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Kinetics and Mechanism of Pentacyanohydroxoferrate(III) Formation from FeL Complexes (L = Triethylenetetraaminehexaacetic Acid and 2-Hydroxy-1,3-diaminopropanetetraacetic Acid)

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Abstract

The kinetics and mechanism of the displacement of two polyaminocarboxylates *viz.*, triethylenetetraaminehexaacetic acid (TTHA) and 2-hydroxy-1,3-diaminopropanetetraacetic acid (HPDTA) from their iron(III) complexes by the cyanide ion have been investigated spectrophotometrically. The forward reactions were carried out in the presence of excess cyanide at pH = 10.5 ± 0.02 for [FeHPDTA(OH)] and 11.5 ± 0.02 for [FeTTHA(OH)$_2$] and $I = 0.25$ M (NaClO$_4$). A variable order dependence in cyanide ranging from one to three was observed in the case of the [FeHPDTA(OH)] complex. In the case of [FeTTHA(OH)$_2$], however, a zero order dependence and only a third order dependence in cyanide was observed at low and high cyanide concentrations, respectively. The reverse reactions exhibited first order dependence on $[Fe(CN)_5OH]^{3-}$ and L^{n-}, but an inverse first order dependence in cyanide. A five step mechanism has been proposed for the FeHPDTA(OH)–CN$^-$ reaction. In the case of the FeTTHA(OH)$_2$–CN$^-$ reaction, however, the first step involves a slow loss of one OH$^-$ followed by five steps envisaged in the HPDTA case. The activation parameters and the effect of ionic strength have been used in support of the proposed mechanism.

$[Fe(CN)_5OH]^{3-}$ reacts with excess cyanide to produce $[Fe(CN)_6]^{3-}$, which further reacts with the released ligand forming $[Fe(CN)_6]^{4-}$ and the oxidation products of the ligands.

Introduction

For some time we have been interested in investigating the kinetics and mechanisms of reactions involving the exchange of polyaminocarboxylate ligands complexed to Ni(II) [1] and Fe(III) [2–4] by a monodentate ligand viz. cyanide ion. Whereas in nickel systems a four step mechanism has been established, in the case of the Fe(III) system a five step mechanism has been suggested for the formation of $[Fe(CN)_5OH]^{3-}$. A feature different than in the Ni(II) system is the existence of two more stages in the reaction involving the formation of $[Fe(CN)_6]^{3-}$ followed by oxidation of the released ligand by hexacyanoferrate(III). The reactants chosen by us so far were monohydroxo-aminocarboxylatoferrate(III) complexes. We thought it worthwhile to study one more monohydroxo- and one dihydroxo-aminocarboxylatoferrate(III) complex *viz.* $[FeHPDTA(OH)]^{2-}$ and $[FeTTHA(OH)_2]^{5-}$ respectively to gain further insight into the mechanism proposed by us earlier and to observe any new features that may arise due to the introduction of a second hydroxy group in a reactant complex. The reactions under investigation are represented by eqn. (1)

$$[FeL(OH)_x]^{3-n-x} + 5\,CN^- \longrightarrow [Fe(CN)_5OH]^{3-} + (x-1)OH^- \qquad (1)$$

where $x = 1$ or 2 for L = HPDTA or TTHA and n = charge on the anion of L respectively.

Experimental

Chemicals

Disodium salt of TTHA (Sigma, U.S.A.), HPDTA (Fluka), ferric nitrate (Thomas and Baker, U.K.), NaClO$_4$ (E. Merck, F.R.G.) and sodium ferricyanide (G.R., S.D.S.) were used for this study. Sodium aquopentacyanoferrate(II) was prepared from sodium nitroprusside by a literature method [5] and was oxidised to aquapentacyanoferrate(III) by H$_2$O$_2$ [6]. Polyaminocarboxylatoferrate(III) complexes were prepared by a method described by us in an earlier communication [1]. Ten percent excess ligand over stoichiometric requirement was added to a solution of ferric perchlorate to ensure complete complexation. Sodium cyanide was determined argentometrically [7]. The pH of the reaction mixture was adjusted by addition of sodium hydroxide or perchloric acid. Buffers were not used in order to minimise complex-

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ity of the reactions system. Tests showed that pH changes during the course of the reaction were negligible.

Equipment

A Toshniwal spectrophotometer model RL-02 with a circulatory arrangement of water for thermostating the cell compartment was used for following the reaction rate. An ultracryostat Model 2 NBE (G.D.R.) was used for maintenance of the desired temperature. A Cary 17-D and Shimadzu UV-190 and UV-240 spectrophotometers were used for repetitive scans of the reaction mixture. pH measurements were recorded on an Elico Digital pH meter Model LI-120.

Kinetic Runs

The rate of formation of $[Fe(CN)_5OH]^{3-}$ was measured at 395 nm (λ_{max} of $[Fe(CN)_5OH]^{3-}$, $\epsilon = 1740\ M^{-1}\ cm^{-1}$) [8] at pH = 11.0 ± 0.02, temperature = 25 ± 0.1 °C and $I = 0.25$ M ($NaClO_4$) in the presence of a large excess of cyanide. Plots of $\log C_A$ versus time in all cases were linear up to about 70% of the reaction. A correction is applied for the absorption of $[FeL(OH)_x]^{3-n-x}$ complexes at 395 nm. It can be derived that

$$C_A = \frac{\epsilon_B C_A{}^0 - A_t}{\epsilon_B - \epsilon_A}$$

where $C_A{}^0$ and C_A represent concentrations of A, *i.e.*, $[FeL(OH)_2]^{3-n-x}$ at $t = 0$ and $t = t$ respectively, B represents $[Fe(CN)_5OH]^{3-}$ and ϵ_A and ϵ_B the molar extinction coefficients of A and B in order. In the following text the complexes will be represented by [FeL] for the sake of simplicity.

Kinetics of Forward Reaction

The forward reaction is favoured thermodynamically, $K_{FeHPDTA(OH)} = 10^{9.45}$ [9], $K_{FeTTHA(OH)_2} = 10^{3.5}$ [10] and β_5 of $[Fe(CN)_5OH] = 10^{43.6}$*. The rate of the forward reaction was measured in the presence of a large excess of cyanide. An interesting feature of the $[FeHPDTA(OH)]^{2-}$ system is the observance of a variable order dependence in cyanide changing from three to one as the cyanide concentration changes from low to high. In the $[FeTTHA(OH)_2]^{5-}$ system, however, a zero order dependence at low and a third order dependence is observed at a high concentration of cyanide (Fig. 1). This zero order dependence has been observed in an aminocarboxylatohydroxoferrate(III) system for the first time. This indicates the loss of one of the two hydroxyl groups present in the $[FeTTHA(OH)_2]^{5-}$ complex.

A rate expression consistent with a variable order dependence in cyanide is given in eqn. (2).

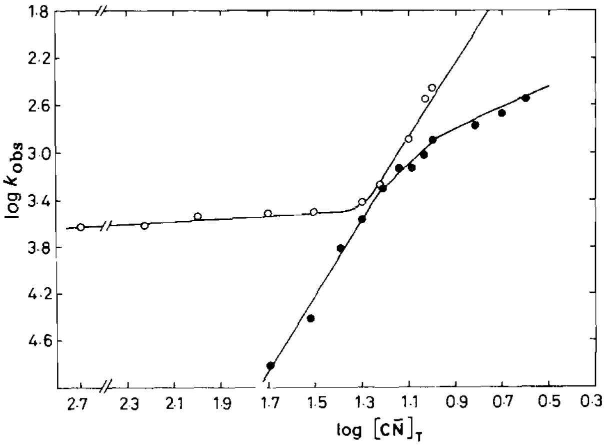

Fig. 1. Cyanide dependence of the observed pseudo-first order rate constants in the reactions of $[FeTTHA(OH)_2]^{5-}$ (○) and $[FeHPDTA(OH)]^{2-}$ (●) with cyanide ion. The reaction conditions are given in Table I.

$$\begin{aligned}\text{Rate} &= \frac{d[Fe(CN)_5OH^{3-}]}{dt}\\ &= k_{obs}[FeL(OH)(CN)_x{}^{2-n-x}]\\ &= k_f[FeL(OH)(CN)_x{}^{2-n-x}][CN^-]^{4-x} \qquad (2)\end{aligned}$$

where n is the charge on the ligand L and x is the number of cyanides attached to $[FeL]^{3-n}$ complexes and can have values 1, 2 and 3 for the HPDTA system, 0 and 3 for the TTHA system. The observed rate constants for both systems are given in Table I. The orders in cyanide are inferred from the slopes of plots of $\log k_{obs}$ *versus* $\log[CN^-]_T$ given in Fig. 1.

Kinetics of Reverse Reaction

The reverse reactions of eqn. (1) are not favoured thermodynamically and it becomes possible to force the reverse reactions only by adding a relatively large excess of ligand compared to $[Fe(CN)_5OH]^{3-}$. The disappearance of $[Fe(CN)_5OH]^{3-}$ follows the rate expression given in eqn. (3).

$$-\frac{d[Fe(CN)_5OH^{3-}]}{dt} = k_r\frac{[Fe(CN)_5OH^{3-}][L^{n-}]}{[CN^-]} \qquad (3)$$

The integrated form of eqn. (3) can be written as eqn. (4)

$$A_i - A_t + A_i \ln\frac{A_i}{A_t} = -\frac{\epsilon}{5}lk'_{obs}t \qquad (4)$$

where $k'_{obs} = k_r[L^{n-}]$, k_r being the reverse rate constant, l is the path length and ϵ is the molar extinction coefficient of $[Fe(CN)_5OH]^{3-}$. The inverse first order dependence in cyanide points to the fact that the step preceding the last step is rate determining. The values of k'_{obs} and k_r are listed in Table II.

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*$\log \beta_5 = 43.9$ determined by authors spectrophotometrically at 25 °C, $I = 0.25$ M ($NaClO_4$) (unpublished work).

TABLE I. Kinetics of Formation of $[Fe(CN)_5OH]^{3-}$ from Mono-aminocarboxylatoferrate(III) Complexes in Presence of Excess CN^- at pH = 11.5 ± 0.02, I = 0.25 M ($NaClO_4$) and Temperature = 25 ± 0.1 °C (pH = 10.5 ± 0.02 for HPDTA reactions)

$10^2 \times [CN^-]_T$ (M), $[FeTTHA(OH)_2]^{5-}$ = $(1.2–2.0) \times 10^{-4}$ M	k_{obs} (s^{-1})	$10^2 \times [CN^-]_T$ (M), $[FeHPDTA(OH)]^{2-}$ = $(1.0–2.5) \times 10^{-4}$ M	k_{obs} (s^{-1})
0.2	1.73×10^{-4a}	2.0	1.42×10^{-5}
0.6	2.32×10^{-4a}	3.0	3.80×10^{-5}
1.0	2.52×10^{-4a}	4.0	1.18×10^{-4}
2.0	2.76×10^{-4a}	5.0	2.65×10^{-4}
3.0	3.07×10^{-4}	6.0	5.22×10^{-4}
5.0	3.43×10^{-4}	8.0	7.13×10^{-4}
6.0	4.73×10^{-4}	9.0	9.21×10^{-4}
7.0	7.20×10^{-4}	10.0	1.21×10^{-3}
8.0	1.25×10^{-3}	15.0	1.60×10^{-3}
9.0	2.63×10^{-3}	20.0	2.05×10^{-3}
10.0	3.61×10^{-3}	25.0	2.55×10^{-3}

[a] Zero order dependence in $[CN^-]$.

TABLE II. Rate constants for the Reaction of $[Fe(CN)_5OH]^{3-}$ with $[TTHA]^{6-}$/$[HPDTA]^{4-}$. $[Fe(CN)_5OH]^{3-}$ = $(0.75–3.0) \times 10^{-4}$ M; pH = 11.0 ± 0.1, Temperature = 25 ± 0.1 °C, I = 1.0 M ($NaClO_4$) for TTHA Reaction. $[Fe(CN)_5OH^{3-}]$ = $(0.7–1.0) \times 10^{-4}$ M, pH = 10.5, Temperature = 25 ± 0.1 °C, I = 0.92 M ($NaClO_4$) for HPDTA Reaction

	$10^9 \times k'_{obs}$ ($M s^{-1}$)	$10^8 \times k_r$ ($= K_5^{-1} k_4$) (s^{-1})
$10^2[TTHA]_T$ (M)		
2.50	0.96	3.24
4.80	1.63	3.39
7.00	2.27	3.24
8.00	2.87	3.51
	Average = 3.35×10^{-8} (s^{-1})	
$[HPDTA]_T$ (M)		
0.05	2.99	5.98
0.10	6.45	6.40
0.12	7.18	5.98
	Average = 6.04×10^{-8} (s^{-1})	

Other Consecutive Reactions Occurring in the Reaction Systems

Two other reactions occur in addition to the forward reaction described in the previous section. As the concentration of $[Fe(CN)_5OH]^{3-}$ increases it begins to react with excess cyanide to form $[Fe(CN)_6]^{3-}$ which in turn reacts with the ligands released in the first stage of reaction to form $[Fe(CN)_6]^{4-}$ and the oxidation products of the ligands [11]. Similar reactions have been shown to occur with other ligand systems *viz.* EDTA, EGTA, NTA [11] and DTPA [12].

A repetitive scan (Fig. 2) of the reaction mixture of the FeHPDTA(OH)–CN^- system shows the formation and/or decay of the species as described in the previous paragraph. The scan of the $FeTTHA(OH)_2$–CN^- system is of a similar type and is, therefore, not given. The rise and fall of the peak at 395 nm and the shift towards the 410–420 nm range along with the existence of an isosbestic at 355 nm shows the conversion of $[Fe(CN)_5OH]^{3-}$ to $[Fe(CN)_6]^{3-}$. Decay of the peak of $[Fe(CN)_6]^{3-}$ in the later part of the reaction is due to the disappearance of this species following reaction with ligands. The spectrum of $[Fe(CN)_6]^{4-}$ is featureless and hence spectral evidence for its formation cannot be provided [13]. However, the ammonium molybdate and thorium nitrate tests [14] are positive in the later part of the reaction and confirm the formation of $[Fe(CN)_6]^{4-}$

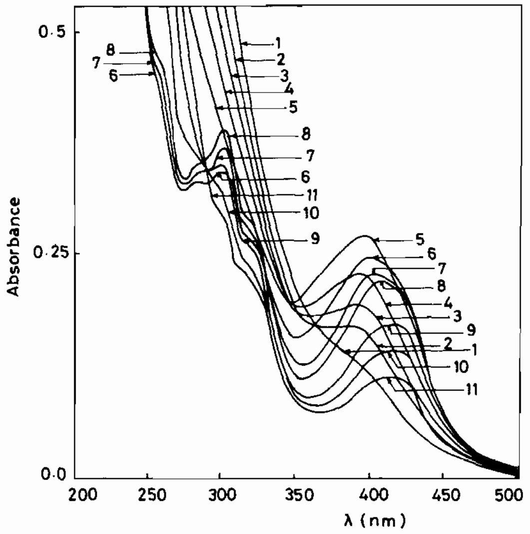

Fig. 2. Repetitive scan of the reaction mixture of $[FeHPDTA(OH)]^{2-}$ and cyanide ion: $[FeHPDTA(OH)]^{2-}$ = 2.5×10^{-4} M, $[CN^-]_T$ = 9×10^{-2} M, pH = 10.5 ± 0.1, I = 0.25 M ($NaClO_4$), temperature = 25 °C. Time (min/h): 1(1), 3(2), 11(3), 21(4), 26(5), 35(6), 1.1(7), 2(8), 3(9), 12(10), 24(11).

The oxidation products of HPDTA and TTHA have not been isolated but based on earlier studies [11] in basic medium they are expected to be carbon dioxide, polybasic aliphatic acids e.g. glycollic acid and simpler aminocarboxylates.

pH Dependence of The Forward Rate

The pH (defined as $-\log[H^+]$ for dilute solutions) profiles for both reactions over the range 9.5 to 12 are shown in Fig. 3. The initial steep portion of the curves reflect the changes in rate as $FeHPDTA(H_2O)$ and $FeTTHA(H_2O)_2$ are converted to FeHPDTA-(OH) and $FeTTHA(OH)_2$ respectively on raising the pH. The relative concentration of various species present as a function of pH are given for the [FeTTHA] complex in Fig. 4 according to a computer program by Perrin and Sayce [15]. The species distribution for the [FeHPDTA] complex is similar but shows the presence of monohydroxo species only and is not given. The limiting values of rate constants are due to the reaction of the two hydroxo complexes with CN^- which is the predominant reacting species present above pH = 9.5 ($K_{HCN} = 9.0$) [16]. Though in earlier investigations on ligand exchange reactions it was possible to resolve the rates by algebraic manipulation [17] it is not possible to do so in these two systems, because of the complexity due to subsequent reactions described in the preceding section.

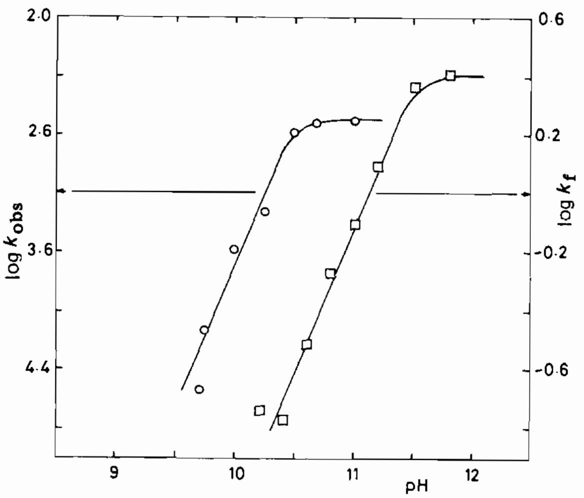

Fig. 3. The effect of pH on the forward reactions of $[FeTTHA(OH)_2]^{5-}$ (□) and $[FeHPDTA(OH)]^{2-}$ (○) with cyanide ion. For $[FeTTHA(OH)_2]^{5-} = 2.0 \times 10^{-4}$ M, $[CN^-]_T = 8 \times 10^{-2}$ M, $I = 0.1$ M ($NaClO_4$), temperature = 25 °C; $[FeHPDTA(OH)]^{2-} = 2.5 \times 10^{-4}$ M, $[CN^-]_T = 0.15$ M, $I = 0.25$ M ($NaClO_4$), temperature = 25 °C.

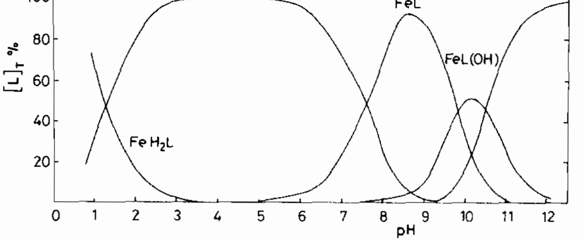

Fig. 4. Species distribution of FeTTHA system as a function of pH. [FeTTHA] = 5×10^{-4} M, $I = 0.1$ M, temperature = 25 °C.

Temperature Dependence of Forward and Reverse Reactions

Activation parameters for the forward and reverse reactions were obtained from the Arrhenius plots drawn in the temperature range 25–45 °C, and are given in Table III. The values obtained for other mono-aminocarboxylato complexes of Fe(III) [2–4] are also consistent with the proposed mechanism.

Ionic Strength: Dependence of Forward Rate

The rate constants for the $[FeHPDTA(OH)]-CN^-$ reaction obeyed the Bronsted eqn. (5) [18]

$$\log k_f = \log k_o + 1.02\, Z_A Z_B \sqrt{I} \tag{5}$$

The values of $Z_A Z_B \approx 5.2$ (Fig. 5). The rate constants for the $FeTTHA(OH)_2$ system, on the other hand, followed the Bronsted–Bjerrum–Christiansen formulation [19].

$$\log k_f = \log k_o + 1.02\, Z_A Z_B \frac{\sqrt{I}}{1 + \sqrt{I}} \tag{6}$$

The values of $Z_A Z_B \approx 7$ (Fig. 6). Both values of $Z_A Z_B$ are close to values expected from the rate determining step envisaged in the proposed mechanism.

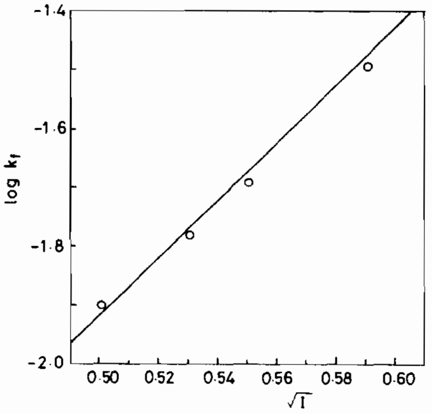

Fig. 5. The effect of ionic strength on the forward rate constants for the reaction of $[FeHPDTA(OH)]^{2-}$ (○) with cyanide ion. $[FeHPDTA(OH)]^{2-} = 2.5 \times 10^{-4}$ M, $[CN^-]_T = 0.15$ M, pH = 10.5 ± 0.1, temperature = 25 ± 0.1 °C.

TABLE III. Activation Parameters

Forward reaction	Reverse reaction
(a) $[FeHPDTA(OH)]^{5-} + 5\,CN^-$ $\longrightarrow [Fe(CN)_5OH]^{3-} + L^{6-}$ $E_a = 33.6$ kJ, $\Delta H^{\neq} = 31.2$ kJ mol^{-1} $\Delta S^{\neq} = -178.4$ JK^{-1}, p$Z = 2.96 \times 10^3$	(b) $[Fe(CN)_5OH]^{3-} + HPDTA^{4-}$ $\longrightarrow [FeHPDTA(OH)]^{2-} + 5CN^-$ $E_a = 47.1$ kJ, $\Delta H^{\neq} = 44.6$ kJ mol^{-1} $\Delta S^{\neq} = -232$ JK^{-1}, p$Z = 4.7$
(c)[a] $[FeTTHA(OH)_2]^{5-} + 5\,CN^-$ $\longrightarrow [Fe(CN)_5OH]^{3-} + L^{6-}$ Zeroth order: $E_a = 43.4$ kJ, $\Delta H^{\neq} = 40.9$ kJ mol^{-1} $\Delta S^{\neq} = -175$ JK^{-1}, p$Z = 4.5 \times 10^6$ cm^{-1} Third order: $E_a = 34.6$ kJ, $\Delta H^{\neq} = 32.2$ kJ mol^{-1} $\Delta S^{\neq} = -127.5$ JK^{-1}, p$Z = 1.4 \times 10^3$ cm^{-1}	(d) $[Fe(CN)_5OH]^{3-} + TTHA^{6-}$ $\longrightarrow [FeTTHA(OH)]^{4-} + 5CN^-$ $E_a = 64.7$ kJ, $\Delta H^{\neq} = 62.2$ kJ mol^{-1} $\Delta S^{\neq} = -178$ JK^{-1}, p$Z = 2.8 \times 10^3$ cm^{-1}
(e) $[Fe(CN)_5OH]^{3-} + CN^-$ $\longrightarrow Fe(CN)_6{}^{3-} + OH$ $E_a = 39.0$ kJ, $\Delta H^{\neq} = 36.5$ kJ mol^{-1} $\Delta S^{\neq} = 1.7$ JK^{-1}, p$Z = 8.6 \times 10^3$ cm^{-1}	

[a] Ref. 4.

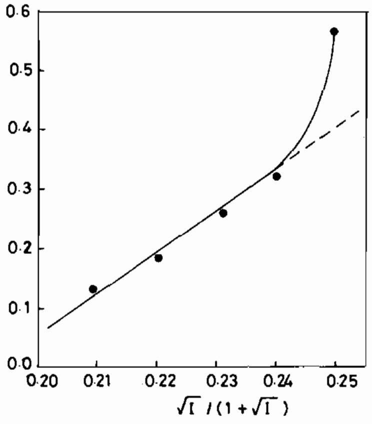

Fig. 6. The effect of ionic strength on the forward rate constants for the reaction of $[FeTTHA(OH)_2]^{5-}$ (●) with cyanide ion. $[FeTTHA(OH)_2]^{5-} = 2 \times 10^{-4}$ M, $[CN^-]_T = 7 \times 10^{-2}$ M, pH = 11.5 ± 0.1, temperature = 25 ± 0.1 °C.

Discussion

The results of forward and reverse rate studies on the reaction of $[FeHPDTA(OH)]^{4-}$ and $[FeTTHA(OH)_2]^{3-}$ with cyanide ion suggest a mechanism given in eqns. (7) to (12). The variable order dependence in cyanide shows that stepwise addition of cyanide ions takes place while the ligands unwarp themselves from the coordination sphere of Fe(III). A new feature of the $[FeTTHA(OH)_2]^{5-}$ system is the observation of zero order kinetics in [cyanide]. This points to a slow loss of one of the two hydroxyl groups in the first step (eqn. (7))* followed by a stepwise mechanism as proposed by us for the reaction of FeL(OH) complexes with cyanide in our earlier communications [2–4] and which is reproduced below in eqns. (8) to (12).

$$[FeL(OH)_2]^{1-n} \xrightarrow[\text{slow}]{k_d} [FeL(OH)]^{2-n} + OH^- \qquad (7)$$

$$[FeL(OH)_2]^{1-n} + CN^- \overset{K_1}{\rightleftharpoons} [FeL(OH)(CN)]^{1-n} + OH^- \text{ (fast)} \qquad (8)$$

$$[FeL(OH)(CN)]^{1-n} + CN^- \overset{K_2}{\rightleftharpoons} [FeL(OH)(CN)_2]^{-n} \text{ (fast)} \qquad (9)$$

$$[FeL(OH)(CN)_2]^{-n} + CN^- \overset{K_3}{\rightleftharpoons} [FeL(OH)(CN)_3]^{-(n+1)} \text{ (fast)} \qquad (10)$$

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*And also a cyanide assisted rapid displacement of OH⁻ according to eqn. (8).

$$[\mathrm{FeL(OH)(CN)_3}]^{-(n+1)} + \mathrm{CN^-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [\mathrm{FeL(OH)(CN)_4}]^{-(n+2)} \text{ r.d.s.} \qquad (11)$$

$$[\mathrm{FeL(OH)(CN)_4}]^{-(n+2)} + \mathrm{CN^-} \overset{K_5}{\rightleftharpoons} [\mathrm{Fe(CN)_5OH}]^{3-} + \mathrm{L}^{n-} \text{ (fast)} \qquad (12)$$

We failed to observe the expected fourth order dependence in cyanide in these two reactions, and, for that matter, in any reaction of FeL(OH) with cyanide investigated so far. Two reasons may be attributed for this behaviour (1) the reaction is too slow to be observed experimentally in the low concentration range of cyanide where fourth order dependence is expected, (2) a stable 1:1:1 complex *viz.* $[\mathrm{FeL(OH)(CN)}]^{1-n}$ is produced immediately following mixing and, therefore, only three cyanides may be added stepwise up to the rate determining step (eqn. (11)) giving rise to observed third, second and first order dependences in cyanide respectively.

It also follows that, (a) where only a third order dependence is seen, as in the case of the $[\mathrm{FeHPDTA(OH)}]^{2-}$ reaction, three cyanides are added simultaneously to the $[\mathrm{FeL(OH)(CN)}]^{1-n}$ intermediate, (b) where only a second order dependence is observed, two cyanides are added to the 1:1:2 intermediate, *viz.* $[\mathrm{FeL(OH)(CN)_2}]^{-n}$ and (c) when only first order dependence is observed one cyanide is added to the 1:1:3 intermediate *viz.* $[\mathrm{FeL(OH)(CN)_3}]^{-(n+1)}$. The formation of similar intermediates has been envisaged in reactions of aminocarboxylato complexes of Ni(II) with cyanide [1]. The relatively low activation energies and highly negative entropies of activation for the forward reactions compared to the reverse reactions point to the fact that the mechanism is an associative rather than a dissociative one and is consistent with the rate determining step given in (eqn. (11)), where bond formation is taking place in the forward reaction and bond breaking in the reverse reaction. The effect of ionic strength provides further support for this mechanistic scheme as discussed earlier (*vide infra*).

In an earlier communication we established a linear free energy relationship between the stepwise rate constants and the stability constants, β_{lmn} of the intermediates reacting in that particular step for FeL–CN⁻ reactions [17] when L = EDTA, HEDTA and DTPA as well as for reactions of a large number of aminocarboxylato complexes of Ni(II) with CN⁻ [1]. Thus it can be shown that

$$\log k_4 = \log k_r\beta_5 - \log \beta_{113} \qquad \text{(1st order)}$$

$$\log K_3k_4 = \log k_r\beta_5 - \log \beta_{112} \qquad \text{(2nd order)}$$

$$\log K_2K_3k_4 = \log k_r\beta_5 - \log \beta_{111} \qquad \text{(3rd order)}$$

$$\log K_1K_2K_3k_4 = \log k_r\beta_5 - \log \beta_{110} \qquad \text{(4th order)}$$

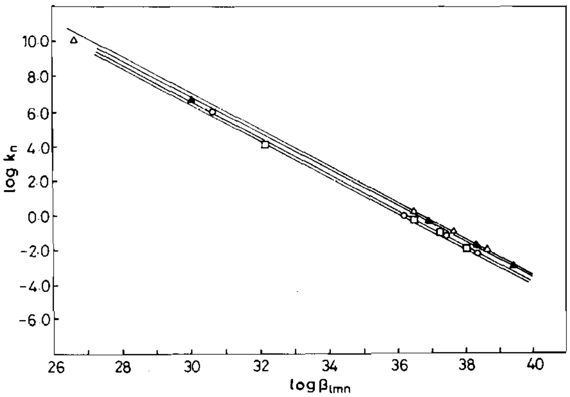

Fig. 7. Plot of log k'_n *vs.* log β_{lmn} ($k'_n = k_4$, k_4K_3, $k_4K_3K_2$ and $k_4K_3K_2K_1$ for the first order, second order, third order and fourth order rate constants and β_{lmn} are β_{113}, β_{112}, β_{111} or β_{110} the overall stability constants for intermediates). The different plots are for (▼) FeHEDTA, (□) FeDTPA, (○) FeEDTA and (△) FeHPDTA.

HPDTA also fits on the plots between log (step rate constants) and log β_{lmn} (Fig. 7).

Finally, the reactions of $[\mathrm{FeL(OH)}]^{n-2}$ complexes with the cyanide ion consist of three distinct stages. The rate constants for the various stages of reaction are given in Table IV.

(1) Conversion of $[\mathrm{FeL(OH)}]^{n-2}$ to $[\mathrm{Fe(CN)_5OH}]^{3-}$ by a five step mechanism.

(2) Conversion of $[\mathrm{Fe(CN)_5OH}]^{3-}$ to $[\mathrm{Fe(CN)_6}]^{3-}$ due to the reaction of the former with excess cyanide.

(3) Conversion of $[\mathrm{Fe(CN)_6}]^{3-}$ to $[\mathrm{Fe(CN)_6}]^{4-}$ and of the ligand released in stage 1 to its oxidation products.

References

1 K. Kumar and P. C. Nigam, *J. Phys. Chem.*, *84*, 140 (1980) and refs. therein.
2 H. C. Bajaj and P. C. Nigam, *Transition Met. Chem.*, *8*, 109 (1983).
3 R. M. Naik and P. C. Nigam, *Transition Met. Chem.*, *10*, 227 (1985).
4 R. M. Naik and P. C. Nigam, *Inorg. Chim. Acta*, *114*, 55 (1986).
5 G. Brauer, 'Handbook of Preparatory Inorganic Chemistry', 2nd edn., Academic Press, New York, 1965, p. 1511.
6 G. Davies and A. R. Garafalo, *Inorg. Chem.*, *15*, 1103 (1976).
7 A. I. Vogel, 'Textbook of Quantitative Analysis', 3rd edn., Longman Green, London, 1982, p. 270.
8 B. Jaseliskis, *J. Am. Chem. Soc.*, *83*, 1082 (1961).
9 K. S. Klausen and O. E. Reuud, *Anal. Chim. Acta*, *57*, 351 (1971).
10 A. E. Martell and R. M. Smith, 'Critical Stability Constants', Vol. 'Amino Acids', Plenum, New York/London, 1974, p. 283.
11 D. G. Lambert and M. M. Jones, *J. Am. Chem. Soc.*, *88*, 4615 (1966).
12 N. Gupta, P. C. Nigam, R. M. Naik, *J. Ind. Chem. Soc.*, 25A, 39 (1986).

TABLE IV. Rate Constants for Various Stages of Reaction

Reaction	Experimental condition
(1) $[\mathrm{FeTTHA(OH)_2}]^{5-} + \mathrm{CN}^-$ $k_\mathrm{d} = 2.64 \times 10^{-4}\ \mathrm{s}^{-1}$ $k_4K_3K_2 = 2.79\ \mathrm{M}^{-3}\ \mathrm{s}^{-1}$	As in Table I
(2) $[\mathrm{FeHPDTA(OH)}]^{2-} + \mathrm{CN}^-$ $k_4 = 1 \times 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ $k_4K_3 = 0.11\ \mathrm{M}^{-2}\ \mathrm{s}^{-1}$ $k_4K_3K_2 = 1.91\ \mathrm{M}^{-3}\ \mathrm{s}^{-1}$	As in Table I
(3) $[\mathrm{Fe(CN)_5OH}]^{3-} + \mathrm{L}^{n-}$ L^{n-}: TTHA^{6-} $K_5^{-1}k_4 = 3.35 \times 10^{-8}\ \mathrm{s}^{-1}$ L^{n-}: $[\mathrm{HPDTA}]^{4-}$ $K_5^{-1}k_4 = 6.04 \times 10^{-8},\ \mathrm{s}^{-1}$	As in Table II
(4)[a] $[\mathrm{Fe(CN)_5OH}]^{3-} + \mathrm{CN}^-$ $k_2 = 3.62 \times 10^{-3},\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$[\mathrm{Fe(CN)_5OH^{3-}}] = 1 \times 10^{-4}$ M $[\mathrm{CN}^-] = (2.0\text{–}10.0) \times 10^{-2}$ M pH = 10.5 $I = 0.25$ M Temperature = 30 ± 0.1 ℃

[a] Taken from ref. 4.

13 A. G. Sharpe, 'The Chemistry of Cyano Complexes of Transition Metals', Academic Press, London, 1976, p. 106.

14 A. I. Vogel, 'Textbook of Macro and Micro Qualitative Inorganic Analysis', vth edn., Ovcent Longman Ltd., New Delhi, 1982, p. 321.

15 D. D. Perrin and I. G. Sayce, *Talanta, 14,* 833 (1967).

16 A. E. Martell, 'Stability Constants of Metal–Ion Complexes', Alden Press, Oxford, 1971, p. 53.

17 R. M. Naik and P. C. Nigam, *Transition Met. Chem., 10,* 220 (1985).

18 K. J. Laidler, 'Chemical Kinetics', 2nd edn., TMH Edition, New York, 1973, p. 220.

19 A. Frost and R. G. Pearson, 'Kinetics and Mechanism', Wiley, New York, 1961, Chap. 7.