

of $D_2O_3(CO)_{10}$ on silica gel but that direct exchange with D_2O or C_6H_5OD does not occur in the absence of silica; extended interaction of $H_2O_3(CO)_{10}$ with H_2O in acetone gives $HO_3(CO)_{10}(OH)$.

- (11) Total deuterium content: % D_2 species + $1/2$ (% HD species).
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 (17) $H_2Re_2(CO)_8$ reacts with PPh_3 in hexane at room temperature in 10 min to give an adduct (ν_{CO} 2104 (w), 2073 (w), 2022 (sh), 2014 (m), 2008 (s), 1980 (m), 1967 (m) and 1949 (m) cm^{-1} (cyclohexane solution) presumed to be $HRe(CO)_4(\mu-H)Re(CO)_4PPh_3$. Attempts to obtain NMR spectra in benzene resulted in decomposition to $HRe(CO)_4PPh_3$; M. A. Andrews and H. D. Kaesz, unpublished observations.
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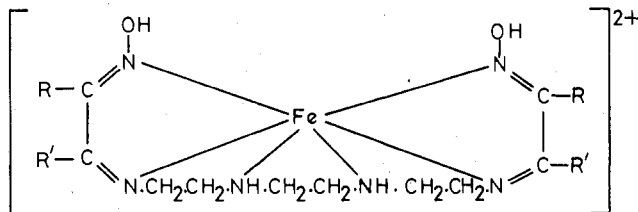
Coupled Electron- and Proton-Transfer Equilibria in Some Iron-Oxime and Related Systems

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Loss of an electron from a complexed metal ion will in general augment the acidity of dissociable protons present on the ligand frame. When the metal-ligand combination is right, oxidation and deprotonation may occur in a coupled manner. The occurrence of such coupled reactions has been postulated in metal ion catalyzed bioreactions.¹ In this work examples of coupled electron and proton reactions are revealed in a variable-pH cyclic voltammetric (CV) study of the low-spin pseudooctahedral iron(II) species^{2,3} $Fe(H_2RR'L)^{2+}$, **1**, which



1

has two dissociable oxime protons.

Experimental Section

A. Preparation of Compounds. The synthesis of $Fe(H_2Me_2L)(ClO_4)_2$ was described earlier.² $Fe(H_2EtMeL)(ClO_4)_2$ was similarly prepared in 70% yield by reacting ferrous sulfate heptahydrate with H_2EtMeL .² Anal. Calcd for $C_{16}H_{32}N_6O_{16}Cl_2Fe$: C, 32.26; H, 5.42; N, 14.12; Fe, 9.38. Found: C, 32.24; H, 5.72; N, 14.10; Fe, 9.20. $Fe(H_2MeEtL)(ClO_4)_2$ was prepared as follows. A 0.49-g sample (0.0033 mol) of triethylenetetramine was added to an ethanolic solution of 0.77 g (0.0066 mol) of isonitrosoethyl ethyl ketone.² An ethanolic solution of 1.21 g (0.0033 mol) of iron(II) perchlorate hexahydrate

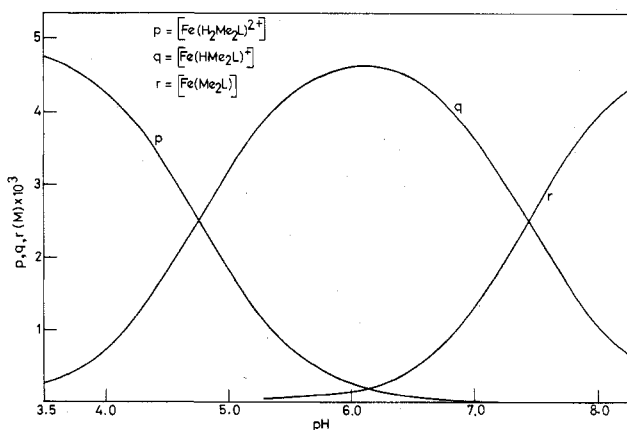


Figure 1. Formation curves of iron(II) species.

was added to the above mixture. The mixture was heated to reflux for 4–5 h with constant stirring. Deep violet crystals deposited in 50% yield. Those were filtered off and were washed with alcohol followed by ether. Anal. Calcd for $C_{16}H_{32}N_6O_{16}Cl_2Fe$: C, 32.26; H, 5.42; N, 14.12; Fe, 9.38. Found: C, 32.14; H, 5.81; N, 14.20; Fe, 9.10. All complexes are indefinitely stable at room temperature.

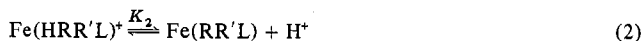
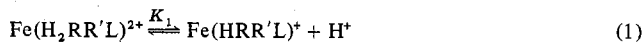
Like $Fe(H_2Me_2L)(ClO_4)_2$ both $Fe(H_2EtMeL)(ClO_4)_2$ and $Fe(H_2MeEtL)(ClO_4)_2$ are diamagnetic. Their electronic and IR spectra² are very similar.

B. pH-metric Titrations. These were done on 40 mL of 0.005 M $Fe(H_2Me_2L)(ClO_4)_2$ with carbonate-free sodium hydroxide solution (0.01 N) at 298 K. Further experimental details and also details concerning treatment of data for obtaining K_1 and K_2 and formation curves are delineated elsewhere.⁴

C. Cyclic Voltammetry and Constant-Potential Coulometry. These were performed in an instrument fabricated in this laboratory, in the same manner as described elsewhere.⁴

Results and Discussion

A. Dissociation of Oxime Protons. The complex $Fe(H_2Me_2L)^{2+}$ was titrated pH-metrically with alkali. From the titration data, the stepwise acid dissociation constants pK_1 and pK_2 corresponding to



were found to be (298 K) 4.75 ± 0.05 and 7.45 ± 0.05 , respectively. The formation curves (Figure 1) were constructed using these equilibrium constants. Up to pH 4, $Fe(H_2Me_2L)^{2+}$ alone makes the major contribution to the solution composition while at pH 8.2 the major species is $Fe(Me_2L)$. The intermediate species $Fe(HMe_2L)^+$ is most important in the narrow pH range 5.6–6.6.

B. Cyclic Voltammetric Results. The case of $Fe(H_2Me_2L)(ClO_4)_2$ will be described first (Table I and Figure 2). All potentials are referenced to the saturated calomel electrode (SCE). The peak separation (ΔE_p) remains close to 60 mV in the entire range of pH (1.55–8.90) and scan rates (0.012–0.213 $V s^{-1}$) studied (Table I). Evidently it is a reversible one-electron transfer.⁵ The one-electron involvement is fully corroborated by constant-potential (oxidation at 0.45 V at room temperature) coulometry in acetate buffer at pH 3.25: 1.14×10^{-5} mol of $Fe(H_2Me_2L)(ClO_4)_2$ in 250 mL of buffer was electrolyzed to complete the oxidation. Amount of electricity consumed was 1.14 C (calculated value 1.10 C).

While ΔE_p remains invariant, the peak potentials and hence their average (\bar{E}_p) shift considerably with pH until pH 8.20 is reached. This pH dependence means that protons are involved in the electrode process. For the general reversible reaction in well-buffered media



Table I. Cyclic Voltammetric Data^{a-c} of Fe(H₂Me₂L)(ClO₄)₂ in Buffers at 25 °C

pH	\bar{E}_p , V	ΔE_p , V	ΔpH	$\Delta \bar{E}_p$, V	m	$E^{\circ\prime}_{298}$, V
Couple: Fe(Me ₂ L) ⁺ -Fe(H ₂ Me ₂ L) ²⁺						
1.55	0.463	0.065				0.64
1.85	0.430	0.065	0.30	0.033	1.9 ± 0.4	0.65
2.65	0.340	0.070	1.10	0.123	1.9 ± 0.1	0.65
3.50	0.245	0.070	1.95	0.218	1.9 ± 0.1	0.66
4.10	0.175	0.070	2.55	0.288	2.0 ± 0.1	0.66
Couple: Fe(Me ₂ L) ⁺ -Fe(HMe ₂ L) ⁺						
5.65	0.015	0.070				0.35
6.35	-0.040	0.070	0.70	0.055	1.3 ± 0.2	0.33
6.55	-0.055	0.070	0.90	0.070	1.3 ± 0.1	0.34
Couple: Fe(Me ₂ L) ⁺ -Fe(Me ₂ L)						
8.20	-0.115	0.070				-0.12
8.65	-0.125	0.070	0.50	0.012	<i>d</i>	-0.13
8.90	-0.128	0.070	0.75	0.015	<i>d</i>	-0.13

^a Concentrations were in the range (1.00-1.13) × 10⁻³ M; scan rates studied in every pH were in the range 0.012-0.213 V s⁻¹; meanings of symbols are as in the text. ^b $E^{\circ\prime}_{298}$ values of three couples were calculated using $m = 2, 1,$ and $0,$ respectively, in eq 4. ^c ΔpH and $\Delta \bar{E}_p$ values were calculated referring to the first entry of pH for each couple. ^d $\Delta \bar{E}_p$ values are very small and no calculation of m is made; evidently it is equal to zero.

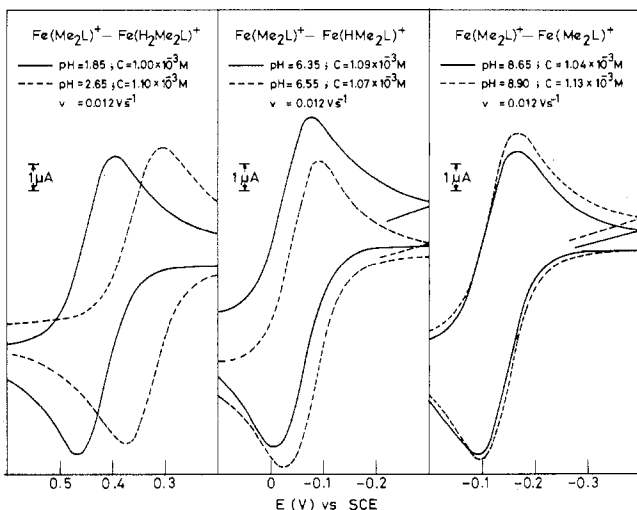


Figure 2. Cyclic voltammograms for one iron system at different pH values.

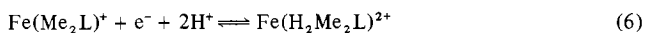
it can be shown^{4,6} that

$$E^{\circ\prime}_{298} = \bar{E}_p + 0.059(m/n)pH \quad (4)$$

$$m = -(n/0.059)(\Delta \bar{E}_p / \Delta pH) \quad (5)$$

where $E^{\circ\prime}_{298}$ is the formal electrode potential of couple (3) and $\Delta \bar{E}_p$ is the shift of \bar{E}_p due to the change in pH by ΔpH . By using eq 5 and $n = 1$, values of m were computed (Table I). The quantities $\Delta \bar{E}_p$ and ΔpH are subject to experimental errors of 5 mV and 0.02 pH unit, respectively. The limits of error on m as shown in Table I correspond to these limits of error in $\Delta \bar{E}_p$ and ΔpH .

At $pH \leq 4.1$, $m = 2$ (Table I). Since the major iron(II) species at $pH \leq 4.1$ is Fe(H₂Me₂L)²⁺, the electrode reaction is



The $E^{\circ\prime}_{298}$ of this electrode reaction is found (eq 4) to be 0.65 ± 0.01 V (Table I). The iron(III) complex Fe(Me₂L)⁺ exists in the deprotonated form even in strongly acidic media. Above pH 4.1 the shift of peak potentials with pH becomes smaller. This happens because the species Fe(HMe₂L)⁺ starts contributing to the solution composition (Figure 1). In the pH

Table II. Cyclic Voltammetric Data^a of Other Iron Systems at 25 °C

pH	\bar{E}_p , V	$E^{\circ\prime}_{298}$, V
Couple: Fe(EtMeL) ⁺ -Fe(H ₂ EtMeL) ²⁺		
1.60	0.465	0.66
2.25	0.388	0.66
3.45	0.250	0.66
Couple: Fe(EtMeL) ⁺ -Fe(EtMeL)		
9.15	-0.175	-0.18
9.45	-0.178	-0.18
Couple: Fe(MeEtL) ⁺ -Fe(H ₂ MeEtL) ²⁺		
1.60	0.433	0.62
2.35	0.350	0.63

^a Since Fe(H₂MeEtL)(ClO₄)₂ decomposes above pH 8.0, the CV data of the couple Fe(MeEtL)⁺-Fe(MeEtL) could not be studied.

Table III. Calculated and Experimental $E^{\circ\prime}_{298}$ values

Couple	Contributions		$E^{\circ\prime}_{298}$, V	
	Electron transfer	Proton transfer	Calcd	Exptl
Fe(III)-Fe(II)				
Fe(Me ₂ L) ⁺ -Fe(Me ₂ L)	-0.13			-0.13
Fe(Me ₂ L) ⁺ -Fe(HMe ₂ L) ⁺	-0.13	0.44	0.31	0.34
Fe(Me ₂ L) ⁺ -Fe(H ₂ Me ₂ L) ²⁺	-0.13	0.72	0.59	0.65
Ni(III)-Ni(II)				
Ni(Me ₂ L) ⁺ -Ni(Me ₂ L)	0.15			0.15 ^a
Ni(Me ₂ L) ⁺ -Ni(HMe ₂ L) ⁺	0.15	0.46 ^b	0.61	0.63 ^a
Ni(Me ₂ L) ⁺ -Ni(H ₂ Me ₂ L) ²⁺	0.15	0.81 ^b	0.96	1.00 ^a
Ni(IV)-Ni(II)				
Ni(Me ₂ L) ²⁺ -Ni(H ₂ Me ₂ L) ²⁺	0.29 ^c	0.41 ^b	0.70	0.71 ^a

^a From ref 4. ^b The acid dissociation constants pK_1 and pK_2 for Ni(H₂Me₂L)²⁺ are 5.90 and 7.80 respectively.⁴ ^c ($E^{\circ\prime}_{298}$)_{e1} and ($E^{\circ\prime}_{298}$)_{e2} (see eq 16) are respectively 0.42 and 0.15 V.

range 5.6-6.6, this becomes the major species. The computed values of m lie close to unity (Table I). The main electrode reaction in the pH range 5.6-6.6 is



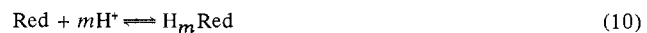
$E^{\circ\prime}_{298}$ for this couple is 0.34 ± 0.01 V (Table I). Above pH 8.2 the peak potentials undergo no further change with pH ($m = 0$). The electrode reaction is



This has $E^{\circ\prime}_{298} = -0.13 \pm 0.01$ V (Table I). Formation curves (Figure 1) also require that the iron(II) species at pH 8.2 is Fe(Me₂L).

The cyclic voltammetric responses for two other iron systems were also studied. The general pattern of behavior is the same as that of Fe(H₂Me₂L)(ClO₄)₂. A few selected results are set out in Table II.

C. Separation of Electron-Transfer and Proton-Transfer Contributions. In this and related works^{4,6} equilibria belonging to type (3) are experimentally identified by cyclic voltammetry. It will be interesting to see whether the observed thermodynamics of such equilibria can be reconstructed from the thermodynamics of two separate equilibria, one involving only electron transfer and other involving only proton transfer. These equilibria are



The formal free energy change $\Delta G^{\circ\prime}_T$ corresponding to eq 3 is given by

$$\Delta G^{\circ\prime}_T = -nFE^{\circ\prime}_T \quad (11)$$

A similar expression holds for (9) for which the free energy change and formal electrode potentials will be designated

Notes

respectively as $(\Delta G^{\circ}_T)_{el}$ and $(E^{\circ}_T)_{el}$. The free energy change in (10) can be written as

$$(\Delta G^{\circ}_T)_{pr} = RT \ln K \quad (12)$$

where K is the dissociation constant of the acid $H_n\text{Red}$ (K is the inverse of the equilibrium constant of eq 10). The equation of free-energy balance

$$\Delta G^{\circ}_T = (\Delta G^{\circ}_T)_{el} + (\Delta G^{\circ}_T)_{pr} \quad (13)$$

can be combined with eq 11 and 12 to yield (at 298 K)

$$E^{\circ}_{298} = (E^{\circ}_{298})_{el} + (0.059/n)pK \quad (14)$$

In the specific cases of equilibria 6 and 7, pK of eq 14 can be expressed respectively as (see eq 1 and 2) $pK_1 + pK_2$ and pK_2 . The values of E°_{298} calculated from eq 14 using experimental values of $(E^{\circ}_{298})_{el}$ and pK for Fe(III)-Fe(II) systems and the corresponding Ni(III)-Ni(II) systems^{4,6} are set out in Table III. The last entry in Table III refers to the Ni(IV)-Ni(II) couple^{4,6}



The electron-transfer couple $\text{Ni}(\text{Me}_2\text{L})^{2+} + 2e^- \rightleftharpoons \text{Ni}(\text{Me}_2\text{L})$ is not known experimentally. However, the two one-electron couples $\text{Ni}(\text{Me}_2\text{L})^{2+} + e^- \rightleftharpoons \text{Ni}(\text{Me}_2\text{L})^+$ and $\text{Ni}(\text{Me}_2\text{L})^+ + e^- \rightleftharpoons \text{Ni}(\text{Me}_2\text{L})$ are well characterized.^{4,6} From consideration of free energy balance it is readily shown that

$$E^{\circ}_{298} = 1/2 [(E^{\circ}_{298})_{el1} + (E^{\circ}_{298})_{el2} + 0.059(pK_1 + pK_2)] \quad (16)$$

where E°_{298} is the redox potential of couple (15), $(E^{\circ}_{298})_{el1}$ and $(E^{\circ}_{298})_{el2}$ are the redox potentials of the one-electron couples, and pK_1 and pK_2 refer to the first and second dissociation of $\text{Ni}(\text{H}_2\text{Me}_2\text{L})^{2+}$.

The agreement between calculated and experimental formal electrode potentials is excellent in all cases (Table III). The separation of the total free energy of reactions of type (3) into electron-transfer and proton-transfer contributions is valid.

Registry No. Fe(H₂EtMeL)(ClO₄)₂, 62107-58-8; Fe-(H₂MeEtL)(ClO₄)₂, 62078-93-7; Fe(H₂Me₂L)(ClO₄)₂, 55758-57-1; Fe(HMe₂L)⁺, 60306-12-9; Fe(Me₂L)⁺, 60196-59-0; Fe(Me₂L), 60306-13-0; Fe(EtMeL)⁺, 62078-91-5; Fe(EtMeL), 62078-90-4; Fe(MeEtL)⁺, 62078-89-1; Ni(Me₂L)⁺, 59980-38-0; Ni(HMe₂L)⁺, 60306-03-8; Ni(H₂Me₂L)²⁺, 55188-31-3; Ni(Me₂L)²⁺, 55188-33-5; triethylenetetramine, 112-24-3; isonitrosoethyl ethyl ketone, 32818-79-4.

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Single-Crystal Electron Nuclear Double Resonance Studies of Silver(II) and Copper(II) Tetraphenylporphyrins

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The importance of understanding the bonding in metal-porphyrins has led us to undertake a comparative study of

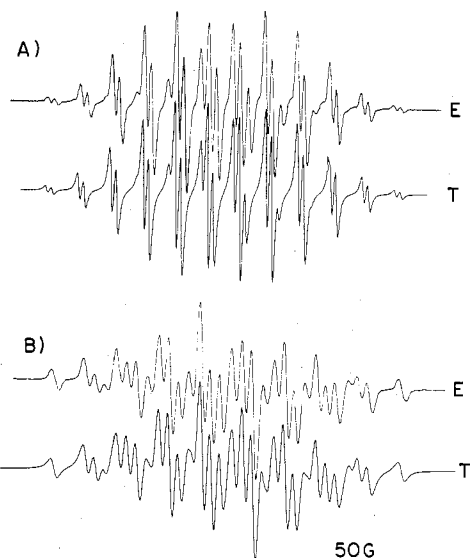


Figure 1. Experimental EPR spectra of AgTPP in (H₂O)ZnTPP (E) and computer simulations (T) employing the spin-Hamiltonian parameters of Table I: (A) H parallel to g_1 ; (B) H along Ag-N axis. Unresolved proton and/or silver isotope interactions were allowed for by using Gaussian line widths of 4 and 6 G, respectively, in simulating (A) and (B).

silver(II) and copper(II) tetraphenylporphyrins (TPP) through the use of electron nuclear double resonance (ENDOR) on oriented, dilute single crystals.¹ The enhanced resolution available from ENDOR² uniquely permits one to map out the odd-electron distribution within these molecules and to compare the M-N bonding in the two systems, and gives information about their geometric configurations as well.

Experimental Section

Metalloporphyrins were prepared by published procedures.³ AgTPP and ⁶³CuTPP, were separately doped into single crystals of (H₂O)ZnTPP by slow evaporation from toluene solution, 1 mol % in dopant. EPR and ENDOR spectra were obtained as described elsewhere.^{4,5} The lowest available temperature, 20 K, gave optimal ENDOR for CuTPP, but AgTPP afforded the best ENDOR at 30 K.

(H₂O)ZnTPP crystals exhibit a single molecule per unit cell, with C_4 , but $\sim C_{4v}$, symmetry. There is a twofold disorder in which the H₂O can point "up" or "down"; the statistically averaged molecule lies in a mirror plane and exhibits C_{4h} symmetry.⁶ This disorder does not affect the EPR or ENDOR spectra, and only one site is observed spectroscopically. Since the g tensors for both dopants are axial,¹ the magnetic field, H , was aligned along g_1 or along g_{\perp} , lying in the molecular mirror plane ($\pm 1^\circ$), by employing the orientation dependence of the EPR signal. Orientation of the field within the molecular plane was obtained from the ENDOR measurements (vide infra).

Results

The angular-dependent EPR spectra of AgTPP and ⁶³CuTPP in (H₂O)ZnTPP give g values in agreement with those reported by Manoharan and Rogers (MR) for an H₂TPP host.¹ The spectra in the (H₂O)ZnTPP host are generally better resolved, in part due to the lower temperatures employed and, for copper, because of our use of isotopically pure ⁶³Cu. In a general orientation the spectra exhibit hyperfine splitting (hfs) from the central metal ion, in some cases with distinguishable patterns arising from ¹⁰⁷Ag and ¹⁰⁹Ag, and from pairs of equivalent pyrrole nitrogens (Figure 1). The metal coupling constants were obtained from EPR; because of considerable overlapping of lines, no effort was made to directly analyze the ¹⁴N pattern (but vide infra).

No evidence of proton hfs is discernible in the EPR (Figure 1); both AgTPP and CuTPP, however, show well-resolved