

# Outer-sphere redox reactions of $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$ complexes. A temperature- and pressure-dependence kinetic study on the influence of the phosphorus oxoanions\*

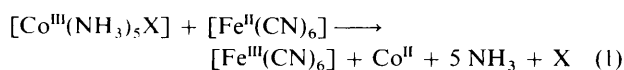
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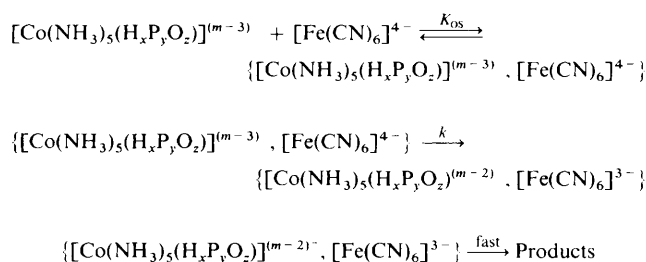
Outer-sphere redox reactions between  $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$  ( $\text{H}_x\text{P}_y\text{O}_z^{m-}$  =  $\text{H}_2\text{PO}_2^-$ ,  $\text{H}_2\text{PO}_3^-$ ,  $\text{HPO}_3^{2-}$ ,  $\text{HP}_2\text{O}_7^{3-}$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\gamma\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$ ,  $\text{-HP}_3\text{O}_{10}^{4-}$ ,  $\text{-P}_3\text{O}_{10}^{5-}$ ,  $\beta\text{-H}_3\text{P}_3\text{O}_{10}^{2-}$ ,  $\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$ ,  $\text{-HP}_3\text{O}_{10}^{4-}$  or  $\text{-P}_3\text{O}_{10}^{5-}$ ) and  $[\text{Fe}(\text{CN})_6]^{4-}$  have been studied as a function of pH,  $\text{H}_x\text{P}_y\text{O}_z^{m-}$  oxoanion, temperature and pressure. The effect of the oxidation state, size, geometry and extent of protonation of the  $\text{H}_x\text{P}_y\text{O}_z^{m-}$  oxoanions on the precursor-complex formation constant, electron-transfer rate constant, and thermal and pressure activation parameters has been investigated. The values obtained indicate that all the precursor-complex formation equilibrium constants,  $K_{\text{OS}}$ , are the same except for the non-linear  $\beta\text{-H}_3\text{P}_3\text{O}_{10}^{2-}$ ,  $\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$ ,  $\text{-HP}_3\text{O}_{10}^{4-}$  and  $\text{-P}_3\text{O}_{10}^{5-}$  oxoanions, where the values are consistently larger, indicating that hydrogen bonding plays a very important role. The electron-transfer rate constant for a series of  $[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$ , with linear oxoanions, increases on decreasing the negative charge on the complex  $\{k^{308} = 0.73 \times 10^3$  and  $(8.5\text{--}11) \times 10^3 \text{ s}^{-1}$  for the  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$  and  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ , respectively $\}$ . For the non-linear  $\beta\text{-P}_3\text{O}_{10}^{5-}$  oxoanions a threshold is observed when the external oxo groups are protonated  $\{k^{308} = 20 \times 10^3$  for  $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$  species and  $0.84 \times 10^3 \text{ s}^{-1}$  for  $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ ,  $\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$  or  $\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$ . The  $\Delta H^\ddagger$  values are within the range expected, while those of  $\Delta S^\ddagger$  and  $\Delta V^\ddagger$  vary considerably with the extent of protonation of the phosphorus oxoanionic ligands, being  $13 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $+36 \text{ cm}^3 \text{ mol}^{-1}$  and  $69 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $+13 \text{ cm}^3 \text{ mol}^{-1}$ , respectively for the  $[\text{Co}(\text{NH}_3)_5(\text{HP}_2\text{O}_7)]\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_2\text{O}_7)]^-$  couple. The  $\Delta V^\ddagger$  values depend strongly on the oxo group distribution of the oxophosphorus ligand  $\{+13$  and  $+32 \text{ cm}^3 \text{ mol}^{-1}$  for  $\beta\text{-}$  and  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$ , respectively $\}$ . Hydrogen bonding and solvent reorganization play a key role in the interpretation of the activation parameters.

Simple outer-sphere redox reactions of type (I) (charges



omitted) have been studied as a function of temperature and pressure.<sup>1</sup> Recently, some studies have been carried out on the effect of steric hindrance of amine ligands both for monodentate and macrocyclic  $\text{N}_5$  systems.<sup>2</sup> Furthermore, a systematic study has been performed for systems having phosphate ligands in different degrees of protonation in the sixth co-ordination position (X), in order to establish possible correlations with charge, degree of protonation, and steric hindrance of the am(m)ine skeleton.<sup>3</sup>

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,<sup>2-6</sup> we have now studied the effect of the nature of the phosphorus ligands on the outer-sphere redox reactions depicted in Scheme 1. Measurements have been carried out at different pH in order to promote differences in the extent of protonation of the oxoanionic ligands. By doing so, both the effects on the precursor formation constants and the electron-transfer rate constants could be studied. The general rate equation derived from this mechanism is (2).<sup>7</sup> All



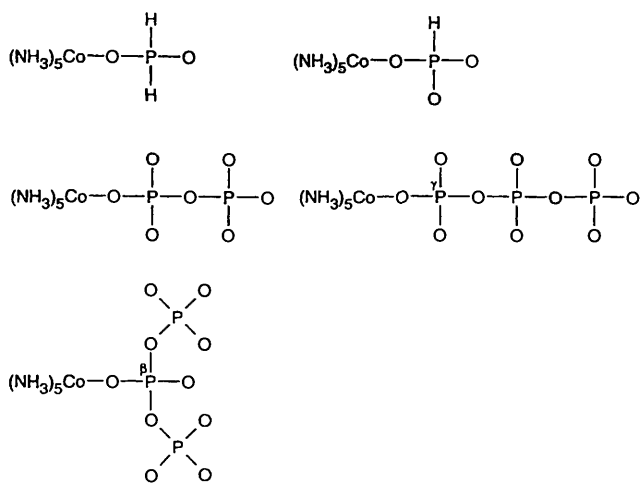
Scheme 1

$$k_{\text{obs}} = \frac{kK_{\text{OS}}[\text{Fe}(\text{CN})_6]^{4-}}{\{1 + K_{\text{OS}}[\text{Fe}(\text{CN})_6]^{4-}\}} \quad (2)$$

the complexes studied allowed the kinetic separation of the encounter-complex formation constant,  $K_{\text{OS}}$ , and the electron-transfer rate constant,  $k$ . Thus, the analysis of the  $[\text{Fe}(\text{CN})_6]^{4-}$  dependence of  $k_{\text{obs}}$  under pseudo-first-order conditions as a function of temperature and pressure enabled us to use the obtained kinetic and activation parameters as a source of mechanistic information on outer-sphere electron-transfer reactions of much more complicated systems. In this respect the existence of large  $K_{\text{OS}}$  constants, even for 2-/-4- systems, demonstrates the importance of hydrogen bonding in the precursor complex species, as found for other systems.<sup>3,8</sup> The

\* Supplementary data available (No. SUP 57143, 10 pp.): observed rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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



values for the rate constants  $k$  seem to depend largely on the extent of protonation of the oxo groups on the periphery of the phosphorus ligands, as found previously for the  $[\text{Co}(\text{NH}_3)_5(\text{HPO}_4)]^+ - [\text{Co}(\text{NH}_3)_5(\text{PO}_4)]$  couple.<sup>3</sup> The oxidation state of the phosphorus centre in the oxoanionic ligand was also found to determine the values obtained for the electron-transfer rate constants, as well as for the associated activation parameters.

## Experimental

### Materials

All materials were reagent-grade chemicals;  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  was recrystallized twice, but all other chemicals were used without further purification. All  $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$  ( $\text{H}_x\text{P}_y\text{O}_z^{m-} = \text{H}_2\text{PO}_2^-$ ,  $\text{H}_2\text{PO}_3^-$ ,  $\text{HPO}_3^{2-}$ ,  $\text{HP}_2\text{O}_7^{3-}$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\gamma\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$ ,  $\gamma\text{-HP}_3\text{O}_{10}^{4-}$ ,  $\gamma\text{-P}_3\text{O}_{10}^{5-}$ ,  $\beta\text{-H}_3\text{P}_3\text{O}_{10}^{2-}$ ,  $\beta\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$ ,  $\beta\text{-HP}_3\text{O}_{10}^{4-}$  or  $\beta\text{-P}_3\text{O}_{10}^{5-}$ ) complexes were prepared according to literature methods,<sup>9</sup> and characterized by UV/VIS and  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopy.

### Buffer solutions

All buffers were prepared according to well established procedures,<sup>10</sup> with concentrations chosen to provide enough buffering for the  $[\text{Fe}(\text{CN})_6]^{4-}$  solutions (from 0.15 to 0.50 mol  $\text{dm}^{-3}$ ). The final pH was set by addition of NaOH or  $\text{HClO}_4$  solutions to the prepared buffers. The chosen pH values were such that, in general, only one of the acid-base equilibrium species of each system is present in solution. Nevertheless, for the  $[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+ - [\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})] - [\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$  equilibria such complete separation is not possible and a pH scan was used instead.

### Instruments

All UV/VIS spectra were recorded on a Hewlett-Packard 8452A spectrometer. pH Measurements were carried out with a Crison 2002 instrument equipped with an Ingold micro electrode. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra were recorded on a Bruker-250 spectrometer. Atmospheric-pressure kinetic runs with  $t_{1/2} > 170$  s were recorded on an HP8452A spectrometer equipped with a thermostatted multicell transport; runs within the 7–170 s range were recorded on this instrument equipped with a High-Tech SFA-11 Rapid Kinetics Accessory; for  $t_{1/2} < 7$  s a Durrum D-110 stopped-flow spectrophotometer was used. For runs at elevated pressure with  $t_{1/2} < 100$  s a laboratory-made stopped-flow instrument equipped with a pressurizing system was used as described previously;<sup>11</sup> for  $t_{1/2} > 800$  s a

pressurizing system and high-pressure cell, fitted on a Beckman UV5230 instrument, as described in the literature<sup>12</sup> were used.

### Kinetics

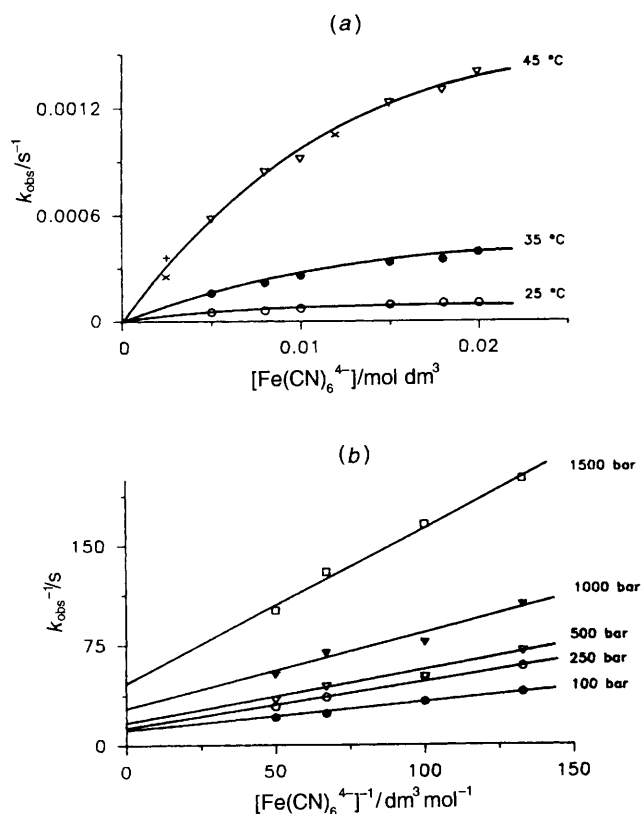
All kinetic measurements were performed under pseudo-first-order conditions with the iron complex in excess over the cobalt complex. Typical cobalt(III) complex concentrations were  $(2-5) \times 10^{-4}$  mol  $\text{dm}^{-3}$ . Solutions were made up by mixing appropriate amounts of the corresponding stock solutions at 1.0 mol  $\text{dm}^{-3}$  ( $\text{LiClO}_4$ ) ionic strength. All solutions were degassed in order to avoid any air oxidation of  $\text{Fe}^{\text{II}}$ , and ethylenedinitrilotetraacetate (edta) was added to the reaction medium to prevent precipitation of the cobalt(II) reaction product.<sup>13</sup> The cobalt(III) complex stock solutions were made up in water in order to avoid any interference from anation reactions with buffer anions during long storage or high-pressure equilibration times. Accordingly, the  $[\text{Fe}(\text{CN})_6]^{4-}$  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 or decomposition during the reaction times was detected.

All the  $k_{\text{obs}}$  values were derived from absorbance *versus* time exponential traces at 420 nm ( $\epsilon = 1023$   $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  for  $[\text{Fe}(\text{CN})_6]^{3-}$ ),<sup>14</sup> using a non-linear least-squares fitting method. For experiments in the presence of added  $[\text{Fe}(\text{CN})_6]^{3-}$  the reactions were followed at 540 nm; under these conditions all the final cobalt(II) products are due to the  $[(\text{edta})\text{Co}^{\text{III}}\text{-NC-Fe}^{\text{II}}(\text{CN})_6]^{5-}$  complex, which shows an absorption maximum at this wavelength.<sup>15</sup> All post-run data fitting was done by unweighted least-squares fit using the desired equations. The values for  $k$  and  $K_{\text{OS}}$  were obtained from a direct fit using equation (2). Alternatively, a double-reciprocal plot was used; the coherence of the two plots was considered as a measure of the quality of the fit. For iteration purposes for systems with more than one oxidizing species, a modification of equation (2), including two (or three) sets of  $k$  and  $K_{\text{OS}}$ , was used. In these instances, the knowledge of one (or two) sets of values for  $k$  and  $K_{\text{OS}}$ , determined at other pH values, was used for starting and checking the validity of the iteration.

## Results

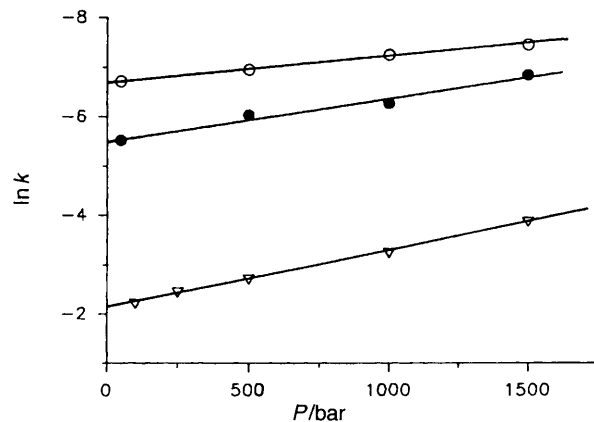
All the observed pseudo-first-order rate constants,  $k_{\text{obs}}$ , measured as a function of the  $[\text{Fe}(\text{CN})_6]^{4-}$  concentrations,  $\text{H}_x\text{P}_y\text{O}_z^{m-}$  ligands, acidity, temperature and pressure are available as SUP 57143. As found for similar systems,<sup>2b,3</sup> no interference from the type and concentration of the buffer solutions or from the amount of edta added was found. Possible effects of added  $[\text{Fe}(\text{CN})_6]^{3-}$  on  $k_{\text{obs}}$  were also tested; none was detected. All these data were fitted by equation (2) (or its reciprocal, see above) and a very good agreement between the fitted and the experimental points was found. Fig. 1 shows selected plots for some of the systems studied. From these plots the first-order electron-transfer rate constants,  $k$ , and encounter-complex formation constants,  $K_{\text{OS}}$ , could be calculated. The errors derived for the first-order rate constants were always in the 5–10% range. Table 1 collects all  $k$  and  $K_{\text{OS}}$  values for the systems studied as a function of the phosphorus oxoanion, temperature and pressure. From standard Eyring and  $\ln k$  *versus*  $P$  plots (Fig. 2), the thermal and pressure activation parameters were obtained, and are summarized along with relevant available literature data in Table 2.

In order to evaluate the pH conditions selected for the study, the values of the acidity constants for all the  $[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$  complexes were taken from the literature.<sup>16</sup> For the  $[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_3\text{O}_{10})]^{(2-x)-}$  ( $x = 1-3$ ),  $[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{PO}_3)]^{x+}$  ( $x = 1$  or  $2$ ) and  $[\text{Co}(\text{NH}_3)_5-$



**Fig. 1** Dependence of  $k_{\text{obs}}$  on  $[\text{Fe}(\text{CN})_6^{4-}]$  for the reduction of  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$  as a function of temperature (a), and for the reduction of  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_2)]^{2+}$  as a function of pressure (b)  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{LiClO}_4$ ). In (a)  $[\text{Fe}(\text{CN})_6^{3-}] = 0.001$  (+),  $0.0025 \text{ mol dm}^{-3}$  ( $\times$ )

$(\text{H}_2\text{PO}_2)]^{2+}$  complexes the variation of  $k$  with pH (3.0–5.0, 2.3–9.0 and 2.0–8.6, respectively) was studied. For the  $\gamma$ - and  $\beta$ -triphosphate complexes,  $[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$ ,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ ,  $[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$  and  $[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$ , the acid–base equilibria merit special comment. The  $K_a$  values for the mono-, di- and tri-protonated complexes are close enough ( $6.3 \times 10^{-4}$ ,  $3.2 \times 10^{-5}$  and  $7.9 \times 10^{-7} \text{ mol dm}^{-3}$  for the  $\beta$  species and  $3.2 \times 10^{-3}$ ,  $4.0 \times 10^{-4}$  and  $2.5 \times 10^{-7} \text{ mol dm}^{-3}$  for the  $\gamma$  species, respectively, at 25 °C)<sup>16a</sup> to prevent the existence of only one major species in solution. For example, at pH 5.0 there is 95% of  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$ , 2.5% of  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$  and 2.5% of  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$ , whereas at pH 3.0 the solution contains 58%  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ , 23%  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$  and 18%  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$ . Con-



**Fig. 2** Plots of  $\ln k$  versus  $P$  for some of the systems studied.  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{LiClO}_4$ ),  $T$  as in Table 2.  $\text{O}$ ,  $[\text{Co}(\text{NH}_3)_5(\text{P}_2\text{O}_7)]^-$ ;  $\bullet$ ,  $[\text{Co}(\text{NH}_3)_5(\text{HPO}_3)]^+$ ;  $\nabla$ ,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_2)]^{2+}$

**Table 1** Kinetic and equilibrium parameters obtained for all the reactions of  $[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$  with  $[\text{Fe}(\text{CN})_6^{4-}]$  as a function of  $\text{H}_x\text{P}_y\text{O}_z^{m-}$ , temperature and pressure.  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{LiClO}_4$ )

$[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$	pH <sup>a</sup>	$P/\text{atm}$	$T/^\circ\text{C}$	$10^3 k/\text{s}^{-1}$	$\bar{K}_{\text{os}}^b/\text{dm}^3 \text{mol}^{-1}$		
$[\text{Co}(\text{NH}_3)_5(\text{HP}_2\text{O}_7)]$	4.3	1	25	0.59	50		
			35	2.0			
			45	7.2			
		100	35	1.8	40		
			500	0.86			
			1000	0.42			
$[\text{Co}(\text{NH}_3)_5(\text{P}_2\text{O}_7)]^-$	7.9	1	25	0.096	45		
			35	0.40			
			45	2.0			
		9.6	50	44	1.2	70	
			500	0.96			
			1000	0.71			
$\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$ $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$	4.3	1	25	0.59	110		
			35	2.2			
			45	6.8			
		5.0	1	25	0.27	120	
			35	0.98			
			45	2.7			
$\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$ $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$	6.0	1	25	0.26	100		
			35	0.74			
			45	2.1			
		7.3	1	35	0.75	110	
			9.0	1	25	0.26	110
				35	0.86		
			45	2.6			

Table 1 (continued)

$[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$	pH <sup>a</sup>	P/atm	T/°C	$10^3 k/\text{s}^{-1}$	$\bar{K}_{\text{os}}^b/\text{dm}^3 \text{mol}^{-1}$			
	8.8	100	35	1.1	95			
		500		0.78				
		1000		0.66				
		1500		0.53				
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$ $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})^-]$	3.0	1	25	1.8	70			
			35	4.9				
			45	11				
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})^-]$	3.6	1	25	1.7	30			
			35	7.2				
			45	18				
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$ $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})^-]$ $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$	5.0	1	25	0.79	25			
			35	3.3				
			45	8.1				
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})^-]$ $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$	6.1	1	45	4.1	30			
			7.1	1		35	0.99	30
						45	3.3	
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$	7.5	1	25	0.24	60			
			35	0.73				
	9.0	1	25	0.18	60			
			35	0.73				
			45	2.7				
		50	44	2.7	70			
		500		1.3				
	1000		0.83					
	1500		0.45					
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_3)]^{2+}$ $[\text{Co}(\text{NH}_3)_5(\text{HPO}_3)]^+$	2.3	1	35	12	60			
			35	11				
			35	9.7				
$[\text{Co}(\text{NH}_3)_5(\text{HPO}_3)]^+$	6.0	1	25	1.1	30			
			35	2.8				
			45	9.4				
	9.0	50	41	4.0	60			
		500		2.4				
		1000		1.9				
		1500		1.1				
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_2)]^{2+}$	4.3	100	41	110	40			
		250		87				
		500		67				
		1000		39				
		1500		21				
	4.8	1	15	4.0	70			
25			12					
35			36					
45			170					
7.5	1	15	5.1	40				
		20	11					
		25	22					
		35	40					

<sup>a</sup> pH 2.0–3.0,  $\text{CClH}_2\text{CO}_2\text{H}-\text{CClH}_2\text{CO}_2^-$ ; 3.0–3.2,  $\text{HCO}_2\text{H}-\text{HCO}_2^-$ ; 3.9–5.5,  $\text{MeCO}_2\text{H}-\text{MeCO}_2^-$ ; 5.9–6.9, citric acid (3-carboxy-3-hydroxypentane-1,5-dioic acid)–citrate; 7.8–9.6, Tris [tris(hydroxymethyl)aminomethane] buffer; 10–11,  $\text{HCO}_3^- - \text{CO}_3^{2-}$ . <sup>b</sup> Average for the indicated conditions.

sequently, although important differences in the values of  $k$  were observed at ambient pressure on changing pH (see Table 1), runs carried out under varying pressure conditions became very erratic, possibly due to differences in the  $\Delta V^\ddagger$  values for the acid–base equilibria. Therefore, for these systems no values of  $k$  could be calculated at elevated pressures. Nevertheless, at room pressure an iteration procedure (see Experimental section) was used in order to fit all data determined at various pH values to estimate the  $k$  values for all the included species (see Table 2).

As seen in Tables 1 and 2, the data obtained for the reduction of  $[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$  clearly indicate that for all the phosphorus oxoanionic complexes the pattern observed for the already published systems<sup>3</sup> with respect to changes in complex charge and extent of protonation is maintained.

On one hand, the range of values found for the first-order electron-transfer rate constants on changing the phosphorus oxoanion (Table 1) is quite significant;  $k$  increases by up to two orders of magnitude on going from  $\text{P}_2\text{O}_7^{4-}$  to  $\text{H}_2\text{PO}_2^-$ . On the other hand, differences introduced by the extent of protonation on the oxoanionic phosphorus(v) ligands are also important. The complexes containing the fully deprotonated  $\text{P}_2\text{O}_7^{4-}$ ,  $\gamma\text{-P}_3\text{O}_{10}^{5-}$  and  $\beta\text{-P}_3\text{O}_{10}^{5-}$  ligands are characterized by the same electron-transfer rate constants. The same is true for the  $\text{HP}_2\text{O}_7^{3-}$  and  $\gamma\text{-HP}_3\text{O}_{10}^{4-}$  complexes; in this case, however, an increase in  $k$  is observed on increasing extent of protonation. This trend is also found for the  $\gamma\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$  complex, but for the  $\beta$  isomers of the triphosphato complexes a threshold is observed up to the  $\beta\text{-H}_3\text{P}_3\text{O}_{10}^{2-}$  oxoanion.

**Table 2** Kinetic and thermal and pressure activation parameters for all the reactions of  $[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$  with  $[\text{Fe}(\text{CN})_6]^{4-}$  as a function of  $\text{H}_x\text{P}_y\text{O}_z^{m-}$ .  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{LiClO}_4$ ), pH conditions as derived from Table 1 data. Available data for similar systems are also included

$[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_y\text{O}_z)]^{(m-3)-}$	$10^3 k^{308}/\text{s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{ mol}^{-1}$ ( $\text{T}/\text{K}^{-1}$ )	Ref.
$[\text{Co}(\text{NH}_3)_5(\text{HP}_2\text{O}_7)]$	2.0	$95 \pm 3$	$13 \pm 10$	$36 \pm 3$ (308)	a
$[\text{Co}(\text{NH}_3)_5(\text{P}_2\text{O}_7)]^-$	0.40	$120 \pm 10$	$69 \pm 22$	$13 \pm 1$ (314)	a
$\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$	$20^b$	—	—	—	a
$\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$	} $0.84^c$	$80 \pm 2^c$	$-44 \pm 6^c$	—	a
$\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$					
$\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$					
$\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$					
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$	} $8.5\text{--}11^d$	—	—	—	a
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$					
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]^-$					
$\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$	$2.0\text{--}2.3^d$	—	—	—	a
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_3)]^{2+}$	0.73	$104 \pm 4$	$31 \pm 1$	$32 \pm 2$ (317)	a
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_3)]^{2+}$	$14^e$	—	—	—	a
$[\text{Co}(\text{NH}_3)_5(\text{HPO}_3)]^+$	2.8	$81 \pm 8$	$-30 \pm 25$	$22 \pm 2$ (314)	a
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_2)]^{2+}$	$36^f$	$73 \pm 12^f$	$-34 \pm 39^f$	$30 \pm 1$ (314)	a
	$40^g$	$94 \pm 6^g$	$33 \pm 20^g$	—	a
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_4)]^{2+}$	5.6	—	—	—	3
$[\text{Co}(\text{NH}_3)_5(\text{HPO}_4)]^+$	2.6	$72 \pm 8$	$-61 \pm 26$	$37 \pm 4$	3
$[\text{Co}(\text{NH}_3)_5(\text{PO}_4)]$	0.28	$107 \pm 22$	$32 \pm 70$	$17 \pm 1$	3
$[\text{Co}(\text{NMeH}_2)_5(\text{HPO}_4)]^+$	59	$86 \pm 14$	$8 \pm 46$	$44 \pm 5$	3
$[\text{Co}(\text{NMeH}_2)_5(\text{PO}_4)]$	3.2	$101 \pm 8$	$32 \pm 27$	$32 \pm 1$	3
$[\text{CoL}(\text{HPO}_4)]^{+h}$	0.73	$57 \pm 10$	$-118 \pm 31$	$36 \pm 2$	3

<sup>a</sup> This work. <sup>b</sup> Estimated from the value at pH 4.3 and the values determined for the  $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]\text{-}[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]$   $[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$  systems (see Fig. 3). <sup>c</sup> Calculated using the values of  $k_{\text{obs}}$  at pH 5.0, 6.0, 7.3 and 9.0 (see Fig. 3). <sup>d</sup> Estimated from the values of  $k_{\text{obs}}$  at pH 3.0, 3.6, 5.0 and 7.1 and the value of  $k$  determined at pH 9.0 for  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$ . <sup>e</sup> Calculated using the values of  $k_{\text{obs}}$  at pH 2.3, 3.0 and 3.9. <sup>f</sup> pH 4.8. <sup>g</sup> pH 7.5. <sup>h</sup> L = *cis*-10-Amino-10-methyl-1,4,8,12-tetraazacyclopentadecane.

The data in Table 1 also suggest that simple cobalt(III) or iron(II) complex charge factors cannot account for the practical lack of differences observed in the values of  $K_{\text{OS}}$ . These values are of the same order of magnitude for all the linear phosphorus oxoanionic groups studied on changing the charge of the complex. As found for other systems,<sup>2c,3</sup> and unlike other simpler systems,<sup>2b</sup> the degree of ion-pair formation during these reactions can be considered to be the same, whatever the nature of the complexes or the charges involved. Nevertheless, it is clear from the values of  $K_{\text{OS}}$  obtained for the non-linear  $\beta\text{-H}_x\text{P}_y\text{O}_z^{(5-x)-}$  ligands that the importance of hydrogen bonding should not be overlooked. For these systems the values found are consistently larger than those for the equivalent  $\gamma\text{-H}_x\text{P}_y\text{O}_z^{(5-x)-}$  linear systems, indicating that the existence of *external* oxo groups in the co-ordination sphere is a very important factor in determining the value of the outer-sphere formation constant,  $K_{\text{OS}}$ .

As seen for other systems,<sup>1-3</sup> the activation enthalpy values do not show any trend, whereas there is a large scatter in the  $\Delta S^\ddagger$  values from  $-34 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{PO}_2)]^{2+}$  to  $+69 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $[\text{Co}(\text{NH}_3)_5(\text{P}_2\text{O}_7)]^-$ . These values are rather surprising since the values for the pressure activation parameter,  $\Delta V^\ddagger$ , are all clearly positive indicating a significant expansion on going to the transition state. Nevertheless, the  $\Delta V^\ddagger$  values are as expected for these outer-sphere redox reactions, and their order of magnitude is that observed for similar systems.<sup>1a,c,d,2a,6a,7</sup> All changes in the  $\Delta V^\ddagger$  values related to the  $\text{H}_x\text{P}_y\text{O}_z^{m-}$  ligand of the cobalt(III) complex clearly indicate that the geometry of the oxoanion, its oxidation state, and its extent of protonation play an important role. The values of  $\Delta V^\ddagger$  for both the fully deprotonated and monoprotonated oxoanionic phosphorus ligands ( $\text{P}_2\text{O}_7^{4-}$ ,  $\text{HP}_2\text{O}_7^{3-}$ ) were obtained only in one case. The value for the fully deprotonated species is significantly smaller than that for the protonated species, similar to what was found for the  $\text{PO}_4^{3-}\text{-HPO}_4^{2-}$  system.<sup>3</sup> This seems to indicate that the presence of *external* oxo groups plays a very important role in electrostriction and solvation effects of reactions between highly charged species. In this respect, differences related to the extent of polymerization are much less important. On the one hand, for the  $\beta\text{-}$  and  $\gamma\text{-}$

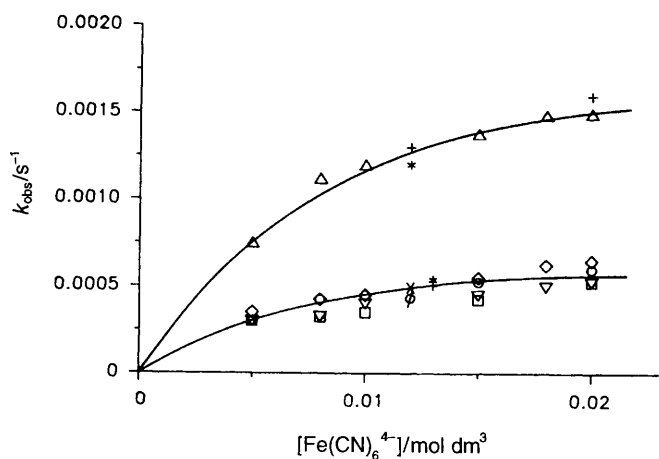
$\text{P}_3\text{O}_{10}^{5-}$  complexes an important difference exists, which clearly has to be related to the geometry of the *external* oxo groups of the ligands. On the other hand, for all the  $\text{PO}_4^{3-}$ ,  $\text{P}_2\text{O}_7^{4-}$  and  $\beta\text{-P}_3\text{O}_{10}^{5-}$  complexes, the values of  $\Delta V^\ddagger$  are practically the same.

## Discussion

The data in Tables 1 and 2 clearly demonstrate important changes in the kinetic and thermodynamic parameters as a function of the phosphorus oxoanionic ligand. In general, the effects observed agree very well with the results obtained for closely related systems,<sup>3</sup> as indicated by the data in Table 2.

A kinetic separation of the first-order electron-transfer rate constant,  $k$ , and the precursor-complex formation constant,  $K_{\text{OS}}$ , was possible according to equation (2). However, the values of  $K_{\text{OS}}$  were found to be too high to be directly related to simple charge factors arising from ion pairing.<sup>17</sup> In particular, for the negatively charged  $[\text{Co}(\text{NH}_3)_5(\text{HP}_3\text{O}_{10})]$  and  $[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$  complexes, the value of  $K_{\text{OS}}$  was found to be practically the same as that for mixtures of the corresponding neutral and positively charged complexes,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{P}_3\text{O}_{10})]$  and  $[\text{Co}(\text{NH}_3)_5(\text{H}_3\text{P}_3\text{O}_{10})]^+$ . It is important to note that the number of *external* oxo groups on the cobalt(III) complex seems to play an important role for species not having any protonation. For example  $K_{\text{OS}}$  at ambient pressure changes from  $60\text{--}70 \text{ dm}^3 \text{ mol}^{-1}$  for the linear  $\gamma\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$  complex to  $100\text{--}110 \text{ dm}^3 \text{ mol}^{-1}$  for the corresponding  $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{P}_3\text{O}_{10})]^{2-}$  species.

The existence of hydrogen bonding has already been held responsible for the large values found for similar systems.<sup>3,8</sup> Although hydrogen bonding between protonated and anionic species is clear, any hydrogen bonding between a fully deprotonated anionic species and a negatively charged ion has to include external solvent water molecules in a way that close contact is avoided. Such interactions can result in the formation of solvent-separated ion aggregates. In this respect the values of  $K_{\text{OS}}$  found for the complexes of the oxoanionic ligands of P<sup>I</sup> and P<sup>III</sup> cannot be interpreted in the same way. Lower polarization of the phosphorus centre, as well as the overall positive charge



**Fig. 3** Dependence of  $k_{\text{obs}}$  on  $[\text{Fe}(\text{CN})_6]^{4-}$  for the reduction of  $\beta\text{-}[\text{Co}(\text{NH}_3)_5(\text{H}_x\text{P}_3\text{O}_{10})]^{(2-x)-}$  as a function of pH at  $I = 1.0 \text{ mol dm}^{-3}$  ( $\text{LiClO}_4$ ) and  $35^\circ\text{C}$ . Upper curve: pH 4.3;  $\Delta$ , no added  $[\text{Fe}(\text{CN})_6]^{3-}$ ;  $+$ ,  $[\text{Fe}(\text{CN})_6]^{3-} = 0.001 \text{ mol dm}^{-3}$ ;  $*$ ,  $[\text{Fe}(\text{CN})_6]^{3-} = 0.002 \text{ mol dm}^{-3}$ . Lower curve:  $\circ$ , pH 9.0, no added  $[\text{Fe}(\text{CN})_6]^{3-}$ ;  $\times$ , pH 9.0,  $[\text{Fe}(\text{CN})_6]^{3-} = 0.001 \text{ mol dm}^{-3}$ ;  $\varnothing$ , pH 9.0,  $[\text{Fe}(\text{CN})_6]^{3-} = 0.0015 \text{ mol dm}^{-3}$ ;  $\nabla$ , pH 7.3, no added  $[\text{Fe}(\text{CN})_6]^{3-}$ ;  $\square$ , pH 6.0, no added  $[\text{Fe}(\text{CN})_6]^{3-}$ ;  $\diamond$ , pH 5.0, no added  $[\text{Fe}(\text{CN})_6]^{3-}$ ;  $+$ , pH 5.0,  $[\text{Fe}(\text{CN})_6]^{3-} = 0.001 \text{ mol dm}^{-3}$ ;  $*$ , pH 5.0,  $[\text{Fe}(\text{CN})_6]^{3-} = 0.002 \text{ mol dm}^{-3}$ .

of the complex, can easily produce important differences; real ion pairing must contribute towards the precursor complex stability in these cases.

All in all, a dead-end type of mechanism, cannot be ruled out,<sup>7,8,18,19</sup> and the existence of a large concentration of unreactive ion pairs has to be considered as a possibility. The situation could be very similar to that found for metalloprotein systems, where modification of some areas of the protein surface leads to an important decrease in the rate of the redox process. Nevertheless, the possibility of modifying the proteins, and measuring their redox potentials, does not apply to our complexes. The presence of added oxidized anion,  $[\text{Fe}(\text{CN})_6]^{3-}$ , had no effect on the observed rate constant,  $k_{\text{obs}}$ , as shown in Figs. 1 and 3. Consequently, the existence of a dead-end, hydrogen bonded, outer-sphere complex between the two negatively charged reactants cannot be ascertained. As a result, although we cannot rule out the existence of such a path in our redox reaction, the possibility of extensive hydrogen bonding in the precursor complex seems to be a much more attractive approach. Therefore the discussion of the results obtained will be made on this basis; the coherence of the observed facts underlines the validity of the proposed mechanism.

Concerning the electron-transfer rate constants,  $k$ , collected in Table 2, it is important to note the wide range of values found,  $(0.4\text{--}40) \times 10^{-3} \text{ s}^{-1}$ , for a relatively narrow family of compounds. Although the driving force could be responsible for the scatter observed,<sup>20</sup> all the important trends related to the oxidation state of the phosphorus in the ligand, extent of protonation, and geometry of the oxophosphorus ligand can be explained in terms of the possible precursor complex interactions and the differences due to hydrogen bonding.

From the data in Table 2, it is clear that the values of  $k$  reach a maximum for the oxoanionic phosphorus(II) ligand complex, diminish on going to the corresponding fully deprotonated complex of the phosphorus(III) ligand and reach a minimum for any of the phosphorus(V) ligand complexes. It is difficult to hold the driving force responsible for these facts, especially when it cannot be measured. Although simple charge factors are an attractive approach, it has to be kept in mind that for the oxoanionic phosphorus(II) ligand complexes any hydrogen-bonding interaction between the free oxo group and a reducing  $[\text{Fe}(\text{CN})_6]^{4-}$  species, *via* an external water molecule, has to be much more localized, for electron-density reasons, than for the

corresponding species of P<sup>III</sup> and P<sup>V</sup>. Direct interaction in protonated species is not possible at this stage.

When the oxoanionic phosphorus(V) ligand complexes are compared it is clear that the differences are very much related to their extents of protonation; the fully deprotonated complexes have practically constant values of  $k$ ,  $[(0.28\text{--}0.86) \times 10^{-3} \text{ s}^{-1}$  at  $35^\circ\text{C}$ ]. Nevertheless, only for the  $\beta\text{-H}_x\text{P}_3\text{O}_{10}^{(5-x)-}$  oxoanion complex, no significant differences are detected within the range  $x = 0\text{--}2$ ; for the  $\gamma\text{-H}_x\text{P}_3\text{O}_{10}^{(5-x)-}$  oxoanionic complexes, no difference is found when  $x = 2$  or 3.

When protonation of the oxoanion {or  $[\text{Fe}(\text{CN})_6]^{4-}$  at  $\text{pH} \leq 5$ } takes place, the possibility of direct hydrogen bonding becomes more important,<sup>18</sup> especially when the proton is more localized [linear  $\text{H}_x\text{P}_3\text{O}_{10}^{(5-x)-}$ ]. On the other hand, the total charge on the cobalt complex becomes more positive and direct interaction is also favoured, provided the same extent of protonation of the iron(II) complex is maintained. Effectively,  $\text{HPO}_4^{2-}$ ,  $\text{HP}_2\text{O}_7^{3-}$  and  $\gamma\text{-HP}_3\text{O}_{10}^{4-}$  complexes show an important increase in electron-transfer rate constant,  $k$ ; the more localized the proton, the larger is the increase. In this respect, the value of  $k$  calculated for the  $\text{H}_2\text{PO}_3^-$  complex shows the same trend, being five times larger than that for the deprotonated species. The lack of differences observed for the  $\beta\text{-P}_3\text{O}_{10}^{5-}$ ,  $\text{-HP}_3\text{O}_{10}^{4-}$  and  $\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$  complexes has probably to be related to the large number of external oxo groups competing for the proton, thus not allowing a proper interaction with the reducing species. A further decrease in pH results in protonation of the complexes, as well as the iron(II) anion. The electron-transfer rate constants could then increase due to the increased possibility of a directly hydrogen-bonded precursor complex. For the  $\beta$ -triphosphato complexes such an increase is only observed for the  $\text{H}_3\text{P}_3\text{O}_{10}^{2-}$  species. Considering the possible localization of the protonation site, the effect of protonation on the oxo groups of the  $\beta\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$  complex has to be fairly similar to the first protonation of the phosphate, diphosphate and  $\gamma$ -triphosphate ligands. Similarly, the lack of differences between the values for the electron-transfer rate constant of the  $\gamma\text{-H}_2\text{P}_3\text{O}_{10}^{3-}$  and  $\text{-H}_3\text{P}_3\text{O}_{10}^{2-}$  complexes (Table 2) has to be related to the fact that protonation has taken place on an internal oxo group. Consequently, no modification of the external oxo group distribution has occurred in this process. Nevertheless, protonation of the  $[\text{Fe}(\text{CN})_6]^{4-}$  anion at this pH is also possible and can account for the differences.

No conclusive discussion of the thermal activation parameters in Table 2 is possible; the values of  $\Delta H^\ddagger$  are all practically the same within the experimental error limits, and these of  $\Delta S^\ddagger$  are scattered around zero, with usually very large errors. Only for the diphosphato system it was possible to determine the activation parameters for the protonation sequence of complexes; in that case the same trend in  $\Delta S^\ddagger$  values as that<sup>3</sup> for  $\text{PO}_4^{3-}\text{-HPO}_4^{2-}$  was found. The values determined for  $\Delta V^\ddagger$  from the pressure dependence of  $k$  are much more reliable and indicative of possible differences in the cobalt(III) complex; the reducing species, being always the same, has to produce an electrostriction/solvational contribution similar for all the systems studied at the same acidity.

As found for the reduction of  $[\text{Co}(\text{NH}_3)_5(\text{PO}_4)]$ , the values of  $\Delta V^\ddagger$  determined for the fully deprotonated  $\text{P}_2\text{O}_7^{4-}$  and  $\beta\text{-P}_3\text{O}_{10}^{5-}$  complexes are small, whereas the value for the  $\gamma\text{-P}_3\text{O}_{10}^{5-}$  complex is of the same magnitude as that obtained for the  $\text{HPO}_4^{2-}$  and  $\text{HP}_2\text{O}_7^{3-}$  complexes. The values found for the fully deprotonated oxoanionic phosphorus-(I) and -(III) ligand complexes are in between these values. That for the fully deprotonated phosphorus(III) ligand is closer to that found for the corresponding phosphorus(V) oxoanion  $\text{PO}_4^{3-}$ . It should, however, be kept in mind that the oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  to  $[\text{Fe}(\text{CN})_6]^{3-}$  is accompanied by a large decrease in electrostriction and an associated volume increase. Allowing for these considerations, it is clear that on going to the transition state the precursor complexes suffer an important

expansion which does not correspond to a intrinsic reorganization, given the almost zero values of  $\Delta S^\ddagger$ . This expansion, consequently, has to be related to a balance between a decrease in electrostriction and an increase in hydrogen bonding. From the data in Table 2, it is clear that this expansion is more pronounced for systems where the external phosphorus(v) centre is less sensitive to changes occurring at the cobalt(III) centre. It seems that solvational factors related to the charge distribution are determining in this respect. The relatively low values of  $\Delta V^\ddagger$  found for the reduction of the  $\text{PO}_4^{3-}$ ,  $\text{P}_2\text{O}_7^{4-}$  and  $\beta\text{-P}_3\text{O}_{10}^{5-}$  complexes indicate that the decrease in electrostriction due to the oxidation of  $[\text{Fe}(\text{CN})_6]^{4-}$  to  $[\text{Fe}(\text{CN})_6]^{3-}$  is less significant, probably due to the lack of protons on these ligands that are essential for effective hydrogen bonding and solvent reorganization within the precursor species. When the size of the amine skeleton,<sup>3</sup> or the distribution of the triphosphate ligand ( $\gamma\text{-P}_3\text{O}_{10}^{5-}$ ) is made less compact, the values of  $\Delta V^\ddagger$  become significantly more positive. The same magnitude of  $\Delta V^\ddagger$  is obtained for the already protonated species of the  $\text{PO}_4^{3-}$  and  $\text{P}_2\text{O}_7^{4-}$  complexes, *i.e.* electrostriction effects are fully realized.

In this respect, on decreasing the oxidation state of the phosphorus centre ( $\text{P}^{\text{V}} \longrightarrow \text{P}^{\text{III}} \longrightarrow \text{P}^{\text{I}}$ ), the volumes of activation for the fully deprotonated complex increase. The above-mentioned reasoning can also explain this trend; the increase in electron density on the phosphorus oxoanion makes it less sensitive to changes taking place on the cobalt(III) centre. Nevertheless, the amount of *external* oxo groups is also increased in the sequence  $\text{P}^{\text{I}} \longrightarrow \text{P}^{\text{III}} \longrightarrow \text{P}^{\text{V}}$ , and this can also be held responsible for the observed facts, especially if hydrogen bonding is responsible for the large positive values found for  $\Delta V^\ddagger$ . These results clearly indicate the important role of solvent reorganization and the fine tuning by hydrogen bonding in outer-sphere electron-transfer reactions.

## Acknowledgements

Financial support from the German-Spanish co-operation projects is acknowledged. M. M. gratefully acknowledges financial support from Direcció General de Investigació Científica y Tècnica and the Direcció General de Universitats de la Generalitat de Catalunya. R. v. E. gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft and the Volkswagen Foundation.

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Received 13th February 1996; Paper 6/01065B