Outer-sphere Redox Reactions of $[Co^{III}\{N_5\}(H_nPO_4)]^{n+}$ $[\{N_5\} = (NH_3)_5$, $(NH_2Me)_5$ or 10-amino-10-methyl-1,4,8,12-tetraazacyclopentadecane] Complexes. A Temperature- and Pressure-dependence Kinetic Study on the Effects of the Different $\{N_5\}$ Groups†

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Outer-sphere redox reactions between $[Co\{N_5\}(H_nPO_4)]^{n+}$ [$\{N_5\} = (NH_3)_5$, $(NH_2Me)_5$ or 10-amino-10-methyl-1,4,8,12-tetraazacyclopentadecane (L)] and $[Fe(CN)_6]^{4-}$ have been studied as a function of pH, $\{N_5\}$, temperature and pressure. The effect of the size of the $\{N_5\}$ skeleton, has been investigated for the $n = 0, 1, 2$ systems in order to establish possible correlations between the size and charge of the cobalt(III) complex and the ion-pair formation constant, the electron-transfer rate constant, and the thermal and baric activation parameters. The values obtained indicate that the ion-pair formation constants are the same, within experimental error, for all the systems studied. The electron-transfer rate constant for a given degree ($n = 1$) of protonation of the $[Co\{N_5\}(H_nPO_4)]^{n+}$ complex increases on increasing the size of the monodentate amines, while an important decrease is observed when they are substituted by the N_5 macrocycle (L) [2.6×10^{-3} s^{-1}, $\{N_5\} = (NH_3)_5$; 59×10^{-3} s^{-1}, $\{N_5\} = (NH_2Me)_5$; 0.73×10^{-3} s^{-1}, $\{N_5\} = L$; respectively at 35 °C]. The activation enthalpies do not show any significant change, neither with decreasing charge on the cobalt complex nor with the size of the amine. The values of $\Delta S^‡$ and $\Delta V^‡$ vary considerably with the degree of protonation of the phosphate ligands and the size of the Co^{III} cavity of the complexes. The opposite trends observed for the values of $\Delta S^‡$ [8 J K^{-1} mol^{-1} for $\{N_5\} = (NH_2Me)_5$ ($n = 1$); −61 J K^{-1} mol^{-1} for $\{N_5\} = (NH_3)_5$ ($n = 1$); 32 J K^{-1} mol^{-1} for $\{N_5\} = (NH_3)_5$ ($n = 0$)] and $\Delta V^‡$ [44 cm^3 mol^{-1} for $\{N_5\} = (NH_2Me)_5$ ($n = 1$); 37 cm^3 mol^{-1} for $\{N_5\} = (NH_3)_5$ ($n = 1$); 17 cm^3 mol^{-1} for $\{N_5\} = (NH_3)_5$ ($n = 0$)] are related to the existence of an important increase in hydrogen bond formation in the cobalt(III) complex on going to the transition state.

Simple outer-sphere redox reactions of the type shown in equation (1) [$n = 2$ or 3; X = H_2O, pyridine (py), Me_2SO,

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

Cl^- or N_3^-] have been studied on several occasions as a function of temperature and pressure.[1,2] Nevertheless, only two attempts to look into the effect of steric hindrance of the amine skeleton have been carried out.[2,3] Furthermore, no studies of this type of reaction carried out on oxoanion-substituted species, such as $[Co\{N_5\}(H_nPO_4)]^{n+}$, are available in order to look into the importance of the changes on the overall charge of the complex in the reaction.

As a continuation of our interest in the effect of steric and electronic factors that could influence or tune the reactivity of transition-metal complexes,[3,4] we have studied the effect of the change of the steric demands of the $\{N_5\}$ skeleton in the outer-sphere redox reaction (2) (L = 10-amino-10-methyl-1,4,8,12-tetraazacyclopentadecane).

$$[Co\{N_5\}H_nPO_4]^{n+} + [Fe(CN)_6]^{4-} \longrightarrow Co^{2+} \text{ products} + [Fe(CN)_6]^{3-} \quad (2)$$

$\{N_5\} = (NH_3)_5$ (n = 0, 1 or 2)
$\{N_5\} = (NH_2Me)_5$ (n = 0 or 1)
$\{N_5\} = L$ (n = 1)

By performing the studies at different temperatures and pressures, we have measured the thermal and baric activation parameters for the different species as a function of pH. For $\{N_5\} = L$ the study for $n = 0$ was not possible given the very rapid hydrolysis reaction of the co-ordinated phosphate group as expected.[5,6] The values for $n = 2$ have been estimated only for the $\{N_5\} = (NH_3)_5$ system at 35 °C and room pressure. The very low pH value necessary for the existence of this species, that prevents the complexation of the Co^{2+} final product with ethylenediaminetetraacetate (edta), produces the subsequent precipitation of cobalt(II) hexacyanoferrate salts and complicates any monitoring of the reaction.

This simple reaction has been chosen in order to be able to separate the encounter-complex formation constant from the electron-transfer rate constant for the mechanism outlined in equations (3)–(5).

$$[Co\{N_5\}(H_nPO_4)]^{n+} + [Fe(CN)_6]^{4-} \overset{K_{OS}}{\rightleftharpoons} \{[Co\{N_5\}(H_nPO_4)]^{n+}\cdot[Fe(CN)_6]^{4-}\} \quad (3)$$

$$\{[Co\{N_5\}(H_nPO_4)]^{n+}\cdot[Fe(CN)_6]^{4-}\} \xrightarrow{k} \{[Co\{N_5\}(H_nPO_4)]^{(n-1)+}\cdot[Fe(CN)_6]^{3-}\} \quad (4)$$

$$\{[Co\{N_5\}(H_nPO_4)]^{(n-1)+}\cdot[Fe(CN)_6]^{3-}\} \xrightarrow{\text{fast}} \text{products} \quad (5)$$

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† *Supplementary data available* (No. SUP 57107, 5 pp.): observed rate constants (k_{obs}) for all the $[Co\{N_5\}(H_nPO_4)]^{n+}$–$[Fe(CN)_6]^{4-}$ systems studied as a function of the $\{N_5\}$ skeleton, pH, temperature, pressure and $[Fe(CN)_6]^{4-}$ concentration. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, pp. xxv–xxx.

The rate law derived from this mechanism is given by equation (6).

$$k_{obs} = \frac{kK_{OS}[\mathrm{Fe(CN)_6}^{4-}]}{\{1 + K_{OS}[\mathrm{Fe(CN)_6}^{4-}]\}} \quad (6)$$

The high charge on the complexes involved allows the kinetic separation of the formation constant of the encounter complex, K_{OS}, and the electron-transfer rate constant, k. Thus, the analysis of the $[\mathrm{Fe(CN)_6}^{4-}]$ 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 outer-sphere electron-transfer reactions of much more complicated systems.

Experimental

Materials.—All materials were reagent grade chemicals. The salt $Na_4[Fe(CN)_6]$ was recrystallized twice, all other chemicals were used without further purification; $[Co(NH_3)_5(PO_4)]$ was prepared as described in the literature.[7]

Preparation of Compounds.—The complex $[Co(NH_2Me)_5(H_2PO_4)][H_2PO_4]_2$ was prepared from the corresponding aqua complex.[4b] The complex $[Co(NH_2Me)_5(H_2O)][ClO_4]_3$ (0.5 g) was dissolved in concentrated H_3PO_4 (7 cm^3) and after continuous stirring for *ca.* 4 days ethanol and diethyl ether were added. The red oil obtained was dissolved in ethanol and taken to dryness; yield 43% {Found: C, 11.35; N, 12.65. Calc. for $[Co(MeNH_2)_5(H_2PO_4)][H_2PO_4]_2\cdot 0.5H_2O$, $C_5H_{32}CoN_5O_{12.5}P$; C, 11.25; N, 13.15%}. UV/VIS (0.1 mol dm^{-3} $HClO_4$): λ/nm 538 (ε 58 dm^3 mol^{-1} cm^{-1}) and 370 (48).

cis-$[CoL(H_2PO_4)][ClO_4]_2$. This complex was prepared from the corresponding chloro complex.[8] The complex *cis*-$[CoLCl][ClO_4]_2$ (0.25 g) and Na_2HPO_4 (0.70 g) were dissolved in water (5 cm^3) and left for *ca.* 20 h. Addition of ethanol and diethyl ether precipitated the excess of Na_2HPO_4 used. The solution was taken to dryness and the residue dissolved in a few cm^3 of ethanol, and the insoluble residue was discarded. The ethanolic solution was taken to dryness to obtain a red oil that converted to a solid on standing, yield 21% (Found: C, 24.75; N, 11.50. Calc. for $C_{12}H_{31}Cl_2CoN_5O_{12}P$: C, 24.10; N, 11.70%). UV/VIS (0.1 mol dm^{-3} $HClO_4$): λ/nm 526 (ε 126 dm^3 mol^{-1} cm^{-1}), 468 (sh) (82) and 360 (162).

Buffer Solutions.—All buffers were prepared according to well established procedures,[9] concentrations were chosen to provide enough buffering for the $[Fe(CN)_6]^{4-}$ solutions. Final pH was set with the addition of NaOH or $HClO_4$ solutions to the prepared buffers. The chosen pH values were such that, in general, predominantly the $[Co\{N_5\}(HPO_4)]^+$ or $[Co\{N_5\}(PO_4)]$ species are present in solution. Only for $\{N_5\} = (NH_3)_5$ was the $[Co\{N_5\}(H_2PO_4)]^{2+}$ redox process estimated at $[H^+] = 0.1$ mol dm^{-3} ($HClO_4$).

Instruments.—All UV/VIS spectra were recorded on an HP8452A instrument; pH measurements were carried out with a Crison 2002 instrument equipped with an Ingold microelectrode. Room-pressure kinetic runs were recorded on an HP8452A instrument equipped with a thermostatted multicell transport. For runs at variable pressure a pressurizing system and a high-pressure cell, fitted on a Beckman UV5230 instrument, as described in the literature were used.[10]

Kinetics.—All kinetic measurements were performed under pseudo-first-order conditions with the iron complex in excess over the cobalt complex. Solutions for the kinetic runs were made up by mixing the 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 oxidation of Fe^{II} and edta was added to the reaction medium to prevent the precipitation of the Co^{2+} reaction product.[11] The cobalt(III) stock solutions were made up in water in order to avoid any interference from anation reactions with buffer anions during long storage. 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 for the study was monitored by UV/VIS spectroscopy; no indication of substitution reactions of the different species occurring during the reaction time was detected.

All k_{obs} values were derived from the obtained absorbance *versus* time exponential traces at 420 nm (ε{$[Fe(CN)_6]^{3-}$} = 1023 dm^3 mol^{-1} cm^{-1}) using a non-linear least-squares fitting method. All post-run fittings were done by unweighted least-squares fit to the desired equations. The values for k and K_{OS} were obtained from a direct fit to equation (6). Alternatively, a double-reciprocal plot was also used, the coherence of the two plots was considered as a measure of the quality of the fitting.

Results

All the observed pseudo-first-order rate constants, k_{obs}, measured as a function of the $[Fe(CN)_6]^{4-}$ concentrations, $\{N_5\}$, acidity, temperature, and pressure are collected in SUP 57107. These values were fitted to equation (6) and a very good agreement (5–10%) between fitted and experimental points was observed. Fig. 1 shows a plot of k_{obs} *versus* $[Fe(CN)_6{}^{4-}]$ for the $\{N_5\} = (NH_2Me)_5$ system. From these plots all the first-order electron-transfer rate constants, k, and encounter complex formation equilibrium constants, K_{OS}, could be calculated. Table 1 collects all k and K_{OS} values for the systems studied as a function of the $\{N_5\}$ skeleton, temperature, acidity and pressure. From standard Eyring and ln k *vs.* p plots the thermal and baric activation parameters summarized in Table 2 were obtained. Fig. 2 shows, the pressure dependence of the rate constants for the $\{N_5\} = (NH_3)_5$ system.

In order to assess the pH conditions chosen for the study, the

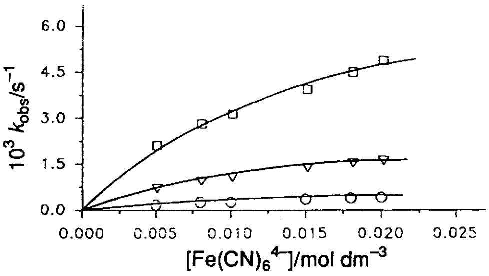

Fig. 1 Plot of k_{obs} *versus* $[Fe(CN)_6{}^{4-}]$ for the $[Co(NH_2Me)_5(PO_4)]$–$[Fe(CN)_6]^{4-}$ system as a function of temperature, $I = 1.0$ mol dm^{-3} ($LiClO_4$); T = 15 (○), 25 (▽) or 35 °C (□)

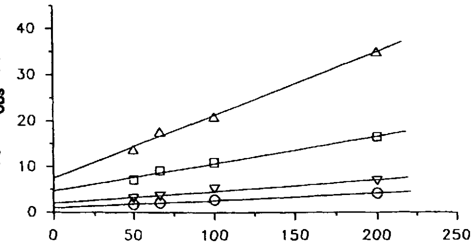

Fig. 2 Plot of $k_{obs}{}^{-1}$ *versus* $[Fe(CN)_6{}^{4-}]$ for the $[Co(NH_3)_5(HPO_4)]^+$–$[Fe(CN_6)]^{4-}$ system as a function of pressure: p = 100 (○), 500 (▽), 1000 (□) or 1500 atm (△)

Table 1 Kinetic and outer-sphere equilibrium parameters obtained for the $[Co\{N_5\}(H_nPO_4)]^{n+}$–$[Fe(CN)_6]^{4-}$ reactions studied as a function of the $\{N_5\}$ skeleton, *n*, temperature and pressure (I = 1.0 mol dm^{-3} $LiClO_4$) (atm ≈ 101 325 Pa)

Species	pH	p/atm	T/°C	10^3k/s^{-1}	K_{OS}/dm^3 mol^{-1}
$[Co(NH_3)_5(H_2PO_4)]^{2+}$	1.0[a]	1	35	5.6	100
$[Co(NH_3)_5(HPO_4)]^{+}$	5.5[b]	1	25	0.81	20
		1	35	2.6	20
		1	45	5.6	35
		100	35	1.0	60
		500	35	0.50	80
		1000	35	0.21	80
		1500	35	0.14	55
$[Co(NH_3)_5(PO_4)]$	9.6[c]	1	25	0.041	50
		1	35	0.28	35
		1	45	0.66	40
		50	45	0.89	60
		500	45	0.71	50
		1000	45	0.46	70
		1500	45	0.37	80
$[Co(NH_2Me)_5(HPO_4)]^{+}$	5.0[b]	1	15	5.1	50
		1	25	12	95
		1	35	59	50
		100	15	5.2	45
		500	15	1.8	70
		1000	15	0.71	55
		1500	15	0.39	100
$[Co(NH_2Me)_5(PO_4)]$	9.6[c]	1	25	0.73	65
		1	35	3.2	55
		1	45	9.0	60
	9.1[d]	100	35	4.0	40
		500	35	2.5	40
		1000	35	1.3	30
		1500	35	0.72	30
$[CoL(HPO_4)]^{+}$	5.0	1	25	0.24[e]	100
		1	30	0.41	90
		1	35	0.73[f]	85
		1	45	1.1[f]	70
		100	45	0.83	90
		500	45	0.44	60
		1000	45	0.26	100
		1500	45	0.12	160

[a] 0.1 mol dm^{-3} $HClO_4$; $[Fe(CN)_6]^{4-} \equiv H_2[Fe(CN)_6]^{2-}$. [b] Acetic acid–acetate buffer. [c] Hydrogen carbonate–carbonate buffer or tris(hydroxymethyl)methylamine (tris) buffer. [d] tris Buffer. [e] k_{obs} Measured indistinctly at pH 5.0 and 4.3 ($MeCO_2H$–$MeCO_2^-$). [f] pH = 4.3 ($MeCO_2H$–$MeCO_2^-$).

Table 2 Kinetic and thermal and pressure activation parameters obtained for the $[Co\{N_5\}(H_nPO_4)]^{n+}$–$[Fe(CN)_6]^{4-}$ reactions studied as a function of the $\{N_5\}$ skeleton and *n* (I = 1.0 mol dm^{-3} $LiClO_4$)

Species	$10^3\,k^{308}$/s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta V^\ddagger(T)$/cm^3 mol^{-1} (°C)
$[Co(NH_3)_5(H_2PO_4)]^{2+}$	5.6	—	—	—(—)
$[Co(NH_3)_5(HPO_4)]^{+}$	2.6	72 ± 8	−61 ± 26	37 ± 4 (35)
$[Co(NH_3)_5(PO_4)]$	0.28	107 ± 22	32 ± 70	17 ± 1 (45)
$[Co(NH_2Me)_5(HPO_4)]^{+}$	59	86 ± 14	8 ± 46	44 ± 5 (15)
$[Co(NH_2Me)_5(PO_4)]$	3.2	101 ± 8	32 ± 27	32 ± 1 (35)
$[CoL(HPO_4)]^{+}$	0.73	57 ± 10	−118 ± 31	36 ± 2 (45)

values of the acidity constants for the $[Co(NH_3)_5(H_nPO_4)]^{n+}$ phosphate complexes were taken from the literature [K_{a1} = 3.09 × 10^{-4} mol dm^{-3}, K_{a2} = 1.23 × 10^{-8} mol dm^{-3} at 45 °C and I = 1.0 mol dm^{-3} ($NaClO_4$)],[12] and that corresponding to the *cis*-$[CoL(H_2PO_4)]^{2+}$ complex was determined by UV/VIS spectroscopy at various wavelengths [K_{a1} = 2.51 × 10^{-4} mol dm^{-3} at 25 °C and I = 1.0 mol dm^{-3} ($LiClO_4$)]. The corresponding values for the $[Co(NH_2Me)_5(H_nPO_4)]^{n+}$ complexes were assumed to be close enough to the above mentioned values as not to affect the species distribution at the pH chosen for the study. For the $[Co(NH_3)_5(H_nPO_4)]^{n+}$ compound a full *k vs.* pH profile has been carried out (Fig. 3) proving the validity of the conditions used.

The data collected in Table 1 indicate that simple cobalt(III) or iron(II) complex charge factors cannot account for the virtual absence of differences observed for the values determined for K_{OS}. These values are of the same order of magnitude on changing pH and $\{N_5\}$ skeleton as well as pressure, indicating that, unlike other systems, the ion-pair formation for these reactions is the same, whatever the complexes or charges involved. Since the investigated systems allow the separation of the contribution of the equilibrium constant for the formation of the encounter complex, the differences between the electron-transfer rate constants for the different species have to be related directly to differences within the encounter complex. In this respect, the kinetic data collected in Table 2 clearly indicate that a definite decrease in the value of *k* is obtained on decreasing the number of acidic protons in the cobalt(III) complex. The same

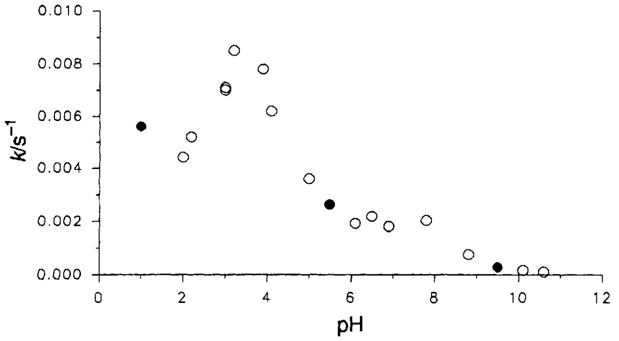

Fig. 3 The pH profile for the $[Co(NH_3)_5(H_nPO_4)]^{n+}$–$[Fe(CN)_6]^{4-}$ reaction; T = 35 °C, p = 1 atm, I = 1.0 mol dm^{-3} ($LiClO_4$). Filled points indicate selected pH for each phosphate species (data in Table 1)

trend has already been observed for similar $[Co(NH_2R)_5X]^{z+}$ (R = alkyl) complexes, and has been associated with the decrease in the electron density of the complex receiving the electron transfer.[3,13] The differences with respect to changes in the $\{N_5\}$ skeleton evidence that, although the increase in the size of the monodentate amines produces an increase in the first-order rate constants of the same order of magnitude as that observed for the $[Co(NH_2R)_5(H_2O)]^{3+}$ complexes,[3] when the skeleton is changed to a macrocyclic N_5 unit an important drop in the value of k is observed.

The thermal activation parameters collected in Table 2 indicate that, although the values of $\Delta H^\ddagger$ for the monoprotonated complexes are slightly smaller than those for the fully deprotonated ones, no definite trends are observed, as expected for this type of reaction. On the other hand, the values obtained from the intercept of Eyring plots produce values of $\Delta S^\ddagger$ that are much smaller than those found for similar pentaam(m)ine systems, such as those indicated in equation (1).[1-3] The values obtained, although having a large error, seem to indicate a trend to higher values for the less protonated systems. The baric activation parameters, $\Delta V^\ddagger$ are all clearly positive as expected for these outer-sphere redox reactions,[14] and their order of magnitude is that observed for similar systems.[1-3] This fact is rather surprising given the negative $\Delta S^\ddagger$ values found for some of the reactions, which would indicate an important space organization on going to the transition state. Even so, an opposite trend that parallels that observed for the activation entropy values is obtained for the measured $\Delta V^\ddagger$, that is, larger positive values are found for the monoprotonated species, $[Co\{N_5\}(HPO_4)]^+$, when compared with the neutral $[Co\{N_5\}(PO_4)]$. As for changes in $\Delta V^\ddagger$ with the size of the $\{N_5\}$ skeleton, the value found for the $[Co(NH_3)_5(PO_4)]$ complex redox reaction is surprisingly low.

Discussion

From the data in Tables 1 and 2 it is clear that both the nature of the $\{N_5\}$ skeleton and the degree of protonation of the phosphate ligand in the $[Co\{N_5\}(H_nPO_4)]^{n+}$ complexes play an important role in the values of the outer-sphere redox rate constants with $[Fe(CN)_6]^{4-}$. The effects observed are in very good agreement with those obtained for the series of $[Co(NH_2R)_5(H_2O)]^{3+}$ (R = H, Me or Et) complexes.[3]

Although these differences should be noticeable both in K_{OS} and k values, data in Table 1 indicate that the values obtained for K_{OS} for the different $\{N_5\}$ skeletons and degrees of protonation are of the same order of magnitude. This similitude disagrees with what has been observed for the same redox reaction of the $[Co(NH_2R)_5(H_2O)]^{3+}$ (R = H, Me or Et) complexes.[3] In those reactions the increase in the basicity and size of the different monodentate amines translated into a significant decrease in the values obtained for K_{OS}, though no differences were observed for the protonation changes on going from aqua to hydroxo species. It seems that not only electrostatic attraction is operative during ion-pair precursor formation and the magnitude of the K_{OS} value clearly relates to hydrogen bonding. This becomes more important on decreasing the positive charge of the cobalt(III) complex and compensates for the differences in coulombic attraction. In this respect, although close contact is commonly held as necessary for the electron transfer,[14b] a water molecule interacting with the two reacting species in the precursor ion-pair has to produce a larger K_{OS} value given the fact that the lesser degree of protonation of the phosphate oxygens helps hydrogen bonding.

The first-order rate constants for the redox process, k, from data in Table 2 indicate that important differences exist on changing the amine skeleton as well as the degree of protonation. Fig. 3 illustrates the effects found for the protonation of the $[Co(NH_3)_5(PO_4)]$ species. In this figure it is clear that two protonation steps at pH 9–10 and 5–7 produce measurable differences in the reaction rate. As for the shape of the profile at pH between 1 and 4, it is important to consider that at these pH values the existence of $[Fe(CN)_6]^{4-}$ as the only reducing species is not guaranteed, at pH < 5 important amounts of the monoprotonated form, $H[Fe(CN)_6]^{3-}$, begin to be present in the reaction medium, its concentration being predominant around pH 3, and at pH 1 the diprotonated form, $H_2[Fe(CN)_6]^{2-}$, becomes the predominant species (K_{a3} = 6.0 × 10^{-3} mol dm^{-3}; K_{a4} = 6.7 × 10^{-5} mol dm^{-3} at 25 °C).[15] It seems clear that the electronic charge density plays a very important role in the reaction rate. While for pH values where the reducing species has a 4− charge (pH = 10.6–4.0) the values of k increase with decreasing electronic density on the oxidizing complex {from $[Co(NH_3)_5(PO_4)]$ to $[Co(NH_3)_5(HPO_4)]^+$}, when the reducing species suffers a drop in charge to 3− or 2− (pH = 4.0–1.0) an important drop in the first-order redox rate constant becomes apparent in spite of the increase in the oxidizing species electron density {from $[Co(NH_3)_5(HPO_4)]^+$ to $[Co(NH_3)_5(H_2PO_4)]^{2+}$}. Nevertheless, the thermodynamics of the electron transfer reaction could also be held responsible for the trends observed by the rationale of Marcus Theory.

Referring to the effects of the $\{N_5\}$ skeleton on the first-order reaction rate constants, k, data in Table 2 clearly show, that although an important increase in the values exists on increasing the cone angle of the monodentate amine [from 2.6 × 10^{-3} s^{-1} for $\{N_5\} = (NH_3)_5$ (94°) to 59 × 10^{-3} s^{-1} for $\{N_5\} = (NH_2Me)_5$ (106°)[16]], as observed for the equivalent aqua complexes, the rate constant obtained for the *cis*-$[CoL(HPO_4)]^+$ complex is much smaller than would be expected if the overall steric hindrance of the molecule has to be held responsible for the effects observed on the monodentate systems. Nevertheless, if one looks into the bonding distances of the equivalent $[Co\{N_5\}Cl]^{2+}$ and $[Co\{N_5\}(H_2O)]^+$ species (Table 3) it is clear that, while the bond distances of the co-ordination sphere of the cobalt(III) complex are increased on going from NH_3 to NH_2Me, when the macrocycle L is introduced a tighter envelope around the metal centre is formed instead. This fact could be held responsible for the difference observed in the first-order rate constants, k, given the different degree of bond stretching necessary to go to the final cobalt(II) compound.[18]

The activation parameters obtained for $\Delta H^\ddagger$ are within the range found for the type of reactions depicted in equation (1).[1-3] These values do not show any special trend, except for the slightly larger values obtained for the $[Co\{N_5\}(PO_4)]$ complexes. Even so, the difference in these values is too small to produce a sensible interpretation.

With reference to the values obtained for $\Delta S^\ddagger$, all of them are very low when compared with the values existing in the literature for similar systems, nevertheless the limited range of temperatures used increases considerably the errors involved.

Table 3 Selected bond distances for relevant $[Co\{N_5\}Cl]^{2+}$ and $[Co\{N_5\}(H_2O)]^{3+}$ complexes

Species	d(Co–Cl)/Å	$d(Co–N_{trans})$/Å	$d(Co–N)_{average}$/Å	Ref.
$[Co(NH_3)_5Cl]^{2+}$	2.286	1.964	1.973	17
$[Co(NH_2Me)_5Cl]^{2+}$	2.283	1.980	1.988	17
cis-$[CoL(Cl)]^{2+}$	2.273	1.982	1.980	8

The fact that the reducing reagent is common to all the reactions presented $\{[Fe(CN)_6]^{4-}\}$, implies that any differences found have to be related to the cobalt(III) species being reduced. The existence of oxo groups in the phosphate ligands of the cobalt(III) complex has to produce an important increase in hydrogen bonding on going from the initial to the transition state, given the stretching in the bonding distances that, according to Marcus Theory, have to take place on going from Co^{III} to Co^{II} complexes. In this respect, the more negative values found for the reactions of $[Co\{N_5\}(HPO_4)]^+$ have to be related to the possibility of further hydrogen bonding due to the existence of an acidic H attached to the phosphate ligand. Again, the more positive values found for the $\{N_5\} = (NH_2Me)_5$ system have to be related to the already existing larger envelope for these species.[4c,8,17] A dead-end mechanism could also be considered for this strongly hydrogen-bonded species. In this case the values determined for $\Delta S^‡$ would be completely meaningless given the fact that the limiting value of k_{obs} would no longer be the electron-transfer rate constant for the system.

The positive values found for $\Delta V^‡$ are those expected for this type of reaction, but they contrast with the negative figures found for some of the $\Delta S^‡$ measured. The existence of the above mentioned inverse relationship in the values of $\Delta S^‡$ and $\Delta V^‡$ (Table 2) points towards a common reason for the two tendencies. If the cobalt(III) complexes form further hydrogen bonds on going to the transition state, as stated above, although an increase in organization will produce more negative $\Delta S^‡$ values, the expected values for the $\Delta V^‡$ data would be positive. That is, hydrogen bonding produces an important increase in the volume due to the inherently 'rigid' reorganization of solvent molecules; the more hydrogen bonds that are formed on going to the transition state, the higher the solvent reorganization and, consequently, an increase in volume is observed. The value found for the $[Co(NH_3)_5(PO_4)]$ reaction is very small, even taking into account these considerations. The impossibility of measuring $\Delta V^‡$ for *cis*-$[CoL(PO_4)]$, given its very fast hydrolysis reaction,[5,6] makes it difficult to assess the difference. Nevertheless, preliminary studies[13] of other fully deprotonated anionic oxophosphorus pentaamminecobalt(III) complexes show values of the same order, indicating that important solvation factors, related with the lack of any acidic protons in the less sterically hindered complex, have to be responsible for the observed results. Further studies in this area are currently under way in order to confirm these assumptions.

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