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Electrochemical Studies of the 8-Quinolinol and 2-Methyl-8-quinolinol Complexes of Iron(II) and -(III) in Dimethyl Sulfoxide

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The iron(II) and -(III) ions form a series of complexes with 8-quinolinol. Four reversible iron(III)–iron(II) redox couples are observed for the group of complexes; the relative concentrations of the species are a function of solution acidity. The reduction potentials for the couples in dimethyl sulfoxide are +0.25 V vs. SCE (Fe^{3+}), −0.05 V (FeQ^{2+}), −0.30 V (FeQ_2^{+}), and −0.60 V (FeQ_3); Q^- represents the anion of 8-quinolinol. With 2-methyl-8-quinolinol iron forms an analogous series of complexes plus a μ-oxo-bridged binuclear compound with a reduction potential of −0.78 V. The reactivity of molecular oxygen and of hydrogen peroxide with the iron(II) complexes with 8-quinolinol has been determined.

The electrochemistry of transition metal complexes in aprotic solvents has become a major interest of our group. As a result, the molybdenum[1,2] and vanadium[3] 8-quinolinol complexes recently have been investigated as models for metalloflavin proteins. The 8-quinolinol ligand (Q^-) also represents a convenient one-molecule functional analogy to the coordinating groups of histidine and tyrosine. Because these amino acids commonly are associated with the transition metal ions in metalloproteins, the redox chemistry of 8-quinolinol complexes should be relevant to the chemistry of the enzymes.

Iron is a common component of metalloenzymes, and therefore studies of the redox chemistry of the iron–8-quinolinol complexes should provide insights to the redox chemistry of iron proteins. Although the common oxidation states of iron are not isoelectronic with the higher oxidation states of molybdenum or vanadium, iron does have a tendency to form oxo-bridged dimers[4-6] such as $[Fe(bpy)_2(H_2O)]_2O^{4+}$ and $[Fe(EDTA)]_2O^{4-}$ and hence forms dimeric complexes with certain 8-quinolinols (as do molybdenum and vanadium). Although formation of oxo-bridged binuclear iron complexes by 8-quinolinol has not been observed, iron(III) readily forms such a complex with 2-methyl-8-quinolinol.[7] The present electrochemical investigation of the iron complexes formed by 8-quinolinol and 2-methyl-8-quinolinol has been carried out in aprotic solvents in the belief that they are more representative of the biological matrix of the metal in a metalloprotein.

Experimental Section

Measurements. Cyclic voltammetric measurements were made with a three-electrode potentiostat constructed with solid-state operational amplifiers[8] or a Princeton Applied Research Corp. (PARC) Model 173D/179 potentiostat/galvanostat coupled to a PARC Model 175 universal programmer. The voltammograms were recorded on a Hewlett-Packard Model 7030A X-Y recorder. Controlled-potential electrolyses were performed using the PARC apparatus or a Wenking Model 61RH potentiostat, with the current–time curves recorded by a Sargent Model SR strip-chart recorder. Electrochemical measurements of air-sensitive solutions were made inside of a Vacuum/Atmospheres Co. Model HE-43-2/HE-193-1 Dri-Lab/Dri-Train inert-atmosphere system filled with nitrogen.

The working electrode for cyclic voltammetry was a Beckman platinum-inlay electrode. For the controlled-potential electrolyses a platinum mesh electrode was used. The auxiliary electrode was a smaller piece of platinum mesh, separated from the cell solution by a fine-porosity frit. The reference electrode consisted of a Ag/AgCl electrode in aqueous tetramethylammonium chloride whose concentration was adjusted to make the electrode potential 0.000 V vs. SCE. The electrode housing was a Pyrex tube which had a small soft-glass cracked-bead tip. The reference electrode was placed inside a Luggin capillary in the cell assembly.

Infrared spectra of the solid complexes in KBr disks were recorded with a Perkin-Elmer Model 621 spectrophotometer. The UV–visible spectra for solutions of the complexes were recorded with a Cary Model 14 spectrophotometer. Magnetic susceptibility measurements of the complexes in solution were made by the NMR method[9] with a Varian Model A-60 or A-60D NMR spectrometer.

Reagents. Reagent grade dimethyl sulfoxide (J. T. Baker) (0.04% water) was used as received. Spectroquality *N,N*-dimethylformamide (Matheson Coleman and Bell) was vacuum distilled over phosphorus pentoxide before use.

Tetraethylammonium hydroxide was obtained from Eastman Organic Chemicals as 25% solutions in methanol and in water. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte and was prepared and purified by established methods.[3]

Preparation of the Complexes. 1. Tris(8-quinolinolato)iron(III). The FeQ_3 complex was prepared by standard methods.[10,11]

2. Bis(8-quinolinolato)iron(II). The $FeQ_2 \cdot 2H_2O$ complex was prepared by published methods[11-13] but with the added precaution that the reactions were carried out in a nitrogen atmosphere.[11]

3. μ-Oxo-bis[bis(2-methyl-8-quinolinolato)iron(III)]. The $[Fe(2\text{-}MeQ)_2]_2O$ complex (2-MeQ^- represents the anion of 2-methyl-8-quinolinol) was prepared by the method of Mabbs et al.[7] Modifications of the procedure included the substitution of ferric chloride hexahydrate for anhydrous ferric chloride and the elimination of the recrystallization from chloroform because it resulted in the chloroform solvate. Anal. Calcd for $Fe_2C_{40}H_{32}N_4O_5$: Fe, 14.69; C, 63.18; H, 4.24; N, 7.37. Found: Fe, 14.60; C, 63.39; H, 4.28; N, 7.38.

The use of ferric perchlorate (G. F. Smith, nonyellow) in place of ferric chloride hexahydrate led to the identical product as confirmed by infrared spectrophotometry. The spectrum for the complex does not exhibit a well-defined absorption peak which can be attributed to the asymmetric Fe–O–Fe stretch, but it does have a shoulder (850 cm^{-1}) attached to the 830-cm^{-1} ligand peak. The shoulder is absent in the spectra of 2-methyl-8-quinolinol, bis(2-methyl-8-quinolinolato)chloroiron(III), and bis(2-methyl-8-quinolinolato)hydroxoiron(III).

4. Bis(2-methyl-8-quinolinolato)hydroxoiron(III). The $Fe(2\text{-}MeQ)_2OH$ complex was prepared by the reaction of stoichiometric amounts of 2-methyl-8-quinolinol (Aldrich) and ferric perchlorate (G. F. Smith, nonyellow) in absolute ethanol. The product was isolated as a black powder. Anal. Calcd for $FeC_{20}H_{17}N_2O_3$: Fe, 14.35; C, 61.72; H, 4.40; N, 7.20. Found: Fe, 13.59; C, 62.80; H, 4.40; N, 7.26.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

The cyclic voltammogram for a 1 mM solution of $Fe^{III}Q_3$ in dimethyl sulfoxide (Me_2SO) (Figure 1a) exhibits a major cathodic couple at −0.60 V vs. SCE and a minor couple at −0.30 V. (The minor couple is observed in cyclic voltammograms of solutions which are at least 10–15 min old.) For both couples the ratio of anodic to cathodic peak heights is near unity, as expected for a reversible process.

Controlled-potential reduction at −0.90 V indicates that the combined reduction peaks correspond to a one-electron process (0.97 e/Fe). Coulometric reduction at −0.50 V indicates that the minor reduction peak accounts for only about 3% of the total. A positive voltammetric scan for a reduced solution (at −0.90 V) exhibits the anodic peaks of both couples. Subse-

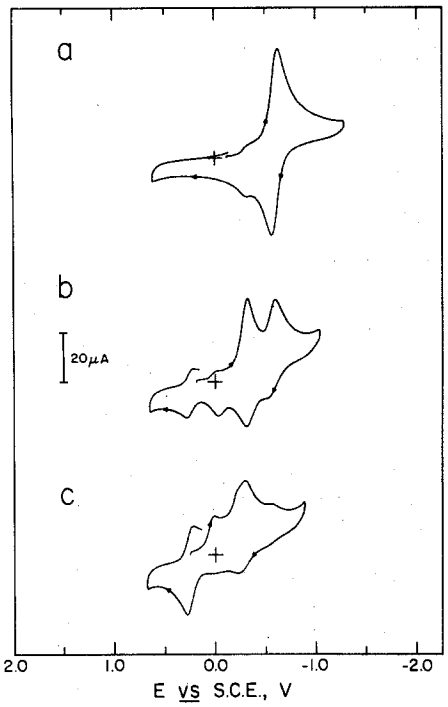

Figure 1. Cyclic voltammograms for 1.0 mM $Fe^{III}Q_3$ in 0.1 M TEAP–Me_2SO: (a) initial solution, (b) after addition of 1 mol of $HClO_4$/mol of FeQ_3, and (c) after addition of 2 mol of $HClO_4$/mol of FeQ_3. Sweep rate 0.1 V/s.

quent oxidation at –0.20 V results in a similar coulometric value and a cyclic voltammogram similar to that for the original FeQ_3 solution.

Addition of water to a solution of FeQ_3 does not have an effect on the cyclic voltammogram. However, the addition of 0.5 mol of tetraethylammonium hydroxide (TEAOH)/mol of FeQ_3 causes the minor couple at –0.30 V to disappear and a small ligand oxidation peak to appear at +0.05 V; the –0.60-V couple remains unchanged.

The addition of acid (aqueous $HClO_4$) to a fresh solution of FeQ_3 has a dramatic effect. The cyclic voltammogram for a solution that contains 0.5 equiv of H^+/mol of FeQ_3 has reduction peaks at –0.325 and –0.625 V with approximately equal heights. Besides the two corresponding oxidation peaks (–0.275 and –0.575 V), the positive part of the cyclic scan has anodic peaks at –0.025 and +0.275 V. On the second negative scan the +0.275-V oxidation peak appears to have a corresponding reduction peak. The addition of 1 mol of H^+/mol of FeQ_3 results in a solution whose cyclic voltammogram is illustrated by Figure 1b. The initial negative scan indicates that there are three species present, with the one that corresponds to the –0.325-V reduction being dominant. The reverse scan exhibits four oxidation peaks, and the second negative scan indicates a fourth reduction peak. Further additions of acid shift the rest potential to more positive values and cause the relative peak heights to change. With 2 equiv of acid added (Figure 1c) the species that correspond to the reductions at –0.075 and –0.325 V appear to be dominant while the reduction peak at –0.625 V (which corresponds to the initial species) is negligible. On the reverse scan the couple at +0.25 V is larger than that for solutions with less acid. Further additions of acid (3 and 4 mol of H^+/mol of FeQ_3) cause the –0.075-V reduction peak to become dominant and the +0.275-V oxidation peak to be the only anodic process. In all cases the reduction peak that corresponds to the oxidation at –0.275 V appears only on the second scan.

When 0.135 g (0.0005 mol) of $FeCl_3 \cdot 6H_2O$ and 0.218 g (0.0015 mol) of 8-quinolinol are dissolved in 25 ml of Me_2SO, a solution is obtained which formally is 20 mM in FeQ_3. The cyclic voltammogram for this solution is similar to that for a solution prepared from solid FeQ_3, to which 3 mol of acid/mol of FeQ_3 has been added. That is, the reduction peak at –0.075 V is dominant and the –0.325-V reduction peak is smaller than that for FeQ_3 without added acid. The voltammograms also differ in that the couple at +0.25 V for FeQ_3 is not present for the synthetic solution. In the latter the couple at –0.05 V appears to be reversible.

Addition of TEAOH to the 1:3 $FeCl_3$–HQ solution gives voltammograms which follow a trend opposite to that for acid additions to the FeQ_3 solution. The height of the –0.325-V reduction peak increases as that at –0.075 V decreases. Further TEAOH additions lead to the appearance of the reduction peak at –0.625 V and its corresponding oxidation peak. With the addition of 3 mol of TEAOH/mol of $FeCl_3$, this is the only couple present; the cyclic voltammogram is identical with that in Figure 1a.

When $Fe^{II}Q_2 \cdot 2H_2O$ is dissolved in Me_2SO, the cyclic voltammogram that is illustrated in Figure 2a is obtained. Reversal of the positive scans at various potentials clearly indicates four reversible couples. With the addition of 0.5 mol of acid/mol of FeQ_2, the rest potential shifts positively, the oxidation peak at –0.575 V disappears, that at –0.275 V becomes smaller, and the anodic peaks at –0.025 and +0.275 V become larger. After the addition of 1 mol of acid/mol of FeQ_2, the oxidation peak at +0.275 V is dominant as shown by Figure 2b. With the addition of 2 mol of acid/mol of FeQ_2, the only species present is that oxidized at +0.275 V (Figure 2c). The corresponding reduction peak is dominant, although there is an equilibrium between the three oxidized species.

When TEAOH is added to a fresh solution of FeQ_2, the equilibrium is shifted completely to the species with a redox couple at –0.60 V (the oxidation peak is observed on the initial positive scan). This is analogous to the couple for the FeQ_3 solution with added base. The cyclic voltammogram for FeQ_2 plus base also is similar to that for FeQ_3 plus base in that free ligand (Q^-) is present as indicated by an oxidation peak at +0.05 V.

A solution which formally is 20 mM FeQ_2 can be made by mixing 0.181 g (0.0005 mol) of $Fe(ClO_4)_2 \cdot 6H_2O$ and 0.14 g (0.001 mol) of 8-quinolinol directly in Me_2SO. The cyclic voltammogram of such a solution exhibits a small anodic shoulder at –0.025 V and a major oxidation peak at +0.275 V for an initial positive scan. The reverse scan exhibits reduction peaks at +0.225, –0.075, and –0.325 V. With additions of base, oxidation peaks that correspond to those of Figure 2a appear along with the reduction peak at –0.625 V. The cyclic voltammogram after 2 mol of TEAOH/mol of $Fe(ClO_4)_2$ has been added indicates that the species which is oxidized at –0.275 V is dominant; with the addition of 3 mol of TEAOH/mol of $Fe(ClO_4)_2$ the species that is oxidized at –0.575 V becomes dominant.

For comparison, the cyclic voltammogram of $Fe(ClO_4)_2$ in the absence of ligand exhibits a reversible couple at +0.25 V.

Solvent effects appear to be minor because the cyclic voltammograms for $Fe(ClO_4)_2$ plus 8-quinolinol in *N,N*-dimethylformamide, and for the solutions that result from base additions, are essentially identical with those in Me_2SO.

On the basis of the cyclic voltammetry the iron complexes formed by 2-methyl-8-quinolinol (Figure 3) are analogous to those formed with 8-quinolinol except for the absence of tris complexes because of steric hindrance.[14] This results in the formation of a stable oxo-bridged binuclear iron(III) complex with 2-methyl-8-quinolinol. The cyclic voltammogram for a 0.5 mM solution of $[Fe^{III}(2\text{-MeQ})_2]_2O$ in Me_2SO (Figure 3a) exhibits a major couple at –0.78 V and minor couples at –0.24 and at –0.53 V. For the major couple the ratio of peak currents approximates unity.

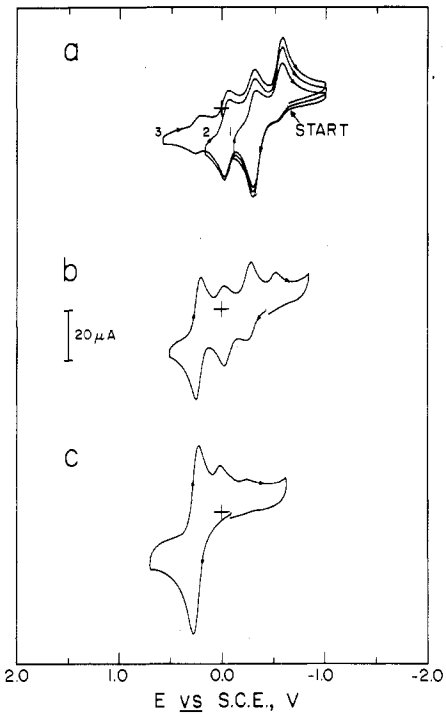

Figure 2. Cyclic voltammograms for 1.2 mM $Fe^{II}Q_2 \cdot 2H_2O$ in 0.1 M TEAP–Me_2SO: (a) initial solution, (b) after addition of 1 mol of $HClO_4$/mol of FeQ_2, and (c) after addition of 2 mol of $HClO_4$/mol of FeQ_2. Sweep rate 0.1 V/s.

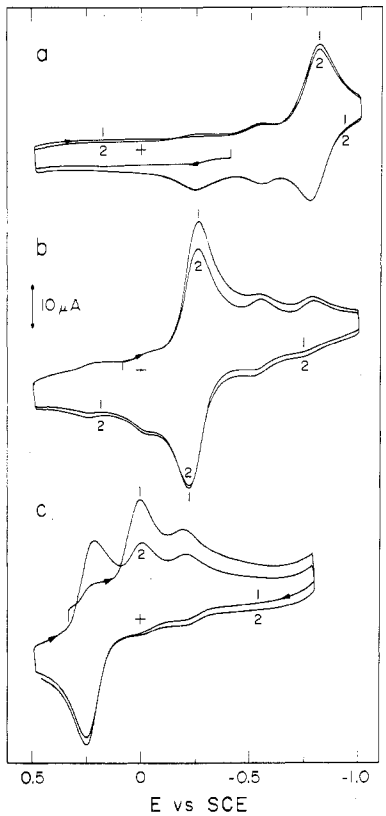

Figure 3. Cyclic voltammograms for 0.5 mM $[Fe^{III}(2\text{-}MeQ)_2]_2O$ in 0.1 M TEAP–Me_2SO: (a) initial solution, (b) after addition of 2 mol of $HClO_4$ per mol of $[Fe(2\text{-}MeQ)_2]_2O$, and (c) after addition of 6 mol of $HClO_4$/mol of $[Fe(2\text{-}MeQ)_2]_2O$. Sweep rate 0.2 V/s.

The addition of 2 mol of H^+/mol of $[Fe^{III}(2\text{-}MeQ)_2]_2O$ results in a solution whose cyclic voltammogram is shown in Figure 3b. The original dominant couple at –0.78 V has been replaced by the couple at –0.24 V. The minor couple at –0.53 V is relatively unchanged. New couples are discernible at +0.25 and –0.03 V. Further additions of acid continue to shift the equilibria to species that are represented by the couples at more positive potentials. The couples at –0.78 and –0.53 V disappear and the one at –0.24 V decreases in peak height.

Table I. UV-Visible Spectrophotometric Data for Iron(III)-8-Quinolinol (Q) and -2-Methyl-8-quinolinol (2-MeQ) Complexes in Me_2SO

Complex	Absorption bands: λ, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	Complex	Absorption bands: λ, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
FeQ_3	368	5.2	$[Fe(2\text{-}MeQ)_2]_2O$[a]	401	8.1
	463	6.1	$Fe(2\text{-}MeQ)_2OH$	380	4.1
	571	4.1		~470	sh
				570	1.7

[a] Molar absorptivity, ϵ, is given per mole of iron; the value is 16.2×10^3/mol of dimer.

The cyclic voltammogram represented by Figure 3c is for a solution that contains 6 mol of H^+/mol of $[Fe(2\text{-}MeQ)_2]_2O$. The initial cathodic scan indicates that the dominant species corresponds to the reduction peak at –0.30 V. Further cycling enhances the couple at +0.25 V. Addition of more acid enhances the magnitude of the +0.25-V couple. When aqueous TEAOH is added to the acidified solution, the equilibria shift back toward the couples with the more negative potentials. However, with the addition of excess base, the couple at –0.78 V does not return to its original peak heights. Instead, the peak heights of the couple at –0.53 V are enhanced.

Controlled-potential electrolysis of a 0.5 mM $[Fe^{III}(2\text{-}MeQ)_2]_2O$ solution at –1.0 V yields a solution whose cyclic voltammogram indicates the elimination of the couple at –0.78 V and its replacement by the couple at –0.53 V. A cyclic voltammogram of the reduced solution after it has stood for several hours (unprotected from air) indicates a partial shift of the equilibria back to the couple at –0.78 V. The couple at –0.53 V matches the reversible couple that is obtained with $Fe^{III}(2\text{-}MeQ)_2OH$ under comparable solution conditions.

The spectrophotometric absorption bands for Me_2SO solutions of isolated 8-quinolinol and 2-methyl-8-quinolinol complexes of iron(III) are summarized in Table I. The single intense band at 401 nm for the binuclear complex $[Fe(2\text{-}MeQ)_2]_2O$ clearly distinguishes it from the mononuclear FeQ_3 and $Fe(2\text{-}MeQ)_2OH$ complexes, which exhibit multiband absorption spectra.

Preliminary studies of these iron–8-quinolinol complexes in combination with molecular oxygen and hydrogen peroxide also have been carried out. When an FeQ_2 solution is combined with 0.25 mol of molecular oxygen/mol of FeQ_2, the resulting cyclic voltammogram exhibits a major reduction peak at –0.625 V for an initial negative scan and major oxidation peaks at –0.575 and –0.275 V on the reverse scan. In a similar experiment with 0.5 mol of O_2 added/mol of FeQ_2, the initial negative scan has reduction peaks at both –0.625 and –0.85 V, of approximately equal height, and corresponding oxidation peaks for both on the reverse scan.

When a 2 mM FeQ_2 solution is made 2 mM in H_2O_2 and 4 mM in methanolic TEAOH, the resultant cyclic voltammogram exhibits the –0.625-V reduction peak on an initial negative scan. An initial anodic scan indicates large oxidation peaks at +0.05 and +0.40 V. When consecutive additions are made to a fresh 2 mM FeQ_2 solution such that it formally contains (a) 1 mM H_2O_2, (b) 1 mM H_2O_2 and 2 mM TEAOH, (c) 2 mM H_2O_2 and 2 mM TEAOH, and (d) 2 mM H_2O_2 and 4 mM TEAOH, the effects are complex. The first addition of H_2O_2 oxidizes the FeQ_2 complex, the addition of

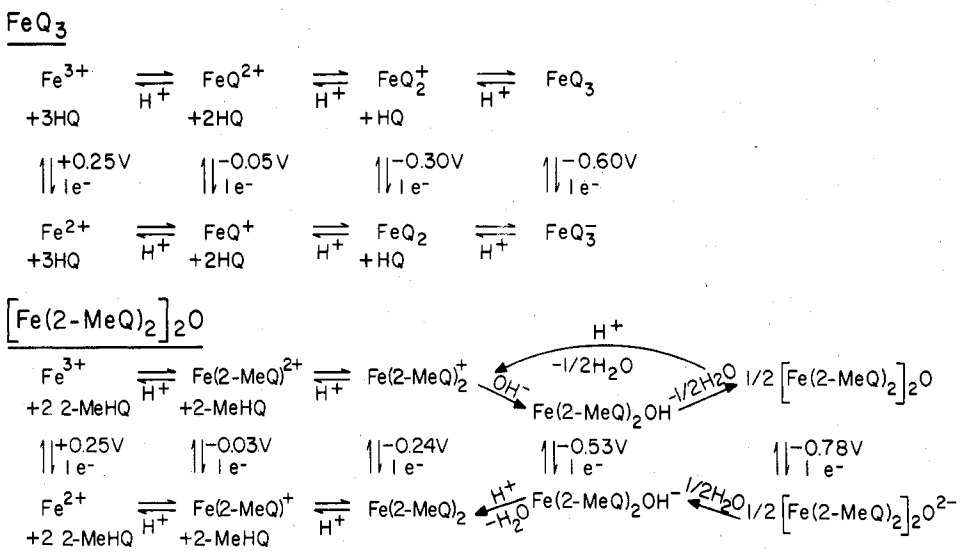

Figure 4. Redox mechanisms for the iron(III) and -(II) complexes formed by 8-quinolinol and by 2-methyl-8-quinolinol in Me_2SO.

OH^- reduces it back to Fe(II), and subsequent additions have analogous sequential effects. The overall result is different from that for the simultaneous addition of H_2O_2 and TEAOH to the FeQ_2 solution.

The addition of 1 mM FeQ_2 to a solution of 6 mM O_2^- causes the height of the oxidation peak for O_2^- (−0.625 V) to be reduced by more than 50%. The cyclic voltammogram also exhibits an oxidation peak at +0.05 V but no iron peaks. Further addition of FeQ_2 (3 mM) causes the O_2^- oxidation peak to disappear. The +0.05-V oxidation peak is only slightly enhanced and the iron couple at −0.60 V appears with relatively small peak heights.

The addition of H_2O_2 and TEAOH to an FeQ_3 solution causes the appearance of a large oxidation peak at +0.05 V but does not affect the iron couple at −0.60 V.

Discussion and Conclusions

The electrochemical data for the iron–8-quinolinol complexes indicate that the number of 8-quinolinol anions (Q^- and 2-MeQ^-) bound to Fe(II) and Fe(III) varies as a function of the amount of acid present. Thus, there are equilibria between at least four species within each oxidation state, and these species also account for four or five reversible redox couples between oxidation states. The probable species and their equilibria are summarized in Figure 4.

In Figure 1a the major couple is due to $Fe^{III}Q_3$, while the minor couple is due to $Fe^{III}Q_2^+$. Addition of a small amount of base shifts the equilibrium completely to FeQ_3. The $Fe^{II}Q_3^-$ that is formed by the reduction of $Fe^{III}Q_3$ appears to be stable within the time frame of cyclic voltammetry. Addition of acid to the initial solution shifts the equilibrium to the more positively charged species, $Fe^{III}Q_2^+$ and $Fe^{III}Q^{2+}$. On the basis of the cyclic voltammogram for $Fe(ClO_4)_2$, the couple at +0.25 V corresponds to uncomplexed iron, $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$.

In a recent study[15] $Fe^{III}Q_3$ was titrated with $HClO_4$. The authors concluded that the acid protonates the nitrogen atom of the ligand to cause it to act as a monodentate ligand. The results of the present study indicate that oxine molecules are not bound to Fe(II) at high acid concentrations.

Similar results are obtained when the iron complexes are formed in Me_2SO by addition of $FeCl_3 \cdot 6H_2O$ and 8-quinolinol. Because the solution becomes acidic from displacement of ligand protons by the iron ions, the cation forms of the iron(III) complexes, FeQ^{2+} and FeQ_2^+, are formed.

The coulometric data for the controlled-potential reduction of FeQ_3 confirm that the −0.60-V couple is a reversible one-electron-per-iron process. By analogy each of the other couples is believed to be a reversible process between an iron(III) and an iron(II) species.

The isolated iron(II) complex, $FeQ_2 \cdot 2H_2O$, upon dissolution forms four species (Figure 2a). The dominant complex is $Fe^{II}Q_2$ (oxidation peak at −0.275 V). The equilibrium

$$2FeQ_2 \rightleftharpoons FeQ^+ + FeQ_3^-$$

undoubtedly exists; the presence of traces of acid or water probably favors the formation of FeQ^+. Apparently, a small amount of free iron, Fe^{2+}, also is formed.

When acid is added to this solution, more ligand anions are protonated and ultimately free Fe^{2+} ion is the dominant species (Figure 2c). Combination of $Fe(ClO_4)_2$ and 8-quinolinol in Me_2SO initially yields Fe^{2+}; the complexation equilibria can be driven toward FeQ_3^- by the addition of base.

The acid–base equilibria for the iron complexes with 8-quinolinol as deduced by cyclic voltammetry are in accord with the conclusions from spectrophotometric data. Spectral monitoring of the titration of $Fe^{III}Q_3$ in Me_2SO with aqueous $HClO_4$ yields data similar to those obtained for $Fe^{III}Q_3$ in a variety of solvents by Tomkinson and Williams.[14] Magnetic susceptibility measurements of $Fe^{III}Q_3$ in Me_2SO yields a value for the magnetic moment, μ_{eff}, of 5.9 μ_B, which indicates the absence of an oxo-bridged species.

When the oxo-bridged binuclear iron(III)–2-methyl-8-quinolinol complex $[Fe(2\text{-}MeQ)_2]_2O$ is dissolved in Me_2SO, the dominant redox couple occurs at −0.78 V and is due to the dimer (Figure 3a). The reduced form of the dimer is stable in the time scale of cyclic voltammetry. The minor couples at −0.24 and −0.53 V are due to $Fe^{III}(2\text{-}MeQ)_2^+$ and $Fe^{III}(2\text{-}MeQ)_2OH$, respectively.

The incremental addition of acid shifts the equilibrium successively to the $Fe(2\text{-}MeQ)_2^+$ (−0.24 V), $Fe(2\text{-}MeQ)^{2+}$ (−0.03 V), and Fe^{3+} (+0.25 V) species (Figure 3b, c) but does not result in significant amounts of $Fe^{III}(2\text{-}MeQ)_2OH$ (−0.53 V). Overall, the redox behavior and the acid–base equilibria of the 2-methyl-8-quinolinol monomeric complexes of iron are similar to those of the 8-quinolinol complexes. This is particularly noticeable in the redox potentials of both series of complexes.

Although the oxo-bridged binuclear iron(III)–2-methyl-8-quinolinol complex is stable in neutral and basic Me_2SO solutions, it does not readily form from the monomeric species. The addition of base to an acidified solution of the bis(2-methyl-8-quinolinol)iron(III) complex initially forms $Fe^{III}(2\text{-}MeQ)_2OH$, which then slowly dimerizes to form $[Fe(2\text{-}MeQ)_2]_2O$. The dimeric reduction product of $[Fe^{III}(2\text{-}$

$MeQ)_2]_2O$ is not stable during a prolonged electrolysis and dissociates to give $Fe^{II}(2\text{-}MeQ)_2OH^-$ as the final product. This behavior is consistent with the absence of known examples of stable oxo-bridged binuclear species of iron(II).

The iron(II) complex, FeQ_2, is oxidized to $Fe^{III}Q_3$ by molecular oxygen. Because only 0.25 mol of O_2 is required/mol of iron(II), oxygen must undergo a four-electron reduction. $Fe^{II}Q_2$ also is oxidized to $Fe^{III}Q_3$ by H_2O_2, but the stoichiometry is not certain. The subsequent addition of OH^- causes the reduction of the iron(III) product species.

The marked decrease in the concentration of O_2^- which occurs upon addition of a small amount of $Fe^{II}Q_2$ implies that the iron complex has a catalytic effect on the decomposition of O_2^-. A similar effect has been observed for the manganese(II)–8-quinolinol complex, MnQ_2.[16] The iron complexes appear to be present only in their tris-chelated forms (–0.60-V couple), which indicates that the solution combination is basic. An oxidation peak at +0.050 V indicates the presence of peroxide ion in the product solution.

From the above results and the fact that peroxide does not have an effect on the electrochemistry of the $Fe^{III}Q_3$ complex, new complexes (such as a peroxo-bridged dimer) apparently are not formed.

Because of the apparent catalytic effect of the $Fe^{II}Q_2$ complex for the decomposition of O_2^- and the redox effects of H_2O_2 and OH^- on the iron–8-quinolinol complexes, additional studies are planned to elucidate the redox mechanisms.

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Registry No. FeQ_3, 14514-43-3; FeQ_2, 15213-83-9; $[Fe(2\text{-}MeQ)_2]O_2$, 51331-59-0; $Fe(2\text{-}MeQ)_2OH$, 61477-50-7.

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Linkage Isomers of Pentaammineruthenium–Hypoxanthine Complexes[1]

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The synthesis of N_3, N_7, and N_9 linkage isomers of a series of pentaammineruthenium(II)– and -(III)–hypoxanthine complexes is reported. Physical measurements of these compounds were made to gain information which might be employed in separating and identifying the metabolites of heavy metals which bind to nucleic acids or their constituent bases. The ruthenium(III) complexes exhibit broad ligand to metal charge-transfer transitions which can be used to assign the isomers. Reduction potentials for these complexes over a broad pH range are presented and are also of use in identifying the complexes. Measurements of the pK_a values of the complexes are reported and were utilized in separating the linkage isomers. A novel N_3 to N_9 isomerization of one of the complexes has been observed to be acid catalyzed.

Introduction

Interactions between transition metals and nucleic acids or their constituent bases have recently been the subject of considerable research. Topics of investigation have tended to center on (1) the role of metals in nucleic acid metabolism,[2-5] (2) the development of new transition metal antitumor agents and the elucidation of their biochemical mechanisms,[6-11] and (3) the selective labeling of nucleic acid bases by heavy metals as an aid in x-ray structure determinations or to facilitate the sequencing of nucleic acids by electron microscopy.[12-15] Other areas of interest have been previously summarized.[16]

Many studies of metal ion interactions with nucleic acids or their constituent bases have been complicated by the availability of numerous metal binding sites. Various spectroscopic (IR,[17] Raman,[18] ESR,[19] NMR,[20-23] CD,[25] UV,[26] visible[16]) and physical methods[27-30] have been employed in efforts to determine the point(s) of metal association. Previous studies with ruthenium–purine complexes indicated that the charge-transfer transitions exhibited by these compounds might be of use in ascertaining the binding site.[31-32] For example, DNA stained with $(NH_3)_5Ru^{III}$ exhibits a charge-transfer absorption band maximum similar to that of $Guo(NH_3)_5Ru^{III}$ indicating preferential binding of the metal to the guanine residues. However, this type of correlation can only be used to determine which bases coordinate the metal ion. Since each base may have several possible binding sites, there remains the additional problem of which sites are involved on a particular base.

The present study was initiated with the goal of synthesizing a series of stable pentaammineruthenium–purine complexes in which the metal binding site could be unequivocally established and to investigate the physical properties of these compounds in order to identify those which might be useful in assigning metal association sites. In particular, we hoped to establish the effect the point of metal attachment has on the ligand to metal charge-transfer (LMCT) bands evident in the electronic spectra of the ruthenium(III)–purine complexes.[16,32] It has been suggested that the energies of these transitions would, to a first approximation, be independent of the coordination site but that the intensities would be site dependent.[31] The relative effect of the metal ion on the acidities of ionizable purine protons has also been used as an indicator of the metal binding site,[14,33] the rule of thumb being that the increase of the acidity of a given proton (relative to the free ligand) is inversely dependent upon the distance between the metal center and the ionizable proton. The