coordinating ability than THF, k_1 at 40 °C was (7.0 ± 0.4) × 10^{-5} s^{-1}, the rate decreased to 28 times slower than the corresponding rate in THF (k_1 = (2.0 ± 0.1) × 10^{-3} s^{-1} at 40 °C). There is precedent for this solvent dependence in the reductive elimination of ethane from bis(phosphine)dimethylpalladium(II).[9,10] The low activation enthalpy barriers and large negative entropies in polar solvents were also attributed to a late transition state that permits coordination of solvent molecules.

Theoretical studies of H_2 reductive elimination from *cis*-$PtH_2(PH_3)_2$ by the GVB,[15] GVB-CI,[14] RHF,[16] and SD-CI[16] methods have appeared. Calculated activation barriers for H_2 elimination are 18.2, 24.1, 42.1, and 29.7 kcal/mol with endothermicities of +15.9, +6.7, +36.9, and +21.5 kcal/mol, respectively. A SCF calculation for *cis*-$PtH_2(PMe_3)_2$ yielded a kinetic barrier of 18.9 kcal/mol,[14] close to that we observe in the noncoordinating 2,2,5,5-Me_4THF solvent (Table I). The calculated exothermicity of −0.6 kcal/mol agrees with our observation that solutions of the complex decompose readily if H_2 is removed (i.e., $\Delta G \sim 0$). On the other hand the predicted stability of the trans isomer over the cis isomer by 23 kcal/mol does not agree with the experimental difference of 0.3 ± 0.1 kcal/mol.[18] If the ΔH^* of 20.0 ± 0.5 kcal/mol in noncoordinating solvents is taken as the intrinsic barrier to reductive elimination of H_2, this permits the estimation (assuming $T\Delta S^\circ \sim 0$ and that solvation differences are small in Me_4THF) of 62 kcal/mol as an upper limit (with DH_m^θ(H-H) = 104 kcal/mol) for the Pt-H bond enthalpy. This agrees closely with the theoretical estimate of 60 kcal/mol[15,30] for the Pt-H dissociation energy. Data reported here should provide a benchmark for future theoretical work.

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Synthetic Model Approach to the Manganese(III) Acid Phosphatase and Its Iron(III)-Substituted Form

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Several reports have described the isolation of red-violet acid phosphatases from plants such as soybean,[1] spinach,[2] and sweet potato.[3] The latter enzyme appears to contain a mononuclear Mn(III) site with thiolate (cysteine) and phenoxide (tyrosine) ligation;[3] histidine residues essential for activity possibly indicate imidazole ligation also.[4] The distinctive spectral properties (λ_{max} = 515 nm, ϵ_M = 2460 L·mol^{-1}·cm^{-1}) have been attributed to ligand-to-metal charge transfer. However, the precise nature of the coordination sphere, the exact origin of the 515-nm band, and even the identity of the metal have been the objects of recent comment.[5,6] In part this has been stimulated by the spectral similarity of acid phosphatase to known iron tyrosinate enzymes (including iron acid phosphatases[5]), its dissimilarity to known Mn(III) thiolates,[6-8] and the lack of Mn(III) phenoxides for comparison. Substitution of Fe(III) into the native enzyme leads to fairly large (53%) retention of activity and noticeable spectral changes (λ_{max} = 525 nm, ϵ_M = 3000);[9] this suggests the native enzyme indeed contains Mn(III). To help answer other outstanding questions, we have employed a synthetic model approach and have sought, for more valid comparisons, a mixed-O,N,S-ligated Mn(III) complex. We herein report the attainment of the first example of such a species, together with its Fe(III) version.

$Mn(acac)_3$, NEt_3, thiosalicyclic acid ($thiosalH_2$), and imidazole (HIm) in a 1:1:2:2 ratio[10] in CH_2Cl_2 at −78 °C yield an intensely red solution. Addition of PPh_4Br and workup yield red-black crystals of $(PPh_4)[Mn(thiosal)_2(HIm)]\cdot 2CH_2Cl_2$ (**1**) in ~25% yield.[11] The Mn is five-coordinate (Figure 1)[12] and square pyramidal with HIm in the apex and *cis* thiolate sulfurs. Complex

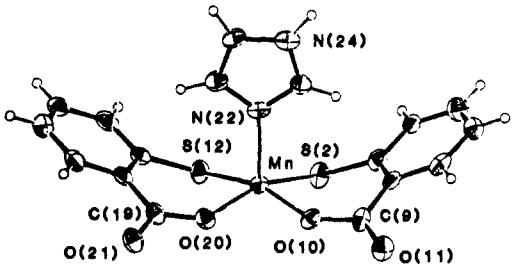

Figure 1. ORTEP projection of the anion of **1**. Pertinent bond distances (Å) and angles (deg): Mn-S(2) 2.2913 (24), Mn-S(12) 2.2752 (25), Mn-O(10) 1.948 (5), Mn-O(20) 1.932 (5), Mn-N(22) 2.176 (6), N(22)-Mn-S(2) 106.25 (17), N(22)-Mn-S(12) 103.39, N(22)-Mn-O(10) 96.07 (22), N(22)-Mn-O(20) 96.11 (22), S(2)-Mn-O(20) 157.59 (17), S(12)-Mn-O(10) 160.54 (17).

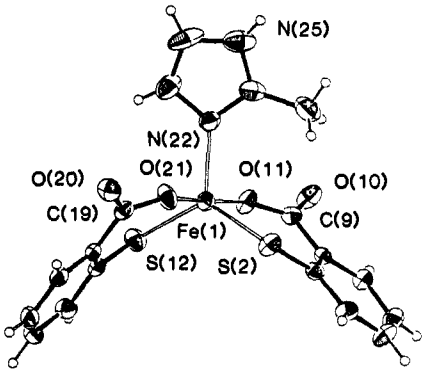

Figure 2. ORTEP projection of the anion of **2**. Pertinent bond distances (Å) and angles (deg): Fe-S(2) 2.2897 (14), Fe-S(12) 2.3010 (14), Fe-O(11) 1.976 (3), Fe-O(21) 1.954 (3), Fe-N(22) 2.065 (4), S(2)-Fe-S(12) 123.36 (6), S(2)-Fe-N(22) 118.07 (11), S(12)-Fe-N(22) 118.53 (11), O(11)-Fe-O(21) 177.02 (13), O(11)-Fe-S(2) 91.01 (9), O(11)-Fe-S(12) 92.32 (10), O(11)-Fe-N(22) 88.50 (14), O(21)-Fe-S(2) 88.46 (11), O(21)-Fe-S(12) 90.42 (10), O(21)-Fe-N(22) 89.16 (14).

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(8) Among the Mn(III) thiolates currently known, $[Mn(edt)_2(HIm)]^-$ (edt = ethane-1,2-dithiolate) is the most similar to **1**. In DMF solution in the presence of excess HIm: λ_{max} (ϵ_M); 596 (815), 392 (8250), 350 (16 400), and 288 (6500).
(9) Kawabe, H.; Sugiura, Y.; Terauchi, M.; Tanaka, H. *Biochem. Biophys. Acta* **1984**, *784*, 81-89.
(10) The acac groups can function as proton acceptors reducing the requirement for added amine.
(11) The crystallographic sample contained two CH_2Cl_2 molecules; the analytical sample dried in vacuo analyzed for one CH_2Cl_2 molecule. Anal. Calcd for $C_{42}H_{34}N_2O_4PS_2Cl_2Mn$: C, 59.23; H, 4.02; N, 3.29. Found: C, 59.71; H, 4.28; N, 3.31%.
(12) Complex **1** crystallizes in space group $P2_1/n$ with (at −155 °C) a = 21.898 (11) Å, b = 13.933 (b) Å, c = 14.065 (6) Å, β = 99.13 (2)°, and Z = 4. 3886 unique reflections with $F > 3\sigma(F)$ were refined to values of discrepancy indices R and R_w of 6.53% and 6.52%, respectively. Anal. Calcd for $C_{24}H_{30}N_3O_4S_2Fe$: C, 52.94; H, 5.55; N, 7.72. Found: C, 52.88; H, 5.69; N, 7.66.

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1 has a solution magnetic moment[13] of 5.11 μ_B consistent with a high spin ($S = 2$) center. The spectrum of 1 in MeCN in the presence of some excess HIm shows bands at 415 (sh, 2940), 450 (2760), and 500 nm (2500).[14]

$FeCl_3$, thiosalH_2, NEt_3, and 2-methylimidazole (2-MeIm) in EtOH in a 1:2:4:2 ratio yield a blue precipitate. Recrystallization from DMF/ether yields blue-black crystals of $(HNEt_3)$[Fe(thiosal)$_2$(2-MeIm)] (2) in 25% yield. The metal is again five-coordinate (Figure 2)[16] but trigonal bipyramidal, no doubt due to the 2-methyl group,[17] with axial oxygen atoms. Complex 2 has a solution moment[13] of 5.93 μ_B consistent with a high-spin ($S = {}^5/_2$) center. In DMF, 2 shows maxima at 290 (13,090), 363 (5775), and 565 nm (5070).

Complexes 1 and 2 are not proposed as perfect models for the native and Fe(III)-substituted enzymes. Tyrosine and cysteine contain phenoxide and alkylthiolate groups, respectively, while thiosal contains carboxylate and arylthiolate functions. This ligand, however, does suppress reduction of the Mn(III), the primary problem in the preparation of Mn(III) thiolates. The conclusions of this work are that spectral properties of Mn(III) thiolates are a function of the total ligand set and that mixed O,N,S-ligation is necessary before spectral characteristics of the native enzyme are approached. The 500-nm (2500) band in 1 is satisfyingly similar to that of the enzyme, 515 nm (2460); the values for 2 and Fe(III)-substituted enzyme are less similar but both show a red shift vs. the Mn forms. Inversely, our results could be considered supportive of mixed O,N,S-ligation in the enzyme. In addition, five-coordination at Mn(III) when thiolate ligands are present represents an interesting contrast to the usual preference of this oxidation level for six-coordination and may be indicative of five-coordination in the enzyme.[18,20]

We believe the visible bands in the spectrum of 1 to be due to S-to-Mn charge transfer (CT). Support for this comes from studies employing salicylate (sal) rather than thiosal. We have made several Mn(III) complexes with this ligand[21] and none exhibit CT bands at >352 nm. The 515-nm enzyme band must presumably be due to S-to-Mn CT, O-to-Mn CT, or a combination of the two. The current status of our modeling work precludes definitive extrapolations to the enzyme spectrum. However, no complex containing a Mn-O(phenoxide) bond has yet shown a CT band in the 500-nm region, whereas such a band is seen when a Mn-S(thiolate) bond is present; on the basis of this we would support the suggestion that the enzyme 515-nm band contains a S-to-Mn CT contribution.[22]

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(13) Measurements were performed in Me_2SO-d_6 using the Evans NMR method.

(14) The slight excess of HIm was required to suppress DMF-for-HIm exchange on the anion; similar behavior is seen[15] for $[Mn(edt)_2(HIm)]^-$.

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(16) Complex 2 crystallizes in space group $P2_1/a$ with (at −158 °C) a = 22.300 (8) Å, b = 12.347 (3) Å, c = 9.419 (2) Å, β = 92.61 (1)°, and Z = 2. 2945 unique reflections with $F > 3\sigma(F)$ were refined to values of R and R_w of 4.76% and 5.31%, respectively.

(17) The change in geometry is undoubtedly due to steric rather than electronic factors associated with the 2-methyl substituent. In TBP geometry, a larger (~120°) N-Fe-S angle is available to accommodate the Me group.

(18) The structure of *T. thermophilus* Mn superoxide dismutase is available[19] and it lends some precedence to the suggestion of similar five-coordination in acid phosphatase.

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(20) It is interesting that Mn(III) and Fe(III) form analogous, five-coordinate complexes with mixed O,N,S-ligation. This might explain why Fe can substitute for the Mn with significant (53%) retention of activity.

(21) Products include $[Mn(sal)_2(salH)]^-$ and $[Mn(sal)_2(HIm)_2]^-$. The CT bands of these species in DMF (λ_{max} (ϵ_M)) are 309 (20950), 320 (sh, 19600), 352 (sh, 8730) and 285 (21400), 322 (sh, 12700), respectively.

(22) This assumes the assignment of sweet potato acid phosphatase as being a Mn(III) enzyme is correct. Our modeling work cannot itself resolve this point but does establish that a mixed-O,N,S-ligated Mn(III) center *could* be responsible for the characteristic spectral features of the enzyme.

Registry No. 1, 103225-95-2; 2, 103225-97-4; $Mn(acac)_3$, 14284-89-0; $[Mn(sal)_2(salH)]^-$, 103225-98-5; $[Mn(sal)_2(HIm)_2]^-$, 103239-84-5; acid phosphatase, 9001-77-8.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters for both complexes (7 pages). Ordering information is given on any current masthead page.

Evidence for Reversible Formation of an Intermediate in the "Spontaneous" Hydrolysis Reaction of *p*-Methoxystyrene Oxide

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The hydrolysis of epoxides may occur by at least three kinetically distinguishable pathways whose rates are functions of the pH of the solution.[1] At low pH the kinetically dominant reaction is usually the acid-catalyzed hydrolysis, and at high pH hydroxide ion can catalyze the reaction by acting as a nucleophile. Many epoxides also undergo reaction at intermediate pH values by pathways whose rates are independent of pH. This latter reaction has become known as the "spontaneous" or "neutral" reaction and often leads to both carbonyl rearrangement products and diols.

The mechanism of the spontaneous reaction of epoxides varies substantially with the structure of the epoxide. For example, this reaction of propylene oxide in water enriched with ^{18}O yielded glycol in which 60-70% of the label was located at the primary center, and this observation was taken as evidence that water acted as a nucleophilic reagent.[1b] Water also appears to act as a nucleophile in the spontaneous reaction of 1,3-cyclohexadiene oxide.[2] In contrast, benzene oxide and naphthalene oxide rearrange completely to phenols in this reaction process, and rate-limiting carbon–oxygen bond fissure leading to dipolar intermediates was proposed on the basis of isotope effect data.[3] In a related reaction, 6-methoxy-1,2,3,4-tetrahydronaphthalene oxide undergoes a spontaneous reaction with rate-limiting hydrogen migration to yield ca. 75% of 6-methoxy-2-tetralone, along with lesser amounts of cis and trans diols.[4] In this latter case, no distinction could be made between a mechanism that involved an intermediate in the carbonyl-forming reaction and a concerted mechanism in which epoxide yielded ketone in a single step. *We have now examined the hydrolysis reactions of p-methoxystyrene oxide* (1) *and a deuterium-labeled derivative and wish to report* ^1H *NMR data that provide evidence for reversible formation of an intermediate in the spontaneous reaction that yields mainly p-methoxyphenylacetaldehyde.*

The rates of reaction of 1 in 0.1 M $NaClO_4$ solutions, at 25.0 °C over the pH range 4.7-13, were fit to the equation $k_{obsd} = k_{H^+}a_{H^+} + k_0$. The values of k_{H^+} and k_0 were determined to be $1.1 \pm 0.1 \times 10^4$ M^{-1} s^{-1} and $3.0 \pm 0.2 \times 10^{-3}$ s^{-1}, respectively.[5] Product studies showed that the acid-catalyzed reaction yielded >95% of glycol product 3, whereas the spontaneous (k_0) reaction proceeded mainly to rearranged aldehyde (Scheme I).

p-Methoxy-*trans*-β-deuteriostyrene oxide (4) was also prepared,[6] and its hydrolysis reactions were studied. The kinetic deuterium isotope effects $k_{H^+}(H)/k_{H^+}(D)$ and $k_0(H)/k_0(D)$ were determined

Scheme I