Substitution Reactions of Di-μ-cyano-bis[tetracyanoferrate(II)] in Aqueous Solution

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Data obtained in a kinetic investigation of the substitution reactions of the binuclear complex ion $[Fe^{II}_2(CN)_{10}]^{6-}$ by X [X = HCN, pyridine (py), and 4-methylpyridine (Mepy)] support the stepwise mechanism in equations (i)—(v)

$$[(NC)_4Fe^{II}(CN)(NC)Fe^{II}(CN)_4]^{6-} + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [(NC)_5Fe^{II}(NC)Fe^{II}(CN)_4(OH_2)]^{6-} \quad \text{(i)}$$

$$[Fe^{II}_2(CN)_{10}(OH_2)]^{6-} + H_2O \xrightarrow{k_9} 2[Fe^{II}(CN)_5(OH_2)]^{3-} \quad \text{(ii)}$$

$$[Fe^{II}_2(CN)_{10}(OH_2)]^{6-} + X \xrightarrow{k_7} [Fe^{II}_2(CN)_{10}X] + H_2O \quad \text{(iii)}$$

$$[Fe^{II}_2(CN)_{10}X] + H_2O \xrightarrow{k_{2X}} [Fe^{II}(CN)_5X] + [Fe^{II}(CN)_5(OH_2)]^{3-} \quad \text{(iv)}$$

$$[Fe^{II}(CN)_5(OH_2)]^{3-} + X \xrightarrow{k_{1X}} [Fe^{II}(CN)_5X] \quad \text{(v)}$$

At 25 °C, $k_3 = (1.25 \pm 0.5) \times 10^{-3}$ s^{-1}, $k_{-3} = 0.165 \pm 0.035$ s^{-1}, $k_{2HCN} = (1.81 \pm 0.07) \times 10^{-3}$ s^{-1}, $k_{7HCN} = 34 \pm 8$ dm^3 mol^{-1} s^{-1}, $k_{7py} = 10 \pm 3$ dm^3 mol^{-1} s^{-1}, and $k_{7Mepy} = 9 \pm 2$ dm^3 mol^{-1} s^{-1}; $\Delta H_3^‡$, $\Delta H_{2HCN}^‡$, $\Delta S_3^‡$, and $\Delta S_{2HCN}^‡$ are 99 ± 4 kJ mol^{-1}, 92 ± 4 kJ mol^{-1}, 52 ± 16 J K^{-1} mol^{-1}, and 31 + 12 J K^{-1} mol^{-1}.

'AQUAPENTACYANOFERRATE(II)' prepared according to Hoffmann[1] has been shown to be dimeric[2] and is oxidised by two one-equivalent steps. One-equivalent oxidation yields a green complex which has an intense absorption in the near-i.r. spectrum ($\lambda_{max.}$ 1 200 nm; ε 10^4 dm^3 mol^{-1} cm^{-1})[2] and a second one-equivalent oxidation gives the purple species $[Fe^{III}_2(CN)_{10}]^{4-}$ ($\lambda_{max.}$ 560 nm; ε 1 600 dm^3 mol^{-1} cm^{-1}).[3] The u.v. and visible spectra of $[Fe^{II}_2(CN)_{10}]^{6-}$ and $[Fe^{III}_2(CN)_{10}]^{4-}$ are similar[2,4] to those of the singly bridged binuclear complexes $[Fe^{II}_2(CN)_{11}]^{7-}$ and $[Fe^{III}_2(CN)_{11}]^{5-}$.

The structure proposed[5] for $[Fe^{II}_2(CN)_{10}]^{6-}$, *i.e.* $[(NC)_4Fe(CN)(NC)Fe(CN)_4]^{6-}$, requires two non-linear cyano-bridges. A recent structure determination of $[(H_3N)_5Co^{III}(CN)Co^{III}(CN)_5]$ has shown[6] that even in singly bridged complexes the deviation from linearity of the bridging cyanide can be as much as 28°.

Our aim was to investigate the substitution reactions of $[Fe^{II}_2(CN)_{10}]^{6-}$ with pyridine (py), 4-methylpyridine (Mepy), and HCN, in the hope that evidence could be obtained for singly bridged intermediates, the presence of which would be evidence for the doubly bridged structure proposed for $[Fe^{II}_2(CN)_{10}]^{6-}$. The substituents HCN, Mepy, and py were chosen since reaction (1) is

$$[Fe^{II}(CN)_5(OH_2)]^{3-} + X \underset{k_{-1X}}{\overset{k_{1X}}{\rightleftharpoons}} [Fe^{II}(CN)_5X]; \; K_{1X} = k_{1X}/k_{-1X} \quad (1)$$

very rapid with $k_{1X} = 344$, 365, and 355 dm^3 mol^{-1} s^{-1} respectively and the equilibrium is well to the right with $K_{1X} = 1.0 \times 10^{10}$, 3.3×10^5, and 3.1×10^5 dm^3 mol^{-1} for X = HCN, Mepy, and py respectively.[7,8] It will be shown that, under our conditions, the back reaction of (1) can be ignored. A further advantage of HCN as a substituent is that a possible intermediate species $[Fe_2(CN)_{11}]^{7-}$ can be prepared directly and its reaction with HCN may be followed independently.

EXPERIMENTAL

All chemicals were AnalaR grade except 4-methylpyridine (Hopkin and Williams, General purpose reagent), NaCN (B.D.H., Laboratory reagent grade), and $Na_2[IrCl_6]\cdot 4H_2O$ (Johnson, Matthey). Water was doubly distilled. Solutions of $Na[ClO_4]$ were standardised by passing samples down an ion-exchange column (Amberlite IR 120) in the acid form and titrating the effluent with standard sodium hydroxide solution.

Samples of $Na_4[Fe^{III}_2(CN)_{10}]\cdot 8H_2O$ were prepared by the oxidation[3] of solutions of $Na_6[Fe^{II}_2(CN)_{10}]$ by Br_2 (Found: C, 19.8; H, 3.7; Fe, 18.0; N, 22.5. $Na_4[Fe^{III}_2(CN)_{10}]\cdot 8H_2O$ requires C, 19.7; H, 2.7; Fe, 18.4; N, 23.0%). The visible spectrum of the iron(III) complex showed a maximum at 560 nm (ε 1 650 ± 50 dm^3 mol^{-1} cm^{-1}), and the i.r. spectrum of a sample in aqueous solution had bands at 2 123 and 2 160 cm^{-1}. It was found that unless the original samples of $Na_6[Fe^{II}_2(CN)_{10}]$ were purified by passage through a Sephadex G25 chromatography column prior to oxidation, the test solutions of $[Fe^{II}_2(CN)_{10}]^{6-}$, which were prepared by reduction of solutions of the iron(III) dimer with ascorbic acid, reacted with all three substituents in two stages. An initial fast reaction ($t_{\frac{1}{2}}$ *ca.* 60 s at 25 °C) accounted for up to 30% of the total absorbance change and was independent of both the concentration and nature of the substituent. This rapid initial reaction was reduced to *ca.* 7% of the total absorbance change when the samples of $Na_6[Fe^{II}_2(CN)_{10}]$ were produced by reduction of solutions of $Na_4[Fe^{III}_2(CN)_{10}]$ which had been prepared from purified samples of $[Fe^{II}_2(CN)_{10}]^{6-}$.

Samples of $Na_7[Fe^{II}_2(CN)_{11}]$ were obtained by reduction

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[1] K. A. Hoffmann, *Annalen*, 1900, **312**, 1.

[2] C. K. Jørgenson and G. Emschwiller, *Chem. Phys. Letters*, 1970, **5**, 561.

[3] J. Espenson and S. P. Wolenuck, *Inorg. Chem.*, 1972, **11**, 2034.

[4] A. D. James and R. S. Murray, unpublished work.

[5] G. Emschwiller, *Compt. rend.*, 1967, **265**, 281.

[6] F. R. Fronczck and W. F. Schaefer, *Inorg. Chem.*, 1974, **13**, 727.

[7] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2084.

[8] A. D. James and R. S. Murray, *J.C.S. Dalton*, 1975, 1530.

of solutions of $Na_5[Fe^{III}_2(CN)_{11}]$ with ascorbic acid. The latter complex was obtained by allowing a solution of $Na_4[Fe^{II}(CN)_6]\cdot 10H_2O$ (2 g) and $Na_3[Fe^{II}(CN)_5(NH_3)]$ (2 g) to equilibrate for *ca.* 10 min at 25 °C before adding a slight excess of Br_2. The purple dimer was separated from the monomeric species on a Sephadex column, evaporated to dryness in a rotary evaporator, and further dried *in vacuo* over $CaCl_2$. The product is hygroscopic (Found: C, 22.0; Fe, 19.6; N, 26.7. $Na_5[Fe^{III}_2(CN)_{11}]\cdot 4H_2O$ requires C, 21.1; Fe, 19.4; N, 26.9%). Better yields of $Na_5[Fe^{III}_2(CN)_{11}]$ were obtained by using a ten-fold excess of $Na_4[Fe^{II}(CN)_6]$ compared to $Na_3[Fe^{II}(CN)_5(NH_3)]$, and by adjusting the pH of the solution to *ca.* 4 prior to the addition of Br_2.

The reactions of $[Fe^{II}_2(CN)_{10}]^{6-}$ with HCN, py, and Mepy were followed spectrophotometrically at 400, 390, and 390 nm respectively {ε 600 and 700 $dm^3 mol^{-1} cm^{-1}$ for $[Fe^{II}_2(CN)_{10}]^{6-}$ at 400 and 390 nm respectively; ε 3 330 and 2 070 $dm^3 mol^{-1} cm^{-1}$ at 390 nm for $[Fe^{II}(CN)_5(py)]^{3-}$ and $[Fe^{II}(CN)_5(Mepy)]^{3-}$ respectively}. The substitution reaction of $[Fe^{II}_2(CN)_{11}]^{7-}$ by HCN was followed spectrophotometrically at 390 nm {ε 800 $dm^3 mol^{-1} cm^{-1}$ for $[Fe^{II}_2(CN)_{11}]^{7-}$}. Optical-density measurements were made using Unicam SP 800 and SP 600 spectrophotometers. Measurements of pH were made using a Radiometer 26 meter.

RESULTS

Substitution of $[Fe^{II}_2(CN)_{10}]^{6-}$ *by* HCN *and* $[CN]^-$.—Repeat scan spectra of reaction mixtures {$[Fe^{II}_2(CN)_{10}{}^{6-}] = 3 \times 10^{-4}$ mol dm^{-3}, [HCN] = 0.02—0.1 mol dm^{-3}, $I = 1.00$ mol dm^{-3}, pH 6.8, and 25 °C} in the 325—500 nm region, over a period of two reaction half-times, showed a sharp isosbestic point at 348 nm, as expected if $[Fe(CN)_6]^{4-}$ and $[Fe^{II}_2(CN)_{10}]^{6-}$ are the only absorbing species. There was no spectral evidence for the formation of $[Fe^{II}_2(CN)_{11}]^{7-}$, the expected intermediate at 390 nm.

Plots of $\ln(A_t - A_\infty)$ against time for absorbance measurements (A) at 400 nm were linear for at least 85% completion of reaction for data obtained at 25, 30, and 40 °C. Linear plots were also obtained for data at lower temperatures where the reaction was followed for *ca.* 1—2 half-times. Values of the first-order rate constants k_{obs} {where $-d[Fe^{II}_2(CN)_{10}]^{6-}]/dt = k_{obs.}[Fe^{II}_2(CN)_{10}]^{6-}$} are given in Table 1. At high concentrations of HCN, $k_{obs.}$ approached a limiting value. Plots of $k_{obs.}{}^{-1}$ against $[HCN]^{-1}$ were linear when [HCN] > 1×10^{-3} mol dm^{-3} (Figure 1) and the gradients and intercepts of these plots at various temperatures are given in Table 2.

TABLE 1

Kinetic data for the reaction of $[Fe^{II}_2(CN)_{10}]^{6-}$ with HCN, py, and Mepy at pH 6.8 ± 0.1 and I = 1.0 mol dm^{-3} ($Na[ClO_4]$) [a]

θ_c/°C	[X]/mol dm^{-3}	$10^5[Fe^{II}_2(CN)_{10}{}^{6-}]$/mol dm^{-3}	$10^4 k_{obs.}$/s^{-1}
(*a*) X = HCN			
25.0	0.136	6	14
	0.057 2	7.5	11.8 [b]
	0.032 7	15	10.5
	0.022 7	15	10.5
	0.016 4	7.5	10.3
	0.011 8	15	8.8
	0.011 4	7.5	8.5
	0.008 0	7.5	8.3
	0.004 86	7.5	6.0
	0.003 24	7.5	5.1
	0.002 73	6	4.4
	0.002 36	10	3.6
	0.001 58	6	2.9
	0.001 18	7.5	2.3
	0.000 72	7.5	1.9
	0.000 24	7.5	1.5
10.0	0.139	5	1.5
	0.026 7	5	1.05
	0.014 5	7.5	0.85
	0.008 9	7.5	0.75
	0.004 93	6	0.62
	0.003 87	5	0.55
	0.001 73	7.5	0.23
	0.001 18	7.5	0.18
	0.000 75	7.5	0.15
	0.000 25	7.5	0.117
15.0	0.139	3.7	3.2
	0.014 4	5	2.2
	0.008 9	5	1.8
	0.004 9	5	1.4
	0.003 9	5	1.2
20.0	0.139	3.5	6.7
	0.139	7.5	5.8
	0.014 4	5	4.5
	0.014 4	2.5	5.0
	0.008 9	4	3.5
	0.006 6	5	3.7
	0.004 5	5	3.0
	0.003 9	5	2.5
	0.002 8	3.5	2.1
30.0	0.139	5	24
	0.014 4	5	15
	0.008 9	5	13
	0.004 9	3.5	10.7
	0.003 9	5	9.2
	0.002 73	5	7.3
40.0	0.139	2.5	86
	0.014 4	2.5	58
	0.008 9	3.5	51
	0.004 9	3.5	33
	0.003 9	3.5	28
(*b*) X = py			
25.0	0.100	15	13.3
	0.100	15	13.6
	0.100	2.5	14.0
	0.050	15	13.0
	0.050	2.5	12.9
	0.025	2.5	11.0
	0.025	15	10.3
	0.017 5	15	9.4
	0.012 5	15	8.3
	0.012 5	2.5	7.9
	0.010 0	2.5	7.1
	0.007 5	30	5.1
	0.007 5	5	5.1
	0.007 5	3.5	5.9
(*c*) X = Mepy			
25.0	0.027 7	5	8.2
	0.020 8	5	9.7
	0.016 7	5	6.7
	0.013 9	3	5.6
	0.010 9	5	5.3
	0.007 6	10	4.2
	0.004 0	5	2.7

[a] Solutions contained 0.8 mol dm^{-3} $Na[ClO_4]$ and phosphate buffer ($[Na^+]_T$ = *ca.* 0.92 mol dm^{-3}. [b] [Ascorbic acid] = 7×10^{-4} mol dm^{-3}; in all other runs [Ascorbic acid] = *ca.* 5×10^{-3} mol dm^{-3}.

Some kinetic runs were carried out at very low concentrations of HCN (<2.36×10^{-3} mol dm^{-3}; the last five entries in Table 1 for data at 25 °C), and for these runs a plot of $k_{obs.}$ against [HCN] was linear with an intercept at [HCN] = 0 of $(1.22 \pm 0.07) \times 10^{-4}$ s^{-1}. The variation of

$k_{obs.}$ with changes in pH at constant cyanide concentration ([HCN] + [CN$^-$] = 0.207 mol dm^{-3}) is shown in Figure 2.

Substitution of $[Fe^{II}_2(CN)_{10}]^{6-}$ *by* py *and* Mepy.—Plots of $\ln(A_\infty - A_t)$ against time were linear for at least 80% completion of reaction for data obtained at 390 nm, and the values of $k_{obs.}$ derived from the gradients of these plots are given in Table 1. Plots of $k_{obs.}^{-1}$ against $[py]^{-1}$ and $k_{obs.}^{-1}$ against $[Mepy]^{-1}$ were linear (Figure 1) and the gradients and intercepts of these graphs are given in Table 2.

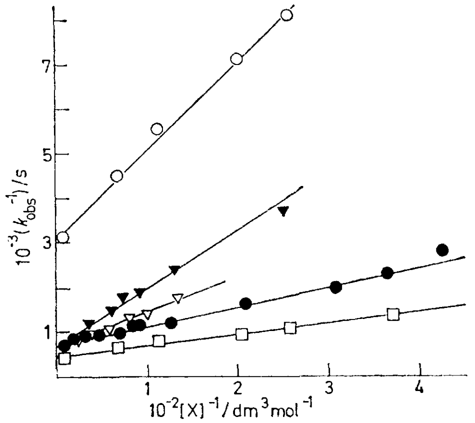

FIGURE 1 Plots of $k_{obs.}^{-1}$ against $[X]^{-1}$. X = HCN, 15 °C (○); Mepy, 25 °C (▼); py, 25 °C (▽); HCN 25 °C (●); HCN 30 °C (□)

TABLE 2

Data obtained from plots of $k_{obs.}^{-1}$ against $[X]^{-1}$

X	$\frac{\theta_c}{°C}$	$\frac{\text{Intercept}}{s}$	$\frac{\text{Gradient}}{\text{mol dm}^{-3}\,s^{-1}}$	$\frac{10^3k_3}{s^{-1}}$
py	25	590 ± 50	9.2 ± 0.5	1.7 ± 0.1
Mepy	25	690 ± 50	12.6 ± 0.5	1.45 ± 0.13
HCN	25	800 ± 30	3.78 ± 0.06	1.25 ± 0.05 *
HCN	10	7 740 ± 720	42.2 ± 4.3	0.130 ± 0.013 *
HCN	15	3 090 ± 204	19.2 ± 0.9	0.32 ± 0.02 *
HCN	20	1 550 ± 108	8.54 ± 0.62	0.64 ± 0.03 *
HCN	30	450 ± 30	2.50 ± 0.02	2.20 ± 0.16 *
HCN	40	103 ± 7	9.48 ± 0.35	9.7 ± 0.7 *

* From these data, $\Delta H_3^‡ = 99 \pm 4$ kJ mol^{-1} and $\Delta S_3^‡ = 52 \pm 16$ J K^{-1} mol^{-1}.

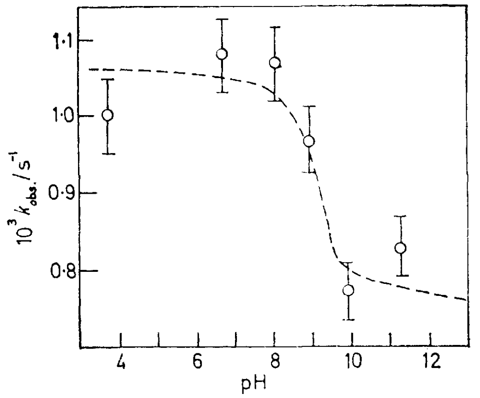

FIGURE 2 Variation of $k_{obs.}$ with pH at 25 °C, [HCN] + [CN$^-$] = 0.207 mol dm^{-3}, $[Fe^{II}_2(CN)_{10}^{6-}] = 1.5 \times 10^{-4}$ mol dm^{-3}, and I = 1.0 mol dm^{-3}

Substitution of $[Fe^{II}_2(CN)_{11}]^{7-}$ *by* HCN.—The reaction of $[Fe^{II}_2(CN)_{11}]^{7-}$ with HCN, (2), was followed spectrophotometrically at 390 nm and plots of $\ln(A_t - A_\infty)$ against time were linear for at least 70% completion of

$$[Fe^{II}_2(CN)_{11}]^{7-} + HCN \xrightarrow{k_{2HCN}} 2[Fe(CN)_6]^{4-} + H^+ \quad (2)$$

reaction with the exception of runs at the lowest ascorbic acid concentration (5 × 10^{-3} mol dm^{-3}). Under these conditions slight initial curvature occurred due to contributions of small amounts of $[Fe^{III}Fe^{II}(CN)_{11}]^{6-}$ to the total optical densities. The conversion of this species into $[Fe^{II}_2(CN)_{11}]^{7-}$ was complete within 1—2 min and the values of k_{2HCN} obtained from the linear region of the plots of $\ln(A_t - A_\infty)$ against time were identical to those obtained when higher concentrations of ascorbic acid were used. Values of k_{2HCN} at different temperatures and concentrations of HCN are given in Table 3. The temperature dependence study gave $\Delta H_{2HCN}^‡ = 92 \pm 4$ kJ mol^{-1} and $\Delta S_{2HCN}^‡$ 31 ± 12 J K^{-1} mol^{-1} respectively. The constant k_{2HCN} was independent of [HCN] in the range $28.3 \times 10^{-3} \geqslant [HCN] \geqslant 0.57 \times 10^{-3}$ mol dm^{-3}, where the initial concentration of $[Fe^{II}_2(CN)_{11}]^{7-}$ was *ca.* 2 × 10^{-3} mol dm^{-3}.

TABLE 3

Kinetic data for the substitution of $[Fe^{II}_2(CN)_{11}]^{7-}$ by HCN [a]

θ_c/°C	10^2[HCN]/mol dm^{-3}	$10^2k_{2HCN}/s^{-1}$
25.0 ± 0.1	28.3 [b]	2.01
	28.3 [c]	1.96
	28.3 [d]	2.10
	14.2	2.18
	2.83	1.94, 1.81 [e]
	1.14	2.02
	0.57	2.07
	28.3	1.94 [f]
	5.7	1.84 [e,f]
	4.8	1.74 [e,g]
20.1	5.7	0.84 [e,g]
15.2	5.7	0.48 [e,g]
10.3	5.7	0.26_2 [e,g]

[a] pH 6.75 ± 0.15, unless otherwise stated; I = 1.0 mol dm^{-3}; $[Fe_2^{II}(CN)_{11}{}^{7-}] = 2 \times 10^{-3}$ mol dm^{-3}. [b–d] [Ascorbic acid] = 0.005, 0.025, and 0.05 mol dm^{-3} respectively; in all other runs [Ascorbic acid] was in the range 0.005—0.10 mol dm^{-3}. [e] Solutions contained 0.8 mol dm^{-3} Na[ClO$_4$]($[Na^+]_T$ = *ca.* 0.91 mol dm^{-3}); in all other runs the ionic strength was maintained with phosphate buffer [($[Na^+]_T$ = *ca.* 0.53 mol dm^{-3}). [f] pH 6.5. [g] pH 6.15 ± 0.1.

Under otherwise comparable conditions, values of k_{2HCN} were consistently lower when Na[ClO$_4$] (0.8 mol dm^{-3}) was present, compared to those obtained where the ionic strength was maintained by the phosphate buffer only. The former conditions were used in experiments from which the data in Table 1 were obtained, and therefore a value of k_{2HCN} of 1.81 × 10^{-2} s^{-1} at 25 °C is used in the Discussion section.

DISCUSSION

The results (excluding those at low concentrations of HCN, see below) are consistent with reactions (3) and (4) and the application of the steady-state treatment to

$$[Fe^{II}_2(CN)_{10}]^{6-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{Intermediate} \quad (3)$$

$$\text{Intermediate} + X \xrightarrow{k_4X} 2[Fe^{II}(CN)_5X] \quad (4)$$

the intermediate leads to (5) and (6). The reciprocal plots described in the Results section then give gradients

$$k_{\mathrm{obs.}} = k_3k_{4\mathrm{X}}[\mathrm{X}](k_{-3} + k_{4\mathrm{X}}[\mathrm{X}])^{-1} \qquad (5)$$

$$k_{\mathrm{obs.}}^{-1} = k_3^{-1} + k_{-3}(k_3k_{4\mathrm{X}}[\mathrm{X}])^{-1} \qquad (6)$$

of $k_{-3}(k_3k_{4\mathrm{X}})^{-1}$ and intercepts of k_3^{-1}. All three substituents gave similar intercepts at 25 °C which supports a scheme where, as in (3), k_3 is independent of the nature of X.

With the exception of $[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-}$, the rates of substitution of monomeric pentacyanoferrate(II) complexes are independent of both the nature and concentration of the substituent at the concentrations of X relative to the concentration of the pentacyanoferrate(II) species used here.[7,9–12] The data in Table 3 show that this is also true for the substitution reaction of the singly bridged species $[\mathrm{Fe^{II}_2(CN)_{11}}]^{7-}$ by cyanide. The dependence of $k_{\mathrm{obs.}}$ on the concentration of X in the substitution reactions of $[\mathrm{Fe^{II}_2(CN)_{10}}]^{6-}$ is therefore probably due to the substitution of a water ligand in an intermediate species. The intermediate cannot be $[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-}$ for the following reasons. If it was, then $k_{4\mathrm{X}}$ would be identical to $k_{1\mathrm{X}}$ [equation (1)], and the gradients of the reciprocal plots would be in the ratio 1.06 : 1.00 : 1.03 for HCN, py, and Mepy respectively, due to the similar values of $k_{1\mathrm{X}}$ for these substituents. The observed ratios for the gradients of these plots are 0.25 : 1.0 : 1.3 respectively. Also, since the dimerisation of $[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-}$ is a second-order process, a reaction scheme involving this species as an intermediate would predict a dependence of $k_{\mathrm{obs.}}$ on the initial concentration of $[\mathrm{Fe^{II}_2(CN)_{10}}]^{6-}$; none was observed (Table 1).

We suggest that the intermediate is the singly bridged complex $[\mathrm{(NC)_5Fe(NC)Fe(CN)_4(OH_2)}]^{6-}$, and the following reaction scheme is proposed:

$$[\mathrm{Fe^{II}_2(CN)_{10}}]^{6-} + \mathrm{H_2O} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Fe^{II}_2(CN)_{10}(OH_2)}]^{6-}$$

$$[\mathrm{Fe^{II}_2(CN)_{10}(OH_2)}]^{6-} + \mathrm{X} \xrightarrow{k_{7\mathrm{X}}} [\mathrm{Fe^{II}_2(CN)_{10}X}] + \mathrm{H_2O} \qquad (7)$$

$$[\mathrm{Fe^{II}_2(CN)_{10}X}] + \mathrm{H_2O} \xrightarrow{k_{2\mathrm{X}}} [\mathrm{Fe^{II}(CN)_5X}] + [\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-}$$

$$[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-} + \mathrm{X} \xrightarrow{k_{1\mathrm{X}}} [\mathrm{Fe^{II}(CN)_5X}]$$

In the case where X = HCN, the unstable protonated species $[\mathrm{Fe^{II}_2(CN)_{10}(CNH)}]^{6-}$ is formed in (7), and this species undergoes the rapid reaction (8). The relative

$$[\mathrm{Fe^{II}_2(CN)_{10}(CNH)}]^{6-} \longrightarrow [\mathrm{Fe^{II}_2(CN)_{11}}]^{7-} + \mathrm{H^+} \qquad (8)$$

gradient of plots of $k_{\mathrm{obs.}}^{-1}$ against $[\mathrm{X}]^{-1}$ depends, in this scheme, on the relative values of $k_{7\mathrm{X}}$ for the three substituents. Thus the value of $k_{7\mathrm{X}}$ decreases as the size of X increases.

Equation (5) predicts that as [HCN] tends to 0, then $k_{\mathrm{obs.}}$ tends to 0, whereas it was found that $k_{\mathrm{obs.}}$ tends to $(1.22 \pm 0.07) \times 10^{-4}\ \mathrm{s^{-1}}$ at 25 °C. When allowance is made for the possibility that the singly bridged complex $[\mathrm{(NC)_5Fe(NC)Fe(CN)_4(OH_2)}]^{6-}$ can undergo bridge cleavage (9), then the results obtained at low concentrations of HCN can be used to obtain values of

$$[\mathrm{Fe^{II}_2(CN)_{10}(OH_2)}]^{6-} + \mathrm{H_2O} \xrightarrow{k_9} 2[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-} \qquad (9)$$

k_{-3} and $k_{-7\mathrm{X}}$ explicitly. Unfortunately, a direct measurement of k_9 was not possible, and the assumption was made that $k_9 = k_{2\mathrm{HCN}}$. Our justification for this assumption is the similarity between the first-order rate constant for cleavage of the cyano-bridge in another singly bridged binuclear complex,[4] $[\mathrm{(NC)_5Fe^{II}(NC)Co^{III}(CN)_5}]^{6-}$ [$(1.6 \pm 0.1) \times 10^{-2}\ \mathrm{s^{-1}}$ at 25 °C, pH 6.7, and $I = 1.0$ mol dm^{-3}] and the value of $k_{2\mathrm{HCN}}$ of $(1.81 \pm 0.08) \times 10^{-2}\ \mathrm{s^{-1}}$. Applying steady-state treatment to $[\mathrm{Fe^{II}_2(CN)_{10}(OH_2)}]^{6-}$, $[\mathrm{Fe^{II}_2(CN)_{11}}]^{7-}$, and $[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-}$, the revised scheme gives (10) and (11). Using $k_3 = (1.25 \pm$

$$k_{\mathrm{obs.}} = k_3(k_{7\mathrm{HCN}}[\mathrm{HCN}] + k_{2\mathrm{HCN}})(k_{-3} + k_{2\mathrm{HCN}} + k_{7\mathrm{HCN}}[\mathrm{HCN}])^{-1} \qquad (10)$$

$$k_{\mathrm{obs.}}(k_3 - k_{\mathrm{obs.}})^{-1} = k_{-3}^{-1}k_{7\mathrm{HCN}}[\mathrm{HCN}] + k_{2\mathrm{HCN}}k_{-3}^{-1} \qquad (11)$$

$0.05) \times 10^{-3}\ \mathrm{s^{-1}}$, $k_9 = k_{2\mathrm{HCN}} = (1.81 \pm 0.08) \times 10^{-2}\ \mathrm{s^{-1}}$, and $k_{\mathrm{obs.}} = (1.22 \pm 0.07) \times 10^{-4}\ \mathrm{s^{-1}}$, k_{-3} was calculated from (10) to be $(1.65 \pm 0.25) \times 10^{-1}\ \mathrm{s^{-1}}$ at 25 °C. A plot of $k_{\mathrm{obs.}}(k_3 - k_{\mathrm{obs.}})^{-1}$ against [HCN] gave an intercept of 0.092 at 25 °C which gives $k_{-3} = 1.9 \times 10^{-1}\ \mathrm{s^{-1}}$. A similar treatment of data obtained at 10.0 °C gave $k_{-3} = (3.2 \pm 0.5) \times 10^{-2}\ \mathrm{s^{-1}}$, and from the values of k_{-3} at 10 and 25 °C, $\Delta H_{-3}^{\ddagger} = 79 \pm 10$ kJ mol^{-1} and $\Delta S_{-3}^{\ddagger} = 4 \pm 25$ J K^{-1} mol^{-1}.

Values of $k_{7\mathrm{py}}$, $k_{7\mathrm{Mepy}}$, and $k_{7\mathrm{HCN}}$ of 9.1 ± 2.0, 10.7 ± 3.0, and 34.8 ± 8.0 dm^3 mol^{-1} s^{-1} respectively at 25 °C were calculated using the gradients of the plots of $k_{\mathrm{obs.}}^{-1}$ against $[\mathrm{X}]^{-1}$ in Table 2, and $k_{-3} = (1.65 \pm 0.25) \times 10^{-1}\ \mathrm{s^{-1}}$. The values of $k_{7\mathrm{X}}$ are smaller and more dependent on the nature of the substituent than the corresponding rate constants $k_{1\mathrm{X}}$ for the substitution of $[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-}$, and probably reflect a more crowded reaction site in the binuclear complex than in the latter species. The lack of spectral evidence for intermediate species where X = HCN is compatible with the relative values of k_3, k_{-1}, and $k_{2\mathrm{HCN}}$ since $k_3 : k_{2\mathrm{HCN}} : k_{-3} = 1 : 14 : 130$.

The decrease in $k_{\mathrm{obs.}}$ of *ca.* 25% between pH and 11.5 is best explained if $k_{7\mathrm{CN}}$ is less than $k_{7\mathrm{HCN}}$. A similar reduction in the rate of substitution of $[\mathrm{Fe^{II}(CN)_5(py)}]^{3-}$ by cyanide was found as the pH increased,[8] and was attributed to the relative values of $k_{1\mathrm{CN}}$ and $k_{1\mathrm{HCN}}$ of 29.3 and 344 dm^3 mol^{-1} s^{-1} respectively. The point of inflection in Figure 2 is consistent with a pK_a for HCN of 8.9.

The value of ΔH_{-3} is similar to that reported[8] for the substitution of $[\mathrm{Fe^{II}(CN)_5(OH_2)}]^{3-}$ by HCN of 71.1 ± 5.4

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kJ mol^{-1}. It has been shown[13] that the enthalpy of activation for the formation of a dibridged binuclear complex from a μ-amido-dicobalt(III) species is *ca.* 8 kcal mol^{-1} less than that for substitution of the corresponding cobalt(III) monomeric complex, and this has been attributed to the proximity of the groups which react to form the second bridge, due to steric effects imposed by the μ-amido-bridge.* It is probable that the deviation from linearity of the bond angle associated with the cyano-bridge in $[Fe^{II}_2(CN)_{10}(OH_2)]^{6-}$ will be less than for the amido-bridge, leading to the observed similarity between the enthalpies of activation for the substitution reactions of the mononuclear and binuclear cyanocomplexes of Fe^{II}.

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* 1 cal = 4.184 J.

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