

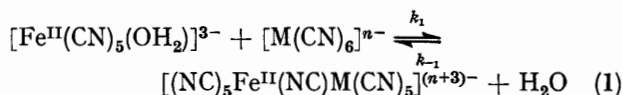
Kinetics of Formation and Bridge Cleavage of Binuclear Complexes derived from the Pentacyanoferrate(II and III) Ions in Aqueous Solution

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Kinetic data for the reaction of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ with $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ to give $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ and $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$ respectively, and the bridge-cleavage reactions of the binuclear complexes, show that these reactions are predominantly dissociative. The bridge-cleavage reaction of $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ is much slower than the corresponding reaction of $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$ and the rate of the former complex is accelerated by the addition of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$.

RECENT interest in cyano-bridged binuclear complexes¹⁻⁹ arises, in part, from their importance¹⁻⁵ as intermediates in inner-sphere electron-transfer reactions. A knowledge of their rates of formation from monomeric species and their stabilities may lead to the correct assignment of mechanism in an electron-transfer reaction.

Here we report the results of a kinetic investigation of the formation and bridge-cleavage reactions of binuclear complexes derived from the aquapentacyanoferrate(II) ion in aqueous solution according to (1),



where M = Fe^{II} or Co^{III}. We have also studied the bridge-cleavage reactions of the binuclear complexes formed in (1) with pyridine (py) and 4-methylpyridine (4Me-py), and the relative rates of bridge cleavage of $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$ and the corresponding iron(III) complex $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ are compared.

EXPERIMENTAL

All the chemicals were AnalaR grade except 4-methylpyridine (Hopkin and Williams, general purpose reagent) and $\text{Na}_4[\text{Fe}(\text{CN})_6]$ (B.D.H., reagent grade). Phosphate buffer solutions containing between 0.8 and 0.9 mol dm⁻³ $\text{Na}[\text{ClO}_4]$ and of total ionic strength 1.00 mol dm⁻³ were prepared using doubly distilled water. The pH of reaction mixtures was measured using a Radiometer type 26 meter. Solutions of $\text{Na}_3[\text{Co}^{\text{III}}(\text{CN})_6]$ of $I = 1.00$ mol dm⁻³ were prepared by adding $\text{K}_3[\text{Co}^{\text{III}}(\text{CN})_6]$ (0.0166 mol) to 1.00 mol dm⁻³ $\text{Na}[\text{ClO}_4]$ (50 cm³, 0.05 mol). The mixture, which was left overnight at 4 °C, was filtered to remove the precipitate of $\text{K}[\text{ClO}_4]$ and the volume of the filtrate was made up to 100 cm³. When calculating the ionic strength of solutions containing $\text{Na}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$, it was assumed that, under the conditions of our experiments, the complex existed predominantly¹⁰ as $\text{Na}^+[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$.

Solutions of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ were prepared⁶ by hydrolysis of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{NH}_3)]^{3-}$ ($t_{1/2} \approx \text{ca. } 40$ s at 25 °C) in aqueous solutions of ascorbic acid (0.01 mol dm⁻³) which was added to prevent¹¹ aerial oxidation of the iron(II) species. The reactions of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ with $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ were followed spectrophotometrically at 450 nm using stopped-flow and recording spectrophotometers.

Samples of $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ and $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ were prepared using the methods reported^{6,11} previously, and solutions of $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$ were prepared by reduction of solutions of $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ with ascorbic acid (0.005–0.01 mol dm⁻³). The bond-cleavage reactions of these binuclear species with py and 4Me-py were followed spectrophotometrically at 390–420 nm using manual and recording spectrophotometers. The substituents py and 4Me-py were chosen because of the large stability constants associated⁷ with the complexes $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{py})]^{3-}$ and $[\text{Fe}^{\text{II}}(\text{CN})_5(4\text{Me-py})]^{3-}$. For similar reasons, azide ion was chosen as the substituent for the bridge-cleavage reaction of $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ which was followed at 560 nm $\{\epsilon \text{ } 3 \text{ } 700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \text{ for } [\text{Fe}^{\text{III}}(\text{CN})_5(\text{N}_3)]^{3-}\}$.

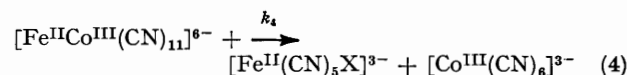
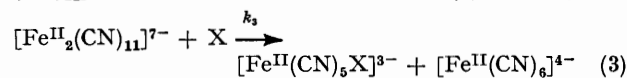
RESULTS

Substitution Reactions of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ by $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$.—Under conditions where $[\text{M}(\text{CN})_6]^{n-} \gg [\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$, the kinetic data obeyed the first-order rate law $-\text{d}[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}/\text{d}t = k_{\text{obs.}}[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ for at least 75% completion of reaction; values of $k_{\text{obs.}}$ at different concentrations of $[\text{M}(\text{CN})_6]^{n-}$ and temperatures are given in Table 1. Plots of $k_{\text{obs.}}$ against $[\text{M}(\text{CN})_6]^{n-}$ were linear and the results are consistent with (2). Values of k_1 and k_{-1} so obtained are included in

$$k_{\text{obs.}} = k_1[\text{M}(\text{CN})_6]^{n-} + k_{-1} \quad (2)$$

Table 1, and from these data ΔH_1^\ddagger and ΔS_1^\ddagger were found to be 15.3 ± 0.3 kcal mol⁻¹ and -8 ± 1 cal K⁻¹ mol⁻¹, and 18.0 ± 1.0 kcal mol⁻¹ and 4 ± 3 cal K⁻¹ mol⁻¹ for the substitution of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ by $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ respectively.†

Bridge-cleavage Reactions of $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ and $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$.—Kinetic data for reactions (3) and (4) where



X = py or 4Me-py obeyed a first-order rate law and values of k_3 and k_4 {where $-\text{d}[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}/\text{d}t = k_3[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ }

* A. D. James, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1974, 1273.

† A. D. James and R. S. Murray, *J.C.S. Dalton*, 1975, 1530 and refs. therein.

‡ K. L. Scott, R. S. Murray, W. C. E. Higginson, and S-W. Foong, *J.C.S. Dalton*, 1973, 2335.

§ K. L. Scott, R. S. Murray, and W. C. E. Higginson, *J.C.S. Dalton*, 1975, 1339.

|| 'Stability Constants of Metal-Ion Complexes,' *Special Publ.*, No. 25, The Chemical Society, 1971.

¶ A. D. James and R. S. Murray, *J.C.S. Dalton*, 1976, 1182.

† 1 cal = 4.184 J.

¹ A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

² J. P. Birk, *J. Amer. Chem. Soc.*, 1969, **91**, 3189.

³ H. Ogino, M. Takahashi, and N. Tanaka, *Bull. Chem. Soc. Japan*, 1974, **47**, 1426.

⁴ P. George, D. H. Irvine, and S. C. Glauser, *Ann. New York Acad. Sci.*, 1960, **88**, 393.

⁵ R. X. Ewall and D. H. Hutchital, *Inorg. Chem.*, 1975, **14**, 494 and refs. therein.

and $-d[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}^{6-}]/dt = k_4[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}^{6-}]$ are given in Table 2. Values of ΔH_3^\ddagger , ΔH_4^\ddagger , ΔS_3^\ddagger , and ΔS_4^\ddagger of 21.9 ± 0.2 kcal mol $^{-1}$, 19.3 ± 0.3 kcal mol $^{-1}$, -2 ± 1 cal K $^{-1}$ mol $^{-1}$, and 7 ± 1 cal K $^{-1}$ mol $^{-1}$ respectively were calculated from these data.

TABLE 1

Kinetic data for the reactions of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ with $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ at pH 6.8

(a) $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$

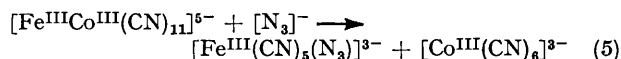
θ_c °C	$10^3[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ ^a mol dm $^{-3}$	10^2k_{obs} ^b s $^{-1}$	k_1 dm 3 mol $^{-1}$ s $^{-1}$	10^2k_{-1} s $^{-1}$
5.0 °	8.30	2.47	0.27 ± 0.02	1.7 ± 1.3 (1.15) ^d
	6.90	2.10		
	5.50	1.65		
	4.20	1.20		
	2.80	1.05		
15.4 °	8.30	9.90	1.14 ± 0.05	5.6 ± 2.9 (4.9) ^d
	6.64	8.50		
	4.43	5.35		
	2.95	4.05		
	1.97	2.80		
25.9 °	8.30	27.5	2.9 ± 0.5	54 ± 12 (17.5) ^d
	6.64	25.5		
	5.53	22.5		
	3.69	16.0		
	2.46	13.0		
1.64	9.0			

(b) $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$

θ_c °C	$10^3[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ^a mol dm $^{-3}$	10^2k_{obs} ^b s $^{-1}$	k_1 dm 3 mol $^{-1}$ s $^{-1}$	10^2k_{-1} s $^{-1}$
5.7 °	8.30	8.0	9.0 ± 0.13	1.4 ± 0.7 (1.41) ^f
	7.10	8.75		
	4.20	5.40		
	2.40	3.45		
	1.30	2.40		
15.8 °	8.30	30.5	26.0 ± 3.2	7.6 ± 1.7 (5.5) ^f
	7.10	23.5		
	4.20	20.0		
	2.40	14.5		
	1.30	9.9		
25.3 °	8.40	67.5	59.0 ± 4.1	19.0 ± 2.1 (18.1) ^f
	6.30	53.5		
	5.60	56.5		
	4.20	44.5		
	2.80	37.0		
2.10	32.0			
1.10	23.0			

^a $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-} = 1 \times 10^{-4}$ mol dm $^{-3}$. ^b Errors in individual rate constants are $\pm 5\%$. ^c Average of two or three experiments. ^d Corresponding values of k_4 , calculated from data in Table 2. ^e Average of four or five experiments. ^f Corresponding values of k_3 , calculated from data in Table 2.

Substitution Reactions of $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ by $[\text{N}_3]^-$.—Reaction (5) was slow $\{-d[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}^{5-}]/dt \leq 1 \times 10^{-4}$ mol dm $^{-3}$ s $^{-1}$ at 25 °C and $I = 1.0$ mol dm $^{-3}$ \} except when $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ was present, and under these conditions



a linear increase in absorbance at 560 nm with time was observed (Figure 1). The values of the zero-order rate constants so derived were directly proportional to $[\text{Fe}^{\text{II}}]$, where $[\text{Fe}^{\text{II}}]$ is the concentration of added $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$.

DISCUSSION

The value of k_1 of 2.9 dm 3 mol $^{-1}$ s $^{-1}$ at 25.9 °C for the substitution reaction of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ by

¹² J. Legros, *J. Chim. phys.*, 1964, **61**, 923.

¹³ J. Legros, *J. Chim. phys.*, 1964, **61**, 911.

¹⁴ H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2080.

TABLE 2

Kinetic data for the substitution reactions^a of $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ and $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$ by py and 4Me-py

(a) $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$

θ_c °C	pH	$10^2[\text{py}]$ ^b mol dm $^{-3}$	$10^2[4\text{Me-py}]$ ^b mol dm $^{-3}$	10^2k_3 s $^{-1}$	
25.0	6.9	9.38		1.58	
	5.3	1.76		1.73	
	6.7	1.76		1.55	
	6.7	1.37		1.67	
	6.7	0.49		1.71	
	6.4	5.3	1.76		0.170
	9.8	5.3	1.76		0.27
	14.7	5.3	1.76		0.46
	19.5	5.3	1.76		1.11
	6.4	6.7		3.48	0.18
9.8	6.7		3.48	0.31	
14.7	6.7		3.48	0.43	
19.5	6.7		3.48	1.05	
25.0	7.0		0.78	1.61	

(b) $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$

θ_c °C	pH	$10^2[\text{py}]$ ^b mol dm $^{-3}$	$10^2[4\text{Me-py}]$ ^b mol dm $^{-3}$	10^2k_4 s $^{-1}$
25.0	6.8	0.94		1.73
24.7	5.3	1.76		1.43
	6.8	1.76		1.60
25.0	6.7	1.37		1.67
	6.7	0.49		1.63
6.4	5.3	1.76		0.127
10.7	5.3	1.76		0.252
14.7	5.3	1.76		0.41
19.5	5.3	1.76		0.80
	7.4	1.76		0.78
	9.5	1.76		0.72
	10.6	1.76		0.85
6.4	6.7		3.48	0.113
10.7	6.7		3.48	0.265
14.7	6.7		3.48	0.43
19.5	6.7		3.48	0.79
24.7	6.7		3.48	1.50
25.0	6.7		7.8	1.57
	7.1		0.65	1.44

^a $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ and $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-} = ca. 1 \times 10^{-3}$ mol dm $^{-3}$. ^b $[\text{py}]$ = total concentration of py and Hpy $^+$ (pK_a 5.2 for Hpy $^+$); $[4\text{Me-py}]$ = total concentration of 4Me-py and 4Me-Hpy $^+$ (pK_a 6.4 for 4Me-Hpy $^+$).

$[\text{Co}(\text{CN})_6]^{3-}$ is about five times greater than the corresponding value of 0.59 dm 3 mol $^{-1}$ s $^{-1}$ at 25.3 °C for the reaction of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ with $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$. These results, together with those for the substitution of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ by $[\text{SO}_3]^{2-}$, $[\text{CN}]^-$, HCN, py, and pz $^+$ (pyrazinium ion) at 25 °C which are 3.3, 29.3, 344, 365, and 550 dm 3 mol $^{-1}$ s $^{-1}$ respectively,¹¹⁻¹⁴ support the suggestion that the charge on the substituent is the most important factor in determining the relative rate of diffusion¹⁵ of the negatively charged substituent towards the intermediate¹⁴ $[\text{Fe}^{\text{II}}(\text{CN})_5]^{3-}$. Thus although it is suggested¹⁰ that at $[\text{Na}^+] = 1.0$ mol dm $^{-3}$ species $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ exists predominantly as the ion pair $\text{Na}^+[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, it appears that the net effect of this more localised charge neutralisation is less than observed for the substitution by $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ which has the same net charge as the latter species.

At 25 °C the values of k_3 and k_4 , the first-order rate constants for the bridge-cleavage reactions of $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ and $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$ by py and 4Me-py, are, within experimental error, identical and independent

¹⁵ Z. Bradic, M. Pribranic, and S. Asperger, *J.C.S. Dalton*, 1975, 353.

of the concentration and nature of the substituent. The similarity of k_3 with the value obtained previously for the first-order rate constant¹¹ for the substitution of

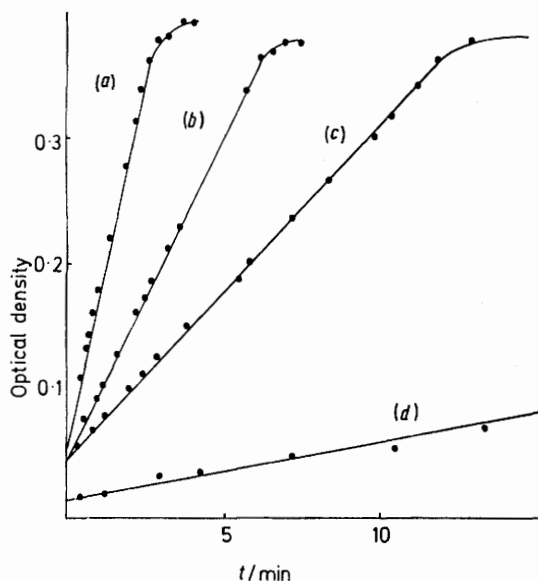


FIGURE 1 Variation of optical density with time at 560 nm for the reaction of $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ (5×10^{-5} mol dm^{-3}) with $[\text{N}_3]^-$ (0.1 mol dm^{-3}) at 25 °C, pH 4, and $I = 1.00$ mol dm^{-3} . $[\text{Fe}^{\text{II}}] = 4 \times 10^{-5}$ (a), 1.6×10^{-5} (b), 0.8×10^{-5} (c), and 0 mol dm^{-3} (d)

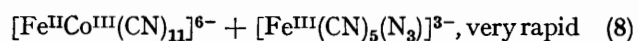
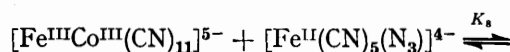
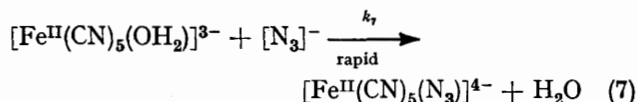
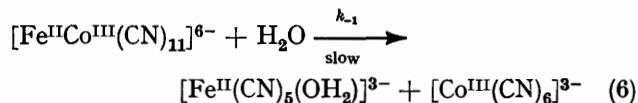
$[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ by HCN of 1.81×10^{-2} s⁻¹ at 25 °C, pH 6.7, and $I = 1.0$ mol dm^{-3} , together with the observation that the values of k_{-1} are in general similar to values of k_3 and k_4 obtained under the same experimental conditions (Table 1), supports the theory that the rate-determining step for the substitution reactions of $[\text{Fe}^{\text{II}}_2(\text{CN})_{11}]^{7-}$ and $[\text{Fe}^{\text{II}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{6-}$ by py and 4Me-py is the dissociation reaction shown in (1).

The two structural isomers $[(\text{NC})_5\text{Fe}^{\text{II}}(\text{CN})\text{Co}^{\text{III}}(\text{CN})_5]^{6-}$ and $[(\text{NC})_5\text{Fe}^{\text{II}}(\text{NC})\text{Co}^{\text{III}}(\text{CN})_5]^{6-}$ undergo bridge-cleavage reactions at significantly different rates, and the value of the first-order rate constant for the former complex, which gives $[\text{Co}^{\text{III}}(\text{CN})_5(\text{OH}_2)]^{2-}$ and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ on hydrolysis, is ca. 400 times smaller¹⁶ than that of the latter. The difference may be attributed to the difference between the strengths of the Fe^{II}-NC and Co^{III}-NC bonds. Both $[(\text{NC})_5\text{Fe}^{\text{II}}(\text{CN})\text{Co}^{\text{III}}(\text{CN})_5]^{6-}$ and $[(\text{NC})_5\text{Fe}^{\text{II}}(\text{NC})\text{Co}^{\text{III}}(\text{CN})_5]^{6-}$ can be oxidised to the corresponding iron(III) binuclear complexes, and the reduction potentials⁷ for these are 0.457 and 0.510 V respectively; the difference probably reflects a greater degree of π bonding in the Fe-CN compared to the Fe-NC bond.

The values of k_3 and k_4 at 25 °C are similar to the value of the corresponding first-order constant of 1.8×10^{-2} s⁻¹ for the solvolysis reaction of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{NH}_3)]^{3-}$ to give $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^3$ and $[\text{NH}_4]^+$. It has been shown that NC and NH₃ groups have similar ligand-field strengths, and for predominantly dissociative reactions correlations between k_3 (and related rate constants) or ΔH_3^\ddagger and factors related to the strength of the metal-ligand bond might be expected. Figure 2 is a plot of the enthalpies

of activation for the substitution reactions of a series of pentacyanoferrate(II) complexes against the corresponding ligand-field strength associated with X, as measured by the energy of the ${}^1A_2 \rightarrow E_2$ (LF) transition.

The results obtained for the substitution reaction of $[\text{Fe}^{\text{III}}\text{Co}^{\text{III}}(\text{CN})_{11}]^{5-}$ by $[\text{N}_3]^-$ ion, where the value of the zero-order rate constants increased as $[\text{Fe}^{\text{II}}]$ increased, are consistent with an iron(II)-catalysed⁶ reaction path, (6)–(8), and are similar to the iron(II)-catalysed substitution reactions of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{NH}_3)]^{3-}$ by substituents



which lead⁶ to large values of K_8 . A value of K_8 of 3×10^3 was calculated from electrode potentials⁷ and

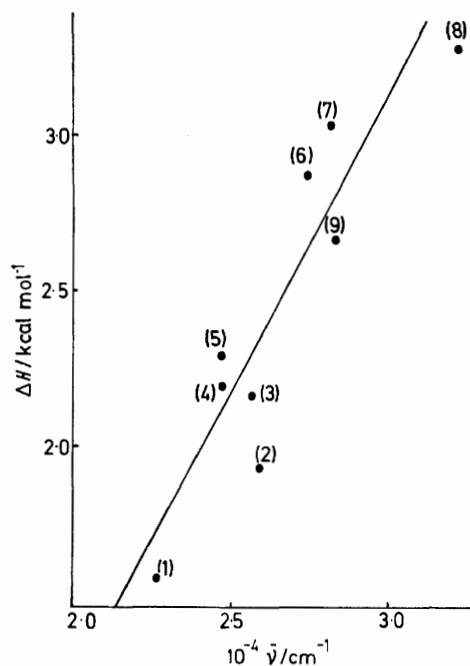


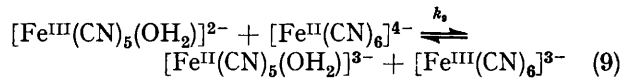
FIGURE 2 Plot of the enthalpies of activation against the energy of the ${}^1A_2 \rightarrow E_2$ (LF) transition for a series of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{X}]$ complexes. X = H₂O (1),¹⁴ $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ (2), $[\text{NO}_2]^-$ (3) (P. A. Rock and J. H. Swinehart, *Inorg. Chem.*, 1966, **5**, 573), $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ (4), NH₃ (5),^{12,13} $[\text{AsO}_2]^-$ (6),¹² $[\text{SO}_2]^{2-}$ (7),¹² $[\text{CN}]^-$ (8),¹³ and dimethyl sulphoxide (9) (N. E. Toma, J. M. Malin, and E. Griesbrecht, *Inorg. Chem.*, 1973, **9**, 2084)

k_{-1} was found to be 1.3×10^{-2} s⁻¹ at 25 °C, pH 6.7, and $I = 1.0$ mol dm^{-3} from the plot of $[\text{Fe}^{\text{II}}]$ against the corresponding values of the zero-order rate constants,

¹⁶ J. Hanzlik and A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1973, **38**, 3019.

in the manner previously⁶ described. The similarity of this value to the above estimates of k_{-1} and k_4 is good evidence that (6) is rate determining, and the bridge-cleavage reaction in the iron(III) binuclear is much slower than for the corresponding iron(II) species.

The rates of substitution of $[\text{Fe}^{\text{II}}(\text{CN})_5(\text{OH}_2)]^{3-}$ and $[\text{Fe}^{\text{III}}(\text{CN})_5(\text{OH}_2)]^{2-}$ by $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ are much slower than that of the electron-transfer reaction¹⁷ (9), where



$k_9 \geq 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25 °C, and by making the assumptions that $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, which has the same net charge as $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$, will substitute at similar rates to the latter and that $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ will substitute more slowly,^{9,18} we conclude that the above electron exchange occurs *via* an outer-sphere mechanism.

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- ¹⁷ R. Strasiw and R. G. Wilkins, *Inorg. Chem.*, 1972, **11**, 2034.
¹⁸ J. H. Espenson and R. Russell, *Inorg. Chem.*, 1974, **13**, 7.