Redox and substitution reactions of *trans*-(diaqua)(N, N'-ethylenebis(salicylideneaminato)cobalt(III) with hexacyanoferrate(II, III): A proton coupled electron transfer reaction

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The electron transfer between *trans*-$[Co(Salen)(OH_2)_2]^+$ (Salen = N, N'-ethylenebis(salicylideneaminato) and $(Fe(CN)_6)^{4-}$ involved a binuclear species, $[(OH_2)Co^{III}(Salen)-(NCFe^{II}CN_5)]^{3-}$, as an intermediate. The kinetics of the formation of this binuclear species and the one formed by the reaction of the title complex with $[FeCN_6]^{3-}$ have been studied at 20-35°C ($I = 0.5$ mol dm^{-3}); the data are consistent with the I_d mechanism. Both spontaneous and H^+ coupled paths are identified for the electron transfer within the binuclear species of hexacyanoferrate(II) which further undergoes electron transfer with $[FeCN_6]^{4-}$ via a second order path.

We have been investigating the kinetics of formation and reactivities of the binuclear compexes, $[N_5Co^{III}O_2CRXM]^{n+}$ where N_5 denotes nitrogen donors, M a substitution labile non-reducing metal ion and $XRCO_2^-$ is generally a bidentate or multidentate ligand[1]. A similar study has been recently reported by Johnson and Balhura[2]. The participation of the precursor binuclear complexes in the innersphere electron transfer reactions of acidoaminecobalt(III) complexes by reducing metal ions like Cr^{2+}, Fe^{2+} are also common[3]. In such cases the rapid formation of the precursors demands high substitutional lability of the reductant metal ion. Also ion-pairs, $\{[(NH_3)_5CoX^{n+}][FeCN_6]^{4-}\}$ (X = OH_2, pyridine, other nonlabile amine ligands)[4-7] are involved as precursors in the outersphere electron transfer reactions of several substitution inert cobalt(III) complexes by hexacyanoferrate(II). Also a cyanide bridged binuclear species, $[(EDTA)-Co^{II}NCFe^{III}CN_5]^{5-}$, was reported to be involved in the oxidation of (ethelenediaminetetraaceta-to)cobalt(II) by hexacyanoferrate(III)[8-10]. The formation of the ion-pairs and cyanide bridged binuclear species as stated above relates to the inertness and lability of Co^{III} and Co^{II} centres respectively.

The (diaqua)(N, N'-ethylenebis(salicylideneaminato)cobalt(III) ($[Co(Salen)(OH_2)_2]^+$ is likely to be prone to ion-pairing due to its low positive charge, *trans* configuration and relatively bulky ligand envelope. However, these properties as well as the charge delocalising effect of the aromatic moieties accentuate the substitutional lability of the bound H_2O ligands favouring the formation of the innersphere binuclear species with $[Fe(CN)_6]^{4-}$. Our aim was to examine the mechanism of reduction of $[Co(Salen)(OH_2)_2]^+$ by $[Fe(CN)_6]^{4-}$ which has not been investigated earlier. In order to elucidate the mechanism, we also investigated the kinetics of complex formation between this cobalt(III) substrate and hexacyanoferrate(III).

Materials and Methods

The $[Co(Salen)(OH_2)_2]ClO_4.H_2O$ was prepared by the published method[11]. Test of Co^{II} in the sample by Kitson's method[12] was negative. The purity of the sample was further checked by analysis of cobalt which agreed satisfactorily with the value calculated by the molecular formula. The samples were stored over fused calcium chloride in dark to avoid photo decomposition. The samples prepared in different batches had identical UV-visible spectra and yielded reproducible kinetic data.

Analar grade chemicals were used for kinetic runs. Sodium perchlorate used for ionic strength adjustments was prepared from Na_2CO_3 and $HClO_4$. Stock solution of $NaClO_4$ was estimated by a combined ion-exchange and alkalimetric procedure. Dowex 50W-X8 resin in H^+ form was used for all ion-exchange experiments. Acetate, MES [2-(N, morpholino)ethanesulphonic acid]

and tris buffers were used for controlling pH. Doubly distilled water was used for preparing solutions and the medium of reaction was 2% (v/v) in methanol. This was necessary to avoid cloudiness of the reaction mixture at the end of the reaction due to the precipitation of the product, Co^{II}(Salen).

The UV-visible spectra were recorded on a JASCO 7800 spectrophotometer. The pH measurements were done with an ELICO digital pH meter model LI 120 equipped with combined glass-Ag/AgCl, Cl^- (2 mol dm^{-3} NaCl) electrode CL51. The meter was standardised using NBS buffers of pH 4.01, 6.86 and 9.20.

pK measurements

90.00 cm^3 (2% v/v in MeOH) of the diaqua complex (5.0 × 10^{-4}, I = 0.5 mol dm^{-3}) was titrated potentiometrically against 0.02 mol dm^{-3} NaOH at 25°C. The ionisation of only one aqua ligand was observed and the pH titration data were analysed using K_w = 1.0 × 10^{-14} and y_{OH^-} = y_{H^+} = 0.7 (to convert a_{H^+} and a_{OH^-} to [H$^+$] and [OH$^-$] respectively). We obtained pK_1 = 9.0 ± 0.05 for the equilibrium (1)

[Co(Salen)(OH$_2$)$_2$]$^+$

$$\underset{K_1}{\rightleftharpoons} [Co(Salen)(OH)(OH_2)] + H^+ \qquad \ldots (1)$$
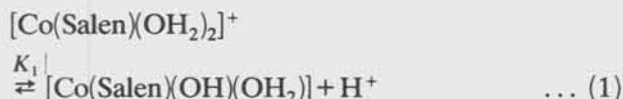
Kinetics

Rate measurements were made on a HITECH (U. K.) SF51 stopped flow spectrophotometer automated by an APPLE IIGS P.C. The pseudo-first order conditions were maintained with respect to pH and [Fe(CN)$_6^{4-}$] and the working wave length was 420 nm (ε = 1023 dm^3 mol^{-1} cm^{-1} for [Fe(CN)$_6$]$^{3-}$)[6]. The reduction of the diaqua complex by [Fe(CN)$_6$]$^{4-}$ displayed biphasic kinetics. The absorbance rapidly increased with time at a shorter time scale while this was followed by a substantially large absorbance increase on a relatively longer time scale. However, the absorbance-time data for the two processes could be fitted to the first order kinetic expression as expected for well resolved kinetics. The observed rate constants for the fast and slow processes (k^f_{obs} and k^s_{obs}) had to be determined from runs taken at different time scales. There was no buffer effect due to acetate and MES buffers; tris buffer had rate retarding effect on the electron transfer reaction. Each rate constant is an average of at least seven measurements.

The kinetics of complexation of the diaqua complex with hexacyanoferrate (III) were studied under pseudo-first order conditions at 430 nm by the stopped flow technique. Only single exponentials characteristic of monophasic first order kinetics were observed. All calculations were made on an IBM 486 PC using a least squares programme; the dependent variable was weighted inversely as its variance.

Stoichiometry of the redox reaction

Known amounts of the diaquacomplex and [Fe(CN)$_6$]$^{4-}$ (in excess) were mixed in acetate buffer. After 60 s, the unreacted [Fe(CN)$_6$]$^{4-}$ and the product [Fe(CN)$_6$]$^{3-}$ were rapidly exchanged by shaking the reaction mixture with Dowex 1 × 8 resin in Cl^- form and the solution filtered. The cobalt(II) content in the filtrate and the resin washings (combined together) was estimated spectrophotometrically as Co(NCS)$_4^{2-}$ by Kitson's method[12]. A standard curve for Co(II) was constructed using CoCl$_2$ which was estimated by complexometric titration using EDTA. The concentration of [Fe(CN)$_6$]$^{3-}$ in the reaction mixture was also estimated spectrophotometrically at 420 nm after acidifying the reaction mixture at the end of the reaction (60s) to pH 1, removing Co^{II} by ion-exchange procedure using Dowex 50W-X8 (H$^+$ form). By this process the diprotonated ethylenediamine, the hydrolysed product of Salen was also retained by the resin. A calibration curve for [Fe(CN)$_6$]$^{3-}$ was also constructed. The analytical data {Δ[Co^{II}]/Fe(CN)$_6^{3-}$] = 1} agreed with the stoichiometry.

$$Co(Salen)(OH_2)_2^+ + Fe(CN)_6^{4-} =$$
$$Co(Salen)(OH_2)_2 + Fe(CN)_6^{3-} \qquad \ldots (2)$$
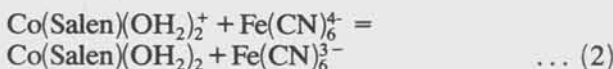
With [Co(Salen)(OH$_2$)$_2^+$] = 2.0 × 10^{-4}, 1.0 × 10^{-3} mol dm^{-3} and [Fe(CN)$_6^{4-}$] = 2.0 × 10^{-3}, 1.0 × 10^{-2} mol dm^{-3} respectively, Co^{II} yields corresponded to 99.2 ± 0.8% reduction.

Results and Discussion

(i) [Co(Salen)(OH$_2$)(NCFeCN$_5$)]$^{3-}$

The initial fast reaction obeyed the empirical relationship

$$k^f_{obs} = (a + b[H^+])[Fe(CN)_6^{4-}]_T \qquad \ldots (3)$$

as (i) k_{obs} versus [Fe(CN)$_6^{4-}$]$_T$ plots at constant pH were linear with statistically insignificant intercept on the rate axis, and (ii) the slopes of such plots increased linearly with increase in [H^f] (see Table 1). This behaviour is consistent with replacement of coordinated H$_2$O by [Fe(CN)$_6$]$^{4-}$ to form [Co(Salen)(OH$_2$)(NCFeCN$_5$)]$^{3-}$ with and without involvement of H$^+$. The dissociation of the binuclear species is, however, not detectable under the experimental conditions. The H$^+$ dependence of

Table 1—Rate constants for the complexation of $[Co(Salen)(OH_2)_2]^+$ with $[Fe(CN)_6]^{4-}$ at $25.0 \pm 0.1°C$, $I = 0.5$ mol dm^{-3})

$10^3[Fe(CN)_6]^{4-}$ (mol dm^{-3})	$k^f_{obs}(s^{-1})$ at $pH =$				
	$(4.18 \pm 0.03)^a$	$(4.48 \pm 0.02)^a$	$(4.75 \pm 0.01)^a$	$(5.26 \pm 0.01)^a$	$(5.75 \pm 0.01)^a$
5.0	$52. \pm 3$	41 ± 3	31 ± 1	26 ± 1	19.4 ± 0.6
7.5	68 ± 3	49 ± 3	47 ± 1	39 ± 1	26.5 ± 0.5
10.5	99 ± 3	73 ± 3	63 ± 3	55 ± 1	37 ± 1
12.5	114 ± 7	92 ± 4	83 ± 2	65 ± 1	48 ± 3
15.0	138 ± 3	116 ± 5	97 ± 2	76 ± 1	63 ± 2
17.5	152 ± 5	132 ± 5	110 ± 2	87 ± 2	72 ± 1
20.5	175 ± 5	151 ± 5	124 ± 3	97 ± 2	81 ± 2
$10^{-3}k^f_{obs}0[Fe(CN)_6^{4-}]_T(dm^3mol^{-1}s^{-1})$					
	9.2 ± 0.6	7.4 ± 0.5	6.3 ± 0.2	5.1 ± 0.2	3.9 ± 0.3

$k_1(dm^3mol^{-1}s^{-1})^b = (4.5 \pm 0.3) \times 10^3$; $k_2'(dm^6mol^{-2}s^{-1})^b = (8.5 \pm 1.6) \times 10^7$
(a) CH_3CO_2Na/CH_3CO_2H buffer; (b) see Eq. (4).

k_{obs} may arise due to two reasons: (i) the protonated substrate may react with $[Fe(CN)_6]^{4-}$, and / or (ii) the unprotonated substrate may react with $\{H[Fe(CN)_6]\}^{3-}$. However, the latter can be discounted on the grounds of the high value of the acid dissociation constant of $\{H[Fe(CN)_6]\}^{3-}$ $\{K = (1.9 \pm 0.1) \times 10^{-3}$ at 25°C and $I = 0.5$ mol dm$^{-3}\}$ (ref. 13). Accordingly Scheme 1 is proposed:

$[Co(SalenH)(OH_2)_2]^{2+} + [Fe(CN)_6]^{4-} \xrightarrow{k_2} [(OH_2)Co(SalenH)NCFeCN_5]^{2-}$

$H^+ \Updownarrow K_2$

$[Co(Salen)(OH_2)]^+ + [Fe(CN_6)]^{4-} \xrightarrow{k_1} [Co(Salen)(OH_2)(NCFeCN_5)]^{3-}$

Scheme 1

for which,

$k^f_{obs} = (k_1 + k_2'[H^+])[Fe(CN_6)^{4-}]_T/(1 + [H+]/K_2)$
... (4)

where $k_2' = k_2/K_2$

It may be noted that the denominator of Eq. (4) essentially reduced to 1 under the experimental conditions consistent with Eq. (3). Values of k_1, and k_2' calculated using Eq. (4) and assuming $1 >> [H+]/K_2$ are collected in Table 1.

(ii) Reversible formation of $[(OH_2)Co(Salen)(NCFeCN_5)]^{2-}$

In order to elucidate the reaction of $[Fe(CN)_6]^{4-}$ we also studied the reaction of hexacyanoferrate(III) with $[Co(Salen)(OH_2)_2]^+$. The UV-visible spectra of the cobalt(III) substrate, $[Fe(CN)_6]^{3-}$ and the mixture of the two (see Fig. 1) showed clear evidence of interaction between them leading to the formation of a binuclear species, $[Co(Salen)(OH_2)(\tilde{N}CFeCN_5)]^{2-}$. The rate constants for the reversible formation of such a species were collected under pseudo-first order conditions at $pH = 4.9 \pm 0.02$ (20.0-30.0°C, $I = 0.5$

Fig. 1—Spectra of $[Co(Salen)(OH_2)_2]^+$ in the presence and absence of $[Fe(CN)_6]^{3-}$ at 25°C, $pH = 5.0$. $I = 0.5$ mol dm^{-3} cell path = 1 cm. (1) $[Co^{III}]_T = 1.0 \times 10^{-4}$ mol dm^{-3}; (2) $[Fe(CN)_6^{3-}]_T = 1.0 \times 10^{-4}$ mol dm^{-3}; (3) $[Co^{III}]_T = 1.0 \times 10^{-4}$ mol dm^{-3} + $[Fe(CN)_6^{3-}]_T = 1.0 \times 10^{-4}$ mol dm^{-3}

mol dm^{-3}) and $0.0025 \leqslant [Fe(CN)_6^{4-}]_T$ (mol dm^{-3}) $\leqslant 0.020$ (see Table 2). At this pH the cobalt(III) substrate and $[FeCN)_6]^{3-}$ (ref. 14) do not undergo protonation to any significant extent. The k_{obs} versus $[Fe(CN)_6^{3-}]_T$ plots were linear with positive gradients and positive intercepts on the k_{obs} axis indicating that both forward and reverse reactions (see Eq. 5) were significant.

$[Co(Salen)(OH_2)_2]^+ + [Fe(CN)_6]^{3-} \underset{k_r}{\overset{k_f}{\rightleftarrows}} [H_2OCo(Salen)(NCFeCN_5)]^{2-}$ ... (5)

$k_{obs} = k_f[Fe(CN_6)^{3-}]_T + k_r$ ... (6)

Values of k_f and k_r were obtained by fitting the rate constants (k_{obs}) to Eq. (6). These and the associated activation parameters are given in Table 2.

Table 2—Rate constants for the complexation of $[Co(Salen)(OH_2)_2]^+$ with $[Fe(CN)_6]^{3-}$

$[Co(Salen)(OH_2)_2^+]_T = 5.0 \times 10^{-4}$, $I = 0.5$ mol dm^{-3}, $\lambda(nm) = 430$

$10^3[Fe(CN)_6^{3-}]_T$ (mol dm^{-3})	$k_{obs}(s^{-1})$ at			
	$20.0 \pm 0.1°$ $(4.92 \pm 0.02)^a$	$25.0 \pm 0.1°$ $(4.88 \pm 0.02)^a$	$30.0 \pm 0.1°$ $(4.92 \pm 0.02)^a$	$35.0 \pm 1°C$ $(4.92 \pm 0.02)^a$
2.50	1.96 ± 0.14	2.34 ± 0.24	4.0 ± 0.1	4.68 ± 0.05
5.50	2.86 ± 0.05	4.54 ± 0.34	6.2 ± 0.5	7.4 ± 0.2
7.55	3.57 ± 0.03	5.34 ± 0.10	8.6 ± 0.1	9.8 ± 0.1
10.5	4.5 ± 0.2	6.4 ± 0.2	10.2 ± 0.4	12.0 ± 0.1
12.5	5.4 ± 0.2	7.5 ± 0.2	12.2 ± 0.3	13.5 ± 0.4
15.5	6.4 ± 0.2	8.9 ± 0.2	14.2 ± 0.3	16.0 ± 0.4
17.5	7.4 ± 0.1	9.8 ± 0.1	16.4 ± 0.2	18.3 ± 0.4
20.0	8.5 ± 0.2	11.1 ± 0.5	18.3 ± 0.4	20.5 ± 0.9
$K_r(s^{-1})$	0.77 ± 0.07	1.5 ± 0.2	2.2 ± 0.2	2.45 ± 0.08
$k_f(dm^3mol^{-1}s^{-1})$	378 ± 9	477 ± 15	806 ± 18	908 ± 15
ΔH^+ (kJ mol^{-1})^b	43 ± 7 (52 ± 8)			
ΔS^+ (JK^{-1}mol^{-1})^b	$-50 \pm 22(-67 \pm 27)$			

^{a} pH values, CH_3CO_2Na/CH_3CO_2H buffer
^{b} unparanthesised values are for formation and paranthesised values are for dissociation of the binuclear species, $[(OH_2)Co(Salen)(NCFeCN_5)]^{2-}$.

(iii)Reduction of $[Co(Salen)(OH_2)_2]^+$ by $[Fe(CN)_6]^{4-}$

The observed rate constants (k_{obs}^s) for the slow reaction between $[Co(Salen)(OH_2)_2]^+$ and $[Fe(CN)_6]^{4-}$ (see Tables 1 and 3) are for the redox reaction. At constant pH, k_{obs}^s versus $[FeCN_6^{4-}]_T$ plots is linear with positive gradient and positive intercept on the k_{obs}^s axis. While the gradient is virtually independent of pH the intercept increases with $[H^+]$. The redox reaction is preceded by the rapid formation of the binuclear complex, $[Co(Salen)(OH_2)(NCFeCN_5)]^{3-}$ which is driven to completion at $[Fe(CN)_6^{4-}]_T$ used. Hence our findings are consistent with Scheme 2 for the redox reaction.
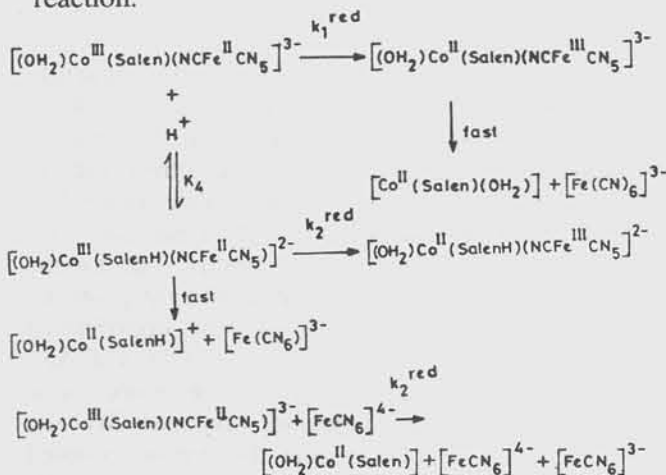
Scheme 2

Accordingly k_{obs}^s is given by Eq. (7) for $K_4[H^+]$ $<< 1$ (i.e. when the binuclear complex is not significantly protonated)

$$k_{obs}^s = k_1^{red} + k_2^{red'}[H^+] + k_3^{red}[Fe(CN)_6^{4-}] \quad \dots (7)$$

where $k_2^{red'} = k_2^{red}K_4$. Values of the rate constants are collected in Tables 3 and 4. The H$^+$ dependence of the redox reaction was insignificant at pH > 5. The temperature dependence of the redox reaction was studied at pH 5.94 (MES buffer), $20.0 \leqslant t/°C \leqslant 35.0$ and the observed rate constants and the rate and activation parameters for the intramolecular (k_1^{red}) and second order (k_3^{red}) paths are collected in Table 4.

The lability of the axially bound H_2O in the *trans*-$[Co(Salen)(OH_2)_2]^+$ (refs. 15, 16) is a contrasting feature considering the kinetic inertness of numerous cobalt(III) complexes. This unusual behaviour has been attributed to the special feature of the Salen and its arrangement in the square plane by which it influences the electron displacement property in the axial direction and hence the kinetic lability of the axially bound ligands[16]. A rate comparison shows that $[Fe(CN)_6]^{4-}$ substitutes the coordinated H_2O in $[Co(Salen)(OH_2)_2]^+ \sim 10$ times faster than $[Fe(CN)_6]^{3-}$. A reverse trend is expected from the consideration of the ionic strength effect. However, ionpairing of the cobalt(III) substrate with 4-ion is electrostatically more favourable than with 3-ion. Hence the observed trend in the reactivity is consistent with the dissociative interchange mechanism involving precursor ion-pair formation. However, substantial ion-pairing of the cobalt(III) substrate with $[Fe(CN)_6]^{4-/3-}$ was not observed. The low values of the activation enthalpy for the formation and dissociation of the binuclear complex of $[Co(OH_2)_2(Salen)]^+$ with

Table 3—Rate constants for the reduction of $[Co(Salen)(OH_2)_2]^+$ by $[Fe(CN)_6]^{4-}$ at $25.0\pm0.1°C$ and $I = 0.5$, $[Co^{III}]_T = 5.0 \times 10^{-4}$ mol dm^{-3}

pH^b	(0.0025)	(0.0050)	(0.0075)	(0.0105)	(0.0125)	(0.0150)	(0.0175)	(0.0250)
4.28±0.2	19.9±0.0.2	24.4±0.1	30.1±0.5	34.0±0.1	37.6±0.1	43.2±0.3	48.2±0.5	51.9±0.4
4.48±0.02	14.4±0.0.2	19.7±0.5	25.8±0.6	31.0±0.4	34.1±0.3	39.2±0.6	43.2±0.6	47.4±0.4
4.75±0.01	12.5±0.1	18.5±0.1	24.9±0.4	31.9±0.3	36.8±0.4	40.6±0.6	45.2±0.8	50.1±0.7
5.26±0.01	10.9±0.1	14.9±0.4	19.9±0.4	25.1±0.2	31.0±0.7	36.0±0.8	40.5±0.8	46.8±1.9
5.75±0.01	8.9±0.1	12.9±0.1	17.3±0.2	22.7±0.3	27.9±0.2	31.9±0.7	37.7±0.6	42.3±0.6
5.94±0.02^c	11.4±0.5	16.9±0.8	24.6±0.7	28.1±0.4	31.9±0.6	37.2±1.1	43.8±0.7	49.4±0.9
7.45±0.03^d	5.9±0.1	8.6±0.5	9.7±0.1	11.0±0.1	11.9±0.1	13.1±0.2	14.0±0.1	15.4±0.1

[a] values under parentheses are $[Fe(CN)_6^{4-}]_T$ (mol dm^{-3}); [b] $4.28 \leqslant pH \leqslant 5.75$, CH_3CO_2Na/CH_3CO_2H buffer; [c] MES buffer; [d] tris buffer

Table 4—Kinetic parameters for redox reaction at $25.0\pm0.1°C$

pH	I^a	S^a	Corr. Coeff.
4.28	0.153±0.0023	18.3±0.3	0.998
4.48	0.100±0.0052	18.9±0.5	0.997
4.75	0.068±0.0043	23.3±0.7	0.995
5.26	0.059±0.0037	19.3±0.5	0.999
5.75	0.0388±0.0033	18.7±0.5	0.999
5.94	0.062±0.009	21.2±0.8	0.996
7.45	0.053±0.0039	5.08±0.3	0.994

$k_1^{red}(s^{-1})^b$ $(5.32\pm0.10)\times10^{-2}$
$k_2^{red}(dm^3mol^{-1}s^{-1})^b$ $(1.6\pm0.2)\times10^3$
$k_3^{red}(dm^3mol^{-1}s^{-1})^b$ 20 ± 2

[a] I and S denote intercept and slope of $k_{obs}^*(s^{-1})$ versus $[Fe(CN)_6^{4-}]_T$ (mol dm^{-3}) plot respectively.
[b] see Eq. (7)

(I)
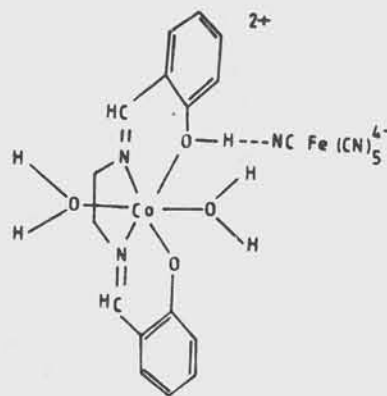
$[Fe(CN_6)]^{3-}$ (see Table 2) reflect the specific effect of the Salen ligand in controlling the energetics of the reaction. The negative values of the activation entropy is in keeping with the entropy loss due to ion-pairing and the solvation demands of the initial state and the transition state of the interchange process. It is further worth noting that the substitutional lability of $[Co(Salen)(OH_2)_2]^+$ is comparable to that of aquacobalamin complex[17] (B12-H_2O^+). However, the mechanism of substitution of the aqua ligand in B12-H_2O^+ by $[Fe(CN)_6]^{4-}$ and several other ligands of varying charge types has been suggested to be D and such reactions are associated with substantially large values of ΔH^* (~80 kJ mol^{-1}) and large positive values of ΔS§ unlike in the present case.

The substitution of H_2O in $[Co(Salen)(OH_2)_2]^+$ by $[Fe(CN)_6]^{4-}$ is H$^+$ catalysed. The acid dissociation constants of $H_2Fe(CN)_6^{2-}$ and $HFe(CN)_6^{3-}$ are $1.2\pm0.5\times10^{-2}$ and $1.9\pm0.1\times10^{-3}$ ($25.0°C$, $I = 0.5$ mol dm^{-3})[13] respectively. Hence such protonated species can be neglected under the present pH conditions. Also the extent of protonation of the cobalt(III) substrate is not significant at pH > 4. However, protonated Salen complex associating with $[Fe(CN)_6]^{4-}$ (see structure I), is presumably of kinetic significance which in consequence, results in rate enhancement.

A comparison of the rate constant for the electron transfer between Co^{III} and Fe^{II} centres within the innersphere binuclear species, $[Co^{III}(Salen)(OH_2)(NCFe^{II}CN_5)]^{3-}$ (~0.05 s^{-1}, see Table 4) with the same for the outersphere ion-pair $[Co(NH_3)_5(OH_2), Fe(CN)_6]^-$ ($k_{ip}=0.1$ s^{-1} at $25.0°C)^{4-6}$ shows that the innersphere effect has no advantage. The electron transfer is, however, mediated by the Salen ligand by reducing electron accepting property of the cobalt(III) centre. It may be mentioned that the electron transfer reaction between (ethylenediaminetretraacetato)cobalt(II) and hexacyanoferrate(III) involves a cyanide bridged binuclear species[8-10], but electron transfer is believed to occur via outersphere mechanism[18].

The electron transfer within the binuclear complex is also subject to H$^+$ catalysis. The kinetic data, however, do not reveal significant protonation of the binuclear species. The coordinated Salen in the successor complex, $[(OH_2)Co^{II}(Salen)(NCFe^{III}CN_5)]^{3-}$, is likely to be more basic than the same in its precursor analogue. We are, therefore led to believe that the proton coupled electron transfer within the binuclear species depicts a concerted process.

It is further interesting to note that the binuclear species also undergoes electron transfer with $[Fe(CN)_6]^{4-}$ via a second order path. There is no

Table 5—Temperature dependence of k^s_{obs} for the reduction of $[Co(Salen)(OH_2)_2]^+$ by $[Fe(CN)_6]^{4-}$

$[Co^{III}]_T = 5.0 \times 10^{-4}$, $I = 0.5$ mol dm^{-3}, $\lambda = 420$ nm.

$10^3[Fe(CN)_6]^{4-}$ (mol dm^{-3})	$10^2 k^s_{obs}$ (s^{-1})[a] at		
	30.0 ± 0.1	35.0 ± 0.1	$40.0 \pm 0.1°C$
2.5	18.1 ± 0.5	28.1 ± 0.5	47.4 ± 1.4
5.5	25.8 ± 0.5	33.4 ± 0.6	58.3 ± 1.4
7.5	36.4 ± 0.7	45.9 ± 0.5	68.7 ± 0.5
10.5	41.4 ± 1.0	58.6 ± 0.8	85.5 ± 1.1
12.6	49.0 ± 0.9	66.9 ± 0.9	98.1 ± 0.8
15.5	56.9 ± 0.6	80.5 ± 1.0	123 ± 3
17.5	63.9 ± 2.0	90.4 ± 1.5	134 ± 3
20.5	75.4 ± 0.5	102 ± 5	146 ± 1
I^b	0.097 ± 0.010	0.157 ± 0.014	0.245 ± 0.020
S^b	31.6 ± 0.9	41.0 ± 1.7	60.0 ± 1.6
ΔH^+ (kJ mol^{-1})^c		$69 \pm 1(50 \pm 2)$	
ΔH^+ (kJ mol^{-1})		$-35 \pm 3(-52 \pm 8)$	

[a] MES buffer, *p*H values: $5.92 \pm 0.01(30°C)$, 5.96 ± 0.01 (35.0°C), $5.92 \pm 0.01(40°C)$

[b] I and S denote intercept and slope of $k^s_{obs}(s^{-1})$ versus $[Fe(CN)_6^{4-}]_T$ plot; $I = k^{red}_1$ and $S = k^{red}_3$ (see equation 7) as under this *p*H conditions the H^+ dependence of k^s_{obs} is negligible.

[c] unparanthesised values are for intramolecular reduction of Co^{III} in the species $[(OH_2)Co(Salen)(NCFeCN_5)]^{3-}$ (k^{red}_1) and paranthesised values are for the reduction of the binuclear species by $[Fe(CN)_6]^{4-}$ in a second order path (k^{red}_3). Values of k^{red}_1 and k^{red}_3 at 25°C (see Table 4) were combined with those in Table 5.

evidence of H^+ catalysis in tris path. However, this is strongly retarded by tris-buffer (see values of I and S in Table 4) unlike other anionic buffers used. We presume that the observed retardation might be linked with blocking of the preferred site of approach of the second $[Fe(CN)_6]^{4-}$ to the binuclear species by the buffer component. The values of the second order rate constant ($k^{red}_2 = 20 \pm 2$ dm^3 mol^{-1}s^{-1}, 25°C, $I = 0.5$ mol dm^{-3}, see Table 4) depict facile electron transfer within the preassembled encounter complex, $\{Fe(CN)_6^{4-}[(H_2O)Co(Salen)(NCFe(CN)_5)]^{3-}\}$. The activation enthalpies (see Table 5) for both the electron transfer steps are low and the corresponding activation entropies are also negative indicating no substantial reorganisation in the transition state. This may be contrasted with very high

ΔH^+ ($= \sim 100$ kJ mol^{-1} and high positive value of ΔH^+ ($= \sim 100$ J K^{-1} mol^{-1}) for the electron transfer reaction of the ion-pair, $[(NH_3)_5CoOOH_2.Fe(CN)_6]^-$ (refs 4 & 6) which follows outersphere mechanism. However, in the present case the electron transfer within the binuclear species is likely to be innersphere while the second order path may involve outersphere mechanism.

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