# Discrete Cyanide-Bridged Mixed-Valence Co/Fe Complexes: Outer-Sphere Redox Behaviour

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The outer-sphere redox behaviour of a series of $[L_nCo^{III}\text{-}NCFe^{II}(CN)_5]^-$ ($L_n$ = *n*-membered pentadentate aza-macrocycle) complexes have been studied as a function of pH and oxidising agent. All the dinuclear complexes show a double protonation process at pH ≈ 2 that produces a shift in their UV/Vis spectra. Oxidation of the different non-protonated and diprotonated complexes has been carried out with peroxodisulfate, and of the non-protonated complexes also with trisoxalatocobaltate(III). The results are in agreement with predictions from the Marcus theory. The oxidation of $[Fe(phen)_3]^{3+}$ and $[IrCl_6]^{2-}$ is too fast to be measured, although for the latter the transient observation of the process has been achieved at pH = 0. The study of the kinetics of the outer-sphere redox process, with the $S_2O_8{}^{2-}$ and $[Co(ox)_3]^{3-}$ oxidants, has been carried out as a function of pH, temperature, and pressure. As a whole, the values found for the activation volumes, entropies, and enthalpies are in the following margins, for the diprotonated and non-protonated dinuclear complexes, respectively: $\Delta V^{\neq}$ from 11 to 13 and 15 to 20 $cm^3\ mol^{-1}$; $\Delta S^{\neq}$ from 110 to 30 and –60 to –90 $J\ K^{-1}\ mol^{-1}$; $\Delta H^{\neq}$ from 115 to 80 and 50 to 65 $kJ{\cdot}mol^{-1}$. The thermal activation parameters are clearly dominated by the electrostriction occurring on outer-sphere precursor formation, while the trends found for the values of the volume of activation indicate an important degree of tuning due to the charge distribution during the electron transfer process. The special arrangement on the amine ligands in the isomer *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]^-$ accounts for important differences in solvent-assisted hydrogen bonding occurring within the outer-sphere redox process, as has been established in redox reactions of similar compounds.

## Introduction

Mixed-valence compounds have been of interest for a long time,[1] given the variable nature of valence localisation (or delocalisation) and the nature and tunability of their MMCT bands.[2] Their potential use as possible electrochromic materials for a variety of situations has already been established.[3,4] As a whole, their redox properties are of great importance, both for their applications and for an understanding of their electronic structure.[5] Despite all these facts, few redox studies on these types of complexes are available in the literature,[6] due primarily to the typically limited stability of the oxidized or reduced species involved in the process. Indeed, few well-characterised discrete (non-polymeric) mixed-valence complexes are known that exhibit redox bistability. In this respect the preparation of a family of well-characterised cyanide-bridged compounds has provided an ideal entry into this field.[7−9]

We have been involved in the study of a number of outer-sphere redox reactions of $Co^{III}$ macrocyclic complexes with $[Fe(CN)_6]^{4-}$, where the importance of solvent reorganisation, in the process, proved to be crucial to differences in the derived thermal and baric activation parameters.[10] Furthermore, the existence of a tight outer-sphere complexation, prior to the rate-determining electron transfer, has been found to be a dominant factor, even in situations where ion-pairing seems very unlikely.[11,12] From these studies, the formation of a discrete $Co^{III}/Fe^{II}$ species, produced by an inner-sphere redox process starting from the reduced $Co^{II}$ macrocyclic complexes and the corresponding $[Fe(CN)_6]^{3-}$ ligand, similar to those detected for the classical $CoEDTA/Fe(CN)_6$ systems has been envisaged.[13] Further studies on these compounds have led us to the full characterisation of a series of molecular mixed-valence $Fe^{II}CNCo^{III}$ complexes with different macrocycles and geometries surrounding the $Co^{III}$ centre.[7−9] During this period, a few redox studies on discrete dinuclear Fe/Ru mixed-valence compounds have appeared,[14,15] but neither the pH

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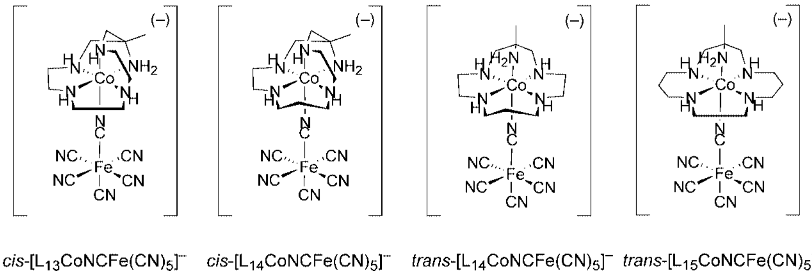

Scheme 1

dependence of such reactions nor the use of transition metal complexes as redox partners has been examined. Furthermore, the stability and full characterisation of the complexes involved was not achieved in some cases.

In this paper we present a mechanistic study of the outer-sphere oxidation processes of the complexes indicated in Scheme 1 with a variety of oxidants such as $S_2O_8^{2-}$, $[Co(ox)_3]^{3-}$, $[IrCl_6]^{2-}$, and $[Fe(phen)_3]^{3+}$. In this case the full characterisation of the reduced and oxidised species has already been carried out; the temperature, pressure, and pH dependence of these reactions has also been investigated.

The differences in macrocycle size and its geometrical wrapping arrangement, are bound to produce important differences in both the electron transfer process and the encounter complex formation equilibrium. The reduction potential of the iron centre being affected by the nature of the wrapped cobalt ion, and the encounter complex affected by the external shape of the macrocycle attached to the cobalt atom.

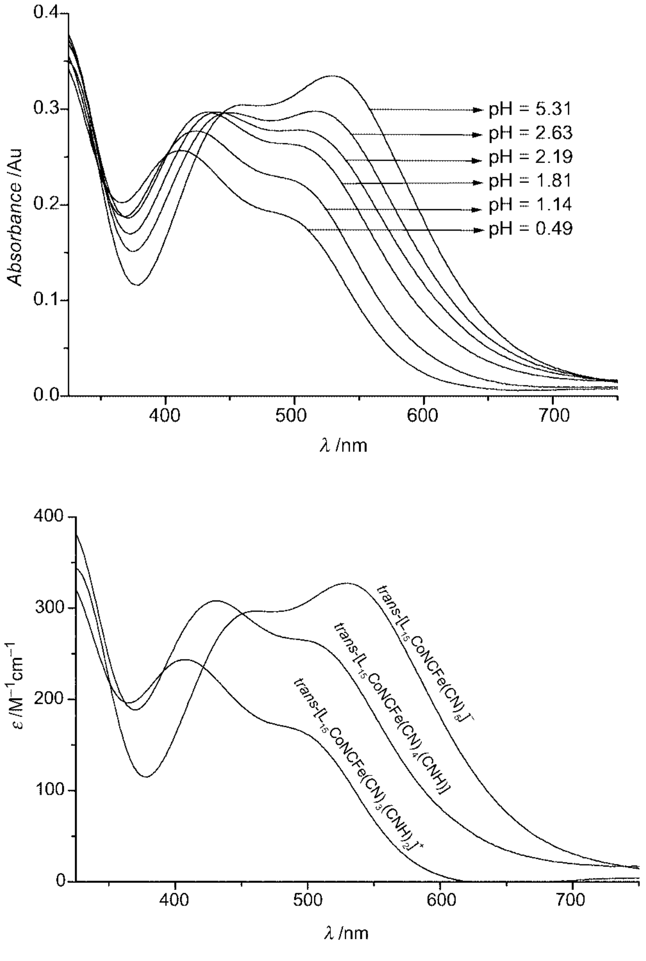

Figure 1. Top: UV/Vis spectral changes obtained for a solution 1 × $10^{-3}$ M of complex *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$ on changing the acidity conditions; bottom: SPECFIT estimation of the UV/Vis spectra of the *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$, *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_4(CNH)]$, and *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ complexes for the same experiment ($T$ = 298 K, $I$ = 1.0 M $LiClO_4$)

## Results and Discussion

### Products

All the complexes have been prepared and characterised according to published procedures[7–9] and there are no aspects that merit special mention. The new *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_5]^-$ complex behaves as the already known derivatives with macrocycles of different sizes. Given the fact that the outer-sphere redox behaviour of these dinuclear complexes was to be studied under different acidity conditions, and that the $[Fe(CN)_6]^{4-}$ moiety of the molecule is likely to undergo protonation at low pH,[16] speciation of the dinuclear complexes as a function of pH has been carried out. Figure 1 (top) shows typical electronic spectral shifts obtained when the solution of the mixed valence complex is taken from a high to low pH. Despite the two sets of different shifts observed in the spectra, for all the complexes studied, the potentiometric titration indicated a double protonation process at pH ≈ 2 that could not be resolved in two different steps. The SPECFIT analysis[17] of the changes shown in Figure 1 (top), indicated the effective presence of two protonation steps with distinct electronic spectra (Figure 1, bottom). The estimated values of p$K_{a1}$ and p$K_{a2}$ are, however, too close for a reliable differentiation, and selecting a pH value that ensured the presence of the monoprotonated complex, $[L_nCo^{III}NCFe^{II}(CN)_4(CNH)]$, as the main species in solution proved impossible.

As a result of this, the study has only been carried out on the complexes $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ and $[L_nCo^{III}NCFe^{II}(CN)_3(CNH)_2]^+$. Table 1 includes all the spectroscopic data and p$\beta_{12}$ values determined spectrophotometrically for the series of dinuclear complexes included in this study. The diprotonated species are less stable than the corresponding non-protonated ones, with respect to de-

Table 1. UV/Vis spectral and $p\beta_{12}$ data determined for the $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ systems included in this study ($T$ = 298 K, $I$ = 1.0 M $LiClO_4$)

| Species | $\lambda_{max}$ [nm] ($\varepsilon$ [$M^{-1}cm^{-1}$]) | $\lambda_{max}$ [nm] ($\varepsilon$ [$M^{-1}cm^{-1}$]) | $\lambda_{max}$ [nm] ($\varepsilon$ [$M^{-1}cm^{-1}$]) | $p\beta_{12}$ |
|---|---|---|---|---|
| *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_5]^-$ | 325(367) | 448(390) | 498(380) | 2.1 |
| *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_4(CNH)_2]^+$ | 319(513) | 390(377) | 478(256) | |
| *cis*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]^-$ | 328(480) | 462(490) | 504(500) | 2.1 |
| *cis*-$[L_{14}Co^{III}NCFe^{II}(CN)_4(CNH)_2]^+$ | 317(555) | 392(375) | 482(270) | |
| *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]^-$ | 324(410) | 440(430) | 513(490) | 2.1 |
| *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_4(CNH)_2]^+$ | 316(457) | 388(352) | 485(207) | |
| *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$ | 328(410) | 462(370) | 530(420) | 2.2 |
| *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_4(CNH)_2]^+$ | 314(320) | 392(211) | 485(135) | |

composition into their $Co^{III}$ and $Fe^{II}$ parents; nevertheless, on neutralization of the resulting solution, a recombination of the two metal centres takes place to form the mixed-valence dinuclear complex.[10] This lesser stability is not surprising, taking into account the increase of positive charge density introduced onto the dinuclear complexes by the double protonation. We have investigated the Fe-centered oxidation processes of these complexes by cyclic voltammetry at pH = 0, where all the compounds are doubly protonated (Table 2).

Table 2. Electrochemical $Fe^{III}/Fe^{II}$ reduction data for the dinuclear complexes studied, protonated species in 1.0 M $HClO_4$, non-protonated in 1.0 M aqueous solution of $LiClO_4$

| Species | $E^0(Fe^{III}/Fe^{II})$ [mV][a] |
|---|---|
| *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_5]$ | 626 |
| *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | 775 |
| *cis*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]$ | 614 |
| *cis*-$[L_{14}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | 778 |
| *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]$ | 644 |
| *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | 775 |
| *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]$ | 612 |
| *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | 773 |

[a] Versus NHE, average value for the anodic and cathodic cyclic voltammogram peaks.

A positive shift of ca. 130−165 mV is observed for all the systems when two of the terminal cyanide ions are protonated on the reduced dinuclear complexes, which is in line with the general rule of increasing reduction potential on increasing the positive charge of the reduced species.[18] The same sort of changes have been observed for the reduction potential of hexacyanoferrates measured at 1.0 M HCl,[19] or when the $\{L_nCo^{III}\}$ moiety is attached to one of the cyanide ligands.[7,8] As for the possible protonation sites of the $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ complexes, it is clear that they have to be at the axial and one of the equatorial positions of the $\{Fe(CN)_5\}$ fragment of the molecule. The protonation of two consecutive equatorial positions cannot be expected to have such similar $pK_a$ values. In this respect the IR spectrum of protonated *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ only shows the peak at 2120 $cm^{-1}$ corresponding to the μ-CN and a rather broad band at 2055 $cm^{-1}$, which indicates the shifting to higher energies, as well as the loss in symmetry, due to protonation (Figure S1, Supporting Information, see also the footnote on the first page of this article).[20,21] In order for the integrity of the complex to be held, which prevents the formation of $Co_3[Fe^{III}(CN)_6]_2$, protonation of the amine groups of the macrocycle must not occur. The amine protons of the macrocycle are structurally (for any of the two possible conformations, *cis* or *trans*) too far away to prevent protonation of any of the equatorial cyanide groups on the iron centre. Furthermore the $^{13}C$ NMR spectrum of a sample of *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$ in 1.0 M $HClO_4$ (Figure S2, Supporting Information) agrees with the integrity of the $Co^{III}$ moiety of the complex.

## Redox Kinetics

It has already been qualitatively established that a well-behaved redox process is observed for the oxidation of the *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$ complex with the $S_2O_8^{2-}$ ion.[7] Despite its high standard potential (2010 mV), the electron transfer mechanism of the peroxodisulfate ion prevents the very fast reaction rate that would be expected,[22] producing a $k_{ex}$ of ca. $10^{-18}$ $M^{-1}$ $s^{-1}$ by the direct application of the Marcus relationship.[23] Furthermore, no dependence on the pH is expected for the reduction potential in the acidity region used for this study. Given that some redox kinetics on dinuclear Ru/Fe mixed-valence compounds had already been studied with this oxidising agent,[24] the kinetics of the redox process between the $S_2O_8^{2-}$ ion and all the $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ systems have also been studied. Figure 2 shows the general kinetic behaviour found for these systems at varying $[S_2O_8^{2-}]$, temperature and pH; second-order rate constants extrapolated at 298 K, and thermal and pressure activation parameters are collected in Table 3.

The reaction of the four dinuclear complexes prepared with $[Fe(phen)_3]^{3+}$ has also been probed, in this case the high reduction potential at pH = 0 (1050 mV)[25,26] produces a redox reaction rate so fast that it cannot be measured even with a stopped-flow system. That is, the spectra measured at 1:1 concentration ratios and at 0.8 ms after mixing correspond exactly to the 1:1 mixture of $[Fe(phen)_3]^{2+}$ and $[L_nCo^{III}NCFe^{II}(CN)_5]^-$. In this case it seems clear that the reaction rate is extremely fast, as ex-

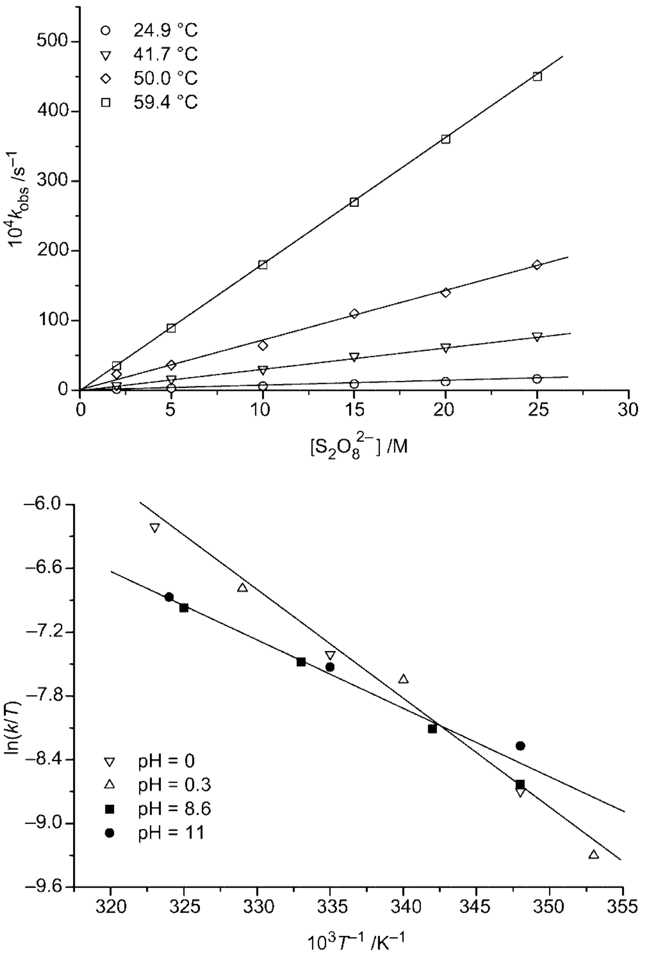

Figure 2. Top: plot of the values of the first-order rate constant, $k_{obs}$, for the $S_2O_8^{2-}$ oxidation of the *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ complex at different temperatures; bottom: Eyring plot derived from the value of the second-order rate constant, $k$, for the *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$ (pH = 8.6 and 11) and *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ (pH = 0.0 and 0.3) plus $S_2O_8^{2-}$ systems ($I$ = 1.0 $\mathrm{M}$ $LiClO_4$)

pected from the calculated value of $E^0$ = 275 mV and the validity of the Marcus relationship for these systems ($k_{ex}\{[Fe(phen)_3]^{3+/2+}\}$ = 1.3 × $10^7$ $\mathrm{M}^{-1}$ $s^{-1}$ and $k_{ex}\{[Fe(CN)_6]^{3-/4-}\}$ = 2.4 × $10^2$ to 2 × $10^4$ $\mathrm{M}^{-1}$ $s^{-1}$),[26,27] which produces an estimated cross reaction rate constant of 7.1 × $10^6$ to 10 × $10^7$ $\mathrm{M}^{-1}$ $s^{-1}$ for the adiabatic redox process occurring on the iron moiety of the dinuclear complex.[28] The instability of $[Fe(phen)_3]^{3+}$ in solutions at higher pH prevented oxidation measurements on the nonprotonated $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ complexes.

The reaction with $[IrCl_6]^{2-}$ was also tried, given the lower potential (892 mV),[29] as well as its independence of pH in the range used for this study. At pH = 0, the transient spectrum measured at 0.8 ms after mixing $[IrCl_6]^{2-}$ and $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ in a 1:1 ratio, effectively shows the presence of an $Ir^{IV}$ oxidising agent which disappears in less than 0.05 s under these second-order conditions. This process could not be observed at pH = 5, where the initial spectrum after mixing corresponds exactly to a 1:1 mixture of the oxidised $[L_nCo^{III}NCFe^{III}(CN)_5]$ complexes and the $Ir^{III}$ species. Taking into account that the redox reaction of $[Fe(CN)_6]^{4-}$ with $[IrCl_6]^{2-}$ has already been measured, and that the values found fit very well with the Marcus relationship,[30] the estimated values of $k_{ex}\{[L_nCoNCFe(CN)_5]^{0/-}\}$ for the different dinuclear systems cannot be smaller than that for the $[Fe(CN)_6]^{3-/4-}$ simple system. Taking into account that the reduction potential of $[Fe(CN)_6]^{3-/4-}$ at 1.0 $\mathrm{M}$ HCl is 688 mV;[19] if a nitrogen atom of one of the cyanide ligands of the hexacyanoferrate(II) has a proton, or an electron-withdrawing $Co^{III}$ centre of the dinuclear complex attached, both the value of $k_{ex}$ and that of $E^0$ seem to increase significantly.

Further inspection of the available oxidants with the appropriate potentials[26] indicated that $[Co(ox)_3]^{3-}$ should be an excellent partner for the process (570 mV[31] and $k_{ex}\{[Co(ox)_3]^{3-/4-}\}$ = 3 × $10^{-7}$ to 1.4 × $10^{-12}$ $\mathrm{M}^{-1}$ $s^{-1}$).[32,33] Consequently, the oxidation of the $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ species with tris(oxalato)cobaltate-

Table 3. Kinetic (extrapolated at 298 K) and thermal and baric activation parameters for the oxidation processes studied ($I$ = 1.0 $\mathrm{M}$ $LiClO_4$)

| Species | Oxidant | $k^{298}$ [$\mathrm{M}^{-1}$ $s^{-1}$] | $\Delta H^{\neq}$ [kJ mol$^{-1}$] | $\Delta S^{\neq}$ [J K$^{-1}$ mol$^{-1}$] | $\Delta V^{\neq}$ [cm$^3$ mol$^{-1}$] |
|---|---|---|---|---|---|
| *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | $S_2O_8^{2-}$ | 6.98 | 114±9 | 114±29 | 12.7±0.8 |
| *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_5]^-$ | $S_2O_8^{2-}$ | 6.24 | 63±3 | 58±10 | 19.6±2.0 |
|  | $[Co(ox)_3]^{3-}$ | 0.121[a] | 65±3 | 86±10 | 14.6±1.1 |
| *cis*-$[L_{14}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | $S_2O_8^{2-}$ | 7.40 | 109±7 | 98±22 | 10.6±1.2 |
| *cis*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]^-$ | $S_2O_8^{2-}$ | 6.80 | 58±6 | 72±20 | 19.7±0.6 |
|  | $[Co(ox)_3]^{3-}$ | 0.128[a] | 68±5 | 73±17 | 16.9±2.2 |
| *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | $S_2O_8^{2-}$ | 5.61 | 80±2 | 2±7 | 1.5±0.1 |
| *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]^-$ | $S_2O_8^{2-}$ | 4.95 | 61±1 | 65±3 | 4.1±0.1 |
|  | $[Co(ox)_3]^{3-}$ | 0.103[a] | 51±2 | 131±8 | 11.5±1.4 |
| *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ | $S_2O_8^{2-}$ | 17.6 | 85±4 | 23±15 | 11.4±0.7 |
| *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$ | $S_2O_8^{2-}$ | 16.2 | 55±5 | 76±16 | 19.1±1.7 |
|  | $[Co(ox)_3]^{3-}$ | 0.113[a] | 63±6 | 90±19 | 17.9±1.9 |

[a] In $s^{-1}$, $K_{OS}$ in the 50−200 $\mathrm{M}^{-1}$ range for all the systems studied.

(III) at pH = 9 was carried out at different temperatures, concentrations, and pressures. Unfortunately, the stability of this complex is not very high and, although it could be used at pH = 9 by adding some EDTA to the solution medium to avoid precipitation of $Co^{2+}$ salts, no studies could be carried out at pH = 0, where the decomposition of the tris(oxalato) complex was too fast when compared with the redox process studied. Figure 3 shows the general kinetic behaviour of the observed reaction rate constants under pseudo-first-order conditions. In this case, as seen in Figure 3, the kinetic behaviour is a bit more complex than with the $S_2O_8^{2-}$ oxidant, and a limiting outer-sphere (OS) precursor formation is observed according to $k_{obs} = (k_{et} \times K_{OS} \times [\text{oxidant}])/(1 + K_{OS} \times [\text{oxidant}])$. The value of $k_{et}$ can be derived from the asymptotic limit of the plots. The temperature and pressure dependence of the derived rate constants produced the thermal and pressure activation parameters are shown in Table 3, together with the corresponding kinetic parameters extrapolated to 298 K.

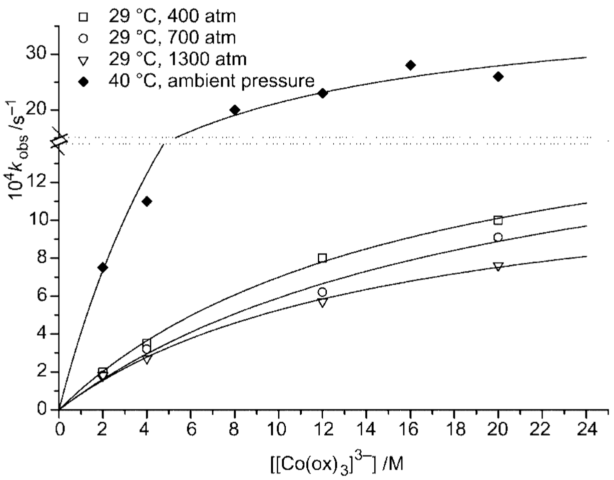

Figure 3. Plot of the values of the first-order rate constant, $k_{obs}$, for the $[Co(ox)_3]^{3-}$ oxidation of the *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_5]^-$ system at different temperatures and pressures and at pH = 9.0 ($I$ = 1.0 M $LiClO_4$)

From a general point of view, the redox reaction with peroxodisulfate as oxidant seems to provide more information about the process studied, because it can be carried out at acidic, alkaline, or neutral pH (i.e. with the doubly protonated and non-protonated dinuclear complexes). A detailed observation of the activation parameters results in a clear differentiation between the non-protonated or diprotonated form of the dinuclear species, despite the minor differences found in $k^{298}$. Activation enthalpies are much higher for the diprotonated complexes and activation entropies are also more positive. These much more positive values for $\Delta S^{\neq}$ found for the $[L_nCo^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ series of complexes, are indicative of the large differences in electrostriction on going from the reactants to the precursor outer-sphere complex involving the $SO_4^{(\cdot)}$ radical ({[1+] + [1−]} at low pH versus {[1−] + [1−]} for the non-protonated complex). These differences are compensated by larger values of $\Delta H^{\neq}$, producing the compensation plot shown in Figure 4, which is a clear indication of the constant reaction mechanism operating for these processes.

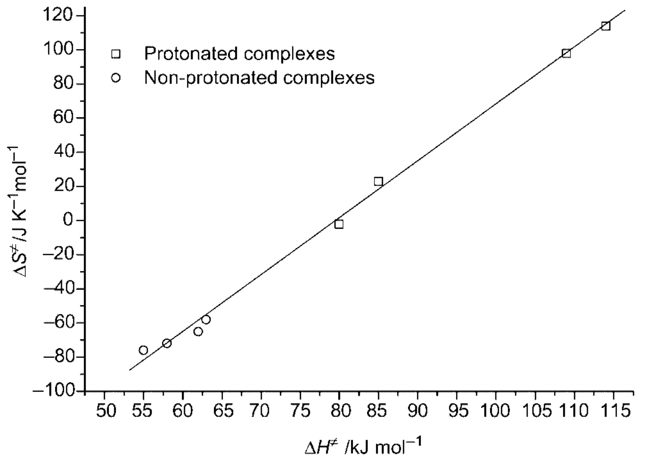

Figure 4. Compensation $\Delta H^{\neq}/\Delta S^{\neq}$ plot for the $S_2O_8^{2-}$ oxidation reactions studied for the *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$/*trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ dinuclear complexes

Another surprising fact is that for the *trans*-arranged dinuclear complexes of the $L_{14}$ and $L_{15}$ macrocycles, the above-mentioned differences in the activation enthalpies and entropies decrease severely. Some ordering, relating to the geometrical arrangement of the macrocyclic ligand, in the transition state, or the precursor complex, must be responsible for the dramatic decrease of the $\Delta S^{\neq}$ values for the reaction with the protonated complex. The relative positions of a protonated equatorial CN group and the facing secondary amine protons of the macrocycle,[7−9] easily allow for a much more ordered positioning of the $SO_4^{(\cdot)-}$ radical in the outer sphere for the $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ complex, producing an important decrease in the $\Delta S^{\neq}$ values. If that is so, the general enthalpic demands for the transition state for the electron transfer on such a precursor are bound to be smaller as seen in the data for all the $[L_nCo^{III}NCFe^{II}(CN)_3(CNH)_2]^+$ complexes in reactions with the $S_2O_8^{2-}$ ion (Table 3).

As for the activation volumes, when the oxidation takes place on the non-protonated species the values determined for $\Delta V^{\neq}$ are more positive. Given that the electrostriction on going to the precursor outer-sphere complex would produce the opposite trend, as explained before, the sequence of values found for $\Delta V^{\neq}$ has to be dominated by the proper electrostriction effect occurring during the electron transfer process on the dinuclear species. At low pH the charge of the complex increases from [1+] to [2+] on electron transfer, while it decreases from [1−] to [0] for the non-protonated complex; consequently, the actual electron transfer process at low pH implies an increase on electrostriction with respect to a decrease at high pH. Nevertheless, the general important expansion observed, for all but the $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ complex, must originate in solvent-assisted hydrogen bonding within the precursor complex, producing an important ordered expansion.[34] This fact also explains the inherent ordering derived from the values of $\Delta S^{\neq}$ that were obtained for the $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ complex in reactions with the $S_2O_8^{2-}$ ion. This expansion/ordering combination must be much smaller for the protonated systems where solvent-assisted hydrogen bonding becomes less important.[10−12] For the $[L_n$-$Co^{III}NCFe^{II}(CN)_5]^-$ system, the values found for the activation entropy at low pH already indicated a unique behaviour of the system. If the possible explanation cited above, derived from the facing secondary amine protons of the macrocycle, is so, solvent assistance for the positioning of the $SO_4^{(\cdot)-}$ radical in the outer sphere of the protonated species should be even less important. As a consequence, the values of $\Delta V^{\neq}$ for those complexes with much less solvent-assisted hydrogen bonding takes place, would tend to the expected contraction values, both from electron transfer electrostriction (specially for the oxidation of the diprotonated species) and inner-sphere contributions.

With respect to the $[Co(ox)_3]^{3-}$ oxidation data in Table 3, the thermal activation parameters are similar to those obtained for the $S_2O_8^{2-}$ oxidation process, with the non-protonated $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ complexes. The fact that, in this case, the values determined for $k^{298}$ correspond to the first-order rate constant (see Figure 3), only relates the activation parameters to the electron transfer process, the outer-sphere equilibrium constant being in the range 50−200 $\text{M}^{-1}$, which is similar to that found for similar systems.[10−12,27,35,36] The values determined for $\Delta H^{\neq}$ are practically the same as those found for the $S_2O_8^{2-}$ reaction, as expected given the small values associated with $\Delta H^0_{OS}$, while those for $\Delta S^{\neq}$ are definitively more negative. Given the fact that no electrostriction related to the outer-sphere precursor complex formation is accounted for, and that no protonated species are present at this pH, the high degree of ordering approaching the transition state has to be related with the above-mentioned formation of solvent-assisted interactions during the electron transfer process. These types of interactions have also been held responsible for the behaviour of other systems,[37] and have explained the ordering/expansion effect detected in the previously discussed $[L_nCo^{III}NCFe^{II}(CN)_5]^-/S_2O_8^{2-}$ redox processes, where outer-sphere electrostriction is held to a minimum. In this respect, the values determined for the activation volumes are positive in all cases and are very similar to those determined for the reaction with the peroxodisulfate anion. Again, the value determined for the *trans*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]^-$ complex is smaller than the rest, although it does not reach the extremely low values found for the peroxodisulfate reaction. Solvent assistance in outer-sphere complexation during electron transfer, can again be held responsible for the this decrease.

In conclusion, we have been able to completely characterise the solution redox behaviour of a complete family of discrete cyano-bridged mixed-valence $Co^{III}/Fe^{II}$ complexes. Further studies are being carried out in order to increase the stabilisation of the $Co^{II}/Fe^{II}$ oxidation state of the complex by tuning of the donor atoms in the macrocycle, which should allow for a wider accessibility of the redox systems.

## Experimental Section

**Products:** All the dinuclear $Co^{III}/Fe^{II}$ complexes have been prepared according to published procedures. The synthesis of *trans*- and *cis*-$[L_{14}Co^{III}NCFe^{II}(CN)_5]^-$ and *trans*-$[L_{15}Co^{III}NCFe^{II}(CN)_5]^-$ (isolated as their $Na^+$ salts) have been reported.[7−9] The analogue *cis*-$[L_{13}Co^{III}NCFe^{II}(CN)_5]^-$ has been prepared by the same procedure starting from *cis*-$[CoL_{13}Cl]^{2+}$.[38] Characterisation data for Na$[L_{13}$-$Co^{III}NCFe^{II}(CN)_5]$: $C_{16}H_{25}CoFeN_{11}Na\cdot 11H_2O$ (707.39): calcd. C 27.17, H 6.70, N 21.78; found C 27.2, H 8.6, N 22.2. $^{13}C$ NMR (62.9 MHz, $D_2O$): δ = 19.6, 49.0, 51.1, 51.9 (× 2), 53.5, 55.8, 56.4, 66.6, 175.0 (× 5), 191.0 ppm. IR (KBr disk): $\tilde{\nu}$ = 2040 (equatorial CN), 2072 (axial CN), 2115 (μ-CN) $cm^{-1}$. UV/Vis ($H_2O$): $\lambda_{max}$ (ε) = 325 (367), 448 (390), 498 nm (380 $\text{M}^{-1}cm^{-1}$). Cyclic voltammogram $E_{1/2}$ (versus NHE; 1.0 M $LiClO_4$) = −543, 626 mV. The oxidants $[Co(ox)_3]^{3-}$ and $[Fe(phen)_3]^{3+}$ were prepared according to published procedures.[39−41] Other chemicals used were analytical grade, commercially available, and were used without further purification. All buffers were prepared according to well-established procedures.[42] The buffer concentration was set to 0.01 M, and final pH values were such that only one of the acid-base equilibrium species of each system was present in solution. Ionic strength was achieved by the addition of $LiClO_4$.

**Acidity Constants:** Potentiometric titrations (1.0 M, $HClO_4$) of the different dinuclear $[L_nCo^{III}NCFe^{II}(CN)_5]^-$ complexes were carried out in order to determine their acidity constants. The solutions were transferred to a 50 mL cell and thermostatted at 25 °C; addition of small amounts of standard 0.1 M NaOH produced successive e.m.f. readings on a Metrohm 713 pH meter (glass and Ag/AgCl reference electrodes). Argon was bubbled through the solution during the experiment to avoid the presence of $CO_2$. The general technique was the same as that described in the literature;[43] even though only one step was detected, the stoichiometry indicated a double deprotonation. Spectrophotometric titrations[44] of the complexes carried out with a Cary 50 instrument produced changes in the UV/Vis spectrum with pH (Figure 1, top) which indicated the presence of two distinct processes. Nevertheless, the p$K_a$ values were too close to allow the selective formation of the monoprotonated complex,[18] and consequently only studies on the non-protonated and diprotonated species were carried out.

**Electrochemistry:** Electrochemical experiments were carried out with an EG&G PAR 263A instrument with a glassy carbon working electrode, a platinum wire secondary electrode and an Ag/AgCl reference electrode; solutions were degassed prior to the cyclic voltammetry experiment. Voltammograms of the complexes were carried out at $1 \times 10^{-3}$ M complex concentration in water (1.0 M $LiClO_4$) and in 1.0 M $HClO_4$ in order to account for differences due to the protonation of the cyanide ligands.

**Kinetics:** The reactions were monitored by UV/Vis spectroscopy in the 800−300 nm range; runs with $t > 170$ s were recorded with an HP8452A instrument equipped with a thermostatted multicell transport; runs within the 7−170 s margin were recorded with an HP8452A or a J&M TIDAS instrument and using a High-Tech SFA-11 Rapid Kinetics Accessory. For the kinetic runs at elevated pressure, a previously described pressurizing system, and cylindrical or pillbox cell were used.[45,46] Observed rate constants were derived from absorbance/time traces at the wavelengths where a maximum increase or decrease of absorbance was observed; Table

S1 (Supporting Information) indicates all the obtained $k_{obs}$ values for all the complexes studied as a function of the reducing and oxidising species, their concentration, pH, temperature, and pressure. No dependence of the observed rate constants on the selected wavelengths was detected, as generally expected for reactions where a good retention of isosbestic points is observed. The general kinetic technique was that previously described; in all cases pseudo-first-order conditions were maintained.[11,12] For reactions involving $[Co(ox)_3]^{3-}$, EDTA was added to the reaction medium to prevent the precipitation of the $Co^{2+}$ reaction product.[10,47]

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