Mixed Iron–Cobalt Binuclear Complexes. Part II.[1] Kinetics of Formation and Dissociation of Binuclear Complexes obtained from *trans*-Aquabis(ethylenediamine)sulphitocobalt(III) and Cyano-complexes of Iron

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The rate of reaction (i) has been studied by stopped-flow spectrophotometry. The rate law (ii) is obeyed at

$$[\mathrm{Fe^{II}(CN)_5(NO)}]^{2-} + [\mathrm{Co^{III}(en)_2(SO_3)(OH_2)}]^{+} \xrightarrow{k_f} [\mathrm{(ON)(NC)_4Fe^{II}CNCo^{III}(en)_2(SO_3)}]^{-} \qquad \text{(i)}$$

$$-\mathrm{d}[\mathrm{Co}]/\mathrm{d}t = k_f[\mathrm{Co}][\mathrm{Fe}] \qquad \text{(ii)}$$

pH 0—6 and 25·0 °C: $k_f = 700 \pm 15\ \mathrm{l\ mol^{-1}\ s^{-1}}$; $\Delta H^{\ddagger} = 59{\cdot}8 \pm 0{\cdot}4\ \mathrm{kJ\ mol^{-1}}$; and $\Delta S^{\ddagger} = 10{\cdot}5 \pm 2{\cdot}1\ \mathrm{J\ K^{-1}\ mol^{-1}}$ [$I = 1{\cdot}00$M (LiClO$_4$)]. With $[\mathrm{Fe(CN)_6}]^{3-}$ and $[\mathrm{Fe(CN)_6}]^{4-}$ as reactants, rate parameters are $k_f = 1\,725 \pm 35$ and $7\,450 \pm 220\ \mathrm{l\ mol^{-1}\ s^{-1}}$, $\Delta H^{\ddagger} = 60{\cdot}7 \pm 0{\cdot}8$ and $56{\cdot}9 \pm 1{\cdot}3\ \mathrm{kJ\ mol^{-1}}$, and $\Delta S^{\ddagger} = 21{\cdot}3 \pm 2{\cdot}5$ and $19{\cdot}7 \pm 3{\cdot}3\ \mathrm{J\ K^{-1}\ mol^{-1}}$, respectively. The rate of the reverse of reaction (i) has been measured by following the displacement reaction (iii) which is first order in the concentration of the reacting binuclear complex and independent of the $[\mathrm{Fe(CN)_6}]^{3-}$ concentration: at 25·0 °C, $k_d = 0{\cdot}113 \pm 0{\cdot}006\ \mathrm{s^{-1}}$ [$I = 1{\cdot}00$M (LiClO$_4$)].

$$[\mathrm{(ON)(NC)_4Fe^{II}CNCo^{III}(en)_2(SO_3)}]^{-} + [\mathrm{Fe^{III}(CN)_6}]^{3-} \xrightarrow{k_d} [\mathrm{(NC)_5Fe^{III}CNCo^{III}(en)_2(SO_3)}]^{2-} + [\mathrm{Fe^{II}(CN)_5(NO)}]^{2-} \qquad \text{(iii)}$$

The dissociation rate constant for the complex $[\mathrm{(NC)_5Co^{III}CNCo^{III}(en)_2(SO_3)}]^{2-}$ has been obtained similarly: $k_d = (3{\cdot}41 \pm 0{\cdot}03) \times 10^{-2}\ \mathrm{s^{-1}}$ under the same conditions. A study of the rate of attainment of equilibrium (iv) in alkaline solution has

$$[\mathrm{Fe^{II}(CN)_6}]^{4-} + [\mathrm{Co^{III}(en)_2(SO_3)(OH)}] \rightleftharpoons [\mathrm{(NC)_5Fe^{II}CNCo^{III}(en)_2(SO_3)}]^{3-} + \mathrm{OH^-} \qquad \text{(iv)}$$

enabled k_d for the dissociation of $[\mathrm{(NC)_5Fe^{II}CNCo^{III}(en)_2(SO_3)}]^{3-}$ to be obtained: $k_d = (2{\cdot}56 \pm 0{\cdot}12) \times 10^{-3}\ \mathrm{s^{-1}}$ at 25·0 °C [$I = 1{\cdot}00$M (NaClO$_4$)]. Equilibrium constants for the formation of these binuclear complexes have been calculated from the kinetic data.

THE identification of mixed iron–cobalt binuclear complexes from reactions of cyanometallates with *trans*-$[\mathrm{Co(en)_2(SO_3)(OH_2)}]^+$ (en = ethylenediamine) is the subject of Part I of this series.[1] Part of the characterisation involved the demonstration that the reaction with $[\mathrm{Fe(CN)_6}]^{4-}$ is measurably slow, showing that the product is a covalently bonded binuclear complex rather than an ion pair. We now report a more detailed kinetic study of the kinetics of reactions of this cobalt(III) complex with $[\mathrm{Fe(CN)_5(NO)}]^{2-}$, $[\mathrm{Fe(CN)_6}]^{3-}$, and $[\mathrm{Fe(CN)_6}]^{4-}$. The equilibrium constant for reaction (1) has been estimated [1]

$$[\mathrm{Fe(CN)_5(NO)}]^{2-} + [\mathrm{Co(en)_2(SO_3)(OH_2)}]^{+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [\mathrm{(ON)(NC)_4FeCNCo(en)_2(SO_3)}]^{-} \qquad (1)$$

by spectrophotometric studies to be $K_a = k_f/k_d = ca.\ 10^4\ \mathrm{l\ mol^{-1}}$. Corresponding values of K_a are even larger for the binuclear complexes obtained from $[\mathrm{Fe(CN)_6}]^{3-}$ and $[\mathrm{Fe(CN)_6}]^{4-}$. Consequently, impracticably low concentrations of such binuclear complexes are necessary to measure dissociation rates in the simplest manner. However, displacement reactions such as (2) were found

$$[\mathrm{(ON)(NC)_4FeCNCo(en)_2(SO_3)}]^{-} + [\mathrm{Fe(CN)_6}]^{3-} \longrightarrow [\mathrm{(NC)_5FeCNCo(en)_2(SO_3)}]^{2-} + [\mathrm{Fe(CN)_5(NO)}]^{2-} \qquad (2)$$

to yield k_d for reaction (1), and similarly for the dissociation of $[\mathrm{(NC)_5CoCNCo(en)_2(SO_3)}]^{2-}$. Such a method could not be used to obtain the rate constant for the dissociation of $[\mathrm{(NC)_5FeCNCo(en)_2(SO_3)}]^{3-}$ since the displacement equilibrium is unfavourable for this binuclear complex with other cyanometallates. However, k_d was obtained from a kinetic study of the partial formation of $[\mathrm{(NC)_5FeCNCo(en)_2(SO_3)}]^{3-}$ from $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Co(en)_2(SO_3)(OH)}]$ in alkaline solution.

RESULTS

Kinetics of Formation of Binuclear Complexes in Acid Solution.—The forward reaction (1) and the corresponding reactions of the cobalt(III) complex with $[\mathrm{Fe(CN)_6}]^{3-}$ and with $[\mathrm{Fe(CN)_6}]^{4-}$ were studied by following the increase in absorption at 420, 480, and 400 nm, respectively, by the stopped-flow technique. In each case the cyano-complex was in considerable excess, and plots of $\log(D_\infty - D_t)$ against time t were linear to greater than 90% completion of reaction, except with $[\mathrm{Fe(CN)_6}]^{4-}$ where slight curvature occurred after *ca.* 70% reaction. Values of $k_{\mathrm{obs.}}$ ($-2{\cdot}303 \times$ gradient) are summarised in Tables 1—3; inspection of the Tables shows that $k_{\mathrm{obs.}}$ is linearly dependent on [Fe], equation (3), where [Co] and [Fe] denote the concentrations of

$$-\mathrm{d}[\mathrm{Co}]/\mathrm{d}t = k_{\mathrm{obs.}}[\mathrm{Co}] = k_f[\mathrm{Co}][\mathrm{Fe}] \qquad (3)$$

mononuclear cobalt(III) and iron complexes, respectively. The effect of varying the acidity was briefly investigated for the reaction involving $[\mathrm{Fe(CN)_5(NO)}]^{2-}$; no dependence on hydrogen-ion concentration was found over the range pH 0—6, nor did absence of air have any effect. The other systems were not completely stable at the lower values of pH, and with $[\mathrm{Fe(CN)_6}]^{4-}$ the instability of solutions in 1M-LiClO$_4$ was sufficient to introduce some error into the final readings of optical density.† Consequently, the rate constants obtained for the system containing $[\mathrm{Fe(CN)_6}]^{4-}$ are less accurate than the others and this applies also to the activation parameters given in Table 4.

Two sets of experiments with $[\mathrm{Co(CN)_6}]^{3-}$ were also made.

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† 1M = 1 mol dm^{-3}.

[1] Part I, K. L. Scott, R. S. Murray, W. C. E. Higginson, and S-W. Foong, *J.C.S. Dalton*, 1973, 2335.

With $[Co(CN)_6{}^{3-}] = 2{\cdot}0 \times 10^{-3}$ and $1{\cdot}1 \times 10^{-2}$M and $[Co(en)_2(SO_3)(OH_2)^+] = 4{\cdot}0 \times 10^{-4}$ and $1{\cdot}0 \times 10^{-3}$M, respectively, the corresponding rate constants $k_{obs.} = 3{\cdot}44 \pm 0{\cdot}12$ and $18{\cdot}5 \pm 0{\cdot}6\ s^{-1}$ were obtained at 25·0 °C and $I = 1{\cdot}00$M (LiClO$_4$). The limited data yield $k_f = 1\ 700 \pm 20\ l\ mol^{-1}\ s^{-1}$, in very good agreement with the value of k_f obtained in the $[Fe(CN)_6]^{3-}$ system.

TABLE 1

Pseudo-first-order rate constants, $k_{obs.}$, for reaction of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ with $[Fe(CN)_5(NO)]^{2-}$ at $I = 1{\cdot}00$M (LiClO$_4$)

θ_c/°C	10^2[Fe]/M	10^3[Co]/M	$k_{obs.}$ [a]/s^{-1}
8·0	1·0	1·0	1·44 ± 0·04 (7)
	1·5	1·0	2·35 ± 0·01 (4)
	4·0	2·0	5·98 ± 0·11 (5)
15·0	0·50	0·70	1·46 ± 0·02 (6)
20·0	0·50	0·70	2·24 ± 0·03 (6)
	1·4	0·70	6·31 ± 0·09 (5)
25·0	0·20	0·40	1·44 ± 0·03 (6)
	0·30	0·50	2·10 ± 0·04 (5)
	0·50	0·50	3·61 ± 0·06 (6)
	1·0	1·0	6·85 ± 0·05 (5) [b]
	1·0	1·0	6·93 ± 0·07 (10)
	1·0	1·0	7·00 ± 0·17 (4) [c]
	1·0	1·0	7·00 ± 0·12 (9) [d]
	1·0	1·0	7·15 ± 0·12 (7) [e]
	1·5	1·0	10·5 ± 0·2 (8)
	2·0	1·0	14·5 ± 0·4 (7)
	3·0	2·0	20·5 ± 0·4 (7)
	3·0	5·0	20·5 ± 0·5 (7)
35·0	0·70	1·0	11·0 ± 0·3 (5)
	1·4	1·0	20·6 ± 0·7 (7)

[a] The number of runs is given in parentheses; pH *ca.* 5·5. [b] $[H^+] = 0{\cdot}02$M. [c] pH *ca.* 6, air-free. [d] $[H^+] = 0{\cdot}97$M. [e] $[H^+] = 0{\cdot}51$M.

TABLE 2

Pseudo-first-order rate constants, $k_{obs.}$, for reaction of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ with $[Fe(CN)_6]^{3-}$ at pH *ca.* 5·5 and $I = 1{\cdot}00$M (LiClO$_4$)

θ_c/°C	10^3[Fe]/M	10^4[Co]/M	$k_{obs.}$ */s^{-1}
10·0	3·0	1·3	1·36 ± 0·02 (7)
	15·0	1·3	6·66 ± 0·12 (7)
15·0	3·0	1·3	2·10 ± 0·03 (4)
20·0	5·0	1·3	5·60 ± 0·08 (6)
	5·0	3·0	5·61 ± 0·03 (6)
25·0	1·0	1·0	1·75 ± 0·06 (8)
	2·5	2·0	4·43 ± 0·07 (4)
	3·0	1·0	5·24 ± 0·06 (5)
	5·0	1·0	8·70 ± 0·15 (7)
	5·0	2·5	8·53 ± 0·14 (6)
	5·0	3·0	8·60 ± 0·18 (6)
	11·0	2·0	19·1 ± 0·3 (4)
	11·0	10·0	18·3 ± 0·2 (7)
	20·0	2·0	35·3 ± 0·5 (5)
	20·0	6·0	33·4 ± 0·3 (5)
30·0	3·0	1·3	7·72 ± 0·1 (3)

* The number of runs is given in parentheses.

Kinetics of Formation of $[(NC)_5FeCNCo(en)_2(SO_3)]^{3-}$ *in Alkaline Solution.*—The reaction of $[Fe(CN)_6]^{4-}$ with *trans*-$[Co(en)_2(SO_3)(OH)]$ was observed spectrophotometrically at 400 nm in the range 0·01—0·96M-NaOH. Variations in D_∞ with $[OH^-]$ were consistent with the establishment of an equilibrium, (4). Equilibrium concentrations of the various

$$[Fe(CN)_6]^{4-} + [Co(en)_2(SO_3)(OH)] \overset{K_b}{\rightleftharpoons} [(NC)_5FeCNCo(en)_2(SO_3)]^{3-} + OH^- \quad (4)$$

light-absorbing species were then calculated from D_∞ by using the initial concentrations of the reactants, together with molar absorption coefficients [1] of 4, 40, and 760 l mol^{-1} cm^{-1} at 400 nm for the complexes in equation (4), taken in order. Initial concentrations were: $[Co(en)_2(SO_3)(OH)] = 6{\cdot}0 \times 10^{-4}$; $[Fe(CN)_6{}^{4-}] = (6{\cdot}0,\ 30,\ \text{and}\ 60) \times 10^{-4}$; and $[OH^-] = 0{\cdot}040 - 1{\cdot}00$M. We find K_b for equation (4) is 217 ± 19 at 25·0 °C and $I = 1{\cdot}00$M (NaClO$_4$).

The rate of approach to the equilibrium position was studied, and plots of log $(D_\infty - D_t)$ against t were linear for at least three half-lives. Conventional spectrophotometry was adequate for measurements at $[OH^-] > 0{\cdot}1$M; below this concentration it was necessary to use the stopped-flow technique. Values of the observed rate constants $k_{obs.}$, obtained from the semi-logarithmic plots, are given in Table 5. The reverse reaction, *i.e.* the approach to equilibrium obtained by making alkaline a solution of the binuclear complex, was followed in one instance and gave a rate constant in satisfactory agreement with that observed for the forward reaction under corresponding concentration conditions. Although perchlorate ion was normally used as the supporting anion, on account of its low tendency to associate with metal complexes, two groups of experiments were made with chloride ions present. A small, but significant, effect was observed, and this raises the question of which anion can best replace hydroxyl ion in studies in which the concentration of the latter is varied. Analysis of the results in Table 5 showed that a rate equation containing at least three terms is required, as in (5), with $k_b = 0{\cdot}38 \pm$

TABLE 3

Pseudo-first-order rate constants, $k_{obs.}$, for reaction of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ with $[Fe(CN)_6]^{4-}$ under air-free conditions at pH *ca.* 6 and $I = 1{\cdot}00$M (LiClO$_4$)

θ_c/°C	10^3[Fe]/M	10^4[Co]/M	$k_{obs.}$ [a]/s^{-1}
8·0	8·0	10·0	13·6 ± 1·0 (6)
10·0	3·0	1·3	6·48 ± 0·08 (5)
15·0	3·0	1·3	9·83 ± 0·13 (5)
18·0	1·0	1·0	3·98 ± 0·16 (7)
	2·0	1·0	8·11 ± 0·13 (8)
	10·0	1·0	37·0 ± 1·6 (8)
25·0	1·0	1·0	7·5 ± 0·2 (7)
	2·0	4·0	15·4 ± 0·3 (7)
	4·0	1·0	28·9 ± 0·5 (4)
	4·0	2·0	29·0 ± 0·2 (2) [b]
	4·0	2·0	29·0 ± 0·2 (5)
	4·0	4·0	29·2 ± 0·6 (7)
	4·0	4·0	28·9 ± 0·3 (7)
	4·0	10·0	28·3 ± 0·3 (2)
	8·0	2·0	62·0 ± 2·0 (5)
	8·0	3·0	63·0 ± 0·7 (2)
	8·0	3·0	62·6 ± 3·0 (4) [b]
	8·0	4·0	59·4 ± 1·2 (3)
	10·0	1·0	74·3 ± 0·9 (6)
30·0	0·50	0·70	5·3 ± 0·07 (6)
	1·0	0·70	11·1 ± 0·2 (6)
35·0	0·50	0·70	7·5 ± 0·17 (5)
	1·0	0·70	15·8 ± 0·5 (7)

[a] The number of runs is given in parentheses. [b] Not air-free conditions.

TABLE 4

Summary of rate parameters for the reactions of cyanoiron complexes with *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ at $I = 1{\cdot}00$M (LiClO$_4$)

Complex	k_f (25 °C) l mol^{-1} s^{-1}	$\Delta H^‡$ kJ mol^{-1}	$\Delta S^‡$ J K^{-1} mol^{-1}
$[Fe(CN)_5(NO)]^{2-}$	700 ± 15	59·8 ± 0·4	10·5 ± 2·1
$[Fe(CN)_6]^{3-}$	1725 ± 35	60·7 ± 0·8	21·3 ± 2·5
$[Fe(CN)_6]^{4-}$	7450 ± 220	56·9 ± 1·3	19·7 ± 3·3

$0{\cdot}01\ s^{-1}$, $k_c = 0{\cdot}25 \pm 0{\cdot}02\ l\ mol^{-1}\ s^{-1}$, and $k_d = (2{\cdot}56 \pm 0{\cdot}12) \times 10^{-3}\ s^{-1}$.

$$k_{obs.} = k_b[Fe(CN)_6^{4-}][OH^-]^{-1} + k_c[Fe(CN)_6^{4-}] + k_d \quad (5)$$

Kinetics of Displacement Reactions involving μ-Cyano-complexes.—The rate of displacement of $[Fe(CN)_5(NO)]^{2-}$ from $[(ON)(NC)_4FeCNCo(en)_2(SO_3)]^-$ by $[Fe(CN)_6]^{3-}$ and by $[Fe(CN)_6]^{4-}$ was studied by stopped-flow spectrophotometry at 480 and 400 nm, respectively. The binuclear complex was prepared by mixing $[Co(en)_2(SO_3)(OH_2)]^+$ with an equivalent or greater amount of $[Fe(CN)_5(NO)]^{2-}$ shortly before the displacement reaction was initiated. The conversion of $[Co(en)_2(SO_3)(OH_2)]^+$ into $[(ON)(NC)_4FeCNCo(en)_2(SO_3)]^-$ was incomplete, especially under the concentration conditions employed in the displacement reaction with $[Fe(CN)_6]^{3-}$. However, the reaction of the displacing hexacyanoferrate with the free $[Co(en)_2(SO_3)(OH_2)]^+$ present occurred so rapidly that it did not interfere with measurement of the rate of the displacement reaction. Final spectra showed that all $[Co(en)_2(SO_3)(OH_2)]^+$ added initially was converted into $[(NC)_5FeCNCo(en)_2(SO_3)]^{n-}$ (n = 2 or 3, depending on the oxidation state of the hexacyanoferrate). Plots of $\log(D_\infty - D_t)$ against t were linear for at least two half-lives, and the first-order rate constants, k_d, obtained from them are given in Table 6. It can be seen that k_d is independent not only of the concentration of the hexacyanoferrate but also of its charge. Evidently a rate expression of the form (6) holds where M′CNCo represents a binuclear μ-cyano-complex, in this case $[(ON)(NC)_4FeCNCo(en)_2(SO_3)]^-$, and $k_d = 0{\cdot}113 \pm 0{\cdot}006\ s^{-1}$ at 25·0 °C, $I = 1{\cdot}00$M ($LiClO_4$), and pH *ca.* 5·5.

TABLE 5

Observed rate constants, $k_{obs.}$, for reaction of *trans*-$[Co(en)_2(SO_3)(OH)]$ with $[Fe(CN)_6]^{4-}$ at 25 °C, $[Co] = 4{\cdot}0 \times 10^{-4}$M, and $I = 1{\cdot}00$M ($NaClO_4$)

$10^3[OH^-]$/M	10^3[Fe]/M	$10^3k_{obs.}$ ^{a}/s^{-1}
10	4·0	154 ± 2 (7)
10	8·0	311 ± 6 (9)
10	8·0	299 ± 3 (5) ^{b}
10	8·0	289 ± 3 (5) ^{c}
15	4·0	104 ± 1 (5) ^{d}
15	4·0	102 ± 2 (7)
15	8·0	204 ± 3 (9) ^{d}
15	8·0	206 ± 2 (6)
20	4·0	74 ± 1 (7)
20	8·0	147 ± 3 (6)
20	8·0	156 ± 2 (10) ^{e}
50	4·0	31·1 ± 0·6 (5)
50	4·0	35·6 ± 1·0 (6)
50	8·0	62 ± 2 (13)
100	4·0	18·5 ± 0·2 (4)
100	8·0	33·9 ± 0·5 (5) ^{e}
200	4·0	10·8 (1)
300	4·0	8·44 (1)
400	1·6	4·91 (1)
400	4·0	7·29 (2)
400	8·0	11·8 (3)
400	10·4	14·6 (1)
400	12·8	17·5 (1)
500	2·0	4·76 (1)
500	2·9	5·14 (1)
500	4·0	6·18 (1)
500	5·0	7·41 (1)
500	7·6	9·63 (1)
500	10·0	12·6 (1)
800	1·6	3·59 (1)
800	4·0	5·15 (2)
800	4·0	5·03 (1) ^{f}
800	8·0	7·56 (1)
800	13·6	11·5 (1)
960	3·0	4·03 (1) ^{g}
960	4·0	4·82 (1)
960	4·8	5·10 (1) ^{g}

[a] The number of runs is given in parentheses. [b] 0·50M-NaCl. [c] 0·91M-NaCl (no $NaClO_4$). [d] $[Co] = 2{\cdot}0 \times 10^{-4}$M. [e] Air-free conditions. [f] Reverse approach to equilibrium. [g] $[Co] = 6{\cdot}0 \times 10^{-4}$M.

TABLE 6

Observed rate constants, k_d, for reaction of $[(ON)(NC)_4FeCNCo(en)_2(SO_3)]^-$ with $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$ at 25·0 °C and $I = 1{\cdot}00$M ($LiClO_4$)

$10^4[Fe(CN)_6{}^{n-}]$ M	$10^4[Fe(CN)_5(NO)^{2-}]$ M	10^4[Co] M	10^3k_b * s^{-1}
(*i*) With $[Fe(CN)_6]^{3-}$ (n = 3)			
25	1·5	1·5	108 ± 4 (5)
50	3·0	3·0	116 ± 2 (3)
100	3·0	3·0	105 ± 4 (5)
200	3·0	3·0	110 ± 4 (5)
200	4·8	1·2	109 ± 3 (5)
(*ii*) With $[Fe(CN)_6]^{4-}$ (n = 4)			
50	10	2·0	110 ± 3 (3)
100	10	2·0	116 ± 3 (4)
100	25	5·0	113 ± 3 (7)
200	10	2·0	118 ± 1 (3)
200	25	5·0	114 ± 4 (5)
250	10	2·0	121 ± 4 (5)

* The number of runs is given in parentheses.

$$-d[M'CNCo]/dt = k_d[M'CNCo] \quad (6)$$

The displacement of $[Co(CN)_6]^{3-}$ from $[(NC)_5CoCNCo(en)_2(SO_3)]^{2-}$ by $[Fe(CN)_6]^{3-}$ was measured at 480 nm in a similar manner. The results are summarised in Table 7 and we conclude that equation (6) again applies, with $k_d = 0{\cdot}0341 \pm 0{\cdot}0003\ s^{-1}$ at 25·0 °C, $I = 1{\cdot}00$M ($LiClO_4$), and pH *ca.* 5·5.

TABLE 7

Observed rate constants, k_d, for reaction of $[(NC)_5CoCNCo(en)_2(SO_3)]^{2-}$ with $[Fe(CN)_6]^{3-}$ at 25 °C and $I = 1{\cdot}00$M ($LiClO_4$)

$10^4[Fe(CN)_6{}^{3-}]$ M	$10^4[Co(CN)_6{}^{3-}]$ M	10^4[Co] M	10^2k_b */s^{-1}
25	1·5	1·5	3·44 ± 0·06 (4)
63	3·0	3·0	3·44 ± 0·06 (5)
100	1·5	1·5	3·38 ± 0·11 (4)
100	3·0	3·0	3·38 ± 0·03 (5)

* The number of runs is given in parentheses.

DISCUSSION

The preliminary kinetic results [1] for the formation of these μ-cyano-complexes are in moderately good agreement with those now reported, with the exception of the earlier experiment at the highest concentration of $[Fe(CN)_6]^{4-}$. Thus, the impression given by the earlier work that $k_{obs.}$ reaches a limit at *ca.* 10^{-2}M-$[Fe(CN)_6]^{4-}$ is erroneous. Although the linear relations now found between $k_{obs.}$ and [Fe] are compatible with a mechanism of type S_N2, the small changes in k_f on changing Fe, the almost identical values of k_f obtained when $[Fe(CN)_6]^{3-}$ is replaced by $[Co(CN)_6]^{3-}$, and the similarities of the activation parameters (Table 4), suggest that the reactions are predominantly of type S_N1. This conclusion accords with the results of other investigations of substitution reactions of sulphitocobalt(III) complexes.[2,3] Since ion pairing is likely between the reactants, the relatively small increase in k_f with increase in the charge of Fe can be ascribed partially to an increase in K_{IP}, the ion-pair stability constant. The full reaction scheme proposed is shown in equations (7)—(9) [$R = (NC)_5$ or $(ON)(NC)_4$]. In solutions of high ionic strength

$$[\mathrm{RFeCN}]^{n-} + [\mathrm{Co(en)_2(SO_3)(OH_2)}]^+ \overset{K_{IP}}{\rightleftharpoons} \underbrace{\{[\mathrm{RFeCN}][\mathrm{Co(en)_2(SO_3)(OH_2)}]\}^{(1-n)+}}_{\text{Ion pair}} \quad (7)$$

$$\{[\mathrm{RFeCN}][\mathrm{Co(en)_2(SO_3)(OH_2)}]\}^{(1-n)+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underbrace{\{[\mathrm{RFeCN}][\mathrm{Co(en)_2(SO_3)}]\}^{(1-n)+}}_{\text{Ion-paired intermediate}} \quad (8)$$

$$\{[\mathrm{RFeCN}][\mathrm{Co(en)_2(SO_3)}]\}^{(1-n)+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{RFeCNCo(en)_2(SO_3)}]^{(1-n)+} \quad (9)$$

the value of K_{IP} is probably less than 10 l mol^{-1}, even for $[Fe(CN)_6]^{4-}$. A value of 6·6 l mol^{-1} has been reported[4] for the formation of $\{Tl[Fe(CN)_6]\}^{3-}$ at $I =$ 3·0M ($LiClO_4$). Under our concentration conditions, the proportion of $[Co(en)_2(SO_3)(OH_2)]^+$ converted into an ion pair with the cyanoferrate would not exceed *ca.* 10% so that a linear relation is to be expected between $k_{obs.}$ and [Fe]. *Ca.* 0·1M-$[Fe(CN)_6]^{4-}$ would be required to show the departure from this relation which the S_N1(IP) mechanism predicts at sufficiently high cyanoferrate concentrations. However, the high contribution of $[Fe(CN)_6]^{4-}$ to the ionic strength, together with its ion pairing with Li^+, the principal cation, render doubtful the interpretation of results obtained at high concentrations of this anion.

The displacement reactions are interpreted as dissociation of the binuclear complex to form the cyanometallate and $[Co(en)_2(SO_3)(OH_2)]^+$ followed by reaction of the latter with the displacing cyanometallate, the sequence of steps being (9 reverse), (8 reverse), (7 reverse), and then, with the displacing cyanometallate, (7), (8), and (9). The lack of dependence of the rate of the displacement reaction on the displacing cyanometallate is a consequence of the higher concentration of the latter, and in most cases its higher k_f value, compared with the cyanometallate liberated by dissociation of the reactant binuclear complex. Under these conditions, scavenging of the liberated aqua-complex is efficient. The mechanistic alternative that the displacing cyanoferrate reacts with the ion-paired intermediate [equation (8)] can be discounted because the highly efficient reaction between these two, which would be required to avoid a kinetic dependence on the displacing cyanoferrate concentration, seems unlikely for reaction of the latter with an ion pair of like overall charge.

According to our proposed mechanism, equations (10) and (11) should hold. The similarity of k_f values and

$$k_f = K_{IP}k_1k_2/(k_{-1} + k_2) \quad (10)$$

$$k_d = k_{-1}k_{-2}/(k_{-1} + k_2) \quad (11)$$

activation parameters for the formation reaction suggests that the step involving bonding by the cyanoferrate [equation (9)] does not contribute markedly to the kinetic behaviour. Hence k_2 must exceed k_{-1} or be of similar magnitude to it. In either case equation (10) can be approximated by $k_f \approx K_{IP}k_1$. The position is less clear for the dissociation of the binuclear complex and depends on the discrimination shown by the five-co-ordinate cobalt(III) intermediate between water and the ion-paired cyanoferrate. We suggest that k_{-1} and k_2 are of the same magnitude and hence that (11) can be replaced by the approximation $k_d \approx k_{-2}$. We have remarked above that K_{IP} is likely to be less than 10 l mol^{-1}, hence this analysis leads to the conclusion that the magnitudes of the measured rate constants k_f and k_d are determined largely by the rate constants for S_N1 dissociation of the cobalt–aqua and cobalt–(μ-cyano) bonds, respectively.

The kinetic behaviour of the reaction between $[Fe(CN)_6]^{4-}$ and $[Co(en)_2(SO_3)(OH)]$ in alkaline solution is summarised by equation (5). We interpret k_d as the rate constant for dissociation of the binuclear complex, as defined in equation (6) in connection with displacement reactions. The constants k_b and k_c evidently relate to formation of the binuclear complex since they appear in terms containing the concentration of $[Fe(CN)_6]^{4-}$. The term in k_b can be assigned to a reaction route in which $[Co(en)_2(SO_3)(OH_2)]^+$ is formed in equilibrium with the dominant species $[Co(en)_2(SO_3)(OH)]$ and then reacts with $[Fe(CN)_6]^{4-}$ as in acidic solutions [equations (7)—(9)]. If this is so, $k_b = k_fK_W/K_H$, where $K_W = [H^+][OH^-] = 1{\cdot}7 \times 10^{-14}$ mol^2 l^{-2} at 25·0 °C and $I =$ 1·00M[5] and $K_H = [Co(en)_2(SO_3)(OH)][H^+]/[Co(en)_2(SO_3)(OH_2)^+] = 5{\cdot}4 \times 10^{-10}$ mol l^{-1}, found by ourselves. By using our value of $k_f = 7\,450$ l mol^{-1} s^{-1}, we obtain $k_b = 0{\cdot}23$ s^{-1}, about half the value obtained directly. Since $[Fe(CN)_6]^{4-}$ is strongly ion paired, even with alkali-metal cations, and k_f was determined in the presence of Li^+ whereas k_b was obtained in the presence of Na^+, we do not consider this discrepancy serious.

The term in k_c appears to imply slow dissociation of hydroxide from the complex $[Co(en)_2(SO_3)(OH)]$, but the detailed mechanism of this reaction path is uncertain. Just as k_b and k_d are the forward and reverse velocity constants for a particular reaction path, so there should be a term $k_e[OH^-]$ in equation (5), where k_e is the reverse reaction-velocity constant corresponding to k_c. Under the conditions of our experiments there was no evidence for such a term. Nevertheless, calculations making use of K_b suggest that the true value of k_d should be *ca.* $1{\cdot}8 \times 10^{-3}$ s^{-1}, *ca.* 70% of that cited, with $k_e =$ *ca.* $1{\cdot}2 \times$

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[2] J. Halpern, R. A. Palmer, and L. M. Blakley, *J. Amer. Chem. Soc.*, 1966, **88**, 2877; H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.*, 1968, **7**, 2535.

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[4] I. F. Mavrin, F. Y. Kul'ba, and V. E. Mironov, *Zhur. fiz. Khim.*, 1967, **41**, 1659.

[5] R. Nasanen and P. Merilainen, *Suomen Kem.*, 1960, **B33**, 149.

10^{-3} l mol^{-1} s^{-1}. Even at the highest hydroxide-ion concentrations employed, the presumed term in k_e should not contribute more than 20% of $k_{obs.}$ and for most experiments its contributions will be negligible.

The rate constants, k_f and k_d, for formation and dissociation of various μ-cyano-complexes are summarised in Table 8. The rate constant for the reaction (12) is not included. This reaction occurred too rapidly for measurement with our stopped-flow apparatus and we conclude that a simple electron-transfer path predominates.

$$[(NC)_5Fe^{III}CNCo(en)_2(SO_3)]^{2-} + [Fe(CN)_6]^{4-} \longrightarrow [(NC)_5Fe^{II}CNCo(en)_2(SO_3)]^{3-} + [Fe(CN)_6]^{3-} \quad (12)$$

Table 8

Summary of formation (k_f) and dissociation (k_d) rate constants in reactions of the complex *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ with cyanometallates, together with the corresponding equilibrium constants (K_a) at 25 °C and $I = 1{\cdot}00$M

	$[Fe(CN)_5(NO)_2]^-$	$[Fe(CN)_6]^{3-}$ and $[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$
k_f/l mol^{-1} s^{-1}	700	1 725	7 450
10^3k_d/s^{-1}	113	34·1	2·56
$10^{-4}K_a$/l mol^{-1}	0·62	5·1	290

To obtain the rate constant for dissociation of a binuclear complex formed from a triply charged cyanometallate, we therefore studied a displacement reaction equivalent to (12), with Co^{III} replacing Fe^{III} in the binuclear complex, and, for experimental convenience, an excess of $[Fe(CN)_6]^{3-}$ in place of $[Fe(CN)_6]^{4-}$ as the displacing anion. It seemed probable that the value of k_d so obtained would be very similar to that for the ligand-dissociation path for reaction (12).

Values of $K_a = k_f/k_d$, the equilibrium constant for formation of these binuclear complexes in acidic solution, are also given in Table 8. The value for the reaction involving $[Fe(CN)_5(NO)]^{2-}$ is in satisfactory agreement with the approximate value, 10^4 l mol^{-1}, obtained previously by spectrophotometric measurements.[1] The considerable increase in K_a with the charge on the cyanometallate is not surprising, but the absolute magnitudes of these stability constants for formation of a cyanide bridge are noteworthy. This work was undertaken with $[Co(en)_2(SO_3)(OH_2)]^+$ as the acceptor complex so that the labilising effect[3] of the sulphito-group would enable equilibria to be attained rapidly. The interesting question whether the presence of this group has a marked effect on the magnitude of the formation constants for cyanide bridges remains to be answered. We note that with $[Fe(CN)_5(NO)]^{2-}$ no change in rate of reaction was observed between pH 0 and 6. This suggests that in this range the sulphito-ligand remains unprotonated, the protonated form presumably being less labile.[6]

The equilibrium constant K_b for the reaction shown in equation (4) can be calculated from the K_a value in Table 8 for formation of $[(NC)_5FeCNCo(en)_2(SO_3)]^{3-}$ in acidic solution, since $K_b = K_aK_W/K_H$ where K_W and K_H have their previous significance and value. We find $K_b = 91$, about one third of the value we obtained from spectrophotometric measurements in alkaline solution. This discrepancy is in the same sense, and presumably has the same origin, as that noted above between rate constants found directly from experiments in alkaline solutions and those calculated from kinetic data obtained in acid solutions. In addition, as discussed above, the value of k_d in Table 8 may be *ca.* 30% greater than the true value; if so, K_a, and hence the value of K_b calculated from it, will be *ca.* 30% too low. We conclude that this numerical discrepancy does not invalidate the mechanistic scheme advanced, but it does indicate that K_a values may be subject to an error of up to 50%.

EXPERIMENTAL

The complex *trans*-$[Co(en)_2(SO_3)(OH_2)][ClO_4]{\cdot}OH_2$ was prepared as described previously.[1] Sodium hexacyanoferrate(II) (reagent grade) was recrystallised from water in subdued light. Dehydration over phosphorus penta-oxide showed a variable water content in successive batches; samples employed in kinetic experiments were standardised against cerium(IV) sulphate by using Ferroin indicator. Potassium hexacyanoferrate(III) (AnalaR), potassium hexacyanocobaltate(III) (reagent grade), and sodium pentacyanonitrosylferrate(2−) dihydrate (AnalaR) were used without further purification. Lithium perchlorate solution was prepared from the carbonate (reagent grade) and perchloric acid (AnalaR) and was recrystallised three times. Stock solutions of sodium hydroxide prepared from AnalaR pellets and, under air-free conditions, from washed reagent-grade sticks gave identical kinetic results; these solutions were standardised against 1·00M-hydrochloric acid by using phenolphthalein. Stock solutions of sodium perchlorate, sodium chloride (both AnalaR), and lithium perchlorate were standardised with 1·00M-sodium hydroxide after ion exchange on a column of Amberlite IR-120(H) resin.

Solutions of the complex cyanides for kinetic experiments on formation of the binuclear complexes in acid solution were freshly prepared by dissolving the solid in water and adding sufficient lithium perchlorate solution and dilute perchloric acid if required to give $I = 1{\cdot}00$M. Solutions of the sulphito-complex were made similarly. In the cases of the potassium salts, a precipitate of potassium perchlorate was removed by filtration before use. These and other rapid-reaction measurements were made by using a Durrum stopped-flow spectrophotometer, model D-110.

The rates of attainment of equilibrium between $[Fe(CN)_6]^{4-}$, *trans*-$[Co(en)_2(SO_3)(OH)]$, and their binuclear product were measured in the range 0·20—0·96M-OH$^-$ by mixing solutions of these reactants together with sodium hydroxide and sodium perchlorate stock solutions in a thermostat, and then transferring a sample into a thermostatted 2-cm optical cell in a Hilger Uvispek H700·9 spectrophotometer. Readings were taken at appropriate intervals of time. Normally, the $[Fe(CN)_6]^{4-}$ solution was added last, but in one case the sodium hydroxide was added last so that the direction of reaction was reversed; in this case the partial conversion of the binuclear complex into $[Fe(CN)_6]^{4-}$ and $[Co(en)_2(SO_3)(OH)]$ was followed. In the range 0·01—0·10M-OH$^-$ the stopped-flow technique was necessary. The readings of D_∞ in this system, from which the equilibrium

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[6] H. Siebert and G. Wittke, *Z. anorg. Chem.*, 1974, **405**, 63.

constant K_b was calulated, were obtained by similar procedures.

In measurements of the rates of displacement reactions, one syringe of the stopped-flow spectrophotometer contained the binuclear complex, formed previously by mixing solutions of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ (denoted by Co in Tables 6 and 7), and the cyanometallate present in lower concentration. The second syringe contained a stronger solution of the displacing cyanometallate, shown in the first column of Tables 6 and 7. The concentrations of reactants given in these Tables are those which would have been present after the final mixing if no reaction had occurred. Both solutions were adjusted to $I = 1{\cdot}00$M with lithium perchlorate; the pH was *ca.* 5·5.

Measurements of pH of reactant solutions were made on a Radiometer type 26 pH meter, standardised against a solution of 0·020M-$HClO_4$ plus 0·98M-$NaClO_4$; this solution was assigned a pH of 1·70. The acid-dissociation constant of *trans*-$[Co(en)_2(SO_3)(OH_2)]^+$ was obtained by titrating solutions in 1·00M-$NaClO_4$ with 1·00M-NaOH at 25·0 °C. From the titration curves, we find $pK_H = 9{\cdot}27 \pm 0{\cdot}02$.

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