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An Unstable Manganese(III) Complex Incorporating Ligand Donor Types Proposed for an Acid Phosphatase from Sweet Potato: (*p*-Nitrobenzenethiolato)[*N*,*N*′-ethylenebis(salicylideneaminato)]manganese(III)

Sir:

Tightly bound manganese in its higher oxidation states (>+2) occurs in a variety of enzymes including pseudocatalase,[1] superoxide dismutase,[2] the oxygen-evolving complex in photosystem II,[3] ribonucleotide reductase,[4] and purple acid phosphatases (PAP).[5,6] On the basis of chemical and spectroscopic evidence, tyrosine, histidine, and cysteine have been proposed as ligands for Mn(III) in sweet potato PAP.[5] The synthetic challenge of preparing a model for this metal site, incorporating mimics for the proposed donors, is a formidable one since Mn(III) in a nitrogen–oxygen environment is generally considered to be an oxidant potent enough to convert thiolate to disulfide rapidly. Manganese thiolate complexes have been prepared previously[7] but none with all of the requisite donor types, and in all structurally characterized cases polydentate ligands containing mercaptide groups have been employed. Also, the known complexes all have more than one thiolate ligand, a situation that tends to stabilize higher oxidation levels. Herein are reported the synthesis, structure, and some properties of the first example of a Mn(III) complex containing mimics for all of the proposed donors in the sweet potato acid phosphatase.

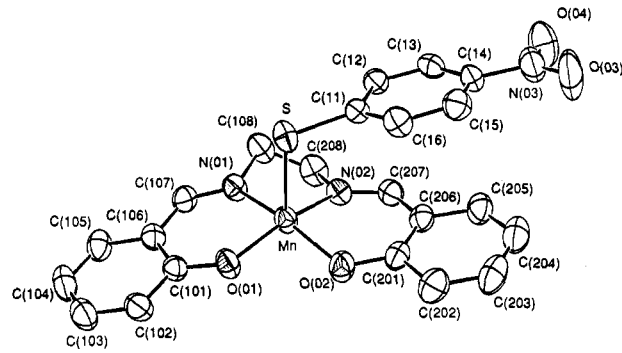

Figure 1. Structure of (*p*-nitrobenzenethiolato)[*N*,*N*′-ethylenebis(salicylideneaminato)]manganese(III) showing the 50% probability thermal ellipsoids and atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Mn–O1, 1.875 (1); Mn–O2, 1.883 (1); Mn–N1, 1.970 (2); Mn–N2, 1.988 (2); Mn–S, 2.4909 (6); S–C11, 1.751 (2); N1–Mn–N2, 81.91 (7); N1–Mn–O1, 91.18 (6); N1–Mn–O2, 161.78 (7); N2–Mn–O1, 160.51 (7); N2–Mn–O2, 89.87 (7); O1–Mn–O2, 91.41 (6); S–Mn–N1, 95.87 (5); S–Mn–N2, 99.78 (5); S–Mn–O1, 99.00 (5); S–Mn–O2, 101.56 (5); Mn–S–C11, 104.33 (7).

Problems with thiolate oxidation were manifest in our initial synthetic efforts. Allowing Mn(salen)Cl (salen = *N*,*N*′-ethylenebis(salicylideneaminato)) to react with $Na(SC_6H_5)$ at room temperature resulted in rapid decoloration of the Mn(III) solutions owing to reduction to Mn(II). Furthermore, a ligand-exchange reaction using Mn(salen)OAc and HSC_6H_5 in MeOH yielded a dark precipitate, which decomposed in the solid state. In contrast, Fe(salen)(SPh)[8] prepared by a similar method was stable enough to purify by recrystallization at room temperature, indicating the instability of the manganese analogue is much greater. However, layering a solution of Mn(salen)OAc in MeOH onto a CH_2Cl_2 solution of HS-*p*-$C_6H_4NO_2$, a less electron-rich thiol, at −14 °C afforded crystalline Mn(salen)(S-*p*-$C_6H_4NO_2$)·CH_2Cl_2 (**1**) in 45% yield.[9] Fortunately, **1** is relatively insoluble in either MeOH or CH_2Cl_2, so that as it forms, it is deposited directly from the reaction mixture prior to extensive decomposition. Crystals suitable for X-ray diffraction studies[10]

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(9) When carried out at room temperature, this reaction results in extensive decomposition and reduced yields.
(10) X-ray analysis: Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with a = 16.685 (3) Å, b = 10.609 (1) Å, c = 13.734 (2) Å, β = 100.80 (1) Å, V = 2388.0 Å^3, ρ_{obsd} = 1.552 g cm^{-3}, ρ_{calcd} = 1.558 g cm^{-3}, Z = 4. With use of 3120 unique observed reflections with Mo Kα (λ = 0.7107 Å) radiation out to 2θ = 50° on a single-crystal X-ray diffractometer, the structure was solved by Patterson and difference Fourier methods and refined with anisotropic thermal parameters to an R index of 0.036. Atomic positional and thermal parameters are provided as supplementary material. Full details will be reported elsewhere.

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and elemental analysis[11] were obtained by this method. For spectral studies described below, Mn(salen)(OC_6H_5) and Mn(salen)(O-*p*-$C_6H_4NO_2$) were prepared by addition of the appropriate phenolate anion to Mn(salen)Cl in MeOH.

The structure of **1**, shown in Figure 1, consists of a five-coordinate Mn(III) atom lying 0.305 Å out of the salen N_2O_2 plane and axially ligated by a thiolate sulfur atom from $^-$S-*p*-$C_6H_4NO_2$. The corresponding out-of-plane displacement in the structure of Mn(salen)Cl is 0.19 Å.[12] Mn-O and Mn-N distances in **1** (see Figure 1 caption) are comparable to those in other Mn(salen)X structures (X = Cl,[12] OAc[13]). The Mn-S bond in **1** is substantially longer than those found in several other manganese(III) thiolate complexes[7] due to its axial postion in this Jahn-Teller-distorted d^4 system. In the structures of $(Et_4N)_2[Mn_2(edt)_4]$,[7a,b] however, one of the unique Mn-(μ-S) bond distances was determined to be 2.606 (2) Å[7a] in one case and 2.632 (2) Å[7b] in the other. Long M-S distances have also been observed in five-coordinate d^9 thiolate complexes.[14] The Mn-Cl distance in Mn(salen)Cl (2.461 Å)[12] is quite close to the Mn-S separation in **1**. The Mn-S-C angle is in between the values for two other transition-metal complexes of $^-$S-*p*-$C_6H_4NO_2$.[15] In contrast to other transition-metal salen species,[16] **1** is mononuclear in the solid state with the closest Mn···Mn separation being 4.14 Å.

Solution stability of **1** is rather limited under normal synthetic conditions, as **1** decomposes with a half-life of 9 min in DMF solution in the presence of room light. In the dark this decomposition is substantially slower; thus, millimolar solutions have a half-life of several hours. Because of this instability, initial characterization of the complex was carried out by using solid samples. Preliminary susceptibility measurements on polycrystalline **1** yielded a magnetic moment of 4.71 μ_B at 281 K, slightly lower than the spin-only value for the high-spin d^4 configuration normally observed for mononuclear Mn(III) complexes.[17] Solid-state reflectance spectra were measured for **1** as well as for a number of other Mn(salen)X complexes including those with X = Cl, OPh, and O-*p*-$C_6H_4NO_2$. All four of these complexes display low-energy absorption bands in the range 620-880 nm.[18] Maxima in this region of the electronic spectrum, as well as at somewhat lower energies, have been assigned to the $^5B_{1g} \rightarrow {}^5A_{1g}$ transition in D_{4h} symmetry for a number of six-coordinate Mn(III) complexes.[19] Several five-coordinate species also displays absorption bands in this spectral region.[19] This transition is considered to correspond to the separation between $d_{x^2-y^2}$ and d_{z^2} orbitals in these Jahn-Teller-distorted d^4 systems. A band at 1160 nm has been reported for Mn(PAP),[4a] outside of the range yet observed for five-coordinate complexes, but consistent with six coordination. The four Mn(salen)X compounds also display shoulders in the region 480-550 nm that are obscured by charge transfer transitions. The position of these bands is consistent with higher energy d-d transition observed for Mn(III) species. Further studies will be required to fully assign the electronic spectra.

In conclusion, a Mn(III) complex of limited stability that incorporates the donor ligands proposed for sweet potato PAP, including a monodentate thiolate group, has been prepared and characterized in the solid state by X-ray crystallography and several physical methods. Compound **1** and related complexes display low-energy electronic absorptions that can be assigned to a transition between d_{z^2} and $d_{x^2-y^2}$ orbitals. Further model studies of this type promise to improve our understanding of the coordination environment and electronic structure of Mn(PAP) and other manganese-containing enzymes.

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Registry No. **1**, 114094-57-4; Mn(salen)(OC_6H_5), 114094-58-5; Mn(salen)(O-*p*-$C_6H_4NO_2$), 114094-59-6; Mn(salen)OAc, 51436-86-3; Mn(salen)Cl, 53177-12-1; acid phosphatase, 9001-77-8.

Supplementary Material Available: Tables of atomic positional and thermal parameters for compound **1** (3 pages). Ordering information is given on any current masthead page.

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(11) Anal. Calcd for $C_{23}H_{20}N_3O_4Cl_2SMn$: C, 49.30; H, 3.60; N, 7.50; Cl, 12.65; S, 5.72; Mn, 9.80. Found: C, 49.39; H, 3.66; N, 7.37; Cl, 12.00; S, 5.85; Mn, 9.59.
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Photodynamics of a Nickel Hydrocorphinoid Model of F_{430}

Sir:

A nickel hydrocorphinoid derivative called F_{430} has recently been identified at the active site of methyl coenzyme M methylreductase (from *Methanobacterium thermoautotrophicum*) and its structure (**1**) has been determined.[1-6] This enzyme catalyzes the final step in the complex series of reactions in the production of methane from carbon dioxide and hydrogen. The potential utility of this process for the chemical or photochemical production of fuels and the catalytic activation of C-H bonds makes the understanding of the mechansims of nickel hydrocorphinoid function of great interest.

Although the hydrocorphinoids are tetrapyrroles, the F_{430} centers in the methyl reductase enzymatic cycle exhibit some unusual properties relative to nickel porphyrins. These include the following: (1) F_{430} can be electrochemically reduced to Ni(I) unlike the more highly conjugated nickel porphyrins, which undergo ring reduction;[7] (2) F_{430} has higher affinity for weak-field axial ligands than most nickel porphyrins;[8-10] and (3) F_{430} has a much greater macrocycle flexibility than nickel porphyrins.[10]

Here we report the results of transient Raman studies of the photodynamics of four- and six-coordinate complexes of a nickel hydrocorphinoid related to F_{430} (see Figure 1). While F_{430} has no in vivo photochemical function, the characterization of ex-

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