Outer-sphere Redox Reactions in Sterically Hindered Pentaam(m)inecobalt(III) Complexes. A Temperature and Pressure Dependence Kinetic Study†

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Outer-sphere redox reactions between $[Co(RNH_2)_5(H_2O)]^{3+}$ and $[Fe(CN)_6]^{4-}$ have been studied as a function of pH, temperature and pressure. The effect of the size of the alkyl substituent on the amine, RNH_2, has been investigated for both the aqua- and the hydroxo-species in order to establish possible correlations between size and ion-pair formation constant, electron-transfer rate constant, and thermal and pressure activation parameters. The values obtained (at 45 °C and ambient pressure) indicate that the ion-pair formation constant decreases with increasing size of R (75, R = H; 40, Me; 23 dm³ mol⁻¹, Et), whereas the electron-transfer rate constant increases in this direction (0.11, R = H; 9.3, Me; 35 s⁻¹, Et). The activation enthalpies do not change, either with decreasing charge on the cobalt complex or with the size of the amine (87, R = H; 79, Me; 84 kJ mol⁻¹, Et). As for the activation volume, although a slight increase is observed on increasing the size of R (26.5, R = H; 29.4, Me; 33.1 cm³ mol⁻¹, Et), it is clear that solvational changes during electron transfer are mainly responsible for the values obtained.

Although the simple outer-sphere redox reaction (1) (n = 2 or 3, m = 0 or 1) has on several occasions[1] been studied as a function of temperature and pressure, the only attempt[2] to look into the effect of steric hindrance on the amines has been done for only one of the five amine groups being substituted, as indicated in reaction (2) (R = Me or Bu^i).

$$[Co(NH_3)_5X]^{n+} + [Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + Co^{2+} + 5NH_3 + X^{m-} \quad (1)$$

$$[Co(NH_3)_4(RNH_2)X]^{2+} + [Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + 4NH_3 + RNH_2 + Co^{2+} + X^- \quad (2)$$

As a continuation of our interest in the effect of pressure on typical inorganic and organometallic reactions,[3] as well as in the effect of steric and electronic factors which could influence or tune the reactivity of transition-metal complexes,[4] we have studied the effect of a systematic increase in the size of all five amine groups for reaction (1). In addition, we have also varied the sixth ligand in the co-ordination sphere of the cobalt(III) complex from H_2O to OH^- by repeating the measurements as a function of pH. This simple reaction has been chosen in order to be able to separate the encounter-complex formation constant, K_{os}, from the electron-transfer rate constant, k, for the mechanism outlined in Scheme 1. The rate equation (3) can be derived for this mechanism under pseudo-first-order conditions. The high charge on the complexes involved allows the kinetic separation referred to. Thus, the analysis of the $[Fe(CN)_6{}^{4-}]$ dependence of k_{obs} under pseudo-first-order conditions as a function of temperature and pressure, enables us to use the obtained thermodynamic and kinetic parameters as a source of information on the effect of steric hindrance on the outer-sphere electron-transfer reactions of more complicated systems.

$$k_{obs} = kK_{os}[Fe(CN)_6{}^{4-}]/\{1 + K_{os}[Fe(CN)_6{}^{4-}]\} \quad (3)$$

Experimental

Materials.—All materials were reagent-grade chemicals. The salt $Na_4[Fe(CN)_6]$ was recrystallized twice, all other chemicals being used without further purification.

Preparation of Compounds.—$[Co(RNH_2)_5(H_2O)][ClO_4]_3$ (R = H, Me *or* Et). The products were prepared as described previously[4b,c] and characterized by UV/VIS spectroscopy [λ/nm (ε/dm³ mol⁻¹ cm⁻¹)]: 491 (47.2), 345 (44.3) for R = H; 510 (65.9), 360 (66.7) for R = Me; 516 (86.7), 364 (86.6) for R = Et.

Buffer Solutions.—All buffers were prepared according to well established procedures,[5] concentrations being chosen to provide enough buffering for the $[Fe(CN)_6]^{4-}$ solutions. The final pH was set by the addition of NaOH or $HClO_4$ solutions to the prepared buffers, 3.9 ($MeCO_2{}^-$–$MeCO_2H$) for the aqua complexes and 7.3 [tris(hydroxymethyl)aminomethane (Tris)] for the hydroxo complexes. The effectiveness of the buffer solutions was checked by measuring the pH value of the final reaction mixture.

Instruments.—All UV/VIS spectra were recorded on a Hewlett-Packard HP8452A instrument. The pH measurements were carried out with a Crison 2002 instrument equipped with an Ingold microelectrode. Atmospheric pressure kinetic runs with $t_{\frac{1}{2}} > 170$ s were recorded on a HP8452A instrument equipped with a thermostatted multicell transport, runs with $7 < t_{\frac{1}{2}} < 170$ s on a HP8452A instrument equipped with a High-Tech SFA-11 rapid kinetics accessory, and those for $t_{\frac{1}{2}} < 7$ s on a Durrum D-110 stopped-flow instrument. For runs at elevated pressure with $t_{\frac{1}{2}} < 100$ s a laboratory stopped-flow

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† *Supplementary data available* (No. SUP 57033, 9 pp.): observed rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: bar = 10^5 Pa.

$$[Co(RNH_2)_5(H_2O)]^{3+} + [Fe(CN)_6]^{4-} \overset{K_{os}}{\rightleftharpoons} \{[Co(RNH_2)_5(H_2O)]^{3+},[Fe(CN)_6]^{4-}\}$$

$$\{[Co(RNH_2)_5(H_2O)]^{3+},[Fe(CN)_6]^{4-}\} \xrightarrow{k} \{[Co(RNH_2)_5(H_2O)]^{2+},[Fe(CN)_6]^{3-}\}$$

$$\{[Co(RNH_2)_5(H_2O)]^{2+},[Fe(CN)_6]^{3-}\} \xrightarrow{\text{fast}} [Fe(CN)_6]^{3-} + Co^{2+} + 5RNH_2 + H_2O$$

Scheme 1 R = H, Me or Et

instrument equipped with a pressurizing system was used as described previously;[6a] for those with $t_{\frac{1}{2}}$ > 800 s a previously described pressurizing system[6b] and high-pressure cell[6c] were used.

Kinetics.—All kinetic measurements were performed under pseudo-first-order conditions with the iron complex in excess over the cobalt complex. All runs were followed at 420 nm where the appearance of $[Fe(CN)_6]^{3-}$ (ε = 1023 dm^3 mol^{-1} cm^{-1})[7] produces a large increase in absorbance [0.1–0.3 units for the cobalt concentration used, *ca.* (2–3) × 10^{-4} mol dm^{-3}]. Solutions for the kinetic runs were made up by mixing appropriate amounts of the corresponding stock solutions at 1.0 mol dm^{-3} ($LiClO_4$) ionic strength. All solutions were degassed in order to avoid any iron(II) oxidation, and ethylenediaminetetraacetate (edta), in a ratio [cobalt complex]:[edta] = 1:2, was added to the reaction medium to prevent precipitation of the cobalt(II) reaction product.[8] The cobalt(III) complex stock solutions were made up in water in order to avoid any interference from anation reactions with edta or buffer anions during long storage or high-pressure equilibration times. Accordingly, the $[Fe(CN)_6]^{4-}$ stock solutions had to be prepared in the corresponding buffers and with the addition of edta to obtain the correct reaction conditions after mixing. The stability of the cobalt(III) complexes in the buffer solutions used was monitored by UV/VIS spectroscopy. No indication of anation reactions of the aqua or hydroxo species occurring during the reaction times was detected.

All k_{obs} values were derived from the obtained absorbance *versus* time exponential traces using a non-linear least-squares fitting method. All post-run fittings were done by unweighted least-squares fit by the desired equations. The values for k and K_{os} were obtained from a direct fit of the data by equation (3) and from the double-reciprocal, $1/k_{obs}$ *versus* $1/[Fe(CN)_6{}^{4-}]$, procedure. The good agreement between the two sets of values was taken as an indication of the quality of the fit; typically, the difference between the obtained values is within 3–8%.

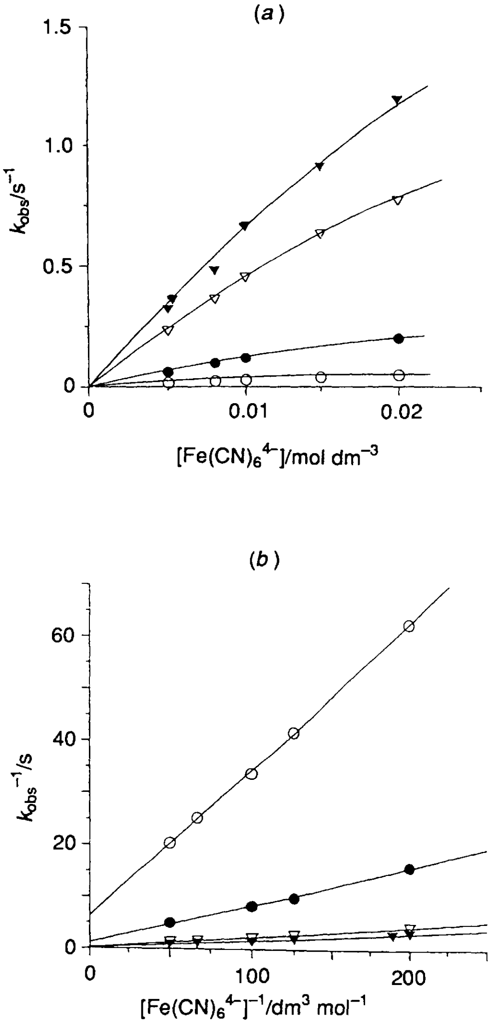

Fig. 1 (*a*) Plots of k_{obs} *versus* $[Fe(CN)_6{}^{4-}]$ for the redox reaction of $[Co(EtNH_2)_5(OH)]^{2+}$ at different temperatures, pH 7.3, I = 1.0 mol dm^{-3} ($LiClO_4$). (*b*) Double-reciprocal plots, $1/k_{obs}$ *versus* $1/[Fe(CN)_6{}^{4-}]$, for the same system. Temperature: 15 (○), 25 (●), 35 (▽) and 45 °C (▼)

Results

All the observed pseudo-first-order rate constants, k_{obs}, measured as a function of the $[Fe(CN)_6]^{4-}$ concentration, R (the substituent), buffer acidity, temperature and pressure have been deposited (SUP 57033). These values were fitted directly by equation (3) and a very good agreement between the fitted and the experimental points was observed. Figs. 1 and 2 show selected k_{obs} *versus* $[Fe(CN)_6{}^{4-}]$ plots for some of the systems studied. From these plots the first-order electron-transfer rate constants, k, and encounter complex-formation equilibrium constants, K_{os}, could be calculated. The errors derived for the first-order rate constants were always 5–10%. Table 1 collects the k and K_{os} values for the systems studied as a function of the amine, temperature, acidity and pressure. From standard Eyring and ln k *versus* P plots, the thermal and pressure activation parameters were obtained, and are summarized along with available literature data in Table 2.

In order to investigate possible interferences from the buffer solutions and the edta added to the reaction medium, some runs were carried out in which the edta concentration, buffer and buffer pH were varied; no meaningful differences were detected (see Table 1 and SUP 57033). No anation reaction of the aquapentaam(m)inecobalt(III) complexes by edta in a 1:2 concentration ratio was observed (provided that the pH was kept lower than 8.5; at higher pH a base-catalysed anation was observed) at ambient pressure or with reactions carried out in the stopped-flow equipment. Nevertheless, when the redox reaction of $[Co(NH_3)_5(OH)]^{2+}$ with $[Fe(CN)_6]^{4-}$ was tried at elevated pressures, especially above 500 bar, using a standard high-pressure cell and spectrophotometer, important discrepancies in the rate constants were detected. In all cases the reactions were too slow and the absorbance changes too small. This was related to a possible base-catalysed substitution reaction of the hydroxo complex under the conditions necessary

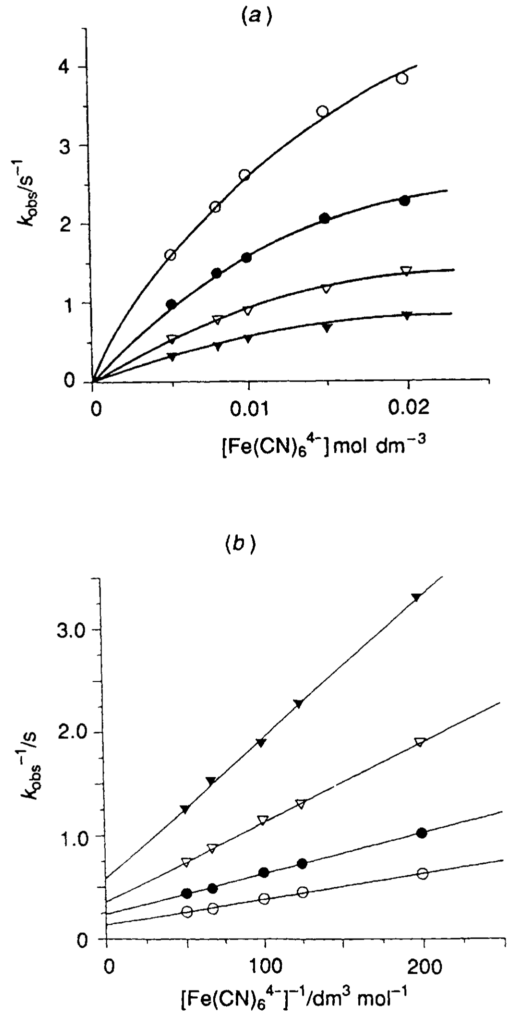

Fig. 2 (*a*) Plots of k_{obs} *versus* $[Fe(CN)_6{}^{4-}]$ for the redox reaction of $[Co(MeNH_2)_5(H_2O)]^{3+}$ at different pressures, pH 3.9, $I = 1.0$ mol dm^{-3} ($LiClO_4$). (*b*) Double-reciprocal plots, $1/k_{obs}$ *versus* $1/[Fe(CN)_6{}^{4-}]$, for the same system. Pressure: 100 (○), 500 (●), 900 (▽) and 1300 bar (▼)

Table 1 Kinetic and equilibrium parameters obtained for all the $[Co(RNH_2)_5X]^{n+} + [Fe(CN)_6]^{4-}$ reactions studied as a function of the amine substituent, R, X (H_2O *versus* OH^-), temperature and pressure at $I = 1.0$ mol dm^{-3} $LiClO_4$

R	X[a]	*P*/ bar	*T*/°C	10^2k/ s^{-1}	K_{os}[b]/ dm^3 mol^{-1}
H	H_2O	1	15	3.2	
			25	11	
			35	35	75 ± 22
			25[c]	13	49 ± 5
H	OH^-	1	15	0.25	
			25	0.81	
			35	5.9	
			45	17	75 ± 30
			15[d]	0.23	30 ± 5
Me	H_2O	1	15	310	
			25	930	
			35	3 500	
			45	6 800	40 ± 4
			15[c]	300	
			25[c]	820	
			35[c]	3 500	36 ± 9
			35[d]	2 500	80 ± 9
			15[e]	300	36 ± 3
		100	25	7.3	
		500		4.1	
		900		2.8	
		1300		1.7	52 ± 7
	OH^-	1	15	7.1	
			25	20	
			35	69	
			45	200	57 ± 26
		100	25	0.12	
		500		0.067	
		900		0.040	
		1300		0.025	75 ± 24
Et	H_2O	1	15	890	
			25	3 500	
			35	7 600	
			45	34 000	23 ± 4
			35[d]	17 000	14 ± 3
		100	25	36	
		500		19	
		900		11	
		1300		7.2	18 ± 1
	OH^-	1	15	15	
			25	64	
			35	300	
			45	1 000	18 ± 7
		100	35	1.2	
		500		0.70	
		900		0.41	
		1300		0.30	25 ± 5

[a] pH 3.9 ($MeCO_2{}^-$–$MeCO_2H$) for X = H_2O, 7.3 (Tris) for OH^-. [b] Average value for the indicated conditions. [c] pH 5.0 ($MeCO_2{}^-$–$MeCO_2H$). [d] pH 4.0 ($HCO_2{}^-$–HCO_2H). [e] pH 3.3 ($CH_2ClCO_2{}^-$–CH_2ClCO_2H).

for the study at elevated pressures. In order to elucidate this possibility further, the stopped-flow redox reaction of $[Co(EtNH_2)_5(OH)]^{2+}$ with $[Fe(CN)_6]^{4-}$ was reinvestigated with the edta added to the former solution instead of to the latter (see Experimental section). In all cases the reproducibility of the absorbance *versus* time traces was poor and only the first few runs gave k_{obs} values in agreement with the previously determined ones. If the solutions were left to stand for long enough at elevated pressures inside the reservoir syringes of the stopped-flow instrument the reaction became slower and the absorbance increase smaller, indicating that the same type of process as that observed for the reaction of $[Co(NH_3)_5(OH)]^{2+}$ with $[Fe(CN)_6]^{4-}$ interferes. No further attempts were made and consequently the activation volume for the latter reaction could not be measured.

Although no pK_a values are available for the $[Co(EtNH_2)_5(H_2O)]^{3+}$ complex owing to its instability under potentiometric titration conditions,[9] the values for $[Co(NH_3)_5(H_2O)]^{3+}$ and $[Co(MeNH_2)_5(H_2O)]^{3+}$ (5.73 and 6.53 at 1.9 °C, respectively)[9] indicate that at the pH used for this study only the hydroxo or aqua complexes are present in the kinetic solutions.

As seen in Tables 1 and 2, the data obtained for the reduction of $[Co(NH_3)_5(H_2O)]^{3+}$ agree extremely well with those published before.[1b] The differences in the first-order electron-transfer rate constants on changing the size of the amine (Table 1) are quite significant for both the aqua and hydroxo complexes. The value of *k* increases by up to two orders of magnitude in going from NH_3 to $MeNH_2$, but significantly less on increasing the steric hindrance from $MeNH_2$ to $EtNH_2$, in the case of the aqua complex. The observed effect is also significantly smaller for the hydroxo complexes.

Since the investigated systems allow the separation of the contribution of the equilibrium constant for the formation of the encounter complex, the difference between the electron-transfer rate constants for the aqua and hydroxo species has to be related to differences within the encounter complex; simple cobalt(III) complex charge factors cannot account for the differences. The difference in the values obtained for these equilibrium constants seems to indicate that the stability of the

Table 2 Thermal and pressure activation parameters for all the $[Co(RNH_2)_5X]^{n+}$ + $[Fe(CN)_6]^{4-}$ reactions studied as a function of the amine substituent, R, and X (H_2O *versus* OH^-) at I = 1.0 mol dm^{-3} $LiClO_4$

R	X[a]	$10^2k^{298}/s^{-1}$	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta V^{‡b}$/cm^3 mol^{-1}
H	H_2O	11	87 ± 2	27 ± 5	
		13	102 ± 5[c]	79 ± 15[c]	26.5 ± 2.4[c]
	OH^-	0.81	109 ± 10	84 ± 30	*d*
Me	H_2O	930	79 ± 7	39 ± 22	29.4 ± 1.6
		820	88 ± 11[e]	69 ± 38[e]	
	OH^-	20	83 ± 3	21 ± 9	32.9 ± 1.3
Et	H_2O	3500	84 ± 6	65 ± 21	33.1 ± 2.0
	OH^-	64	102 ± 1	95 ± 2	30.6 ± 2.8[f]

[a] pH 3.9 ($MeCO_2^-$–$MeCO_2H$) for X = H_2O, 7.3 (Tris) for OH^-. [b] T = 25 °C unless stated. [c] Ref. 2, I = 0.5 mol dm^{-3}, pH 3.8 ($MeCO_2^-$–$MeCO_2H$). [d] Not determined due to edta interference (see Results). [e] pH 5.0 ($MeCO_2^-$–$MeCO_2H$). [f] T = 35 °C.

outer-sphere complex diminishes on increasing the bulk of the substituent R on the amines in the $(RNH_2)_5$ moiety of the complex. Although a charge dilution over the increasing bulkiness of the RNH_2 ligands can account for less-effective ion-pair formation, the differences are not very large, especially when the large errors involved in the kinetically determined values of the equilibrium constants are taken into account.

The parameters collected in Table 2 show no definite trends, neither in the activation enthalpy, nor in the activation entropy values. From the activation volumes it is clear that the value is definitely larger on increasing the size of the amine (RNH_2, with R = H, Me or Et) both for the aqua and the hydroxo species. The differences between the aqua and the hydroxo species for the same amine are not significant, especially when taking into account that, owing to the significantly different rates of the reactions, different instruments and/or reaction temperatures had to be employed.

Discussion

From the data in Tables 1 and 2 it is clear that the nature of the amine substituents in the aquapentaam(m)inecobalt(III) complexes plays an important role in determining the reaction rate constants. The observations of this study are in very good agreement with those obtained for the effect of steric hindrance of the same amines in the anation reactions of $[Co(RNH_2)_5(H_2O)]^{3+}$ by several entering anions.[4c,d]

Although the changes on going from $(NH_3)_5$ to $(MeNH_2)_5$ are significant, both sterically (cone angles 94 and 106°, respectively)[10] and electronically (pK_a = 9.32 and 10.72, respectively)[11] resulting in a large effect on the investigated reactions, a further increase in the length of the alkyl chain of the amine to $(EtNH_2)_5$ (cone angle 106°, pK_a = 10.72) does not produce such a large effect. For the same reason, when the $(NH_3)_5$ group is replaced by $(NH_3)_4(RNH_2)$ no significant differences are expected. This is in excellent agreement with what is observed for redox reactions of $[Co(NH_3)_4(RNH_2)Cl]^{2+}$ systems.[2]

The mentioned differences should be noticeable in both the K_{os} and k values for these systems. The data in Table 1 clearly show that, on increasing the basicity and size of the amines, a significant decrease in K_{os} is observed. This can probably be attributed to the weaker hydrogen-bonding interaction between the cobalt(III) complex and its redox partner and the greater steric congestion of the formed outer-sphere precursor complex. In addition, charge dilution on increasing the size of the alkyl chains in the RNH_2 ligands, as mentioned above, will also contribute to a decrease in K_{os}.

In the case of the rate constant for the electron-transfer process, k, the results are more difficult to interpret. The simple electronic nature of the RNH_2 and H_2O or OH^- ligands makes it difficult to believe that such a large effect exists as observed. It seems that the redox reaction takes place only when the reductant contacts the cobalt(III) centre and the orbital symmetry is preserved.[12] The increase in steric hindrance, and consequently in the bulk, on the cobalt(III) complex produces an important increase in the electron-transfer rate constant. The differences observed in terms of the basicity of the amines suggest that the $[Fe(CN)_6]^{4-}$ reductant responds to the overall skeleton and electronic distribution of the amine ligands around the cobalt(III) centre. As a result, electron transfer from the $[Fe(CN)_6]^{4-}$ to a cobalt(III) centre with a richer external electron density, produced by a less basic amine, is less favoured.

On the other hand, for the reactions carried out at a pH where the cobalt(III) species is mainly $[Co(RNH_2)_5(OH)]^{2+}$, the increase in the overall electron density on the oxidant species produces a significant decrease in the electron-transfer rate constant. This is in good agreement with the arguments presented above, as well as with preliminary results obtained for a series of outer-sphere redox reactions performed with $[Co(NH_3)_5(PO_4)]$ at different pH values.[13] The fact that the K_{os} value does not show any such tendency with changes in the charge of the cobalt(III) complex is a clear indication that not only electrostatic attraction is operative during ion-pair precursor formation. The main factors determining the magnitude of K_{os} seem to be related to hydrogen bonding and/or steric requirements as stated above.

The $\Delta H^‡$ values fall in the rather narrow range expected for these reactions. The $\Delta S^‡$ and $\Delta V^‡$ values are clearly positive for all the systems studied and also in the range expected on the basis of literature values.[1b,2] Despite the fact that the $\Delta S^‡$ values vary considerably with the different complexes in Table 2, they do not show any trend that could be correlated either with the size or the electronic characteristics of the amine, nor with the deprotonation of the aqua ligand. In this respect the values obtained for $\Delta V^‡$ are perhaps more indicative. For all systems studied the values are in the range 27–33 cm^3 mol^{-1}, and are in perfect agreement with those obtained for similar systems.[1a–c,2] This indicates that, even though the nature of the co-ordination sphere of the cobalt(III) complex is continuously changed along the series, volume changes mainly associated with the $[Fe(CN)_6]^{4-}$–$[Fe(CN)_6]^{3-}$ redox pair can be held responsible for the observed activation volumes.[1,2] Arguments have been presented[2] in favour of an overall volume increase of *ca.* 65 cm^3 mol^{-1} associated with the rate-determining electron-transfer reaction in Scheme 1. Recent electrochemical measurements at elevated pressure[14] have revealed reaction volume data for these and related redox systems which support the magnitude of the expected overall volume change given above. It follows that the transition state for the electron-transfer process lies approximately halfway between the initial and final states from a molar volume point of view. That is, the solvation spheres of both oxidant and reductant have been modified to an extent where the electron-transfer process would require the minimum changes in the reactant and product co-ordination spheres.

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