Kinetics of Ethylenediamine Exchange in Pentacyano(ethylenediamine)-ferrate(II)

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Rate constants (k_{-1}) and activation parameters for the release of ethylenediamine (en) and monoprotonated ethylenediamine (Hen) co-ordinated to the $[Fe(CN)_5]^{3-}$ moiety are reported, together with the corresponding stability constants. The rates of formation (k_f) of the complexes have been evaluated indirectly. The results confirm previous predictions of a dissociative mechanism where the basicity of the ligand determines k_{-1}, whilst only the charge on the ligand effects k_f.

IN a previous paper [1] we described the properties of a salt containing the ion $[Fe(CN)_5(Hen)]^{2-}$ (Hen = monoprotonated unidentate ethylenediamine). As shown in the present work, this ion can be deprotonated at pH 10, thus providing an adequate system for studying the kinetics of exchange of en and Hen^+ in unidentate ethylenediamine complexes. The difference in reactivity between en and Hen^+ in the complex formation reactions with Cu^{2+} and Ni^{2+} has been studied by several workers.[2-4] In these labile systems, however, the rate of ring closure from the unidentate species is fast, and only chelate species $[M(en)]^{2+}$ and $[M(en)_2]^{2+}$ are characterized. The specific rates for the reaction M^{2+} + en are much higher than those for $M^{2+} + Hen^+$, the difference being attributed to the ring-closure stage. To our knowledge, the present is the first report of kinetic data on simple $M + en \rightleftharpoons [M(en)]$ and $M + Hen^+ \rightleftharpoons [M(Hen)]^+$ equilibria for unidentate ethylenediamine complexes.

The pentacyanoferrate(II) complexes of ammonia and methylamine have been previously studied.[5,6] A value of 4.8×10^4 dm^3 mol^{-1} for the stability constant of the amine complex at 25 °C and pH >7.7 was found.[5] This value is in reasonable agreement with the rate constant reported for the release of NH_3 from the complex, 1.75×10^{-2} s^{-1},[6] since typical values for the rate of substitution of various uncharged ligands are of the order of 3×10^2 dm^3 mol^{-1} s^{-1}; combining both figures, an estimate is obtained for the stability constant, which is of the same order of magnitude as the previously reported value.[5] The release of $NMeH_2$ is slower, $k = 2.9 \times 10^{-3}$ s^{-1}, the difference having been ascribed to the different basicity of NH_3 and $NMeH_2$.[6] As no large differences are expected between the rate constants for the reverse reactions,[7,8] the stability of the methylamine complex should be correspondingly higher.

We have made a study of the dissociation kinetics of en from $[Fe(CN)_5(Hen)]^{2-}$ in the range pH 7—12. This pH range proved suitable for fully characterizing the reactivity of both the protonated and deprotonated co-ordinated ethylenediamine. The results are compared with previous predictions [6] regarding basicity–rate constant relations, and with those related to the influence of the charge on the ligand.[8] The kinetic data were supplemented by a determination of the stability constants for both complexes and thus the rates of substitution of en and Hen^+ on $[Fe(CN)_5(OH_2)]^{3-}$ could be estimated indirectly.

EXPERIMENTAL

All chemicals employed were analytical reagents. The salt $Na_2[Fe(CN)_5(Hen)]\cdot 6H_2O$ was prepared as described previously.[1]

Kinetics.—The rate of formation of either $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_5(py)]^{3-}$ from $[Fe(CN)_5(Hen)]^{2-}$ and CN^- or pyridine was measured on a Spectronic 600E spectrophotometer in a thermostatted optical cell, following in the first case the decrease in absorbance at 402 nm {maximum of $[Fe(CN)_5(Hen)]^{2-}$, ε 475 dm^3 mol^{-1} cm^{-1}}, and in the second case the increase in absorbance at 365 nm {maximum [9] of $[Fe(CN)_5(py)]^{3-}$, ε 3 720 dm^3 mol^{-1} cm^{-1}}. Measurements were made in the range pH 7—12, using either borax–potassium dihydrogenphosphate or –sodium carbonate buffers. The ionic strength was maintained at I = 1 mol dm^{-3} through the addition of sodium perchlorate. Runs were performed in the range 10—30 °C.

Equilibrium Competition Studies.—Adequate amounts (*ca.* 10 mg per 100 cm^3) of $Na_2[Fe(CN)_5(Hen)]\cdot 6H_2O$ were dissolved in a solution containing known amounts of en, Hen^+, and pyridine, together with sufficient $Na[ClO_4]$ to ensure I = 1 mol dm^{-3}. In the case of measurements close to the pK_a value of Hen^+ (10), the pH was fixed by the relative amounts of en and Hen^+. At lower alkalinities, the above buffers were used. Spectral changes at 365 nm were followed at 25 °C until equilibrium was attained. The concentration of $[Fe(CN)_5(py)]^{3-}$ was calculated from its molar absorption coefficient, and the difference from its initial concentration was attributed to $[Fe(CN)_5(Hen)]^{2-}$. When necessary, corrections were made to take into account the absorption of this latter ion at 365 nm (ε 230 dm^3 mol^{-1} cm^{-1}).

RESULTS AND DISCUSSION

Table 1 contains the pseudo-first-order rate constants, $k_{obs.}$, obtained at various pyridine concentrations and pH

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values for several temperatures, corresponding to reaction (1). Values obtained at pH 10.7 for reaction (1) with cyanide ion are shown in Table 2. In the whole range of pH studied, $k_{\mathrm{obs.}}$ showed the same dependence on the concentration of the incoming ligand as found by

TABLE 1

Rate constants, $k_{\mathrm{obs.}}$, at various pyridine concentrations, pH, and temperatures; $I = 1.0$ mol dm^{-3} (Na[ClO$_4$])

θ_c/°C	10[py]/ mol dm^{-3}	pH	$10^3k_{\mathrm{obs.}}$/s^{-1}
10.0	1.0	7.2	1.08
14.0	1.0	7.2	1.16
20.0	1.0	7.2	6.35
25.0	1.0	7.2	10.4
30.0	1.0	7.0	19.7
25.0	1.0	8.0	10.2
25.0	1.0	9.0	9.79
25.0	1.0	9.5	8.70
25.0	1.0	9.8	8.07
25.0	1.0	10.0	7.53
25.0	1.0	10.7	5.83
25.0	1.0	11.2	5.59
25.0	1.0	11.8	5.46
25.0	1.0	12.7	5.95
25.0	0.01	11.8	3.25
25.0	0.005	11.8	2.90
25.0	1.4	7.2	10.4
25.0	0.5	7.2	10.1
25.0	0.1	7.2	9.79
25.0	0.05	7.2	9.77
25.0	0.02	7.2	8.40
25.0	0.01	7.2	7.1
25.0	0.005	7.2	5.3

TABLE 2

Rate constants, $k_{\mathrm{obs.}}$, at various Na[CN] concentrations and temperatures; $I = 1.0$ mol dm^{-3} (Na[ClO$_4$]), and pH 10.7

θ_c/°C	10^2[NaCN]/mol dm^{-3}	$10^3k_{\mathrm{obs.}}$/s^{-1}
10.0	1.00	0.307
	7.51	0.560
	20.0	0.595
	50.2	0.602
15.0	50.2	1.28
20.0	1.00	1.21
	7.51	2.16
	20.0	2.46
	50.2	2.45
25.0	0.51	3.20
	1.03	3.00
	8.24	4.37
	15.2	4.50
	20.0	4.62
	30.7	5.00
	39.9	5.10
	50.2	5.15

$$[\mathrm{Fe(CN)_5(en)}]^{3-} + \mathrm{py} \longrightarrow [\mathrm{Fe(CN)_5(py)}]^{3-} + \mathrm{en} \qquad (1)$$

previous workers[8-10] for other $[\mathrm{Fe(CN)_5L}]^{(3-n)-}$ ions, reacting with either cyanide, methylpyrazinium, or other ligands. This has been interpreted as proof that the dissociative mechanism in equations (2) and (3) is operative,

$$[\mathrm{Fe(CN)_5L}]^{(3-n)-} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [\mathrm{Fe(CN)_5}]^{3-} + \mathrm{L}^n \qquad (2)$$

$$[\mathrm{Fe(CN)_5}]^{3-} + \mathrm{L}'^m \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Fe(CN)_5L'}]^{(3-m)-} \qquad (3)$$

where the charge born by the ligands L and L′ can be positive, zero, or negative.

In fact, the mechanism can be either dissociative or of the dissociative-interchange type (D or I_d), using the terminology of Langford and Gray.[11] Equilibrium (4),

$$[\mathrm{Fe(CN)_5}]^{3-} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Fe(CN)_5(OH_2)}]^{3-} \qquad (4)$$

although kinetically irrelevant, is displaced far to the right; moreover, it is also probable that $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$ is generated in a single concerted step, formally equal to reactions (2) + (4), the activation energy of which is independent of the nature of the incoming ligand (see, however, ref. 8). In this scheme, $k_{\mathrm{obs.}} = k_{-1}k_2[\mathrm{L}'^m]/k_1[\mathrm{L}^n] + k_2[\mathrm{L}'^m]$, which simplifies to $k_{\mathrm{obs.}} = k_{-1}$ in the saturation plateau of Figure 1.

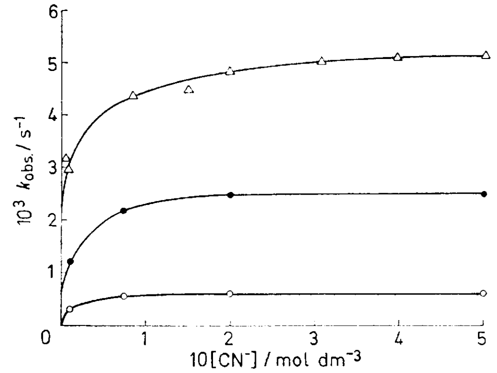

FIGURE 1 Variation of $k_{\mathrm{obs.}}$ with [CN$^-$] at various temperatures ($I = 1$ mol dm^{-3}, pH 10.7): (△), 25.0; (●), 20.0; and (○), 10.0 °C

Our own data on the present system are wholly consistent with the foregoing mechanism, as shown by the constancy of $k_{\mathrm{obs.}}$ in the saturation region, even when cyanide is substituted for pyridine, and also by the linearity of the plot of $(1/k_{\mathrm{obs.}})$ against (1/[L]) at constant ethylenediamine concentration (Figure 2). The new feature appearing in our system is the dependence of the rate constant on pH, shown in Figure 3 for $k_{\mathrm{obs.}}$ in the saturation plateau, *i.e.* for k_{-1}. We have interpreted the data in Figure 3 by means of the reaction scheme in equations (5)—(7), followed by reaction (3), where

$$[\mathrm{Fe(CN)_5(Hen)}]^{2-} \xrightarrow{k_{\mathrm{H}}} [\mathrm{Fe(CN)_5}]^{3-} + \mathrm{Hen}^+ \qquad (5)$$

$$[\mathrm{Fe(CN)_5(Hen)}]^{2-} \overset{K_{\mathrm{A}}}{\rightleftharpoons} [\mathrm{Fe(CN)_5(en)}]^{3-} + \mathrm{H}^+ \qquad (6)$$

$$[\mathrm{Fe(CN)_5(en)}]^{3-} \xrightarrow{k_0} [\mathrm{Fe(CN)_5}]^{3-} + \mathrm{en} \qquad (7)$$

L′ = CN$^-$ or py. According to this scheme, the dependence of k_{-1} on [H$^+$] should be as in equation (8). A

$$k_{-1} = (k_{\mathrm{H}}[\mathrm{H}^+] + k_0K_{\mathrm{a}})/([\mathrm{H}^+] + K_{\mathrm{a}}) \qquad (8)$$

good fit of equation (8) to the data in Figure 3 was obtained by using $k_{\mathrm{H}} = 1.04 \times 10^{-2}$ s^{-1} (*i.e.* the maximum

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[10] Z. Bradic, D. Pavlovic, I. Murati, and S. Asperger, *J.C.S. Dalton*, 1974, 344.

[11] C. Langford and H. B. Gray, ' Ligand Substitution Processes,' W. A. Benjamin, New York, 1965.

value, at high acidities), $k_0 = 5.60 \times 10^{-3}$ s^{-1} (*i.e.* the constant value ensuing at high pH), and pK_a 10.

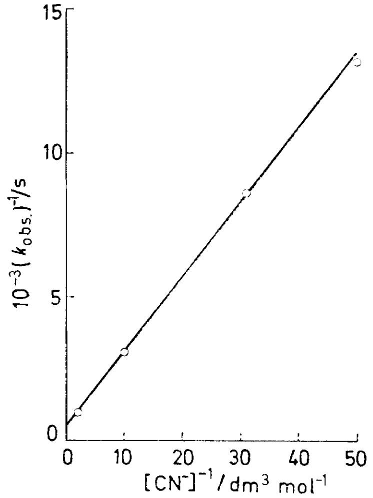

FIGURE 2 Variation of $(1/k_{obs.})$ with $1/[CN^-]$ at 25 °C, $I = 1$ mol dm^{-3}, pH 10.7, and [en] = 0.1 mol dm^{-3} (Data presented are not included in Table 2.)

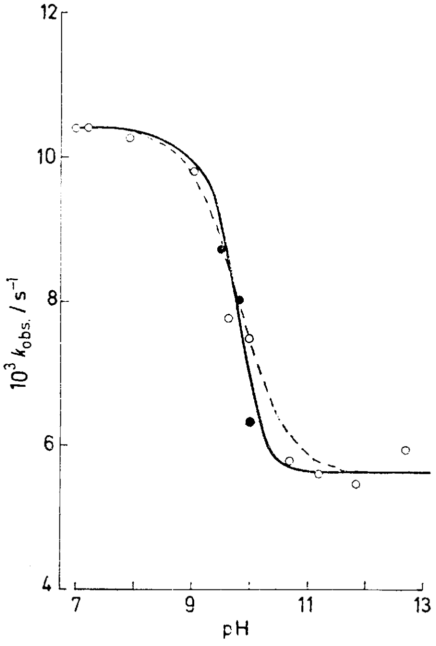

FIGURE 3 Variation of $k_{obs.}$ with pH at 25 °C and $I = 1$ mol dm^{-3}: (○), [py] = 0.1 mol dm^{-3}; (●), [CN$^-$] = 0.5 mol dm^{-3}; (——), experimental; (— — —), calculated from equation (8)

We also attempted to measure the pK_a of the reacting ion at 25 °C and $I = 1$ mol dm^{-3} by potentiometric titration, obtaining a value of *ca.* 10.5; the origin of the discrepancy is not clear, although the poor definition of the inflection point casts some doubt on the latter value. As shown below, the results of the equilibrium competition studies also point to a pK_a of *ca.* 10 under our experimental conditions. In fact, any change in acidity of the ligand on co-ordination should show up as a corresponding change in the stability constants of $[Fe(CN)_5(Hen)]^{2-}$ (K_H) and $[Fe(CN)_5(en)]^{3-}$ (K_0), as these are related through equation (9). We measured K_H and

$$K_0/K_H = K_a \text{ (co-ordinated en)}/K_a \text{ (free en)} \quad (9)$$

K_0 at several pH values and $I = 1$ mol dm^{-3} using the procedure described in the Experimental section. Table 3 shows the results thus obtained. The equilibrium constant is approximately independent of pH; only at pH < 8, when the equilibrium $H_2en^{2+} \rightleftharpoons Hen^+ + H^+$ begins to be important, was there an apparent marked decrease in the stability of the Hen$^+$ complex relative to the py complex. Using the reported value[7] for the stability constant of the pyridine complex, the values for K_H and K_0 in Table 3 were calculated. These values are similar to those of the ammonia and methylamine complexes.

TABLE 3

Composition of equilibrium mixtures of pyridine and ethylenediamine complexes at various pH and at 25 °C

pH	[py]	[en]	$[Fe(CN)_5(py)^{3-}]/$	10^4K *
	mol dm^{-3}		$[Fe(CN)_5\{(H)en\}^{n-}]$	mol dm^{-3}
10.7	0.147	0.985	1.10	4.4
9.0	0.100	0.630	1.30	4.0
8.0	0.120	0.746	1.35	3.9

* Stability constant for the ethylenediamine complex, $([Fe(CN)_5\{(H)en\}^{n-}]/[Fe(CN)_5(py)^{3-}])([py]/[en])K_{py}$, where the stability constant for the pyridine complex $K_{py} = 3.3 \times 10^5$ mol dm^{-3}.

In our media, the pK_a of free Hen$^+$ at 25 °C was found to be 9.9, which is close to other literature values {*e.g.* pK_a 9.98 (Hen$^+$) and 7.28 (H_2en^{2+}), in 0.5 mol dm^{-3} $K[NO_3]$}.[12] Thus, equation (9) would predict a pK_a for co-ordinated Hen$^+$ of *ca.* 9.9, in good agreement with the kinetic data. It should be pointed out that the predicted pK_a is not very sensitive to small differences between K_0 and K_H; a factor of 2 between the stability constants would amount to a shift of 0.3 units in pK_a.

Rate Constants for Dissociation of the Protonated and Deprotonated Complexes (k_H *and* k_0).—In Table 4 we show the values of k_{-1} for various amines, together with the corresponding activation parameters. The data for en and Hen$^+$ were calculated from Eyring plots in the range 10—30 °C. Both ligands may be placed between NH_3 and $NMeH_2$, as far as k_{-1} at 25 °C is concerned.

Toma and Malin[6] assumed that the only relevant factor in defining the value of k_{-1} was the basicity of the ligand, and proposed the relation $k_{-1} = A - B\text{p}K_a$, where p$K_a$ refers to the conjugate acid. The agreement of the rate constant found for en is reasonable; however, the precision of the data and the changes in pK_a in the various media do not warrant a more detailed analysis. On the other hand, the influence of charge on the rate constant k_{-1} can be placed on an approximately quantitative basis by using the above relation to estimate the expected rate constant for an uncharged amine with a conjugate acid having pK_a 7.3 (*i.e.* the value for H_2en^{2+}).

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[12] A. Vacca and D. Arenave, *J. Phys. Chem.*, **1967**, **71**, 1495.

The expected rate constant is 3.8×10^{-2} s^{-1}, which is 3.6 times larger than the experimental value.

From the data in Table 4 it can be seen that k_H is higher than k_0 because of a larger $\Delta S^\ddagger[\Delta(\Delta S^\ddagger) = 13$ J K^{-1} mol^{-1}]. Although probably not much higher than the precision of the data (see for instance ref. 13), we feel that the difference $\Delta(\Delta S^\ddagger)$ is significant, and it is highly suggestive that this value lies close to the change of entropy accompanying protonation of free ethylenediamine, which is 14.2 J K^{-1} mol^{-1} when corrected for statistical weight.[12] This parallelism has been proposed as a diagnostic tool for dissociative mechanisms.[13] It is also possible that this difference implies the existence of an intramolecular hydrogen bond between the co-ordinated Hen$^+$ and cyanide. This is akin to the intramolecular proton-transfer mechanism proposed for the aquation of $[Cr(CN)(OH_2)_5]^{2+}$ and related complexes.[13,14]

TABLE 4

Kinetic parameters for the release of various ligands

Outgoing ligand	10^4k_{-1} [a] / s^{-1}	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}	Ref.
Nitrosobenzene	0.016	*ca.* 118	*ca.* 42	*b*
Sulphite	0.57	*ca.* 120	*ca.* 76	*c*
Dimethyl sulphoxide	0.75	111	46	*d*
N-Methyl-pyrazinium	2.8	115	75	9
Pyrazine	4.2	111	59	9
4,4′-Bipyridine	6.2	111	67	9
Isonicotinamide	7.3	109	59	9
Pyridine	11.0	104	46	9
4-Methylpyridine	11.5	100	38	9
NN-Dimethyl-*p*-nitrosoaniline	12.0			8
Methylamine	29.0	96	29	6
Ethylenediamine (en)	51.5	97	38	*e*
Hen$^+$	104	100	50	*e*
Ammonia	175	93	33	6

[a] At 25 °C. [b] Calculated from data at 25 and 50 °C (ref. 7 and D. Pavlovic, I. Murati, and S. Asperger, *J.C.S. Dalton*, 1973, 602). [c] Calculated from data at 25 and 43 °C (refs. 7 and 10). [d] H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, 1973, **12**, 2084. [e] This work.

Second-order Rate Constants (k_f) *for the Reaction of* en *and* Hen$^+$ *with* $[Fe(CN)_5(OH_2)]^{3-}$.—Bradic *et al.*[8] have already pointed out that the only factor relevant to the rate of formation of the various $[Fe(CN)_5L]^{n-}$ complexes from $[Fe(CN)_5(OH_2)]^{3-}$ is the charge on the incoming ligand. Thus $k_f(SO_3^{2-}) < k_f(CN^-) < k_f$(neutral amines) $< k_f$(methylpyrazinium ion). On these grounds, we would expect values of *ca.* 3×10^2 dm^3 mol^{-1} s^{-1} for k_f(en) and *ca.* 5.5×10^2 dm^3 mol^{-1} s^{-1} for k_f(Hen$^+$). These expectations are surprisingly close to the values obtained by combining the respective k_{-1} with the stability constant K, *i.e.* $k_f(\text{en}) = 3.3 \times 10^2$ dm^3 mol^{-1} s^{-1} and $k_f(\text{Hen}^+) = 6.2 \times 10^2$ dm^3 mol^{-1} s^{-1}. This is strong evidence in favour of the contention of Bradic *et al.*[8] These calculations are equivalent to evaluating the competition factors $k_1(\text{Hen}^+)/k_1(\text{L})$ and $k_1(\text{en})/k_1(\text{L})$, where L = py or CN$^-$. This can also be done from the plots of $(1/k_{obs.})$ against $(1/[L])$ (Figure 2). For L = CN$^-$, the expected competition factors are *ca.* 15 and 9, whilst the actual values obtained are 18 and 12.

The second-order rate constants, k_f, are directly related to the respective k_1 values through equation (10),[8] where

$$k_f = k_1K_{H_2O} \qquad (10)$$

K_{H_2O} is the equilibrium constant for reaction (11).

$$[Fe(CN)_5(OH_2)]^{3-} \rightleftharpoons [Fe(CN)_5]^{3-} + H_2O \qquad (11)$$

Equation (10) predicts that the k_f values should be sensitive only to factors affecting the process embodied in k_1, which has been proposed to be diffusion controlled.[7,8]

Protonation of Co-ordinated Cyanide.—Complexes of the $[Fe(CN)_5]^{3-}$ moiety with aromatic amines undergo reversible protonation at cyanide at low pH.[9] Attempts to observe protonation of $[Fe(CN)_5(Hen)]^{2-}$ in acidic solutions failed, as decomposition of the complex ensues at pH < 5, apparently with release of co-ordinated cyanide. However, this phenomenon is indicative that protonation might take place, resulting in labilization of cyanide as HCN (*cf.* ref. 13). Furthermore, solutions of $[Fe(CN)_5(Hen)]^{2-}$ salts are alkaline, and this fact can be explained only if protonation on cyanide takes place, with a pK_a of the order of 5 or higher. It is also suggestive that in the thermal decomposition of $Na_2[Fe(CN)_5(Hen)]\cdot6H_2O$,[15] ethylenediamine release is followed, at *ca.* 200 °C, by release of HCN, indicating probably a prior proton transfer from Hen$^+$ to co-ordinated cyanide.

Conclusions.—The origin of the relatively high stability of the Hen$^+$ complex with respect to the NH_3 complex is seen to be traced to changes both in k_1 and k_{-1} arising from the positive charge of the ligand, which overcomes the predicted decrease in stability due to the lower basicity. The activation entropy of step (2) (k_{-1}) for en and Hen$^+$ gives some support to the idea that intramolecular hydrogen bonding can be an important factor in the latter case. As a result of the balance of charge and basicity effects, the stabilities of the complexes of en and Hen$^+$ are similar, and thus the acidity of Hen$^+$ co-ordinated to the $[Fe(CN)_5]^{3-}$ moiety is similar to that of free Hen$^+$. This is different from the case of positively charged complex ions containing Hen$^+$, *e.g.* *cis*-$[CoCl(en)_2(Hen)]^{2+}$; in this case the pK_a of co-ordinated Hen$^+$ is sensibly lower, lying closer to that of free H_2en^{2+}.[16]

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