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Mononuclear Cyano- and Hydroxo-Complexes of Iron(III)

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A detailed investigation of the iron(III)–cyanide and iron(III)–hydroxide systems has been made in $NaClO_4$ media at 25 °C, using combined UV–vis spectrophotometric and pH-potentiometric titrations. For the $Fe(III)/OH^-$ system, use of low total Fe(III) concentrations ($\leq 10\ \mu M$) and a wide pH range ($0 \leq pH \leq 12.7$) enabled detection of six mononuclear complexes, corresponding to the following equilibria: $Fe^{3+}(aq) + rH_2O \Leftrightarrow Fe(OH)_r^{(3-r)+}(aq) + rH^+(aq)$, where $r = 1$–6 with stability constants (log $^*\beta_{1r}$) of –2.66, –7.0, –12.5, –20.7, –30.8, and –43.4, respectively, at $I = 1$ M ($NaClO_4$). It was also found to be possible to measure, for the first time, stability constants for most of the following equilibria: $Fe^{3+}(aq) + qCN^-(aq) \Leftrightarrow Fe(CN)_q^{(3-q)+}(aq)$, despite a plethora of complicating factors. Values of log $\beta_{1q} = 8.5$, 15.8, 23.1, and 38.8 were obtained at $I = 1.0$ M ($NaClO_4$) for $q = 1$–3 and 6, respectively. No reliable evidence could be obtained for the intermediate ($q = 4$ or 5) complexes. Similar results were obtained for both systems at $I = 0.5$ M($NaClO_4$). Spectra for the individual mononuclear complexes detected for Fe(III) with OH^- and CN^- are reported. Attempted measurements on the $Fe(II)/CN^-$ system were unsuccessful, but values of log $\beta_{16}(Fe(CN)_6^{4-}) = 31.8$ and log $\beta_{15}(Fe(CN)_5^{3-}) \approx 24$ were estimated from well established electrode potential and other data.

Introduction

Iron(III)–cyanide complexes are of considerable practical importance. For example, $Fe(CN)_6^{3-}$ has been identified as a source of cyanide mobility in the environment[1,2] because of its relative lability and its sensitivity toward photolysis.[1,3] On the other hand, sparingly soluble "Prussian blue" ($Fe(II)/Fe(III)/CN^-$) compounds are thought to be a major pathway for the immobilization and detoxification of anthropogenic cyanide.[1,2]

Although Fe(III) is a "hard" metal ion and cyanide a "soft" ligand,[4] the $Fe(III)/CN^-$ complexes are extremely strong,[3,5] with an overall formation constant $\beta_{16}(Fe(CN)_6^{3-}) \approx 10^{44}$. However, no quantitative thermodynamic data are available for any other $Fe(III)/CN^-$ species in aqueous solution,[3,5] and it has been implied[5,6] that the lower order ($q < 6$) mononuclear complexes may not exist appreciably, because of the predominance of $Fe(CN)_6^{3-}$. Yet, in addition to two aqueous polynuclear species ($Fe_2(CN)_{10}^{4-}$ and $Fe_2(CN)_6^{\circ}$),[3] the complexes $Fe(CN)_2^+$, $Fe(CN)_3^0$, and $Fe(CN)_4^-$ have been reported in dimethyl sulfoxide solutions.[7]

Particular difficulties exist in detecting and quantifying the lower order $Fe(CN)_q^{(3-q)+}$ complexes in aqueous solution. At low pH values, H^+ will compete with Fe(III) for CN^- (pK_a(HCN) ≈ 9.2),[5,8] and there is a risk of cyanide loss by volatilization (Henry's law constant for HCN ≈ 0.02 MPa kg mol^{-1} at 25 °C).[9] At high pH values, OH^- will compete strongly[10] with CN^- for Fe(III) and/or form mixed $Fe(CN)_q(OH)_r^{(3-q-r)+}$ complexes. In addition, the total concentrations of Fe(III) and CN^- must be kept low to avoid precipitation of FeOOH(s),[10] cyanide polymerization,[11] complications associated with "polynuclear" complexes,[3] and "Prussian blue" formation (by reduction of Fe^{3+}, and possibly $Fe(CN)_6^{3-}$, by CN^-).[3] These features severely curtail the accessible experimental conditions for investigating the $Fe(III)/CN^-$ system. For example, a potentially attractive set of conditions

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for measuring Fe(III)/CN^- complexation such as mixing 1 M CN^- with $[Fe(III)]_T \geq 0.01$ M[12] in 1 M $HClO_4$ results in Prussian blue precipitation.[3,13]

Because HCN is such a weak acid,[8] the Fe(III)/OH^- complexes are so strong,[10] and the solubility of "ferric hydroxide" (FeOOH)[14] so low,[10] it is essential to quantify the Fe(III)/OH^- system under comparable conditions before studying the Fe(III)/CN^- system. Of course, Fe(III)/OH^- complexes are important in their own right: they dominate Fe(III) chemistry under most biological, environmental, and physiological conditions.[15,16] Such species are, for example, the major reactive heavy metal component of soils[17] and are significant in the binding (adsorption) and transport of many other species in the environment.[17] The behavior of Fe(III) at high pH is also of special interest since Fe(III) is a significant contaminant in strongly alkaline Bayer process[18] "liquors", in NH_3 leachates used in Cu(II), Ni(II), and Co(II) extraction,[19] and in the CN^- solutions employed in gold leaching.[20]

Not surprisingly, therefore, the Fe(III)/OH^- system has been extensively investigated. The available quantitative data have been reviewed frequently,[10,21−24] most recently by Byrne et al.[25] At reasonably low $[Fe(III)]_T$ and pH, the species $FeOH^{2+}$, $Fe(OH)_2^+$, and $Fe_2(OH)_2^{4+}$ have been reasonably well characterized by potentiometry[10,26] and UV−vis spectrophotometry.[27,28] However, at higher $[Fe(III)]_T$ in neutral or mildly alkaline solutions, the species formed are not well understood,[10,21] due to their number and complex stoichiometries, their slow kinetics of interconversion, and the sparing solubility of FeOOH(s).[21,25,29] At high pH values, although there is probably considerable simplification of Fe(III) speciation (as occurs for Al(III)[30]), the complexes formed are poorly characterized.[10] The only formation constants currently available, for $Fe(OH)_3^0$ and $Fe(OH)_4^-$, have been derived from solubility measurements.[10,25] No evidence appears to exist for any higher order mononuclear complexes in solution, although $Fe(OH)_6^{3-}$ is reported to exist in the solid state.[31,32]

As noted, the Fe(III)/OH^- and Fe(III)/CN^- systems were investigated under the same conditions, employing a wide pH range. To minimize precipitation and polymerization, $[Fe(III)]_T$ was kept at ≤ 10 μM. However, although polynuclear species are avoided at these low concentrations, the solutions remain supersaturated with respect to FeOOH(s).[10] Fortunately, the precipitation rate of FeOOH(s) is slow, so, providing experiments can be done quickly and homogeneous equilibrium is established rapidly, valid thermodynamic data for the homogeneous equilibria can be obtained.[33]

The technique chosen for the present study was UV−vis spectrophotometry, mostly in a long path length cell, combined with simultaneous pH measurements, as used previously to study the hydrolysis of Pb(II).[34] As Fe^{3+}(aq), Fe(III)/OH^- species, and $Fe(CN)_6^{3-}$ all show reasonably strong charge-transfer bands,[3,10] it is reasonable to expect that other Fe(III)/CN^- species would also.[7]

Experimental Section

All solutions were made from high purity water (Millipore MilliQ system) and deoxygenated and decarbonated by boiling and cooling under high purity N_2.

Fe(III)/OH^- System. Iron(III) stock solutions (~0.1 M) were prepared from $Fe(ClO_4)_3$ (BDH, U.K., LR, 98%) and analyzed (±0.2%) as rapidly as possible by titration against ETDA (BDH, U.K., concentrated volumetric standard) using variamine blue indicator.[35] Diluted stock solutions ($[Fe(III)]_T \sim 0.01$ M in 1 M $HClO_4$) were then prepared immediately from such solutions. Working solutions of $[Fe(III)]_T \approx 2-10$ μM in 1 M $HClO_4$ were prepared as required. Titrant solutions contained 1 M NaOH (for measurements at $I \approx 0.5$ M) or 1 M NaOH and 1 M $NaClO_4$ (for measurements at $I \approx 1$ M) to allow for the decrease in I due to neutralization, where I ($=1/2\sum[i]z_i^2$) is the stoicheometric ionic strength maintained by addition of appropriate amounts of $NaClO_4$ (BDH, AR, purity ≥ 99.0%). Titrations were performed in combined potentiometric−spectrophotometric titration cells[34] with optical path lengths (cm) of 10.76 ± 0.05, 0.74 ± 0.01, and 0.0909 ± 0.0005. The titration vessel was sealed with a snug-fitting PTFE lid machined with five standard taper joints to accommodate the glass and reference electrodes, N_2 inlet, and a calibrated (NIST-traceable) mercury thermometer.

Electronic spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer with an integration time of 1 s.

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Table 1. Present Stability Constants (log $^*\beta_{1r}$ Values)[40] of the $Fe(OH)_r^{(3-r)+}$(aq) Complexes at 25 °C[a]

I/M	log $^*\beta_{11}$	log $^*\beta_{12}$	log $^*\beta_{13}$	log $^*\beta_{14}$	log $^*\beta_{15}$	log $^*\beta_{16}$
0.5	-2.9 ± 0.1	-6.8 ± 0.5	-13.3 ± 1.2	-21.9 ± 1.8		
	(10.8)	(20.5)	(28)	(33)		
1.0	-2.66 ± 0.03	-7.0 ± 0.3	-12.5 ± 0.9	-20.6 ± 0.7	-30.8 ± 0.8	-43.4 ± 0.7
	(11.11)	(20.6)	(28.9)	(34.5)	(38.0)	(39.2)

[a] Numbers in parentheses are log β_{1r}values.[41] Uncertainties are overall standard deviations (σ).

Solutions were stirred with a PTFE-coated magnetic bar driven by a magnetic rotor (Metrohm, type E402) mounted at 90° to the cell.[34] The cell temperature was maintained at 25.0 ± 0.05 °C by a refrigerated circulator-thermostat (Grant Instruments, U.K., model SB3/74GB).

Hydrogen ion concentrations were measured in situ using a glass electrode (Metrohm, model 6.0101.000) and a Ag/AgCl reference electrode[36] in conjunction with a salt bridge containing 1 or 5 M $NaClO_4$. Potentials were measured to ±0.1 mV with a high impedance digital voltmeter of in-house construction. Glass electrodes (GEs) were calibrated ex situ in terms of $[H^+]$ using 0.01000 M H^+ in $NaClO_4$ at the appropriate I before and after each titration. Electrodes were checked for Nernstian behavior by occasional strong acid–strong base titrations. All titrations were performed under N_2. Titrant was added from a piston buret (Metrohm Dosimat, model 665, calibrated accuracy ±0.1%), and potentials were measured after 1–5 min of equilibration.

Spectra were recorded between 190 and 820 nm, with and without Fe(III) at pH values as similar as possible to minimize errors. Duplicate experiments were performed at each I and $[Fe(III)]_T$. Concentrations were such that >90% of the absorbance (A) readings fell in the range $0.2 < A < 1$. Experiments were performed immediately after solution preparation to minimize precipitation of FeOOH(s). Blank (background) spectra were obtained by titrating $HClO_4$ with NaOH at the desired I, as described previously.[34] Detailed spectral analysis was performed over the region 230–500 nm using the SPECFIT program.[37,38] The wavelength range was chosen such that the background absorbance did not exceed 0.1 over the pH range being considered.

Fe(III)/CN$^-$ System. Blank spectra were obtained by titrating 1 M $HClO_4$ with 1 M NaCN (for $I \approx 0.5$ M) and 1 M NaCN + 1 M $NaClO_4$ (for $I \approx 1$ M). Deaeration with N_2 was stopped at titration commencement to minimize HCN volatilization. The GE was calibrated ex situ, but at pH < 2, it was assumed $[H^+] = [H^+]_T$. Spectra (200–500 nm) were analyzed by SPECFIT assuming $pK_a(HCN) = 9.01$ and 9.02 at $I = 0.5$ and 1.0 M ($NaClO_4$), respectively.[8]

Results and Discussion

Iron(III) Hydrolysis. Significant spectral changes occurred over the pH range examined (Figure S1). However, at $[Fe(III)]_T = 10\ \mu M$ and a fixed pH, absorbances decreased with time: a worst-case situation is shown in Figure S2. The rate of change in A (Figure S3) depended on pH and $[Fe(III)]_T$ and is consistent with the precipitation of FeOOH(s).[10]

These changes were sufficiently small and slow such that reliable spectra could be obtained over short intervals. In a 10.76 cm cell, for example (Figure S2), for $t \leq 10$ min, ΔA was ≤ 0.01 (corresponding to $\Delta A \leq 0.001$ in a 1 cm cell). Hence, at $4.5 \leq pH \leq 11$, all titrations were discontinued after 10 min, with many such titrations being performed over successive narrow pH ranges. Following ~30 min of thermal and electrochemical equilibration prior to titration commencement, the GE was given ~60 s to stabilize, following each addition of OH^-, before the spectrum and the pH were recorded simultaneously. Note that, after initial equilibration, the GE responds very rapidly (tens of seconds) to small changes in pH. In more acidic or basic solutions, titrations could be performed conventionally. To further check for possible precipitation-related complications,[29] a few solutions were acidified to their initial pH following titration with OH^-. The original spectra were recovered within the limits of experimental error ($\Delta A < 0.01$ in a 10.76 cm cell). Additional uncertainty may exist due to adsorption of Fe(III) onto the glassware. Although literature data suggest adsorption ($\leq 20\%$ at 3 μM Fe(III))[39] might affect the results, the independence of the constants with respect to $[Fe(III)]_T$ indicates it is not significant for the present experiments (Table S1).

Background-subtracted spectra at $230 \leq \lambda/\text{nm} \leq 500$ (Figure S1) show isosbestic points and changes consistent with seven species at $0 \leq pH \leq 12.7$. Comparisons with literature spectra[27] indicate Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^+$ were detectable. No $Fe_2(OH)_2^{4+}$ was evident since its characteristic peak at 335 nm[27] was absent and the isosbestic point between Fe^{3+} and $FeOH^{2+}$ ($\lambda_{max} = 264$ nm) was well defined.[28] SPECFIT optimization of the whole data set converged using a model with only the mononuclear species $Fe(OH)_r^{(3-r)+}$ ($0 \leq r \leq 6$) present. The stability constants[40,41] so obtained are summarized in Table 1. Excellent correlation between the observed and predicted spectra was obtained (Figure S4). The constants and the quality of the fits (Table S1) were independent of $[Fe(III)]_T$ over the range 2–20 μM and at $0 \leq pH \leq 12.7$, indicating the absence of any significant polynuclear species within the truncated time frame of the experiments.

The major value of this study of the Fe(III)/OH^- system lies in its characterization of the higher order ($r \geq 3$) mononuclear complexes. More precise studies (employing higher concentrations and more conventional mensuration) already exist for the lower order complexes,[10,25] although the present values are in good agreement with them. Specifically, the present log $^*\beta_{11}$ values (Table 1) lie close

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(41) $\beta_{1q} = [FeL_q^{(3-q)+}]/[L^-]^q\ [Fe^{3+}]$ corresponding to the following equilibrium: $Fe^{3+} + qL^- \Leftrightarrow FeL_q^{(3-q)+}$, where L = OH^- or CN^-.

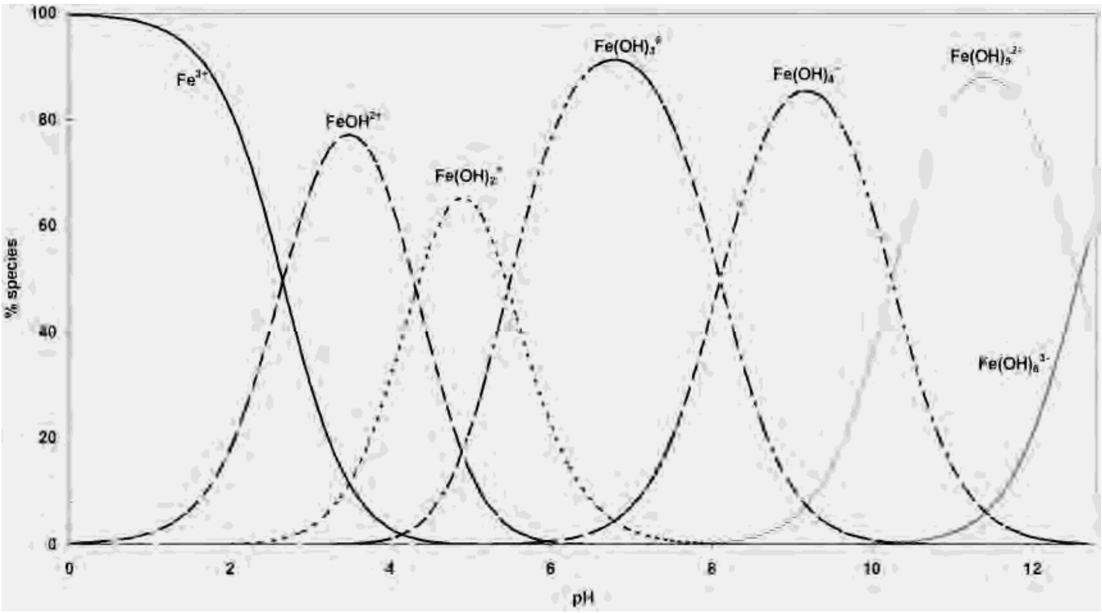

Figure 1. Speciation diagram of the Fe(III)/OH^- system at $[Fe(III)]_T \leq 10\ \mu M$, $I = 1$ M ($NaClO_4$), 25 °C, using the stability constants from Table 1. These solutions are supersaturated with respect to FeOOH(s) at higher pH values.

to or within the spread (-2.62 to -2.74 at $I \approx 0.7$ M($NaClO_4$))[25] of apparently reliable results reported under similar conditions. As noted by Byrne et al.,[25] the formation of $Fe(OH)_2^+$ is much less well characterized. Earlier values[26,42] appear to be unreliable, and log $*\beta_{12} > -7$ at $I \approx 1$ M is probably more realistic.[25] This value is in good agreement with the present estimate (Table 1), despite UV−vis spectrophotometry being somewhat insensitive[27] to $Fe(OH)_2^+$.

As for many metal ions, the Fe^{3+}/OH^- system has been little studied at high pH.[10,43] The generally accepted estimates[10] of log $*\beta_{13} = -12.6$ and log $*\beta_{14} = -21.95$ at $I = 1.0$ M and 25 °C were derived from a critical analysis of the then available solubility data. Subsequently, Byrne et al.[25] have suggested log $*\beta_{13} \leq -13.6$ might be more appropriate. Liu and Millero[44] report log $*\beta_{13} \approx -15$ and log $*\beta_{14} \approx -23$ at $I = 0.7$ M and 25 °C, although careful examination (e.g., Figure 3[44]) suggests these values do not accurately reproduce their data. The present results for log $*\beta_{13}$ and log $*\beta_{14}$ (Table 1) lie close to or within this spread of values.

More importantly, as noted by the authors themselves,[44] the solubility (log$[Fe(III)]_T$) versus pH curves of Liu and Millero have a slope that is significantly >1.0 at high pH, indicative of the presence of complexes of higher order than $Fe(OH)_4^-$. Using the appropriate mass balance equations, assuming only mononuclear complexes to be present and ignoring activity coefficients, it is readily shown that $[Fe(III)]_T = K_{sp}(\sum\beta_{1r}[OH^-]^r)$.[45] Taking goethite as the solid phase ($pK_{sp} \approx 41.5$)[21] and the present β_{1r} values (Table 1) gives log$[Fe(III)]_T \approx -7.4$ at $[OH^-] = 0.01$ M, which is in reasonable agreement with the solubility reported by Liu and Millero[44] at this pH, the highest measured. As already noted, the existence of $Fe(OH)_6^{3-}$ in solution is consistent with reported solid state compounds containing this ion.[31,32] Even so, it is clear that the present values of $*\beta_{15}$ and $*\beta_{16}$ (Table 1), which appear to be the first quantitative estimates of these constants, require further studies at high pH employing solubility and other techniques to properly validate them.

The variation of the stepwise formation constants ($K_{1r} = \beta_{1r}/\beta_{1r-1}$) with the number of OH^- ligands exhibits a smooth decrease, indicative of the stepwise replacement of bound water by OH^- without major changes of coordination geometry.[24] A typical species distribution at low $[Fe(III)]_T$ derived from the present stability constants (Table 1) is given in Figure 1. At higher pH values, it differs markedly from that given by Baes and Mesmer,[10] as would be expected from the detection of the two extra higher order complexes in this work.

The SPECFIT-derived spectra for the individual $Fe(OH)_r^{(3-r)+}$(aq) complexes are shown in Figure 2. Those for Fe^{3+}(aq), $FeOH^{2+}$(aq), and $Fe(OH)_2^+$(aq) are in reasonable agreement with previous reports[27] (Table 2). For $Fe(OH)_4^-$, only a broad band with a shoulder at ~264 nm was seen. This differs from Bunchuk et al.[46] who reported $\lambda_{max} \approx 340-345$ nm, possibly due to the presence of polynuclear species at their much higher $[Fe(III)]_T$ (~200 μM). Kamnev et al.[47] report an intense band with λ_{max} at 230 nm, obtained by mixing $FeCl_3$ and FeOOH in alkali, which they attributed to $Fe(OH)_4^-$ but which is similar to the present spectrum of $Fe(OH)_6^{3-}$ (Figure 2).

It is notable that λ_{max} is red-shifted between Fe^{3+} and $FeOH^{2+}$ whereas for the higher order complexes it is

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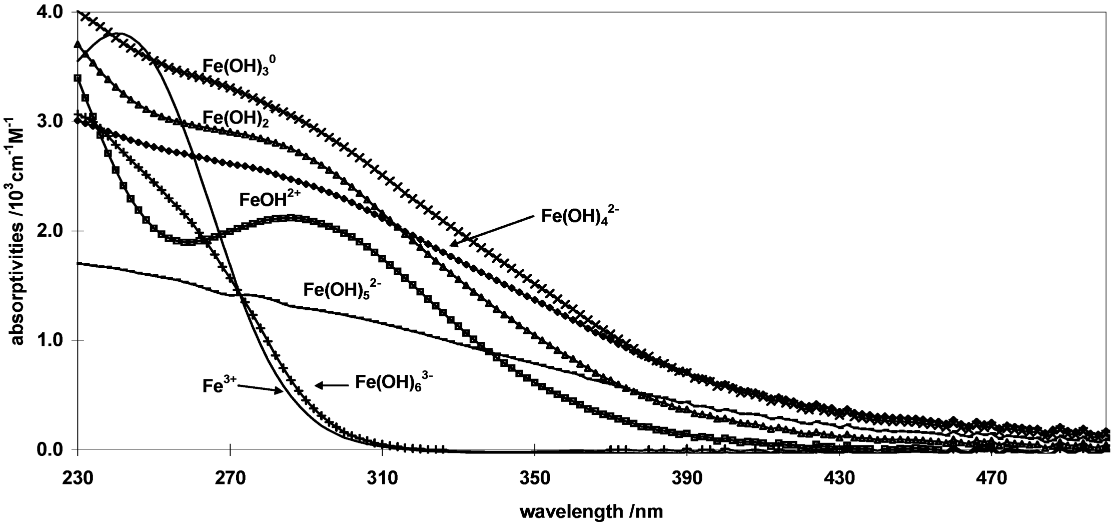

Figure 2. Spectra of the $Fe(OH)_r^{(3-r)+}$(aq) complexes at 25 °C, $I = 1$ M ($NaClO_4$), as calculated by SPECFIT.

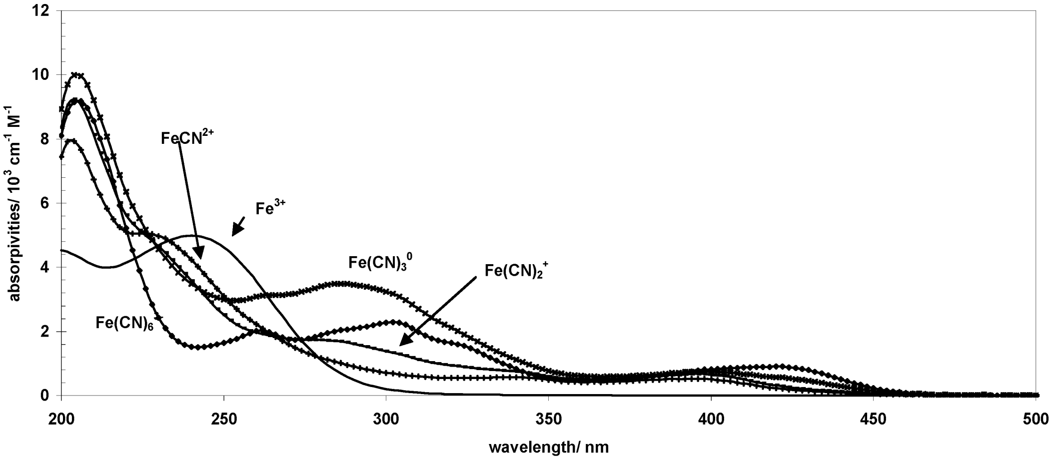

Figure 3. Spectra of the $Fe(CN)_q^{(3-q)+}$(aq) complexes as calculated by SPECFIT at $0 \leq [CN^-]_T/M \leq 0.5$, $0 \leq pH \leq 8$ $[Fe(III)]_T = 0.5$ mM, $I = 1$ M ($NaClO_4$). Spectra for Fe^{3+} and $Fe(CN)_6^{3-}$ are identical to those of solutions prepared from compounds containing these ions (Table 4).

Table 2. Present and Literature Values of the Peak Positions (λ_{max}'s) and Absorptivities (ϵ_{max}'s) for the $Fe(OH)_r^{(3-r)+}$(aq) Complexes at 25 °C

	λ_{max}/nm		estimated $\epsilon_{max}/10^3\ M^{-1}\ cm^{-1}$	
species	present	literature[a]	present	literature[a]
Fe^{3+}	240	240	3.8	4.2
$FeOH^{2+}$	286	297	2.1	2.0
$Fe(OH)_2^+$	~272[b]	297[c]	2.9[b]	1.8[c]
$Fe(OH)_3^0$	~252[b]		3.5	
$Fe(OH)_4^-$	~264[b]		2.7	
$Fe(OH)_6^{3-}$	< 230		> 3.1	

[a] $I = 0.1$ M (Na, $HClO_4$).[27] [b] Shoulder. [c] Inferred only, not measured.[27]

generally blue-shifted (Figure 2 and Table 2). As the d−d transitions are both orbitally- forbidden and spin-forbidden, the significant bands for high spin Fe(III)/OH^- complexes are attributable to ligand-to-metal charge transfer (LMCT) processes, consistent with the relative ease of reduction of Fe(III) to Fe(II).[48] Even assuming a constant coordination number of 6, the changes in the electronic transition energies as OH^- replaces H_2O in $Fe(OH)_r(H_2O)_{6-r}^{(3-r)+}$ are unlikely to be straightforward given the changes in local symmetry and charge that occur. On the other hand, that $Fe(OH)_6^{3-}$ does not absorb appreciably at $\lambda > 320$ nm (Figure 2) is consistent with the greater π-donor strength of OH^- cf. H_2O and the colorless salts containing this ion.[31,32]

Iron(III)−Cyanide Complexes. Significant UV−vis spectral changes were seen when CN^- was added to acidic solutions at $[Fe(III)]_T \approx 10\ \mu M$. However, the data were difficult to analyze due to the spectral complexity and the relatively low signal-to-noise ratio associated with the use of the long path length cell.[34] Low pH measurements were therefore made at $[Fe(III)]_T \approx 0.2-20$ mM in shorter path length cells (Figure S5). At $3.5 \leq pH \leq 7.3$, spectra were irreproducible, presumably due to kinetic and precipitation effects. At higher pH values, spectra were identical to those of $Fe(CN)_6^{3-}$ (Figure S5).

Global analysis of the complete data set (Table S2) with SPECFIT indicated the presence of four mononuclear complexes: $FeCN^{2+}$, $Fe(CN)_2^+$, $Fe(CN)_3^0$, and $Fe(CN)_6^{3-}$. The stability constants[41] for these complexes are listed in Table 3; they appear to be the first quantitative estimates for any Fe(III)/CN^- complex in aqueous solution, other than β_{16}. The present result of $\beta_{16} \approx 39$ (Table 3) lies well within

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(48) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

Table 3. Present Stability Constants (log β_{1q} Values)[41] for the $Fe(CN)_q^{(3-q)+}$ Complexes at 25 °C[a]

I/M	log β_{11}	log β_{12}	log β_{13}	log β_{16}
0.5	8.55 ± 0.06	16.0 ± 0.2	22.2 ± 0.5	39.0 ± 0.9
1.0	8.5 ± 0.1	15.8 ± 0.8	23.1 ± 0.2	38.8 ± 0.7

[a] Uncertainties are overall standard deviations (σ).

the wide spread of values reported for the standard state constant ($31 \leq \log \beta_{16}° \leq 53$) derived from thermodynamic cycles.[3,49] Being based on direct measurement, it should be more realistic.

It is of particular note that the currently accepted values[49] of the (conventional) standard Gibbs energies of formation ($\Delta_f G°$) at 25 °C of Fe^{3+}(aq), CN^-(aq), and $Fe(CN)_6^{3-}$(aq), respectively, −4.6, 172.4, and 729.3 kJ mol^{-1}, predict log $\beta_{16}° = 52.6$. Although considerable ionic strength and ion pairing effects would be expected for a reaction involving so many charged species, this value seems far too high by comparison with the present result and with other estimates.[3] It suggests significant errors exist in one or more of the $\Delta_f G°$ values. As has been pointed out,[3] even log $\beta_{16}° = 44$, estimated by some earlier authors, is inconsistent with the known chemistry since it suggests, incorrectly, that FeOOH(s) is soluble in concentrated CN^- solutions. In contrast, the present value is broadly consistent with this observation (see following paragraphs).

Models including $Fe(CN)_4^-$ and $Fe(CN)_5^{2-}$ failed to converge, except for one experiment at $I = 0.5$ M($NaClO_4$) that gave log $\beta_{14} \approx 29$ and log $\beta_{15} \approx 33$. (These values must be regarded with caution: they are mentioned only because of the absence of any other estimates). The failure to reliably detect these species can be attributed to the truncated accessible experimental range, the predominance of $Fe(CN)_6^{3-}$ at higher pH and [CN^-], and possibly kinetic effects. Certainly, with the exception noted, no spectral features consistent[50−53] with the well characterized $Fe(CN)_5H_2O^{2-}$ were observed. Inclusion of mixed $Fe(CN)_q(OH)_r^{(3-q-r)+}$ complexes in the models also resulted in nonconvergence, nor was the characteristic spectrum ($\lambda_{max} = 385$ nm, $\epsilon = 1800$)[50] of $Fe(CN)_5OH^{3-}$ observed under the conditions employed (Figure 3). As the spectra and stability constants of the individual species were independent of pH, mixed species were not significant over the concentration ranges and time scales investigated. Similarly, the absence of polynuclear species under the present conditions (Table S2) was confirmed by the independence of the data on $[Fe(III)]_T$.

Table 4. Spectral Characteristics of the $Fe(CN)_q^{(3-q)+}$(aq) Complexes at 25 °C

	λ_{max}/nm		$\epsilon_{max}/10^3$ M^{-1} cm^{-1}	
species	present	literature	present	literature
Fe^{3+}	240	240[a]	4.9[b]	4.2[a]
$FeCN^{2+}$	204		7.9	
	228		5.0	
	392		0.5	
$Fe(CN)_2^+$	204		9.2	
	226[c]		5.0	
	280		1.9	
	396		0.7	
$Fe(CN)_3^0$	206		10.0	
	264		3.1	
	286		3.5	
	398		0.8	
$Fe(CN)_6^{3-}$	206	200[d]	9.2	∼11[d]
	262	260[d]	2.0	1.4[d]
	302	301[d]	2.3	1.6[d]
	320	321[d]	1.6	1.2[d]
	420	420[d]	0.9	1.1[d]

[a] $I = 0.1$ M (H, $NaClO_4$).[27] [b] Value differs slightly from that in Table 2 due to minor optical differences between the solutions and deconvolution errors. [c] Shoulder. [d] Reference 54.

Details of the spectra of the individual Fe(III)/CN^- complexes detected are given in Table 4 and Figure 3. The spectral variations from Fe^{3+}(aq) to $Fe(CN)_6^{3-}$(aq) reflect the complicated changes that are likely to occur in the electronic energy levels[54,55] as the weak π-donor H_2O is replaced by the strong π-acceptor CN^- in the coordination shell of Fe(III).

Figure 4 plots the predominance diagram of the Fe(III)/OH^-/CN^- system at $[Fe(III)]_T = 10$ μM using the stability constants in Tables 1 and 3, and assuming supersaturation with respect to FeOOH(s). Cyanide remains bound to Fe(III) down to very low pH levels providing $[CN^-]_T$ remains reasonably high. However, Figure 4 also shows that CN^- is unable to compete with OH^- for Fe(III), even at low pH, unless the [CN^-]/[OH^-] ratio is very high (e.g., 10^9 at pH = 3). At high pH, despite the great stability of $Fe(CN)_6^{3-}$, OH^- largely displaces CN^- from the Fe(III). Figure 4 suggests that under typical environmental conditions, and even in most cyanide wastewaters (where $[CN^-]_T$ is usually quite small), Fe(III)/OH^- species will predominate over Fe(III)/CN^- species. Hence, barring the precipitation of Prussian blues, CN^- would be expected to be quite mobile in the environment.

Separate experiments established that both neutral (pH ∼ 7) and alkaline (pH ∼ 13) solutions of 0.3 mM $K_3Fe(CN)_6$ released CN^- (detected using the gold colloid[56] and Prussian blue[57] methods) and precipitated FeOOH(s). No OCN^- was detected (via the cobalt acetate test[57]). After ∼5 weeks at 25 °C, the neutral solution was ∼75% decomposed, while only trace quantities of $Fe(CN)_6^{3-}$ remained at pH ∼ 13.

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(49) *Selected Values of Chemical Thermodynamic Properties*; Wagman, D. D., et al., Eds.; Technical Note 270; National Bureau of Standards: Washington, DC, 1968.

(50) Espenson, J. H.; Wolenuk, S. G., Jr. *Inorg. Chem.* **1972**, *11*, 2034−2041.

(51) Gale, R.; McCaffery, A. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1344−1351.

(52) The spectrum reported for $[Fe(CN)_5H_2O]^{2-}$ by Gale and McCaffery[51] differs completely from that given by Espenson and Wolenuk.[50] According to the latter, and consistent with the spectral characteristics, the preparation method employed by Gale and McCaffery produces a hydrate containing $Fe_2(CN)_{10}^{4-}$. Numerous kinetic studies involving $[Fe(CN)_5H_2O]^{2-}$ have been reported,[53] but the equilibrium constant for the replacement of H_2O by CN^-, corresponding to β_{15}, does not appear to have been reported.

(53) Stochel, G.; van Eldik, R.; Hejmo, E.; Stasicka, Z. *Inorg. Chem.* **1988**, *27*, 2767−2770 and references therein.

(54) Alexander, J. J.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4260−4271.

(55) Naiman, C. S. *J. Chem. Phys.* **1961**, *35*, 323−328.

(56) Hindmarsh, K.; Nicol, M. J. In *Cyanide: Social, Industrial and Economic Aspects*; Young, C. A., Tidwell, L. G., Anderson C. G., Eds.; Minerals, Metals and Materials Society: New Orleans, 2001; pp 151−162.

(57) Svehla, G. *Vogel's Textbook of Macro and Semimicro Qualitative Inorganic Analysis*, 5th ed.; Longman: London, 1979.

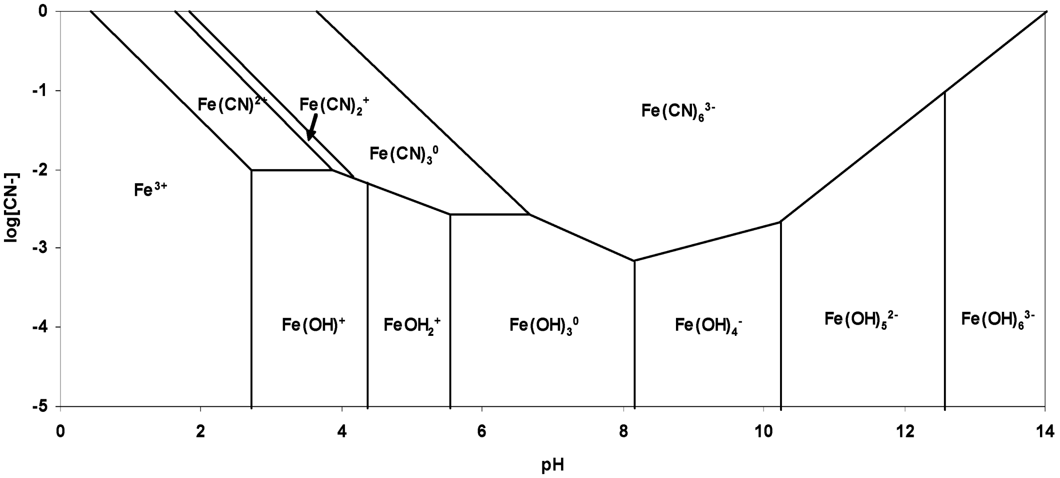

Figure 4. Predominance diagram for the Fe(III)/CN$^-$/OH$^-$ system, with $[\mathrm{Fe(III)}]_T = 10$ μM, $I = 1$ M (NaClO$_4$), $E_H \sim 0.5$ V, 25 °C. The system is supersaturated with respect to FeOOH(s) at higher pH values.

This result confirms that the stability constant of $\mathrm{Fe(CN)_6}^{3-}$ cannot be significantly greater than the solubility product of FeOOH (p$K_{sp} \approx 41.5$).[21]

The Fe(II)/CN$^-$ System. Addition of CN$^-$ to an acidified solution of 0.26 mM $\mathrm{Fe^{II}(NH_4)_2(SO_4)_2}$(aq) produced a rise in absorbance centered on ~217 nm, attributable[48] to the formation of $\mathrm{Fe(CN)_6}^{4-}$. Further investigation of the Fe(II)/CN$^-$ system over a wide range of conditions produced no clearly defined isosbestic points nor any other evidence for other species. Attempts to extend the measurements to $[\mathrm{Fe(II)}]_T \approx 0.5$ mM produced a white precipitate of $\mathrm{Na_2Fe_2(CN)_6}$,[3] which slowly turned dark blue upon the addition of sufficient CN$^-$ or on contact with air. From calculations using the spectrophotometrically determined onset of precipitation, the log $^*K_{sp}$ value of $\mathrm{Na_2Fe_2(CN)_6}$(s) was estimated to be -11.1 ± 0.3 based on the following reaction:

$$\mathrm{Na_2Fe_2(CN)_6(s) + 6H^+ \Leftrightarrow 2Fe^{2+} + 2Na^+ + 6HCN} \quad (3)$$

The present direct determination of $\beta_{16}(\mathrm{Fe(CN)_6}^{3-})$, hereafter abbreviated $^{\mathrm{III}}\beta_6$, can be combined with electrode potential data to estimate $^{\mathrm{II}}\beta_6°$ for the following equilibrium:

$$\mathrm{Fe^{2+}(aq) + 6\ CN^-(aq) \Leftrightarrow Fe(CN)_6{}^{4-}(aq)}$$

Using usual thermodynamic procedures, it is readily shown that

$$\log {}^{\mathrm{II}}\beta_6° = \log {}^{\mathrm{III}}\beta_6° + \{(E°_{\mathrm{CN}} - E°_{\mathrm{Fe}})F/2.303RT\}$$

where $E°_{\mathrm{CN}}$ and $E°_{\mathrm{Fe}}$ are, respectively, the standard electrode potentials for the following processes:

$$\mathrm{Fe(CN)_6{}^{3-}(aq) + e^- \Leftrightarrow Fe(CN)_6{}^{4-}(aq)}$$

$$\mathrm{Fe^{3+}(aq) + e^- \Leftrightarrow Fe^{2+}(aq)}$$

and other symbols have their usual meanings. Substitution of the well established values[58] of $E°_{\mathrm{CN}} = 0.361$ V and $E°_{\mathrm{Fe}} = 0.771$ V, and ignoring activity coefficient effects, gives $\log {}^{\mathrm{II}}\beta_6° = 38.8 - 7.00 = 31.8$ at 25 °C. This value falls within the wide range reported in the literature ($24 \leq \log {}^{\mathrm{II}}\beta_6° \leq 35$)[3,49] but, being based on direct measurements, should be more reliable. Finally, it can be noted that the equilibrium constant $\log {}^{\mathrm{II}}K_6$ for the reaction $[\mathrm{Fe(CN)_5OH_2}]^{3-} + \mathrm{CN^-} \Leftrightarrow [\mathrm{Fe(CN)_6}]^{4-}$ has been determined on a number of occasions, with values ranging from 7.7 to 10.1 ("best" value = 8.3).[5] This gives an estimate of $\log {}^{\mathrm{II}}\beta_5 = \log {}^{\mathrm{II}}\beta_6 - \log {}^{\mathrm{II}}K_6 \approx 24$.

Conclusions

UV−vis spectrophotometry of the Fe(III)/OH$^-$ system at $[\mathrm{Fe(III)}]_T \leq 10$ μM reveals the presence of only the mononuclear complexes $\mathrm{Fe(OH)}_r^{(3-r)+}$ ($r = 1-6$) at $1.0 \leq$ pH ≤ 12.8. The Fe(III)/CN$^-$ system was difficult to study because of competing reactions, but $\mathrm{Fe(CN)}_q^{(3-q)+}$ complexes ($q = 1-3$, 6) were detected. Only inconclusive evidence was obtained for the intermediate species ($q = 4$ or 5), and mixed Fe(III)/CN$^-$/OH$^-$ or polynuclear complexes were not detected under the present conditions. No spectrophotometric evidence could be obtained for Fe(II)/CN$^-$ complexes other than $\mathrm{Fe(CN)_6}^{4-}$. An estimate of the formation constants of $\mathrm{Fe(CN)_6}^{4-}$(aq) and $\mathrm{Fe(CN)_5}^{3-}$(aq) could be made using the present value for $\mathrm{Fe(CN)_6}^{3-}$(aq) and well established electrode potential and other data.

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Supporting Information Available: Additional figures and tables This material is available free of charge via the Internet at http://pubs.acs.org.

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(58) *Standard Potentials in Aqueous Solutions*; Bard, A. J., Parsons, R., Jordan, J., Eds., Marcel Dekker: New York, 1985.