chemical effects lead to a 1/1 product mixture, the carboxylate substituents on **1** and **2** remote from the stereocenters by several methylene units impose a diastereomer selection of up to 8/1. The success of this first attempt to study acyclic equilibrium stereoenforcement encourages a more thorough investigation of the phenomenon.

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[16] **Note Added in Proof**: The diacid **1** equilibrates to a 50/50 mixture of diastereomers in benzene at 60 °C in a reaction catalyzed by toluenesulfonic acid.

A Binuclear Iron Peroxide Complex Capable of Olefin Epoxidation

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Nature has utilized structurally similar metalloprotein sites for reversible oxygen binding and for oxygen activation; myoglobin and cytochrome P450 constitute one such carrier/activator pair which has heme sites,[1] while hemocyanin and tyrosinase have binuclear copper sites.[2] There are as yet no examples of a binuclear nonheme iron dioxygen activating enzyme corresponding to hemerythrin,[3] though methane monooxygenase may have such a site on the basis of the similarity of its EPR spectrum with those of semimethemerythrins.[4] Based on this analogy, we are studying the capability of synthetic binuclear iron complexes to activate the O–O bond, and we report our initial results in this paper.

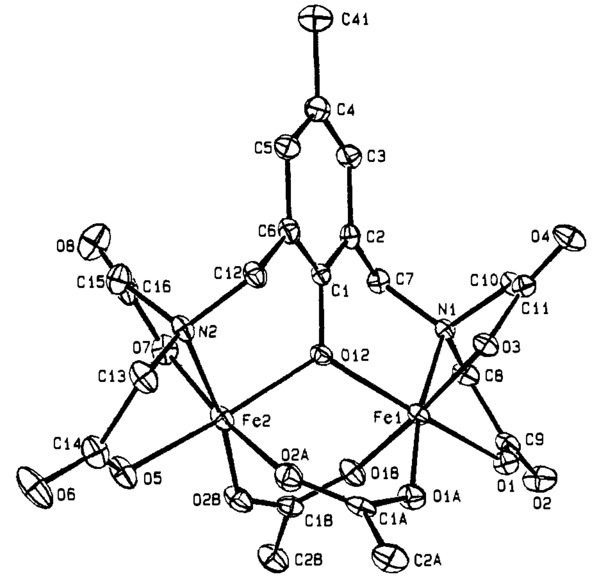

Figure 1. ORTEP plot of the structure of $[Fe_2L(OAc)_2]^-$, showing 50% probability ellipsoids. Representative distances (Å): Fe1–O12, 1.997 (2); Fe2–O12, 2.019 (2); Fe1–N1, 2.151 (2); Fe2–N2, 2.158 (2); Fe1–O1, 1.996 (2); Fe1–O3, 1.966 (2); Fe2–O5, 1.973 (2); Fe2–O7, 1.954 (2); Fe1–O1A, 1.970 (2); Fe1–O1B, 2.050 (2); Fe2–O2A; 2.049 (2); Fe2–O2B, 1.970 (2); Fe1–Fe2, 3.442 (0). Angle Fe1–O12–Fe2, 117.9 (1)°.

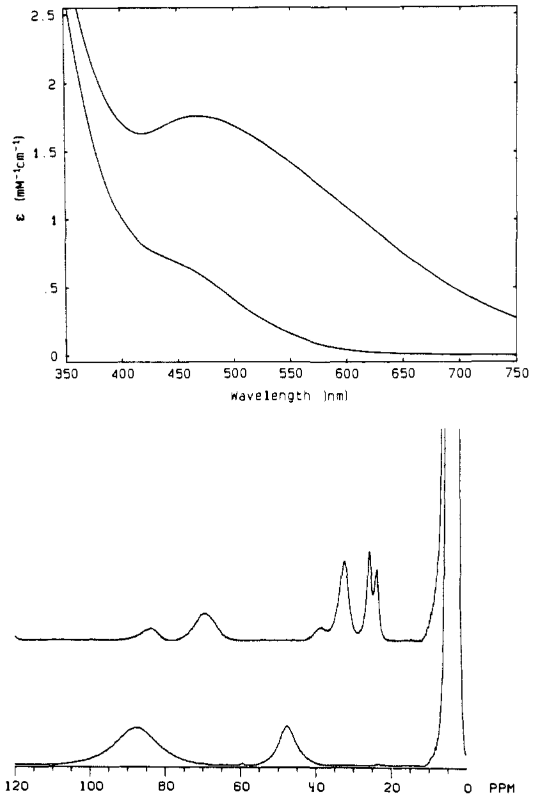

Figure 2. (Top) Visible spectra of 0.72 mM $[Fe_2L'(OAc)_2]^-$ (lower trace) and 0.72 mM $[Fe_2L'(OAc)_2]^-$ + 0.2 M H_2O_2 (upper trace) in methanol with 50 mM 1:1 HOAc/NaOAc. (Bottom) ^1H NMR spectra of $[Fe_2L'(OAc)_2]^-$ in MeOH-d_4 with 50 mM HOAc/NaOAc (lower trace) and $[Fe_2L'(OAc)_2]^-$ + H_2O_2 in Me_2SO-d_6 with 50 mM HOAc/NaOAc (upper trace).

The complex $(Me_4N)[Fe_2L(OAc)_2]$[5] is obtained by addition of acetate at pH 5 to $[Fe_2L(OH)(H_2O)_2]$[6] and metathesis with Me_4NCl. X-ray crystallography[7] shows that the phenolate and the two acetates bridge the iron centers to give a confacial bioctahedral structure (Figure 1) similar to that found for $[(HBpz_3Fe)_2OH(OAc)_2]^+$.[8] This triply bridging unit appears to be a common structural feature for binuclear complexes[9] and

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[5] Abbreviations: L, *N,N'*-(2-hydroxy-5-methyl-1,3-xylylene)bis(*N*-carboxymethylglycine); OAc, acetate; $HBpz_3$, hydrotris(pyrazolyl)borate; L', *N,N'*-(2-hydroxy-5-chloro-1,3-xylylene)bis(*N*-carboxymethylglycine); bpmp, 2,6-bis[[bis(2-pyridylmethyl)amino]methyl]-4-methylphenol; acac, acetylacetonate; TPP, *meso*-tetraphenylporphin; OTf, triflate; EDTA, *N,N,N',N'*-ethylenediaminetetraacetate; Cl_2HDA, *N*-(4,6-dichloro-2-hydroxybenzyl)-*N*-(carboxymethyl)glycine.

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[7] The complex crystallized out of water as $(Me_4N)[Fe_2L(OAc)_2]\cdot H_2O$ in the monoclinic space group $P2_1/a$ with the following cell constants: *a*, 25.963 (15) Å; *b*, 9.603 (3) Å; *c*, 12.278 (3) Å; *β*, 96.34 (3)°. The structure was determined from 2304 out of a total of 4878 reflections with $r = 3.56\%$ and $r_w = 3.99\%$. Complete details of the structure will be published elsewhere. Elemental analysis for $(Me_4N)[Fe_2L(OAc)_2]\cdot H_2O$ calculated for $C_{25}H_{37}Fe_2N_3O_{14}$: C, 41.98; H, 5.21; N, 5.91. Found: C, 41.86; H, 5.23; N, 5.87.

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Table I. Epoxidation Reaction Yields[a] for Q[Fe$_2$L(OAc)$_2$] + H$_2$O$_2$

substrate	epoxide yield	byproduct yield
cyclohexene	1.6	3-cyclohexenol, 0.9; 3-cyclohexenone, 0.4
styrene	3.2	benzaldehyde, 1.5
cis-stilbene	2.5 (cis:trans, 5:95)	

[a] Yields expressed in turnover numbers, moles of product per mole of complex. Products were identified by gas chromatography. Reaction conditions: 1 mM complex + 1 M alkene under N$_2$ in DMF with 50 mM H$_2$O$_2$ for 45 min.

one that is also found in the active site of hemerythrin.[10]

The chloro analogue of this complex, (Me$_4$N)[Fe$_2$L′(OAc)$_2$], exhibits a visible spectrum with a shoulder near 450 nm, due to a phenolate-to-Fe(III) charge-transfer transition (Figure 2). Its NMR spectrum shows isotropically shifted features at 48 and 88 ppm assigned by deuterium substitution to the phenolate meta and the acetate methyl protons, respectively (Figure 2). The integration shows that two acetates bind per binuclear complex as in the crystal structure. The methylene protons are not observed because of their proximity to the paramagnetic centers.

Addition of H$_2$O$_2$ to [Fe$_2$L′(OAc)$_2$]$^-$ results in the development of a new visible absorption maximum near 470 nm (Figure 2); laser excitation (514.5 nm) into this band shows the enhancement of a Raman feature at 884 cm^{-1} consistent with its assignment to the peroxide O–O stretch. Thus, this band probably arises from a peroxide-to-Fe(III) charge-transfer transition, as observed in other Fe(III)–peroxide complexes.[11-13] The NMR spectrum of the complex also reflects changes in coordination chemistry (Figure 2[14]). The acetate methyl resonance shifts to 33 ppm, and the meta protons appear as discreet features at 27 and 25 ppm. The remaining broad features are due to the methylene protons of the ligand. The integration of the meta and methyl peaks shows that only one acetate remains coordinated in this complex, suggesting that the peroxide has replaced one acetate. This replacement would also destroy the C_2 symmetry of the parent complex and explain the observed nonequivalence of the meta H's in the NMR spectrum of the peroxide complex. A possible structure for this complex is that found for [Co$_2$bpmp(OAc)O$_2$](ClO$_4$)$_2$ where the cobalt ions are bridged by phenolate, acetate, and peroxide.[15]

The peroxide complex can catalyze the disproportionation of H$_2$O$_2$ to O$_2$ and water. In the absence of an oxidizable substrate, the complex slowly destroys itself. In the presence of alkenes, epoxides along with byproducts of autoxidation are observed (Table I). The epoxide constitutes 10% of the H$_2$O$_2$ consumed in the reaction. The epoxidation of *cis*-stilbene by the binuclear complex results in 95% *trans*- and 5% *cis*-epoxide, similar to the results found for Fe(acac)$_3$/H$_2$O$_2$ epoxidation[16] but opposite to those of the Fe(TPP)Cl-, iron(III) bleomycin-, and Fe(OTf)$_3$-catalyzed reactions with PhIO where *cis*-stilbene yields predominantly or exclusively *cis*-epoxide.[17-19]

Interestingly, the mononuclear analogue, Fe(Cl$_2$HDA)(H$_2$O)$_2$,[20] binds neither acetate nor peroxide, suggesting a requirement for a binuclear unit for forming such complexes. The Fe(Cl$_2$HDA)(H$_2$O)$_2$/H$_2$O$_2$ mixture does not epoxidize alkenes but does catalyze peroxide disproportionation and one-electron oxidations such as the conversion of *o*-dianisidine and 2,4,6-tri-*tert*-butylphenol to their corresponding cation radicals. This comparison suggests that, at least for this family of ligands, a binuclear iron unit is required for the epoxidation chemistry. This is the only characterized iron(III) peroxide complex thus far shown to effect epoxidations. The other known iron(III) peroxide complexes,[21] e.g., [Fe(TPP)OOFe(TPP)],[22] [Fe(TPP)O$_2$]$^-$,[13] and the peroxide complex of [Fe(EDTA)],[23] have not been shown to epoxidize olefins. Efforts to understand the structure and reactivity of the binuclear peroxide complex and to compare this complex with other nonheme iron systems, such as Fe(acac)$_3$[16] and Fe(II)/CH$_3$CN,[24] that react with H$_2$O$_2$ to yield species capable of olefin epoxidation are continuing.

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Photogenerated Semi-Enone Radical Anions:[1] A New Perspective on the Reactions of 10-(Hydroxymethyl)-2-octalone Tosylate

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Since Stork's 1961 report[2] on the lithium-liquid ammonia reductive transformation of octalone tosylate **1** to the cyclopropyl ketone **6**, the nucleophilic character of the β-carbon of "semi-enone"[1] radical anions has been generally accepted. Parallel behavior would be anticipated for semi-enone radical anion of **1** generated by alternative electron-transfer processes. Indeed, electrochemical[3] and lithium dimethyl cuprate[4] reactions of octalone sulfonate esters yield the expected cyclopropyl ketones, providing experimental support for this hypothesis. In direct contrast to these results, *we report that the major product from photomediated electron-transfer to enones* **1** – **4** *is 10-methyl-*

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[1] The term "semi-enone" is introduced here to denote the radical anion of an α,β-unsaturated ketone, parallel to the designation of semidione and semiquinone to the corresponding diketone and quinone radical anions.

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