TTF molecules are named hereafter as molecules A and B (see Figure 1). The atomic parameters of one of the two ethylene groups of molecule A and both ethylene groups of molecule B indicate their positional disorder. The perchlorate anion also has large thermal parameters, suggesting molecular rotation as frequently observed in such similar cation radical salts as $(TMTTF)_2ClO_4$[8] and $(TMTSF)_2ClO_4$[9] (TMTTF, tetramethyltetrathiafulvalene; TMTSF, tetramethyltetraselenafulvalene). X-ray diffuse spots indicating the doubling of the lattice constant c below ca. 100 K suggest the ordering of the molecular orientation of ClO_4^- at low temperature. The molecular plane of molecule A is almost parallel to that of molecule B. The dihedral angle of the two least-squares planes is 2.9°. The mode of intermolecular overlapping is shown in Figure 2a. Figure 2b shows the molecular arrangement viewed along the direction parallel to the molecular plane.

Unlike the other organic metals with column structures, $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ exhibits only a slight intermolecular overlapping (see Figure 2). As shown in Figures 1 and 2b, the molecules B′, A, and B″ are approximately on the same plane at $z = -1.4$. Similarly the molecules A′, B, and A″ are approximately on the plane $z = {}^1/_4$. Thus the molecules related to A by symmetry operations and those related to B are alternately arranged side by side to form a strip along the a axis. This arrangement is in contrast with the face to face stacking typically observed in organic metal systems. The intermolecular S–S contacts in the strip are short compared with the van der Waals distance (3.70 Å). They are given in Figure 1. The shortest distance is 3.34 Å, which is reduced to 3.317 Å at 153 K. Similar side by side arrangement and intermolecular short S–S contacts are found in $(BEDT\text{-}TTF)_2PF_6$.[10] There are also some short S–S contacts between the molecules arranged along the $[10\bar{2}]$ direction. Thus the crystal has a two-dimensional nature, which is consistent with the anisotropy of the conductivities.

Recently we have made the band-structure calculation in order to obtain a better understanding of the two-dimensional conducting properties. The 2s and 2p atomic orbitals of C and the 3s and 3p atomic orbitals of S were used. The intermolecular overlap integral of HOMO is largest along $[10\bar{2}]$ and smallest along [102]. As shown in Figure 2, there is no face to face overlapping along $[10\bar{2}]$ (B‴, A, A′, ...). In spite of the shortest S···S distance, the overlap integrals along [100] are in the middle of the others. This is due to the $p\pi$ character of the HOMO. In an organic metal with face to face stacking, the Fermi surface is expected to be a plane. In fact, the band calculation in TTF-TCNQ gave one-dimensional plane Fermi surface.[11] Similar one-dimensional band structure has been obtained even in the organic superconductor $(TMTSF)_2X$ (X: ClO_4, PF_6, BF_4, ...).[12] However, owing to the two-dimensional molecular arrangement, the band-structure calculation of $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ leads to a very different band structure, indicating that this compound is a two-dimensional organic semimetal or a narrow-gap semiconductor.[13]

The importance of the intermolecular contacts between chalcogen atoms has been already revealed in some low-dimensional conductors. Underhill and Ahmad have found a new type of highly conducting planar platinum complex, $Li_{0.75}[Pt(C_4N_2S_2)_2]\cdot 2H_2O$, where the conduction pathway is considered to be formed by intermolecular contacts of the sulfur atoms of the ligands.[14,15] The crystals of the organic superconductors $(TMTSF)_2X$ suggest the importance of the formation of the two-dimensional Se–Se "sheet-network".[16] The crystal structure of $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ suggests a way to introduce a two-dimensional interaction in the organic conductors, which will be effective in the design new organic metal systems.

Registry No. $(BEDT\text{-}TTF)_2ClO_4\cdot(C_2H_3Cl_3)_{0.5}$, 83314-73-2.

Supplementary Material Available: Table of atomic coordinates (2 pages). Ordering information is given on any current masthead page.

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A Totally Synthetic (Nonporphyrin) Iron(II) Dioxygen Carrier That Is Fully Functional under Ambient Conditions

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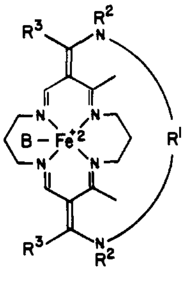
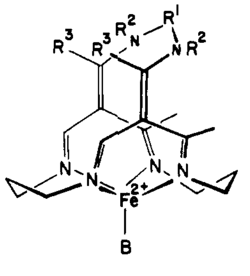
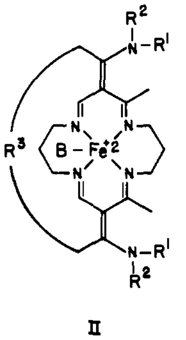
The iron–oxygen chemistry that is well-known among heme proteins has long remained without parallel among the usual coordination compounds of that metal. Even the history of nonporphyrin iron(II)–dioxygen carriers is fraught with misinterpretation and uncertainty.[1] Only relatively recently have unchallenged examples of such iron–dioxygen carriers been reported. Baldwin and Huff[2] synthesized an iron(II) complex with a hindered 14-membered macrocycle that showed reversible O_2 binding in anhydrous solvents at −85 °C but lost all trace of reversible binding by −50 °C. The only other example was our lacunar iron(II) complex[3] of structure I (R^1 = *m*-xylylene; $R^2 = R^3 = CH_3$). The O_2 adduct of this complex shows complete reversibility up to temperatures of about −35 °C, and the O_2 adduct is still detectable at temperatures above 0 °C. We now report iron-based O_2 carriers that are fully functional under ambient conditions.



Ia



Ib



II

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[1] In 1927, Kunz and Kress (*Chem. Ber.* **1927**, *60*, 367) claimed reversible dioxygen binding by a diindigoiron(II) complex, which as shown by Larkworthy (*J. Chem. Soc.* **1961**, 4025), turned out to exhibit reversibility only so long as excess iron pentacarbonyl reagent was present. Bis(dimethylglyoximato)iron(II) was subsequently reported to bind dioxygen reversibly (Drake, J. F.; Williams, R. J. P. *Nature (London)* **1958**, *182*, 1084), but later work failed to confirm these results (Davies, R. C., Ph.D. Thesis, Wadham College, Oxford, 1963; cf. ref 14).

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Table I. Analytical Data and Magnetic Moments in Acetonitrile Solution[a] for Lacunar Iron(II) Complexes

structure I											
R^1	R^2	R^3	B	formula	μ_{eff}, μ_B[a]		C, %	H, %	N, %	Fe, %	Cl, %
m-xylylene	CH_3	CH_3	Cl	$C_{28}H_{40}N_6ClPF_6Fe$	5.09	calcd	48.26	5.78	12.06		5.09
						found	48.22	5.93	12.00		5.01
m-xylylene	benzyl	CH_3	CH_3CN	$C_{42}H_{51}N_7P_2F_{12}Fe$	5.04	calcd	50.46	5.14	9.81	5.59	
						found	50.44	5.16	9.39	5.72	
m-xylylene	CH_3	phenyl	CH_3CN	$C_{40}H_{47}N_7P_2F_{12}Fe\cdot 0.5EtOH$	5.12	calcd	49.52	5.10	9.82	5.59	
						found	49.27	4.95	9.62	5.60	
m-xylylene	benzyl	phenyl	CH_3CN	$C_{52}H_{55}N_7P_2F_{12}Fe\cdot 2.5MeOH$	4.99	calcd	54.41	5.43	8.16	4.65	
						found	54.28	5.17	8.26	4.54	
CH_3	CH_3	$(CH_2)_8$	Cl	$C_{28}H_{48}N_6ClPF_6Fe$	5.05	calcd	46.38	6.67	11.59	8.15	
						found	46.50	6.90	11.52	8.15	

[a] As measured by the Evans ^1H NMR method at 301.6 K in C^2H_3CN with acetone reference.

It is clear that both the protein *and* the heme prosthetic group of the natural oxygen carriers, e.g., myoglobin, play crucial roles in facilitating reversible dioxygen binding by their iron derivatives. This facilitative role of the protein has been elucidated through studies employing the device of keeping the same basic ligand as occurs in nature (the porphyrin) while exploring the role of the protein by variations in such factors as solvent, temperature, and substituents on the porphyrin itself.[4,5] In research directed toward our goal to use new (nonporphyrin) ligand systems in the design and synthesis of iron(II)–dioxygen carriers, additional considerations are of primary importance.

Attention was first drawn to lacunar iron complexes (structure I) because $E_{1/2}$ for their Fe^{2+}/Fe^{3+} couple falls very close to those of the natural oxygen carriers.[6] However, initial failure to observe reversible dioxygen binding to the iron complex led to complementary studies on the O_2 adducts of cobalt lacunar complexes[7] and the CO adducts of the iron lacunar complexes.[8] These studies showed (1) that the affinities of the complexes for gaseous ligands could be controlled by varying the substituents R^1, R^2, and R^3 and (2) that the ligands tended to generate extremely great O_2 affinities. For example, the cobalt complex of the lacunar ligand having $R^1 = (CH_2)_6$ and $R^2 = R^3 = CH_3$ has an oxygen affinity equal to that of iron-containing myoglobin. Since the dioxygen affinity of the iron derivative is usually about 100 times that of the corresponding cobalt derivative, this suggests that the iron lacunar complexes might have exceptionally large K_{O_2} values. The lacunar iron complex previously reported to be an O_2 carrier (R^1 = *m*-xylylene, $R^2 = R^3 = CH_3$) was chosen because it produced much reduced O_2 and CO affinities for cobalt(II) and for iron(II), respectively.[9]

The oxygenation behavior is presented here for four new iron(II) lacunar complexes, whose elemental analyses are reported in Table I. The complexes were synthesized by modifications of procedures described earlier.[8] The ligands were prepared on nickel(II) and then removed and allowed to complex to iron(II). Like their congenors, these iron(II) complexes are high spin (Table I), and the $ClPF_6$ salts are uni-univalent electrolytes in acetonitrile (λ 125–150 Ω^{-1} mol^{-1} cm^2 at 1 mM). It is therefore concluded that the iron is five-coordinated with either solvent or, in the $ClPF_6$ salts, with the chloride ion occupying the axial site opposite the cavity, which remains vacant prior to O_2 binding.

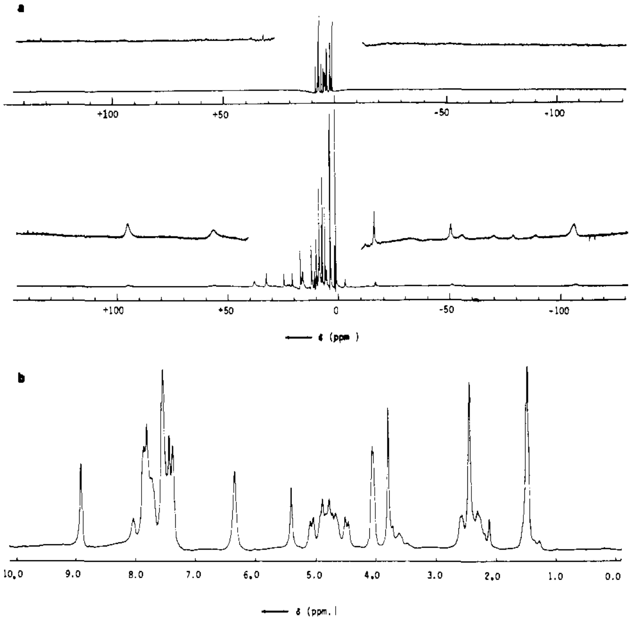

Figure 1. (a) bottom ^1H NMR spectrum of the iron(II) lacunar complex I, R^1 = *m*-xylylene, $R^2 = CH_2C_6H_5$, $R^3 = C_6H_5$ in pyridine-$^2H_5$ at −20.0 °C. Paramagnetically shifted and broadened as expected for high-spin iron(II) (vertical expansion ×8 is inset). Upper; ^1H NMR spectrum of the same solution at the same temperature on the same vertical expansion scales but after exposure to 748 torr of O_2, conditions leading to >97% oxygenation. (b) expanded plot of the 0–10-ppm region of ^1H NMR spectrum in Figure 1a, top.

Table II. Stability toward Autoxidation of Various Dioxygen Adducts of Structure I (R^1 = *m*-xylylene, B = 1-methylimidazole)[a]

R^1	R^3	$t_{1/2}$	T_{max},[b] °C
CH_3	CH_3	<1 min	−35
$CH_2C_6H_5$	CH_3	~3 min	−15
CH_3	C_6H_5	~15 min	−5
$CH_2C_6H_5$	C_6H_5	~24 h	~20

[a] Solvent is acetone, 1-methylimidazole, water = 3:1:1 by volume at 20 °C, under 1 atm of O_2. [b] T_{max} is the highest temperature at which K_{O_2} can be measured precisely by slow-equilibration techniques.

Three of the new compounds were designed to provide a progressive increase in the hydrophobic bulk in the vicinity of the O_2 binding site while, hopefully, perturbing the O_2 affinity as little as possible. Therefore R^2 and R^3 were varied while R^1 was held constant (*m*-xylylene). Hindering access to the cavity with bulky groups should retard autoxidation processes occurring by either of two broad categories of possible mechanisms: (1) dissociation of O_2^- from the O_2 adduct[10,11]—the polar transition states should be stabilized by the action of polar solvent molecules; (2) out-

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[9] As indicated, the unhindered lacunar cobalt complexes show K_{O_2} values as large as those of FeMb. Since FeMb has a $K_{O_2} \approx 10^2$ times that of CoMb, we could anticipate $K_{O_2} \approx 10^2$ $torr^{-1}$ for the lacunar iron complex. It would be very difficult to remove the O_2 from such an adduct in solution ($P_{50} \approx 0.01$ torr). Further, the enhanced O_2 affinity may be accompanied by dioxygen activation, in which case autoxidation might be accelerated.

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Table III. Thermodynamic Properties[a] of the O_2 Adducts of Lacunar Iron(II) Complexes

R^1	R^2	R^3	B	solvent	ΔH, kcal/mole	ΔS, eu	K_{O_2}, torr^{-1} (−20 °C)
CH_3	CH_3	$(CH_2)_8$	Cl	acetone	−14.2 ± 0.5	−64 ± 2	0.019
m-xylylene	$CH_2C_6H_5$	CH_3	py	APW[b]	−12.9 ± 0.8	−63 ± 2	0.003
m-xylylene	CH_3	C_6H_5	py	APW[b]	−14.2 ± 0.3	−65 ± 1	0.011
m-xylylene	$CH_2C_6H_5$	C_6H_5	py	APW[b]	−17.5 ± 0.4	−76 ± 2	0.050

[a] Standard state of 1 torr. [b] APW = acetone-pyridine-water = 3:1:1 by volume.

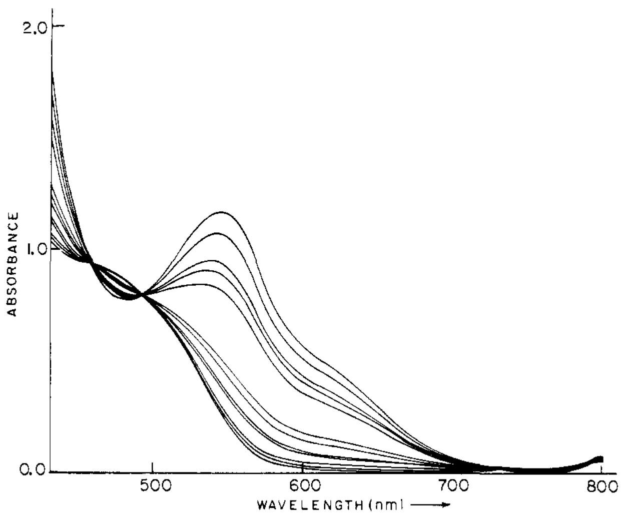

Figure 2. Visible spectral changes accompanying formation of the O_2 adduct of the Lacunar-2 complex of iron(II) (structure II, $R^1 = R^2 = CH_3$, $R^3 = (CH_2)_8$); acetone, $T = -20$ °C, $P_{O_2} = \sim 0$, 4.6, 12, 22, 38, 67, 99, 150, 300, and 760 torr.

er-sphere electron transfer[12] from the iron(II) deoxy complex to free O_2—the exchange would be facilitated by the close approach of the exchanging species.

The formation of O_2 adducts by these iron derivatives is signaled by the appearance of a characteristic electronic spectral pattern with absorption maxima near 520 and 620 nm. Proton NMR spectral studies on solutions of the O_2 adducts reveal the usual ligands signals, establishing the diamagnetic character of the adducts (Figure 1). Further, the ESR signals characteristic of the autoxidation products, which are the subject of ongoing studies, are absent.

Table II shows the progressive stabilization toward autoxidation that accompanies this systematic increase in the bulk of the substituents in the vicinity of the cavity within which the O_2 binds. The maximum temperatures at which we can perform precise K_{O_2} determinations, T_{max}, is a revealing, if rather practical, indicator of the durabilities of the O_2 adducts. This requires the spectral behavior of a solution containing the complex and various partial pressures of O_2 to remain sharply isosbestic for several hours. Clearly each increase in steric bulk leads to a substantial increase in durability until, in the case where R^2 = benzyl and R^3 = phenyl, the O_2 complex can be studied at room temperature (20 °C) and above in a partial (20%) aqueous solution. If the water is excluded from the solvent, the reversibility is further enhanced and evidence for autoxidation at room temperature disappears. Considerable reversibility remains at +37 °C in this solvent.

The values of $t_{1/2}$ for autoxidation at room temperature in the presence of 1 atm of O_2 (solvent = 3:1:1 acetone-1-methylimidazole-water) offer a rough quantitation of the effect. The half-lives were estimated from spectral changes accompanying oxygenation–deoxygenation cycles at 20 °C. Clearly the benzyl- and phenyl-substituted complex constitutes the first example of a nonporphyrin iron derivative that it capable of forming a dioxygen adduct reversibly at room temperature.

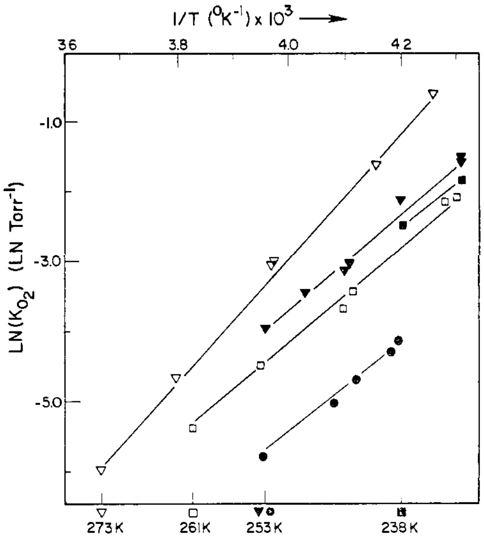

Figure 3. Van't Hoff plots for reaction of dioxygen with complexes of structures I and II: (■) R^1 = *m*-xylyene, $R^2 = R^3 = CH_3$; (▼) $R^1 = R^2 = CH_3$, $R^3 = (CH_2)_8$; (●) R^1 = *m*-xylylene, $R^2 = CH_2C_6H_5$, $R^3 = CH_3$; (□) R^1 = *m*-xylylene, $R^2 = CH_3$, $R^3 = C_6H_5$; (▽) R^1 = *m*-xylylene, $R^2 = CH_2C_6H_5$, $R^3 = C_6H_5$.

The *m*-xylylene summarizes was maintained for the four iron complexes whose behaviors are given in Table II in an effort to minimize changes in the dioxygen affinity. Table III summarizes the results of lengthy equilibrium studies on the new complexes. K_{O_2} was measured over much of the available temperature range (above −40 °C) for each complex by a method described earlier,[7] and the enthalpy and entropy changes associated with oxygenation were estimated. K_{O_2} values are listed in Table III for −20 °C and may be compared with an extrapolated value of 0.02 (± 0.002) torr^{-1} for the lacunar iron–dioxygen carrier reported earlier[3] (R^1 = *m*-xylylene, $R^2 = R^3 = CH_3$). Bearing in mind the fact that K_{O_2} for cobalt lacunar complexes can be caused to change over a range of 10^5 by changing R^1 alone, the O_2 affinities for the iron complexes described here do indeed change relatively little. For three of the complexes, K_{O_2} remains of the same magnitude, but the complex having R^2 = benzyl and R^3 = methyl shows an anomalously low dioxygen affinity.

The complex of the novel structure II has also yielded a reversible iron–dioxygen carrier at moderate temperatures. Structure II differs from I in the point of attachment of the bridging group (R^3 instead of R^1), and this results in placing the bridge more nearly above the metal atom. Studies on the cobalt complex[13] revealed a reduced O_2 affinity, and this motivated us to explore O_2-binding ability of the iron complex.[9] The isosbestic spectral behavior of this novel complex at −20 °C is shown in Figure 2 (maxima at 545 and 630 nm and isosbestic points at 458, 493, and 730 nm). The K_{O_2} values reported for this case (Table III) indicate a substantial O_2 affinity even though the axial ligand is chloride. The O_2 adduct appears to be stable toward autoxidation up to about −15 °C, and it is detectable at 20 °C, where its half-life is a few minutes.

The Van't Hoff plots in Figure 3 show the magnitudes of K_{O_2}, their variation with temperature, and the temperature ranges over

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which we were able to measure them with precision for each of the new complexes. The upper limit is determined by the decomposition reaction, which is evidenced by the onset of nonisosbestic behavior in sets of spectral scans. It should be noted that the thermodynamic parameters ΔH and ΔS remain constant when R^3 changes from CH_3 to phenyl, whereas both parameters change when benzyl is substituted for the methyl group at R^2. Studies on the cobalt(II) lacunar complexes[13] commonly give values of ΔS in the region -62 ± 3 eu, essentially the entropy of dioxygen.[14] The benzyl-phenyl derivative appears to involve substantial reorganization within the complex in addition to removing the degrees of freedom of dioxygen. The alteration in ΔH suggests that the reorganization enlarges the void so as to enhance the O_2 binding.

The new complexes open many new possibilities. The structural modifications we have used are trivial compared to those that are possible, and future studies will almost certainly address such subjects as the use of simple iron coordination compounds in the energy-efficient reduction of dioxygen and the selective oxygenation of organic substrates.[15]

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(15) Support by the National Institutes of Health and the National Science Foundation is gratefully acknowledged. The aid of the staff and use of the facilities of the Cooperative Institute for Research in Environmental Sciences of the University of Colorado in the preparation of this paper is deeply appreciated.

Oxidation-Reduction Catalytic Activity of a Pentaammineruthenium(III) Derivative of Sperm Whale Myoglobin

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The extent to which the oxidation-reduction properties of a metalloprotein can be manipulated by the attachment of redox-active inorganic groups to polypeptide chain ligands is a matter of current interest in our laboratory. Our initial studies in this area have centered around pentaammineruthenium(III) (a_5Ru^{3+}) and pentacyanoferrate(II) derivatives of horse heart cytochrome *c*.[2-6] In accord with Matthews (who has studied the a_5Ru^{3+} derivatives of several proteins),[7-10] we have found that a_5Ru^{3+} has a strong preference for surface-accessible histidine residues; furthermore, we have been able to establish that a_5Ru–His(protein) complexes possess considerable kinetic stability (with respect to dissociation) in *both* Ru^{II} and Ru^{III} states. In recent experiments we have found that three a_5Ru^{3+} groups can be attached to sperm whale myoglobin and that the ligand-binding and oxidation-reduction properties of $(a_5Ru^{3+})_3Mb$ or Ru_3Mb are dramatically

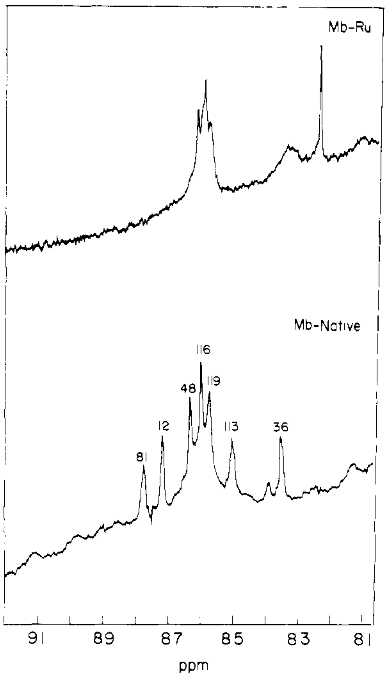

Figure 1. Proton NMR spectra (Bruker WH500) of Mb and Ru_3Mb in the region of imidazole ^1H(C-2) resonances (D_2O/DCl, pH 5.5; internal DSS). Prominent peaks attributable to the C-2 proton resonances of His-12, His-81, and His-113 in the spectrum[11] of native Mb are absent in the Ru_3Mb spectrum.

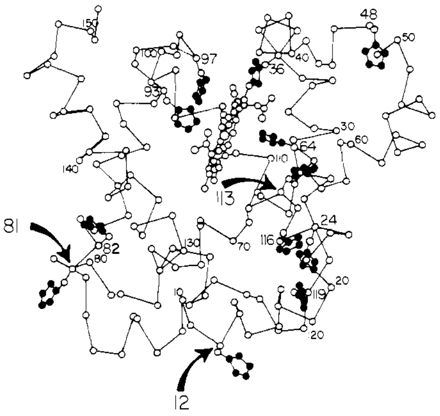

Figure 2. Drawing of the Mb structure that highlights the three a_5Ru^{3+} binding sites. The shortest His-113 imidazole edge to heme edge distance is roughly 12 Å. The His-12 and His-81 imidazole edge–heme contacts are all over 15 Å.

Table I. Reactivity Parameters for Oxidations Catalyzed by Ru_3Mb and Related Species at 25 °C

substrate	pH	E°, mV[a]	catalyst	K_m, M	k_{cat}, s^{-1}
ascorbate	5.5	55	Ru_3Mb	1.5×10^{-5}	0.60
			Ru_3apoMb	1.9×10^{-5}	0.0063
			a_5RuIm^{3+}	1.3×10^{-5}	0.0035
durohydroquinone	7	65	Ru_3Mb	2.8×10^{-5}	0.30
			Ru_3apoMb	1.1×10^{-4}	0.058
hydroquinone	7[b]	120[b]	Ru_3Mb	1.1×10^{-4}	0.0042

[a] Versus NHE. [b] At pH 5 (E° = 360 mV) catalytic turnover is not observed.

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