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Coordination Chemistry of Microbial Iron Transport Compounds. 15.[1] Electrochemistry and Magnetic Susceptibility of Iron(III)–Hydroxamate and –Thiohydroxamate Complexes

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The electrochemical reduction of hydrox*a*mate and thiohydrox*a*mate complexes of ferric ion as well as the corresponding hydrox*i*mate complexes has been examined by cyclic voltammetry on hanging mercury drop electrodes. In all cases the ferric complexes have been found to undergo reversible or quasi-reversible reductions under suitable conditions. Deprotonating the hydroxamato complexes stabilizes the Fe(III) vs. the Fe(II) state, while replacing the carbonyl oxygen by sulfur stabilizes the Fe(II) vs. the Fe(III) state. This makes biological iron release by reduction even easier for thiohydroxamate than for hydroxamate siderophores. The magnetic susceptibilities of tris(thiobenzohydrox*a*mato)iron(III) as well as the tris(ethylenediamine)cobalt(III) salt of tris(thiobenzohydrox*i*mato)iron(III) have been measured over the temperature range 5–71 K. Contrary to previous reports, there is no evidence of spin crossover. The ferric thiohydrox*a*mato and thiohydrox*i*mato complexes obey Curie–Weiss ($\chi = C/(T - \Theta)$, $\Theta = -3$ K) and Curie laws, respectively, in this temperature range and contain high-spin iron(III) with magnetic moments of $\sim 5.4\ \mu_B$.

Introduction

The siderophores are low-molecular-weight compounds which are manufactured by microbes to facilitate uptake of ferric iron. The insolubility of ferric hydroxide at physiological pH and the essential nature of iron for microbial growth apparently engendered the production of a wide range of powerful sequestering agents for ferric ion—the siderophores. The general properties of these agents[2,3] and the role of iron in microbial physiology[4] have been the subjects of recent reviews. The functional groups in these siderophores are the hydroxamate and catecholate bidentate chelating groups as found in ferrichromes,[5] ferrioxamines,[6] and enterobactin.[7] Recently cupric and ferric complexes of *N*-methylthioformhydroxamic acid have been isolated from culture broths of *Pseudomonas fluorescens*;[8,9] however, the function of these complexes is not fully understood.

As part of our interest in siderophore electrochemistry, we previously examined the cyclic voltammetric behavior of ferric hydroxamate complexes in comparison with that of ferric enterobactin, a naturally occurring catechol-based siderophore.[10] The only previous report of ferric hydroxamate electrochemistry was that of Keller-Schierlein and co-workers in 1960.[11] Our studies were performed to clarify the iron release mechanism from siderophores, which is thought to occur via reduction of Fe(III) to the weakly bound Fe(II) state. We have subsequently extended these studies to the ferric thiohydroxamate system in order to determine the effect of thio substitution on the electrochemical behavior of the siderophores and to examine the possible role reduction plays in iron release from thiohydroxamate siderophores.

Recently Murray et al.[12] reported the variable-temperature magnetic susceptibility data for some ferric tris(thiobenzohydroxamato) complexes. They found that these complexes display spin-crossing behavior in the temperature range ~100–300 K. In contrast, we report here variable-temperature magnetic susceptibility data for such compounds in the temperature range ~5–71 K, which show Curie or Curie–Weiss behavior with no indication of spin-crossover behavior. The compounds studied include tris(thiobenzohydroxamato)iron(III) and the tris(ethylenediamine)cobalt(III) salt of tris(thiobenzohydroximato)ferrate(III). We also describe the electrochemical behavior of the ferric complexes of *N*-methylbenzohydroxamate, its thio analogue *N*-methylthiobenzohydroxamate, acetohydroxamate, and the N-deprotonated hydroxamates.

Experimental Section

Synthesis of Compounds. Tris(acethydroxamato)iron(III), tris(benzohydroxamato)iron(III), tris(thiobenzohydroxamato)iron(III), tris(*N*-methylbenzohydroxamato)iron(III), and tris(*N*-methylthiobenzohydroxamato)iron(III) were prepared by literature methods.[13–15] Sodium tris(benzohydroximato)ferrate was prepared from sodium hydroxide and the corresponding hydroxamato complex[15] and was recrystallized from water; $[Co(en)_3][Fe(PhC(S){=}N(O))_3]$ was prepared from $[Co(en)_3]I_3$ and potassium tris(thiobenzohydroximato)ferrate as reported eariler and gave satisfactory elemental analyses.[16]

Physical Measurements. Electrochemical measurements were performed using the three-electrode configuration. Triangular waves were generated by the Princeton Applied Research (PAR) 175

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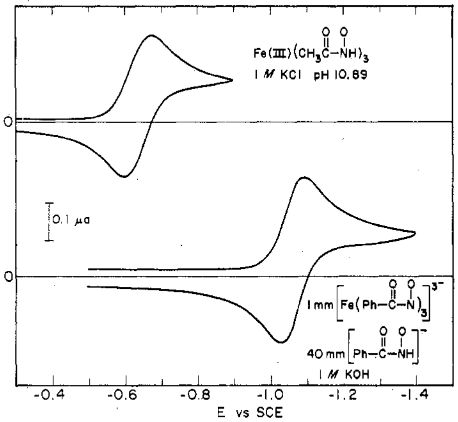

Figure 1. Cyclic voltammograms of 10^{-3} M solutions of tris(acethydroxamato)iron(III) (upper) and sodium tris(benzohydroximato)ferrate(III) (lower), in water.

Table I. pH Dependence of the Tris(acethydroxamato)iron(III) Reduction Potential by Cyclic Voltammetry[a]

pH	E, mV vs. SCE	ΔE,[b] mV	pH	E, mV vs. SCE	ΔE,[b] mV
12.29	−802	95	9.20	−525	70
11.90	−755	90	8.70	−500	70
11.32	−696	78	8.17	−466	69
11.00	−660	75	7.50	−434	74
10.00	−588	71	7.00	−388	95
9.65	−554	68			

[a] [Fe(III)] = 1 mM; [acethydroxamate] = 20 mM. The scan rate was 100 mV/s on a hanging mercury drop in 1 M KCl, 0.05 M each in potassium phosphate and sodium borate buffer. [b] Potential separation between cathodic and anodic peak currents.

programmer in conjunction with the PAR 173 potentiostat: a hanging mercury drop working electrode, a platinum wire auxiliary, and a saturated calomel electrode (SCE) reference electrode were employed. Unless otherwise noted, all potentials are reported vs. SCE and are uncorrected for liquid junction potentials. The supporting electrolyte for acethydroxamate solutions was 1 M KCl, which was 0.05 M each in sodium borate and potassium phosphate; for benzohydroxamate solutions, 1 M KOH was used as supporting electrolyte. In both cases a ligand:metal ratio of 40:1 was employed. Cyclic voltammograms in CH_3CN used 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

Magnetic susceptibility measurements were obtained with a PAR Model 155 vibrating-sample magnetometer used with a homogeneous magnetic field produced by a Varian Associates 12-in. electromagnet capable of a maximum field strength of 12.5 kG. A liquid helium Dewar produced sample temperatures in the range 5–80 K which were measured by a calibrated GaAs diode approximately 1 cm above the sample (~60 mg) in a sample holder machined from Kel-F rod. The magnetometer was calibrated with $HgCo(NCS)_4$,[17] and the resulting susceptibilities were corrected for underlying diamagnetism.[18]

Results and Discussion

Electrochemistry. The cyclic voltammogram (CV) of tris(acethydroxamato)iron(III) is shown in Figure 1, top, in which a single quasi-reversible, pH-dependent, one-electron wave is observed, with a peak separation of 70 mV (at a 100 mV/s scan rate). At pH 7 the observed formal potential E_f is −388 mV vs. SCE, decreasing by 60 mV/pH unit to pH 11.5. This pH dependence of the ferric tris(acethydroxamate) reduction potential in the region pH 7–11 is consistent with protonation of the electrogenerated ferrous complex by one proton. Above pH 11, ionization of the N protons of the ligand becomes significant, leading to much greater potential change with pH (Table I). Above pH 12 the CVs become increasingly ill-behaved, precluding quantitative assessment of the relevant dissociation constants. The CV of the N-deprotonated complex, sodium tris(benzohydroximato)ferrate(III), similarly exhibits a reversible one-electron wave (peak-to-peak separation of 62 mV), but with $E_f = -1.055$ V (Figure 1, bottom). Preparative reduction on a mercury pool of the ferric solutions, which are deep orange, reversibly yielded solutions of the ferrous complexes, which are colorless. An iron wire immersed in a ferrous acetohydroxamate solution at pH 10.89 (with a ligand to metal ratio of 20:1) exhibited a potential of −664 mV vs. NHE after correction to unit concentrations in ferrous ion and acetohydroxamate monoanion (using the known acid association constants).[19] This potential is consistent with that calculated from the $E°$ of the Fe(II)/Fe(0) couple and the known ferrous acethydroxamate formation constant (vide infra).[19] The large overpotential for dihydrogen evolution precludes interference from this couple.

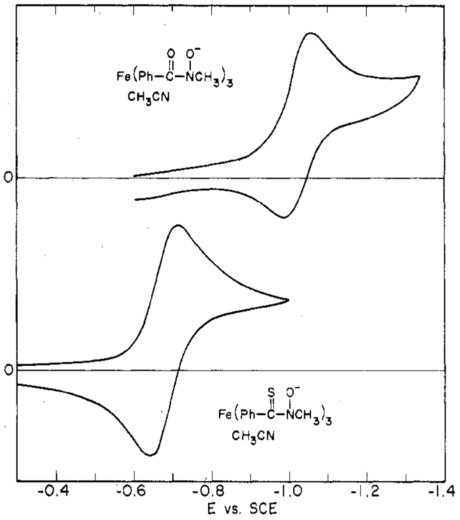

Figure 2. Cyclic voltammograms of 10^{-3} M solutions of tris(*N*-methylbenzohydroxamato)iron(III) (upper) and tris(*N*-methylthiobenzohydroxamato)iron(III) (lower), in acetonitrile.

Due to insolubility in water, the *N*-methylbenzohydroxamato and *N*-methylthiobenzohydroxamato ferric complexes were examined in acetonitrile. The CV of tris(*N*-methylbenzohydroxamato)iron(III) is shown in Figure 2, top, where a quasi-reversible wave ($E_a - E_c = 70$ mV) is found with $E_f = -1.025$ V; in Figure 2, bottom, the CV of the analogous thio compound tris(*N*-methylthiobenzohydroxamato)iron(III) is shown, for which a quasi-reversible one-electron wave is observed at −675 mV, with a peak-to-peak separation of 70 mV. Preparative reduction to the ferrous state again eliminated the deep color characteristic of the ferric complexes.

For reversible *n*-electron couples, peak separations of 59/*n* mV are predicted at 25 °C.[20] For such couples, the average of the peak potentials can be identified with the reduction potential to within an excellent approximation. By this criterion, several of the observed CVs must be considered quasi-reversible; nevertheless, formal potentials were estimated as the average of the peak potentials. Ionization of the N protons of the ferric complex considerably lowers the reduction potential of the N-deprotonated tris(benzohydroximato)ferrate(III) complex with respect to that of the tris(acethydroxamato)iron(III) complex.

The reduction potential of the ferric to the ferrous complex is related to the stability constants K_{Ox} and K_{Red} by the relation

$$E_f^{complex} - E_f^{aquo} = -(RT/nF)\log(K_{Ox}/K_{Red}) \qquad (1)$$

where K_{Ox} and K_{Red} are the stability constants of the oxidized and reduced species, respectively, and $E_f^{complex}$ and E_f^{aquo} are the reduction potentials of the complex and the aquo ion, respectively.[21] Presumably the greater part of the K_{Ox}–K_{Red} difference observed is attributed to the greater electron-donating ability of an N-deprotonated hydroximate group, which

Table II. Molar Magnetic Susceptibilities of Thiobenzohydroxamato and Thiobenzohydroximato Ferric Complexes[a]

Fe(thiobenzohydroxamate)$_3$H$_2$O		[Co(en)$_3$] [Fe(thiobenzohydroximate)$_3$]	
T, K	χ_m', cgs	T, K	χ_m', cgs
5.0	0.505	5.7	0.660
8.0	0.347	8.3	0.446
20.2	0.155	17.3	0.204
31.4	0.104	31.0	0.114
42.0	0.0798	44.5	0.0816
50.1	0.0683	63.3	0.0576
59.3	0.0580		
73.5	0.0471		

[a] A magnetic field of 2.5 kG was used. No field dependence of χ_m' was observed in the range 2.5-KG.

would lead to stronger complexation of a powerful Lewis acid such as Fe(III).

From the standard potential of an iron wire immersed in a ferrous acetohydroxamate solution (and the reduction potential from the CV), the stability constant of the ferric complex can be estimated. By combining the half-cells ($\mathcal{E}°$ values)

$$\mathrm{Fe}^0 + 3\mathrm{L}^- = \mathrm{Fe}^{\mathrm{II}}\mathrm{L}_3 + 2\mathrm{e}^- \qquad (2a)$$

$$\mathrm{Fe}^{\mathrm{III}} + \mathrm{e}^- = \mathrm{Fe}^{\mathrm{II}} \qquad (2b)$$

$$\mathrm{Fe}^{\mathrm{III}}\mathrm{L}_3 + \mathrm{e}^- = \mathrm{Fe}^{\mathrm{II}}\mathrm{L}_3 \qquad (2c)$$

$$\mathrm{Fe}^0 = \mathrm{Fe}^{\mathrm{II}} + 2\mathrm{e}^- \qquad (2d)$$

one obtains the potential for the cell

$$\mathrm{Fe}^{\mathrm{III}} + 3\mathrm{L}^- = \mathrm{Fe}^{\mathrm{III}}\mathrm{L}_3 \qquad (3)$$

which defines the stability constant via

$$\Delta G = -RT \ln K = -nF\mathcal{E}° \qquad (4)$$

Equations 2b and 2d represent the standard half-cell potentials of the Fe(III)/Fe(II) and Fe(II)/Fe(0) couples, respectively, and are pH independent.[22] The half-cell potential in eq 2c is the reduction potential determined in the CV experiment (when 244 mV is added to convert to $\mathcal{E}°$ values vs. a normal hydrogen electrode). Thus with the half-cell potential of eq 2a, the stability constant of the tris(acethydroxamato)iron(III) complex can be calculated. From our data a stability constant log β_3 of 28.2 is obtained, compared with the literature value of 28.3 determined by pH titration.[19]

Although the precision of this approach is probably not as great as that available via other techniques (the above excellent agreement is probably fortuitous), this method is of utility for the rapid determination of stability constants with moderate precision. From the reduction potential determined by CV and the K_{Ox} value above, the stability constant log β_3 of the ferrous tris complex is estimated to be 8.6. This value corresponds to the equilibrium constant for the reaction $\mathrm{Fe}^{2+} + 3\mathrm{L}^- = \mathrm{FeL}_3^-$ and is consistent with (a) the value of log β_2 (8.5) for the ferrous bis complex[19] and (b) the fact that the ferrous tris complex only forms in significant amount at high free-hydroxamate concentrations ($K_3 \approx 1.3$ for the ferrous tris complex).

Comparison of the CV data for the tris(N-methylbenzohydroxamato)iron(III) and its thio analogue tris(N-methylthiobenzohydroxamato)iron(III) reveals that substitution of sulfur for carbonyl oxygen raises the reduction potential by 400 mV, consistent with the greater basicity of oxygen relative to sulfur and probably due in some part to the relatively greater affinity of a soft acid such as Fe(II) for a soft base ligand such as sulfur—in contrast to a hard base such as oxygen.

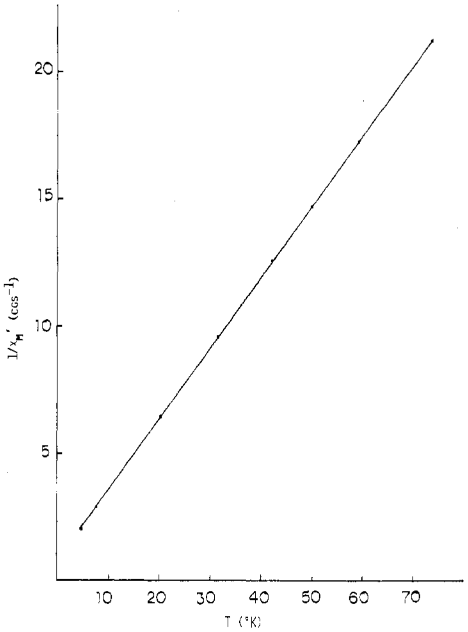

Figure 3. Inverse molar susceptibility vs. temperature for tris(thiobenzohydroxamato)iron(III)–water.

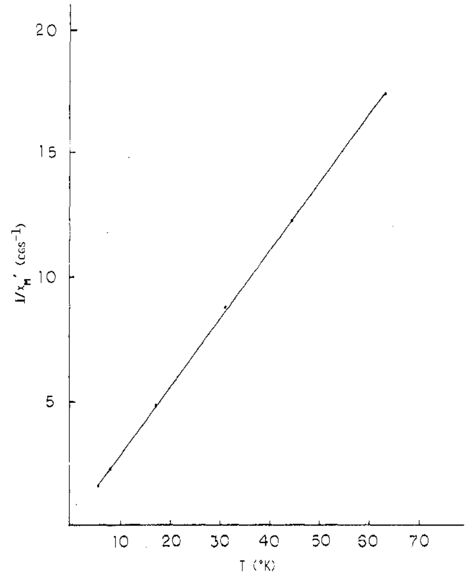

Figure 4. Inverse molar susceptibility vs. temperature for tris(ethylenediamine)cobalt(III) tris(thiobenzohydroximato)ferrate(III).

Magnetic Properties. The magnetic behavior of tris(thiobenzohydroxamato)iron(III) and the tris(ethylenediamine)cobalt(III) salt of tris(thiobenzohydroximato)ferrate(III) is given in Table II. The inverse molar susceptibilities of the two compounds as functions of temperature are shown in Figures 3 and 4, respectively. The tris(ethylenediamine)cobalt(III) salt of tris(thiobenzohydroximato)ferrate(III) displays Curie behavior within experimental error in the range 5–70 K, while tris(thiobenzohydroxamato)iron(III) displays Curie–Weiss [$\chi = C/(T - \Theta)$] behavior in the same temperature range with a Weiss constant $\Theta = -3$ K. We see no sign of the spin state change recently reported by Murray et al.[12] The magnetic moments of the two compounds were calculated from the slopes of the inverse molar susceptibility vs. temperature plots (Figures 3 and 4) to be 5.4 μ_{B}—only slightly lower than the room-temperature value of 5.5–5.6 μ_{B}.[14,23]

Deprotonation of the N hydrogens in tris(thiohydroxamato)iron(III) complexes should increase the ligand field, and consequently it is expected that the deprotonated form, tris(thiohydroximato)ferrate(III), would display spin-crossover behavior, if it occurred, at a relatively higher temperature than the corresponding neutral species. We have found such behavior for the tris(hydroxamato)cobalt(III) and tris(hydroximato)cobaltate(III) salts;[24] however, the μ_{eff} values of *both* the neutral and the trianionic forms of tris(thiobenzohydroxamato)iron(III) remain constant down to ~5 K.

In summary, results of this study show that (1) both the hydroxamate and the thiohydroxamate complexes of ferric ion, as well as the corresponding deprotonated hydrox*i*mate and thiohydrox*i*mate complexes, show reversible or quasi-reversible electrochemical behavior under suitable conditions, (2) deprotonation of the hydroxamate complex stabilizes the Fe(III) vs. the Fe(II) state, (3) the replacement of the carbonyl oxygen by sulfur stabilizes the Fe(II) state relative to the Fe(III) state (which makes biological iron release by reduction even easier for thiohydroxamate than for hydroxamate siderophores), and (4) the thiohydroxamate and thiohydrox*i*mate complexes of Fe(III) display high-spin magnetic moments down to 5 K.

Acknowledgment. This research is supported by the NIH. We thank Dr. Norman Edelstein for experimental assistance with the magnetic susceptibility measurements and the U.S. AID for a fellowship to K.A.-D.

Registry No. Tris(acethydroxamato)iron(III), 14587-53-2; Fe(thiobenzohydroxamato)$_3$, 31375-72-1; $[Co(en)_3][Fe(\text{thiobenzohydroximato})_3]$, 68024-55-5; sodium tris(benzohydroximato)ferrate(III), 23683-81-0; tris(*N*-methylbenzohydroxamato)iron(III), 68024-56-6; tris(*N*-methylthiobenzohydroxamato)iron(III), 68069-75-0.

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Electronic Structure of Mixed-Valence Ions: ESCA and MO Calculations on $[\eta^5\text{-}C_5H_5Fe(CO)]_2\text{-}\mu\text{-}Ph_2P(CH_2)_nPPh_2^{m+}$ (n = 1, 2; m = 0, 1)

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The ESCA spectra of the title compounds are presented and compared to the results of parameter-free Fenske–Hall molecular orbital calculations. The calculations are used both to calculate ESCA satellite intensities via the sudden approximation and to describe the valence electronic structure. The results of the sudden approximation, which predict no satellites of intensity greater than 10% of the main peak, are in good agreement with the ESCA spectra, where no satellites are discernible. However, using the same theoretical results, we find that the Hush model predicts a single intense satellite, which is in disagreement with the full MO sudden approximation and the ESCA spectra. The description of the valence electronic structure is in good agreement with previous results for the cyclic voltammetry, for the carbonyl stretching frequencies, and for the crystal structures. However, they suggest that oxidation of the neutral species involves removal of an Fe–Fe nonbonding electron rather than removal of an electron from the Fe–Fe σ bond.

Introduction

The dimers $[CpFe(CO)]_2Ph_2P(CH_2)_nPPh_2^{m+}$ (n = 1, 2; m = 0, 1) (Cp = $\eta^5\text{-}C_5H_5$, Ph = C_6H_5) have been synthesized and characterized by Haines and du Preez.[1] These compounds, which have a bridging diphosphine group and two bridging carbonyls, possess approximate C_{2v} symmetry, as shown in Figure 1. The neutral species are thought to have a single Fe–Fe bond, while the oxidized species are thought to have a one-electron Fe–Fe bond.[1,2] Thus, these latter species would be delocalized mixed-valence complexes (class IIIa in the terminology of Robin and Day[3]).

Although one might expect a delocalized mixed-valence metal dimer to show a single metal ESCA peak and a localized dimer (class II) to show two metal ESCA peaks, Hush has suggested that a delocalized dimer could have an ESCA spectrum like that of a localized dimer.[4] According to Hush, the ionization of a core electron on the metal will cause the formally delocalized valence electron to localize on one of the two metal centers (now differing by a core electron). The ratio of the intensity of the peak at low binding energy to that at high binding energy is proportional to the electronic coupling integral (J in Hush's notation). Thus, for strongly coupled metal centers one might expect a main ESCA peak and a weaker satellite, while for weakly coupled metals (but still delocalized) one would expect to see two nearly equal ESCA peaks.

In this work we have examined the ESCA spectra of the title compounds to test Hush's model for rather strongly

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