyridine.

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(16) X-ray analysis: Compound **1**·2CH$_3$CN crystallizes in the monoclinic space group $P2_1/c$, with a = 17.401 (4) Å, b = 12.692 (2) Å, c = 21.777 (3) Å, β = 112.25 (2)°, V = 4451.4 Å^3, and Z = 4. Data collection at 173 K out to $2\theta = 50°$ with Mo Kα radiation yielded 4137 reflections with $I > 3\sigma(I)$. The structure was solved by a combination of Patterson and direct methods (SHELXS86, G. Sheldrick) and refined by using 555 parameters to final R (R_w) values of 6.6% (7.8%).

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0020-1669/90/1329-2193\$02.50/0

manganese coordination complexes.[9,10] The Mn^{III}-O_{oxo} bond distances in **1** (1.751 (4), 1.757 (4) Å) can be compared to the corresponding lengths in $[Mn_2O(O_2CCH_3)_2(HB(pz)_3)_2]$ (**3**) (1.773 (2) Å),[6a] $[Mn_2O(O_2CCH_3)_2(tacn)_2]^{2+}$ (**4**) (1.80 (1) Å),[6b] $[Mn_2O(O_2CCH_3)_2(bpy)_2(H_2O)_2]$ (**5**) (1.777 (12) Å, 1.788 (11) Å),[6c] $[Mn_2O(phthal)_2(py)_2]$ (**6**) (1.71 (1) Å),[10] $[Mn_2(\mu\text{-}O)(CN)_{10}]^{6-}$ (**7**) (1.723 (4) Å),[9] and $[Mn_4(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(H_2O)_2(tphpn)_2]^{4+}$ (**8**) (1.766 (1), 1.777 (2) Å).[18] Bent Mn–O–Mn bridges are observed for complexes that contain carboxylate bridging groups in addition to the bridging oxo atom (**3**–**5**) whereas linear Mn–O–Mn bridges are observed in complexes that lack additional bridging groups (**6**–**8**). However, unlike these latter complexes, the angle at the bridging oxo group in **1** is nonlinear (168.4 (2)°), presumably in order to reduce strain on the bridging Schiff base ligand. By inspection of the bond distances to Mn(1) and Mn(2) (Figure 1 caption) it is evident that compression along the Mn–(μ-O) axes is accompanied by elongation perpendicular to these axes.[19]

Preliminary magnetic susceptibility data for a powdered sample of **1** were collected at a field strength of 5 kG in the temperature range 6–280 K. The data were fitted well by the theoretical expression derived from an isotropic spin exchange Hamiltonian $H = -2JS_1{\cdot}S_2$,[20] where $S_1 = S_2 = 2$, using the following parameters: $J = -120$ cm^{-1}; $g_1 = g_2 = 2.0$; $p = 3.0\%$.[21] The magnitude and sign of the magnetic exchange constant J are comparable to values determined for compounds that contain the Fe^{III}–O–Fe^{III} core.[17] Molar magnetic moments are substantially less for **6** (μ_{eff}/Mn = 0.71 μ_B at 298 K) and **7** (μ_{eff}/Mn = 0.41 μ_B at 298 K) than for **1** (μ_{eff}/Mn = 1.44 μ_B at 280 K), owing to the likelihood that **6** and **7** have exchange-coupled low-spin manganese centers ($S_1 = S_2 = 1$).[22,23] By comparison to **1**, magnetic interactions for compounds that possess the $[Mn(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2Mn]^{2+}$ core are much weaker. For example the J values for **3** and **4** are −0.5 and +9 cm^{-1}, respectively. Weak magnetic interactions for these latter complexes, which have smaller Mn–O–Mn angles (125 and 118°, respectively), have been attributed to the lack of a d_{z^2}–d_{xz}[24,25] superexchange pathway. For compound **1** the d_{z^2}–d_{z^2} pathway is inoperative since these orbitals are vacant. Furthermore, with a nearly linear geometry, the "crossed" d_{z^2}–d_{xz} interaction is not likely to be an important contributor to antiferromagnetic exchange. This leaves the d_π–p_π–d_π (d_{xz}–d_{xz} or d_{yz}–d_{yz}) superexchange pathway as the probable dominating antiferromagnetic pathway for **1**.

Interestingly, in the solid state, compound **1** can be converted back to the Mn^{II} starting material (**2**) with heating under vacuum, according to infrared and EPR spectroscopic results. In DMF solution, **1** will revert to compound **2** at room temperature within 17 h. However, neither the above solid-state process nor the solution process is accompanied by evolution of dioxygen,[26] and thus the fate of the bridging oxo atom has not been determined. Similar observations have been reported for other iron[27,28] and manganese[13i] compounds, and dioxygen loss has been postulated, but not verified experimentally. An intermediate in the solution decomposition of **1** displays a 16-line EPR spectrum that is nearly identical with spectra reported for a bis(μ-oxo) $Mn^{III}Mn^{IV}$ complex[5a] and a compound that was postulated to be a $(Mn^{II}Mn^{III})(\mu\text{-peroxo})(Mn^{II}Mn^{III})$ species.[13i] Further characterization of the solution chemistry of **1** is under way.

In conclusion, a novel binuclear Mn^{III} complex with biologically relevant donors and a single oxo bridge has been isolated. A further understanding of the magnetic behavior and unusual reactivity properties of **1** may provide insight into both structural and functional aspects of the active sites of manganese-containing enzymes.

Acknowledgment. This work was supported by Grant No. GM382751-01 from the National Institute of General Medical Sciences. W.H.A. is grateful for a Searle Scholars Award (1986–1989).

Registry No. **1**, 126948-73-0; **1**·$2CH_3CN$, 126948-74-1; **2**, 101056-16-0.

Supplementary Material Available: Tables of atomic positional and thermal parameters and intramolecular distances and angles for **1** (10 pages). Ordering information is given on any current masthead page.

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Department of Chemistry
University of California
Berkeley, California 94720

Cary A. Kipke
Michael J. Scott
Joel W. Gohdes
William H. Armstrong*

Received March 7, 1990