Mechanistic aspects of the chemistry of mononuclear Cr$^{III}$ complexes with pendant-arm macrocyclic ligands and formation of discrete Cr$^{III}$/Fe$^{II}$ and Cr$^{III}$/Fe$^{II}$/Co$^{III}$ cyano-bridged mixed valence compounds†

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The kinetics and mechanism of the redox reaction between [Fe$^{II}$(CN)$_6$]$^{4+}$ and the macrocyclic ligand complex [CrCl(L$_{15}$)]$^{2+}$ (L$_{15}$ = 6-methyl-1,4,8,12-tetraazacladecan-6-amine) has been studied at different pH values. In acidic solution, the expected redox process occurs with no formation of any of the possible Cr$^{III}$/Fe$^{II}$ mixed valence complexes, as those seen for the Co$^{III}$ species of the same family, due to the enhanced lability of the Cr$^{III}$ species formed on Fe$^{II}$ to Fe$^{III}$ oxidation. In alkaline conditions, the formation of the complex [Cr(L$_{15}$)(OH)$_2$]$^+$ takes place as an initial step that precedes a simple substitution process producing the expected cyano-bridged Cr$^{III}$/Fe$^{II}$ complex. In this species the potentially pentadentate ligand, L$_{15}$, has a tetradentate coordination mode with a protonated exocyclic primary amine group and the redox potential is shifted to more negative values, thus disfavouring a redox driven reaction; the equivalent complex [CrCl(HL$_{14}$)(H$_2$O)]$^+$ (L$_{14}$ = 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine) has been prepared by the same method and characterized by X-ray crystallography. The final [Fe$^{II}$(CN)$_6$]$^{4+}$ substituted complex, [[(HL$_{15}$)(OH)Cr$^{III}$NC]Fe$^{II}$(CN)$_6$]$^{2+}$ shows pK$_a$ values of 3.8 and 7.4, as expected for the aqua and amino ligands, respectively. Its characterization indicated its Class II mixed valence character with a very intense MMCT band at 350 nm showing a much larger extinction coefficient than that observed for the Co$^{III}$ complexes of the same family. This fact is in good agreement with the much larger Cr$^{III}$–Fe$^{II}$ (t$_2$g–t$_2$g) coupling through cyanide bridging petridentate ligands expected for these complexes. The fully mixed metal/valence/ligand trimetallic complex [[(HL$_{15}$)(OH)Cr$^{III}$NC]L$_{15}$Co$^{III}$NC]Fe$^{II}$(CN)$_6$]$^{2+}$ has been prepared following the same procedures and the results are comparable. The final complex has the same Class II mixed valence character and its electronic spectrum shows the characteristics of both the Fe$^{II}$-to-Cr$^{III}$ and Fe$^{II}$-to-Co$^{III}$ CT bands. The study allows the application of the redox and/or substitutionally driven methodology, already described and kinetically designed, for the preparation of discrete mixed valence complexes of inert centres, so avoiding the unpredictable nature of other approaches seen in the past.

Introduction

The existence of metallic mixed-valence compounds is a well known feature of inorganic chemistry, and those involving cyanide-bridged polymeric motives represent the oldest examples.1,2 The determination of the electronic structure and properties of such complexes is much more recent. There are several key studies that have been crucial in our understanding of mixed valence chemistry.3–6 These type of complexes can be used as general multi-electron donor/acceptor systems,7 compounds with useful macroscopic properties (such as magnetism),8,9 photoinduced electron transfer devices (involving the MMCT band to give a charge separated species),10 and from a fundamental standpoint for understanding electronic delocalization between metal centres.4 From a preparative perspective, control of the mechanism by which the mononuclear components assemble into a single mixed valent form is vital in order to avoid intractable mixtures of oligonuclear compounds; many being isomeric mixtures.11

We have been involved for some time in the preparation of a full series of discrete Class II mixed valence cyanide-bridged complexes of type [[LCo$^{III}$NC]Fe$^{II}$(CN)$_{6-n}$]$^{4-6n}$ (where L represents a pentadentate ligand), as well as in their formation mechanism and redox reactivity.12–17 Strictly, these heterometallic compounds do not adjust to the term “mixed-valence”, as referring to compounds in which at least two ions of the same element are present in different oxidation states. Nevertheless, in the literature these complexes are classified as such given their

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internal electron transfer capabilities, similar to those found in homometallic analogues. Their anchoring on TiO₂ surfaces has also been carried out in order to check its plausible use as DSSC sensitizers, and their encapsulation in silica matrixes has also been achieved with some results that perfectly mimic the reactivity seen in solution. The reaction sequence for the formation for all these di- (Co<sup>III</sup>/Fe<sup>II</sup>), tri- (Co<sup>III</sup>₂/Fe<sup>II</sup>) and even tetranuclear (Co<sup>III</sup>₃/Fe<sup>II</sup>) complexes has been fully established and the relative importance of the competing redox- and substitutionally-driven mechanisms pinpointed (Scheme 1). As a consequence, subtle features related to the two mechanisms, as well as the dramatically different conditions needed for the isolation of the complexes, has been clarified and better understood.

Following this line we have decided to move further with the incorporation of inert metals, other than Co<sup>III</sup>, which also might generate a mixed-valence complex in concert with ferrocyanide and which may have novel magnetochemical and photochemical properties. The most obvious alternative to Co<sup>III</sup> is Cr<sup>III</sup> a viable redox active MMCT acceptor from hexacyanoferrate(ii) upon photoexcitation. It is apparent that the much greater photolability of Cr<sup>III</sup> is a considerable challenge to be met: this has already been noted with the simplest reaction of this type: [Cr<sup>III</sup>(NH₃)₅(OH₂)]<sup>3+</sup> with [Fe<sup>II</sup>(CN)₆]<sup>4-</sup>.

In this paper we present the full characterization and the kinetics and mechanistic study of the formation of the Class II mixed-valence complex [[(HL₁₅)(OH)Cr<sup>III</sup>NC]Fe<sup>II</sup>(CN)₅]⁻ (Scheme 2). The synthesis incorporates Cr<sup>III</sup> mononuclear “building blocks”, characterized for the first time by single-crystal X-ray analysis, in the reaction with [Fe<sup>II</sup>(CN)₆]<sup>4-</sup>. The relative importance of the possible redox and substitutionally driven processes for the Cr<sup>III</sup> building blocks has been fully established, which has allowed a mechanistic study of the formation of the mixed trimetallic [[(HL₁₅)(OH)Cr<sup>III</sup>NC]L₁₃Co<sup>III</sup>NCFe<sup>II</sup>(CN)₄]<sup>2+</sup> complex, also characterized. This first discrete fully unsymmetrical (both metal and encapsulating ligand) species of this family prepared, allows for a novel study of the characteristics of the MMCT bands in relation with the redox potentials obtained for the assemblies. Scheme 2 collects the reactivity and the compounds (charges omitted for clarity) to be dealt with.
The above mentioned assembly processes are found to be substitutionally driven only at alkaline pH, in contrast with the simpler systems involving Co\textsuperscript{III} macrocyclic centres. Consequently, the solution behaviour of the [CrClL\textsubscript{14}]\textsuperscript{+} (n = 14, 15) systems (Scheme 2) at this pH over long periods has also been studied. Under these conditions, base-hydrolysis (substitution) of the pendant primary amine by a hydroxyl ligand has been observed. This behaviour is in contrast to the corresponding Co\textsuperscript{III} chemistry of ligands from the same family.\textsuperscript{25} The Cr\textsuperscript{III} complex obtained for n = 14 after acidification, trans-III-[Cr(HL\textsubscript{15})(H\textsubscript{2}O)Cl][ClO\textsubscript{4}], has also been characterized via single-crystal X-ray analysis.

**Experimental**

**Safety note**

Although we have experienced no problems with the compounds in this work, perchlorate salts are potentially explosive and should only be handled in small quantities, never scraped from sintered glass frits and never heated whilst in the solid state.

**Preparation of compounds.** The known mononuclear trans-II-[CrClL\textsubscript{15}](ClO\textsubscript{4})\textsubscript{2} complex has been prepared according to published procedures,\textsuperscript{24} as well as the Co\textsuperscript{III}/Fe\textsuperscript{III} the mixed valence dinuclear complex Na{(cis-V-L\textsubscript{15}Co\textsuperscript{III}NC)Fe\textsuperscript{III}(CN)}\textsubscript{2}, also known.\textsuperscript{15} The trans-II and cis-V N-based isomeric forms are defined in Scheme 1 and follow the established nomenclature developed for cyclam analogues.\textsuperscript{26}

trans-III-[CrClL\textsubscript{15}](ClO\textsubscript{4})\textsubscript{2}. Complexation of Cr\textsuperscript{III} with the macrocycle followed the same preparative procedure described for its trans-II isomer.\textsuperscript{28} Isolation of the trans-III form was achieved in the work up of the reaction. The final orange-red band eluted from a strongly acidic Dowex 50 W × 2 column (3 M HCl eluent) was collected and most of the acid removed on a rotary evaporator. The concentrated solution was then diluted to ca. 0.25 M ionic strength, and re-chromatographed. Elution with 2 M HCl produced a single red band that was concentrated to 1 cm\textsuperscript{3} and further addition of acetone (500 cm\textsuperscript{3}) produced the desired compound as crystals suitable for X-ray work. Its elemental analysis agrees with the [CrClL\textsubscript{15}](ClO\textsubscript{4})\textsubscript{2} formulation: 27.35% C (calcd 27.21), 13.13% N (calcd 13.22), 5.69% H (calcd 5.52). Its electronic spectrum in water showed peaks at 368 nm (110 M\textsuperscript{-1} cm\textsuperscript{-1}), 438 nm (37 M\textsuperscript{-1} cm\textsuperscript{-1}) and 516 nm (72 M\textsuperscript{-1} cm\textsuperscript{-1}). The solution of the complex in 0.1 M NaClO\textsubscript{4} showed a peak at 340 nm (4000 M\textsuperscript{-1} cm\textsuperscript{-1}) and a shoulder at 416 nm (1320 M\textsuperscript{-1} cm\textsuperscript{-1}). Its X-ray crystal structure determination was carried out in order to fully characterize the form of the macrocyclic ligand around the metal centre.

\[
\text{Na}\{(HL\textsubscript{15})(OH)Cr\textsuperscript{III}NC)Fe\textsuperscript{III}(CN)}\]_{2}\text{ClO}\textsubscript{4}. Solutions of trans-II-[CrClL\textsubscript{15}](ClO\textsubscript{4})\textsubscript{2} (10 × 10\textsuperscript{-3} M, 100 cm\textsuperscript{3}) and K\textsubscript{2}[Fe(CN)\textsubscript{5}] (30 × 10\textsuperscript{-3} M, 50 cm\textsuperscript{3}) were combined and the pH adjusted to 9 with 2 M NaOH. The reaction mixture was left to react for ca. 24 h at 60 °C. The reaction mixture was then diluted to 750 cm\textsuperscript{3} and loaded onto a Sephadex DEAE anion exchange column protected from the light to minimise photodecomposition. After washing with water, elution with 0.1 M NaClO\textsubscript{4} produced a single coloured anionic band (ca. 100 cm\textsuperscript{3}) which was collected. The addition of cold ethanol (ca. 1000 cm\textsuperscript{3}) produced the precipitation of the complex (50% yield) which was filtered off and dried in vacuo. The elemental analysis of the solid agrees with the Na{[(HL\textsubscript{15})(OH)Cr\textsuperscript{III}NC)Fe\textsuperscript{III}(CN)}\textsubscript{2}·3H\textsubscript{2}O formulation: 32.95% C (calcd 32.79), 24.97% N (calcd 24.36), 6.43% H (calcd 6.32).

The electronic spectrum of the complex in water shows a peak at 353 nm (2500 M\textsuperscript{-1} cm\textsuperscript{-1}) and a shoulder at 416 nm (1320 M\textsuperscript{-1} cm\textsuperscript{-1}). The differential pulse voltammetry (DPV) of a 1 × 10\textsuperscript{-3} M solution of the complex in 0.1 M NaClO\textsubscript{4} shows a signal at 670 mV (vs. NHE) corresponding to the Fe\textsuperscript{III}/II couple; no signal of the Cr\textsuperscript{III}/II couple has been detected. The IR spectrum showed relevant bands at 2960 cm\textsuperscript{-1} (br, protonated amine), 2107 cm\textsuperscript{-1} (w, bridging CN) and 2048 cm\textsuperscript{-1} (str, terminal CN).

\[
\text{Na}\{(HL\textsubscript{15})(OH)Cr\textsuperscript{III}NC)Fe\textsuperscript{III}(CN)}\]_{2}\text{ClO}\textsubscript{4}. An aqueous solution of Na{[(cis-V-CO\textsuperscript{III}L\textsubscript{14}NC)Fe\textsuperscript{III}(CN)}\textsubscript{2} (16 × 10\textsuperscript{-3} M, 100 cm\textsuperscript{3}) was mixed with trans-II-[CrClL\textsubscript{15}](ClO\textsubscript{4})\textsubscript{2} (16 × 10\textsuperscript{-3} M, 50 cm\textsuperscript{3}), both adjusted to pH 9–10 by the addition of 2 M NaOH. The resulting mixture was heated at 65 °C for 5–6 h and diluted to 500 cm\textsuperscript{3} before being loaded onto a Sephadex C-25 cation exchange chromatography column protected from light to avoid decomposition. Some undefined material non-retained by the column was discarded. Elution with 0.1 M NaClO\textsubscript{4} gave three well separated bands. Both the first and second band show the spectral characteristics of a mixed valence Cr/Cu/Fe species and are associated to the trans- (first band, minor) and cis- (second band, major) possible isomeric forms of compound [{(HL\textsubscript{15})(OH)Cr\textsuperscript{III}NC)Fe\textsuperscript{III}(CN)}\textsubscript{2}·3H\textsubscript{2}O]. Aqueous solutions of {cis-V-L\textsubscript{15}Co\textsuperscript{III}NC}Fe\textsuperscript{III}(CN)\textsubscript{2} (16 × 10\textsuperscript{-3} M, 50 cm\textsuperscript{3}) were combined and the pH adjusted to pH 9–10 by the addition of 2 M NaOH. The resulting mixture was heated at 65 °C for 5–6 h and diluted to 500 cm\textsuperscript{3} before being loaded onto a Sephadex C-25 cation exchange chromatography column protected from light to avoid decomposition. Some undefined material non-retained by the column was discarded. Elution with 0.1 M NaClO\textsubscript{4} gave three well separated bands. Both the first and second band show the spectral characteristics of a mixed valence Cr/Cu/Fe species and are associated to the trans- (first band, minor) and cis- (second band, major) possible isomeric forms of compound [{(HL\textsubscript{15})(OH)Cr\textsuperscript{III}NC)Fe\textsuperscript{III}(CN)}\textsubscript{2}·3H\textsubscript{2}O].

\[
\{[(HL\textsubscript{15})(OH)Cr\textsuperscript{III}NC)Fe\textsuperscript{III}(CN)}\textsubscript{2}\text{ClO}\textsubscript{4}\}_{2}\cdot 3H_2O.
\]

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Acidity constants determination. Potentiometric titrations were conducted at 298.1 ± 0.1 K using NaClO4 1.0 M as supporting electrolyte. KOH solutions were obtained from Aldrich and standardized with potassium hydrogenphthalate. The reference electrode was a Ag/AgCl system in a saturated KCl solution. A CRISON 5204 glass electrode, coupled with a CRISON GLP22+ pH meter, was calibrated (in a 1 M NaClO4 medium) by titration of previously standardized solutions of HClO4 with CO2−. HClO4 and KOH solutions were used to adjust the pH values. The observed spectral pH changes were used to calculate the protonation constants.30 Titration curves, (pH range 2.0–11.0), were repeated and treated either as a single set or as separated curves without significant variations in the value of the acidity constants. Finally, the sets of data were combined and treated simultaneously to give the final stability constants. The concentration of the desired complex was of 1.25 × 10−4 M in all titrations.

For spectrophotometric titrations the absorption spectra were recorded on a Cary 50 instrument; HClO4 and KOH solutions were used to adjust the pH values. The observed spectral pH changes as a function of pH were analysed with the SPECFIT software.31

Physical methods. Elemental analyses were carried out by the Serveis Científico-Técnicos de la Universitat de Barcelona. UV-vis spectra were recorded on HP5482A, Cary50 or J&M TIDAS instruments depending on the circumstances, as indicated. IR spectra were recorded on a Nicolet 520 FT-IR instrument as KBr dispersions. Electrochemistry experiments were carried out with a PAR EG&G 263A instrument using a glassy carbon working electrode, a Ag/AgCl (3 M KCl) reference electrode and a platinum wire counter electrode on 1 × 10−3 M solutions of the sample using 1.0 M NaClO4 as supporting electrolyte unless otherwise stated. All potential values are given vs. NHE once corrected for the reference electrode used.

Crystallography. trans-III-[CrCl(HL14)(H2O)](ClO4)3. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a MAR345 diffractometer with an image plate detector. Its cell constants at 293 K were determined from 313 reflections (3 < 2θ < 31°) and refined by least-squares method. Intensities were collected with graphite MoKα radiation, using ω – 2θ scan-technique. 41669 reflections were measured in the range 2.76 ≤ 2θ ≤ 32.41° 6564 of which were unique (Rint = 0.053) and 5157 observed (I > 2σ(I)). Lorentz-polarization and absorption corrections were made.

trans-III-[CrCl(HL15)(H2O)](ClO4)3. A crystal (0.3 × 0.5 × 0.6 mm) was mounted on a quartz capillary and data were collected on an Enraf Nonius CAD4 diffractometer with MoKα radiation operating in the ω – 2θ scan mode. A unique set of data comprising 2419 reflections (1930 observed) was collected and an empirical absorption correction (y-scans) was applied. All calculations were performed with the SHELX suite of programs. Structures were solved by direct methods, using SHELXS,32 and refined by full-matrix least-squares method with SHELX-97 computer program,33 using 41669 reflections. The function minimized was Σwi[|Fobs|−|Fcal|]2, where wi = σ(2)/[(σ(2) + (0.044P)2 + 2.4045P)2], and P = (|Fobs|2 + 2|Fcalc|2)/3. f, f′ and f″ were taken from international tables of X-ray crystallography.44

### Table 1 Crystal structure data for complexes trans-III-[CrClL13](ClO4)3 and trans-III-[CrCl(HL14)(H2O)](ClO4)3

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
<th>R1 (%)</th>
<th>wR2 (%)</th>
<th>Dcalc (g cm−3)</th>
<th>V (Å3)</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-III-<a href="ClO4">CrClL13</a>3</td>
<td>C32H48Cl2N2O12</td>
<td>0.0589</td>
<td>0.0636</td>
<td>1.662</td>
<td>4235(2)</td>
<td>8</td>
</tr>
<tr>
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<td>0.0636</td>
<td>1.662</td>
<td>4235(2)</td>
<td>8</td>
</tr>
</tbody>
</table>

All H atoms were included at estimated positions and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which are linked. For [CrCl(HL15)(H2O)](ClO4)3, 2H2O both perchlorate anions were rotationally disordered. These were refined in different orientations (with complementary occupancies) all attached to a common Cl atom and with the aid of tetrahedral restraints. Crystal and refinement data are summarized in Table 1, and selected bond lengths and angles in the caption of Fig. 1.

Kinetics. All reactions were followed by UV-vis spectroscopy in the full 800–300 nm range. Observed rate constants were derived from the absorbance vs. time traces at wavelengths where a maximum increase and/or decrease of absorbance was observed.34 No dependence of the observed rate constant values on the selected wavelengths was detected, as expected for reactions where a good retention of isosbestic points is observed. The general kinetic technique is that previously described,35,36,37 pseudo-first order conditions were used for the studies.38 The concentration of the mononuclear chromium complex (the minor component of the reaction) was kept in the range (3–5) × 10−3 M, and rate constants were found independent on its concentration. The concentration of the hexacyano reactant was kept in the (5.0–150) × 10−3 M range for both [FeII(CN)6]4− and [(cis-V-L15)CoIII(NC)FeII(CN)] complexes. Rate constants were determined by the use of Specfit software.39 Acetate, PIPPS3 and borax buffer solutions were prepared at I = 0.2 M for pH 5 and 9, respectively. Final I = 1.0 M was achieved with NaClO4.40 Atmospheric pressure runs were recorded on a Cary50 or a HP8452A instrument, equipped with a thermostatted multi-cell transport. For runs carried out at elevated pressures an already described pressurizing cell system setup was used connected to a TIDAS J&M instrument.34 All the values obtained for the first order rate constants as a function of the metal complex, temperature, pressure and different reactant concentrations are collected in Table S1 (ESI).†

Results and discussion

Mononuclear CrIII “building block” complexes

The preparation and isolation of [CrClL13]3+ in its minor trans-III isomeric form (Fig. 1a) agrees with the results obtained for the already described CoIII analogues, and can be related with
the relative stability of the different N-based isomeric forms governed by the match between the cavity size of the ligand in its configuration and the metal ion radius. The complex may be compared directly with its N-based trans-II isomeric form reported previously. The effect of the more rigid arrangement of the N2–Cr–N3 units translates to an expected increase of the N2–Cr–N1 and N3–Cr–N4 angles and the consequent decrease of the remaining N1–Cr–N4 angle value. For the analogous CoIII complexes a number of different isomeric forms of the \{CoIIIL15\} unit have been identified including trans-II, trans-III and cis-VI depending on the pH of the reaction. In this respect, a solution of either of the two isomeric forms (trans-II and trans-III) of [CrClL15]2+ at alkaline pH immediately affords the same UV-vis spectrum regardless of the starting material, indicating (as seen their CoIII analogues) the establishment of a fast equilibrium between the two hydroxo species (Fig. 2a).

When equilibrated solutions are left for long periods or higher temperatures, significant changes occur in the UV-vis spectra, in contrast to the [CoL15(OH)]2+ complexes where no further reaction had been observed (Fig. 2b). Given the larger size of the CrIII cation a dissociatively activated trans to cis isomerization process could be proposed producing a cis-VI form, as identified for the [CoClL15]2+ and [RhClL15]2+ analogues. Nevertheless, the changes in the electronic spectrum are too important to be explained invoking a simple isomerisation process in which the same set of donor groups is maintained. At this point it is interesting to note that a similarly slow change in the electronic spectrum is observed when the related complex trans-I-[CrClL14]+ is reacted in alkaline solution producing, on acidification, the complex trans-III-[CrCl(HL14)(H2O)]3+ (Fig. 1b). It is apparent that a base-catalysed dissociation of the pendant amine from the Cr ion has occurred i.e. the macrocyclic ligand has become tetradentate coordinated. The X-ray crystal structure of trans-III-[CrCl(HL14)(H2O)](ClO4)3·2H2O finds the complex cation on a mirror plane, which bisects the metal centre, chloro and aqua ligands which are in trans positions. One perchlorate anion is on a mirror plane while the other is on a general site. Both are severely disordered. A water molecule is on a general site and hydrogen bonded to the aqua ligand. The macrocycle adopts the trans-III configuration, importantly with the protonated ammonium group in an equatorial position on the six-membered chelate ring. It is clear that the secondary amines (N2 and its symmetry partner N2¢) have retained their configuration during dissociation of the pendant amine. In its tetradentate coordinated (cyclam)

![Fig. 1](image-url)  
(a) Drawing of cations (a) trans-III-[CrClL15](ClO4)2. Selected coordinate bond lengths (Å) and angles (°): Cr–N5, 2.062(3); Cr–N3, 2.066(3); Cr–N2, 2.074(3); Cr–N4, 2.075(3); Cr–Cl, 2.3095(11); N5–Cr–N3, 93.46(11); N5–Cr–N2, 91.32(12); N3–Cr–N2, 81.33(13); N5–Cr–N1, 175.20(11); N2–Cr–N1, 96.65(12); N3–Cr–N4, 80.77(12); N2–Cr–N4, 172.07(12); N1–Cr–N4, 83.03(12); N5–Cr–Cl, 94.40(9); N2–Cr–Cl, 96.98(9); N1–Cr–Cl, 90.16(8); N4–Cr–Cl, 90.95(9); and (b) trans-III-[CrCl(HL14)(H2O)](ClO4)2·2H2O. Selected coordinate bond lengths (Å) and angles (°): Cr–O1, 1.997(4); Cr–N2, 2.064(4); Cr–N1, 2.044(4); Cr–Cl, 2.288(2); O1–Cr–N2, 90.6(1); O1–Cr–N1, 87.9(2); N2–Cr–N2¢, 93.9(2); N1–Cr–N1¢, 95.3(2); N2–Cr–N1, 85.4(2); N2–Cr–N1¢, 178.4(2); O1–Cr–Cl, 179.4(1); N1–Cr–Cl, 92.5(1); N2–Cr–Cl, 89.0(1)). Primes denote symmetry operation x, 1/2 – y, z.

![Fig. 2](image-url)  
(a) [CoClL15](OH)2+ isomeric mixture; trans-II[CoClL15]+; trans-III[CoClL15]+. (b) [CrClL15](OH)2+ isomeric mixture; trans-II[CrClL15]+; trans-III[CrClL15]+.
form the Cr–N bond lengths in trans-III-[CrCl(HL14)(H2O)]+ are comparable with those found in the pentadentate coordinated compound trans-III-[CrClL14]+ (2.06–2.08 Å).[^46] The Cr–O (1.997(4) Å) bond is significantly shorter than the corresponding coordinated primary amine in pentadentate coordinated trans-III-[CrClL14]+ due to the greater covalency radius of the O-donor.

The potentiometric titration of finally equilibrated solutions of trans-II-[CrClL14]+ has been conducted and three distinct pKₐ values (3.2, 5.3 and 8.8) obtained, in support of the [Cr(HL14)(H₂O)]⁺ formulation. The values of 3.2 and 5.3 agree with those for other diaqua macrocyclic complexes of the same type.[^47,48] As for the value of 8.8, this has been related with the protonation of the primary amine, 2 units more acidic than for the free macrocycle[^49] as would be expected from the electrostatic effect on the metal centre on the pendant amine, even taking into account the increased stability of the RNH₃⁺ group by hydrogen bonding interactions with the hydroxo ligand (see related Scheme 3 below).

Summarizing, when any of the [CrClL14]⁺ species are dissolved at alkaline pH they convert rapidly to the corresponding monohydroxo-pentaamine derivatives trans-III-[CrClL14(OH)]⁻. From then on, the mixture evolves at a much slower rate compared to that of the [CrClL14]⁺ –[CrCl(HL14)(H₂O)]⁺ complex where the macrocycle is tetracoordinated (Scheme 1) by comparison with the reactivity and spectroscopy of the structurally characterized L₁₄ analogue.

Kinetic studies

Oxidation of [Fe⁶(OCN)]⁺ with [Cr⁶⁺Cl₄L₁₄]⁺. The outcome of reaction of [Fe⁶(CN)]⁻ with the chromium(III) mononuclear complexes trans-II and trans-III-[CrCl⁶⁺L₁₄]⁺ at acidic pH does not produce the expected mixed valence compound [((HL₁₄)(OH)Cl⁶⁺NC)Fe⁶(CN)]⁻. It is thus clear that the operation of the redox driven mechanism (Scheme 1, top) observed for the Co³⁺ analogues is not taking place. When the reaction is carried out at pH 4 (thus avoiding any mononuclear Cr⁶⁺ building block reactivity, see above) the formation of a precipitate takes place immediately with the simultaneous appearance of [Fe⁶(CN)]⁻, as seen in the UV-vis spectrum (λ max ~420 nm). In the presence of EDTA no precipitate is formed. This indicates that free Cr⁶⁺ is rapidly formed by outer sphere ferrocyanide reduction, and once it is liberated forms an insoluble precipitate with the hexacyanoferrate(III/II) anions present in the reaction.

Re-oxidation of the chromous ion is very likely but this precipitate was not characterised further. If the chromium ion is sequestered by EDTA, precipitation is averted but the desired mixed valence complex does not form either. Consequently the neat oxidation of [Fe⁶(CN)]⁻ by either of the two forms of trans-[Cr⁶⁺Cl₄L₁₄]⁺ was studied at (i) pH 4 and I = 1.0 M (NaClO₄) in acetate or PIPPS buffers, (ii) in the presence or absence of EDTA, and (iii) in the presence or absence of oxygen. Although some differences were obtained with respect to the quality of the absorbance–time traces (increase of the peak at 420 nm of the hexacyanoferrate(III) anion) no relevant changes were evident with respect to the pseudo-first order (iron in excess) rate constants. The presence of EDTA only prevented the appearance of a minor very fine precipitate in the final reaction mixture that only interfered as a small drift in the final absorbance readings; for very similar reasons, the use of PIPPS was preferred vs. that of acetate also in order to minimize drift in the final absorbance. With respect to the presence or absence of air in the reaction mixture the qualitative differences are much more obvious. Even though the observed rate constants for the initial absorbance changes obtained are independent of the presence of oxygen, further increase of the absorbance at 420 nm is observed in air until practically all [Fe⁶(CN)]⁻ is in excess used is up. Aerial oxidation of the Cr⁶⁺ initially formed produces a Cr⁶⁺ species capable of oxidizing the Fe⁶⁺ centre in a catalytic process. When the system is kept rigorously oxygen-free only a stoichiometric amount of [Fe⁶(CN)]⁻ is oxidized after the studied reaction. At longer times the oxidation of Cr⁶⁺ to Cr⁶⁺ cannot be avoided and an increase of the concentration of hexacyanoferrate(III) is observed. As a summary the best quality absorbance–time traces were obtained with the use of PIPPS buffer, in the presence of EDTA and in air. Fig. 3 shows the typical spectral changes for such reaction conditions and the trend of the values of kₑₙ₁, with the concentration of the excess reactant. Table 2 collects the derived kinetic and activation parameters. It is important to note that no significant differences exist in the values obtained for the reaction rate constants with the oxidant in its trans-II-[CrCl⁶⁺L₁₄]⁺ or trans-III-[CrIII⁺Cl₄L₁₄]⁺ forms.

As seen in the results, the values of k, Kₐ₁, ΔH˚, ΔS˚ and ΔV˚ found for the redox process between any of the trans-[CrCl⁶⁺L₁₄]⁺ complexes and hexacyanoferrate(II) agree very well with the outer-sphere nature of the redox process. The fact that both complexes have the same redox potential (see Table 3 below) leads to the same kinetic and activation parameters for the process with both starting materials. The data also agree with the available data in the literature for the reduction of Co³⁺ complexes of the same family ([Co⁶⁺L₁₄]: n = 14, 15; cis, trans).[^50] The value of the activation enthalpy is larger, as expected for the lower reduction potential of the Cr³⁺ centre, ~850 mV vs. ~200 mV for the Co³⁺ centre (calculated from the differences observed between the chloro and the mixed valence complexes of the same acceptor group).[^52] The values found for ΔS˚ and ΔV˚ agree with a dominant expansive disorganization on the chromium centre on reduction and consequent re-sizing of its coordination sphere. The effect of the contraction on the iron centre seems to be fully counterbalanced by the decrease of the change of the {Fe(CN)₆}⁻ unit, as already observed for similar situations.[^12,13,52]

Substitution by [Fe⁶⁺(CN)₄(N)X]⁺ on trans-[Cr⁶⁺(L₁₄)(OH)]⁺. When the reaction indicated in the previous section was repeated
actuation of a pure (slow) substitutional mechanism for the formation of mixed valence Cr III/FeII building blocks studied.

### Table 2 Kinetic and activation parameters for the reactions between the different \{XFe\textsuperscript{i}(CN)\textsubscript{6}\} and \{Cr\textsuperscript{iii}L\textsubscript{15}\} building blocks studied

<table>
<thead>
<tr>
<th>{Cr\textsuperscript{iii}L\textsubscript{15}}</th>
<th>{XFe\textsuperscript{i}(CN)\textsubscript{6}}</th>
<th>pH</th>
<th>\textsuperscript{121}k/s\textsuperscript{–1}</th>
<th>(K_{\text{eq}}^a/M\textsuperscript{–1})</th>
<th>(\Delta H^a/kJ\textsuperscript{mol}\textsuperscript{–1})</th>
<th>(\Delta S^a/J\textsuperscript{mol}\textsuperscript{–1}K\textsuperscript{–1})</th>
<th>(\Delta V\textsuperscript{b}/cm\textsuperscript{3}\textsuperscript{mol}\textsuperscript{–1}K\textsuperscript{–1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-II-[Cr\textsuperscript{iii}ClL\textsubscript{15}]\textsuperscript{2–}</td>
<td>{Fe\textsuperscript{ii}(CN)\textsubscript{6}}\textsuperscript{4–}</td>
<td>4</td>
<td>(5.0 \times 10^4)</td>
<td>10</td>
<td>120 ± 6</td>
<td>64 ± 20</td>
<td>24.7 ± 0.7 (1%0)</td>
</tr>
<tr>
<td>trans-I-[Cr\textsuperscript{iii}ClL\textsubscript{15}]\textsuperscript{2–}</td>
<td>{Fe\textsuperscript{ii}(CN)\textsubscript{6}}\textsuperscript{4–}</td>
<td>9</td>
<td>(3.0 \times 10^4)</td>
<td>175</td>
<td>89 ± 4</td>
<td>–75 ± 11</td>
<td>–9.0 ± 0.3 (1%0)</td>
</tr>
<tr>
<td>trans-[Cr\textsuperscript{iii}(L\textsubscript{15})(OH)\textsubscript{2}]\textsuperscript{2–}</td>
<td>{Fe\textsuperscript{ii}(CN)\textsubscript{6}}\textsuperscript{4–}</td>
<td>9</td>
<td>(2.1 \times 10^4)</td>
<td>170</td>
<td>96 ± 1</td>
<td>–36 ± 2</td>
<td>Not measured</td>
</tr>
<tr>
<td>trans-[Cr\textsuperscript{iii}(L\textsubscript{15})(OH)\textsubscript{3}]\textsuperscript{1–}</td>
<td>{cis-[V–L\textsubscript{15}Co\textsuperscript{ii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}]}</td>
<td>1.8 \times 10^4</td>
<td>10</td>
<td>36 ± 10</td>
<td>–207 ± 40</td>
<td>Not measured</td>
<td></td>
</tr>
</tbody>
</table>

* Average for the temperatures studied. a For the reverse process.

### Table 3 Characterization data for the new mixed valence complexes. Relevant literature data from other complexes of the same family are included for comparison

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{MMCT}}(\epsilon)/\text{nm (M}^{-1}\text{cm}^{-1}))</th>
<th>(E^a(/\text{Fe}\textsuperscript{iii}/\text{ii})/\text{mV})</th>
<th>(E^b(/\text{Cr}\textsuperscript{iii}/\text{ii})/\text{mV})</th>
<th>(E^c(/\text{Co}\textsuperscript{iii}/\text{ii})/\text{mV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[[(HL\textsubscript{15})H(OH)]Cr\textsuperscript{iii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}]</td>
<td>406 (2900)</td>
<td>765</td>
<td>–600*</td>
<td>—</td>
</tr>
<tr>
<td>[[(L\textsubscript{15})OH]Cr\textsuperscript{iii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}]</td>
<td>350 (2750)</td>
<td>650</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>cis-[[[(HL\textsubscript{15})H(OH)]Cr\textsuperscript{iii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}]</td>
<td>405 (4450)</td>
<td>890</td>
<td>–680</td>
<td>–495</td>
</tr>
<tr>
<td>cis-[[[(L\textsubscript{15})OH]Cr\textsuperscript{iii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}]</td>
<td>340 (4000), 490 (500 sh)</td>
<td>800</td>
<td>—</td>
<td>–495</td>
</tr>
<tr>
<td>cis-[V–L\textsubscript{15}Co\textsuperscript{ii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}]</td>
<td>500 (380)</td>
<td>625</td>
<td>—</td>
<td>–545</td>
</tr>
<tr>
<td>trans-II-L\textsubscript{15}Co\textsuperscript{ii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}</td>
<td>530 (420)</td>
<td>600</td>
<td>—</td>
<td>–580</td>
</tr>
<tr>
<td>trans-III-L\textsubscript{15}Co\textsuperscript{ii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}</td>
<td>515 (940)</td>
<td>800</td>
<td>—</td>
<td>–530</td>
</tr>
<tr>
<td>trans-III-[Cr\textsuperscript{iii}ClL\textsubscript{15}]</td>
<td>—</td>
<td>—</td>
<td>–845</td>
<td>—</td>
</tr>
<tr>
<td>trans-II-[Cr\textsuperscript{iii}ClL\textsubscript{15}]</td>
<td>—</td>
<td>—</td>
<td>–850</td>
<td>—</td>
</tr>
<tr>
<td>[Fe\textsuperscript{ii}(CN)\textsubscript{6}]</td>
<td>—</td>
<td>—</td>
<td>465</td>
<td>—</td>
</tr>
</tbody>
</table>

* This work, according to the acid–base behaviour determined. a Observed only on cathodic sweeps. b Not observed in the electrochemical window available.

at pH 9 neither precipitation nor any reaction occurs at short reaction times, but when long reaction times or high temperatures are used some meaningful changes take place after the time allocated for the formation of the mixed valence complex [[(L\textsubscript{15})OH]Cr\textsuperscript{iii}(NC)Fe\textsuperscript{ii}(CN)\textsubscript{5}] correspond to the substitutionally driven mechanism (Scheme 1, bottom) where a simple slow substitution of an OH\textsuperscript{–} by [Fe\textsuperscript{ii}(CN)\textsubscript{6}]\textsuperscript{4–} has occurred.

Fig. 3 (a) UV-vis spectral changes for the oxidation of [Fe\textsuperscript{ii}(CN)\textsubscript{6}]\textsuperscript{4–} (5 \times 10\textsuperscript{–5} M) with trans-II-[Cr\textsuperscript{iii}ClL\textsubscript{15}]\textsuperscript{2–} (5 \times 10\textsuperscript{–5} M) (60 °C, [EDTA] = 5 \times 10\textsuperscript{–5} M, pH = 4.0 PIPPS (0.25 M), I = 1.0 M(NaClO\textsubscript{3}); (b) plot of the values of \(k_{\text{obs}}\) obtained as a function of the concentration of [Fe\textsuperscript{ii}(CN)\textsubscript{6}]\textsuperscript{4–}.
fact, the \{Cr\textsuperscript{II}(L\textsubscript{15})\} being too labile toward dissociation during the reaction with [Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsuperscript{3-} within the outer sphere complex.\textsuperscript{15,20}

With these results in hand plus the recent report on the actuation of a fully substitutionally driven mechanism for the preparation of Co\textsuperscript{III}/Fe\textsuperscript{II} polynuclear aggregates,\textsuperscript{11} the reaction of trans-[Cr\textsuperscript{III}(L\textsubscript{15})](OH)\textsubscript{3}\textsuperscript{+} with the known dinuclear mixed valence Co\textsuperscript{III}/Fe\textsuperscript{II} complex \{[cis-V-L\textsubscript{15}Co\textsuperscript{III}NC]Fe\textsuperscript{II}(CN)\textsubscript{5}\}, instead of [Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsuperscript{4-}, was also carried out at pH = 9. Again a simple equilibrium substitution process takes place, as observed for similar non-redox favourable processes leading to trinuclear species of this family.\textsuperscript{11} The changes in the UV-vis spectrum are very similar and the variation of the values of the pseudo-first order rate constants observed is shown in Fig. 4b. In this case the process leads to an equilibrium of the starting reaction mixture with the final Cr\textsuperscript{III}/Fe\textsuperscript{II}/Co\textsuperscript{III} trinuclear complex, as seen by the definite intercept in the plot and the increase of Δ(Absorbance) with the concentration of the iron complex. The values of the relevant kinetic and activation parameters measured are also collected in Table 2. The values found for these parameters agree with the expected for a substitution process on a \{Cr\textsuperscript{III}(N\textsubscript{4})\} core as before\textsuperscript{46,53,55} despite the increase of an order of magnitude in the rate constant measured for the formation process. It is notable that this fact cannot be either related with an increased basicity of the cyanide nitrogen atoms, with respect to [Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsuperscript{4-}, or to the stability of the final complex, given the equilibrium process established (K\textsubscript{eq} = 2.8, average for the four temperatures studied). As for the values obtained for the reverse process it is clear that it has a very different character from the forward one showing, in this case, an important ordering for the transition state leading to an parallel decrease in the value of ΔH\textsuperscript{‡}. Nevertheless, these values have to be taken very cautiously given the very large method errors involved in the measurement of the intercept of a non-linear fit.\textsuperscript{57}

In any case, the fairly large values found for the K\textsubscript{eq} constants from the two previously discussed substitution reactions agree very well with the involvement of the macrocyclic amine protons in the outer-sphere coordination in these type of complexes,\textsuperscript{12,20,37,55} that also have to have some effect on the values determined for ΔS\textsuperscript{‡} as stated before.

**Characterization of the mixed valence complexes**

Once the kinetic and mechanistic information of the reaction of the Cr\textsuperscript{III} building blocks with [Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsuperscript{4-} was available, the characterization of the final compounds formed in the substitution reaction by [Fe\textsuperscript{II}(CN)\textsubscript{6}](X)\textsuperscript{+} on trans-[Cr\textsuperscript{III}(L\textsubscript{15})(OH)\textsubscript{3}]\textsuperscript{+} has been pursued. In the reaction of any of the [Cr\textsuperscript{III}ClL\textsubscript{15}]\textsuperscript{2+} isomeric forms with [Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsuperscript{4-} the final compound isolated after column work up corresponds to the mixed valence Cr\textsuperscript{III}/Fe\textsuperscript{II} complex, \{[Cis-V\{OH\}Co\textsuperscript{III}NC]Fe\textsuperscript{II}(CN)\textsubscript{5}\}. This species shows a very intense new band in the UV-vis spectrum that is associated with the Class II mixed valence character expected.\textsuperscript{21} The complex is light sensitive and the long standing needed for obtaining X-ray quality crystals invariably lead to decomposition of the sample.\textsuperscript{22,23} Even if the compound is kept in the dark the appearance of polymeric material also occurs, probably due to the presence of a potentially bridging OH\textsuperscript{-} ligand in the complex. The ion chromatographic behaviour of the complex is very pH dependent indicating a variable charge of the complex in water, given the existence of an acidic aqua ligand whose deprotonation produces a mononanoan that is held on the DEAE column. Similarly, the UV-vis spectrum of the mixed valence complex shows a significant pH dependence. The determination of the two relevant pK\textsubscript{a} values for the system (eqn (1a) and (1b), Scheme 3 above) has been carried out via potentiometric and spectrophotometric titrations (Fig. 5).

\[
\text{[(HL}_{15})*(H,O)\text{Cr}^{III}\text{NC})\text{Fe}^{II}(CN)_{5}]^{+} \rightarrow \text{[(HL}_{15})*(OH)\text{Cr}^{III}\text{NC})\text{Fe}^{II}(CN)_{5}]^{+} + H^{+} \quad (1a)
\]

\[
\text{[(HL}_{15})*(OH)\text{Cr}^{III}\text{NC})\text{Fe}^{II}(CN)_{5}]^{+} \rightarrow \text{[(HL}_{15})*(OH)\text{Cr}^{III}\text{NC})\text{Fe}^{II}(CN)_{5}]^{2+} + H^{+} \quad (1b)
\]

For the first process the value of pK\textsubscript{a1} has been determined as 3.8 with a significant spectral shift of the MMCT transition to higher energies upon deprotonation due to the increase in electron density on the Cr\textsuperscript{III} centre. This increase on the pK\textsubscript{a1} value with respect to the parent [Cr\textsuperscript{III}H\textsubscript{15}*(H,O)\textsuperscript{+}]\textsuperscript{4+} building block can be related with the increase of electron density on the Cr\textsuperscript{III} ion on coordination of a [Fe\textsuperscript{II}(CN)\textsubscript{6}]\textsuperscript{4-} unit. For the second process the value of pK\textsubscript{a2} has been determined as 7.3 and produces no UV-vis spectral changes.
so it involves the pendant primary amine. This increase on acidity from the parent [CrIII(HL15)(H2O)]4+ building block cannot be related to simple electrostatic considerations, these should produce the opposite effect as for the equilibrium indicated above. A possible explanation of this fact can be related with the very different arrangement of the macrocyclic ligand around the M III centre.

The redox potentials determined by differential pulse voltammetry (Fig. 6a), as well as the electronic spectroscopic data, collected in Table 3, agree with the Class II mixed valence formulation of this species. For the dinuclear complex $[[[(HL_{15})(H_2O)Cr^{III}(NC)]Fe^{III}(CN)_5]$, a positive shift of the FeIII/II potential relative to ferrocyanide is seen due to the influence of the CrIII centre. A putative CrIII/II signal is only observed (−600 mV) on a cathodic sweep when the aqua ligand is present and the exocyclic amine is protonated. Deprotonation to the hydroxo complex, $[[[(HL_{15})(OH)Cr^{III}(NC)]Fe^{III}(CN)_5]$ , shifts the CrIII/II signal outside the available potential window (−1.0 V vs. NHE) in water. This fact is qualitatively in good agreement with the shift at longer wavelength for the fully protonated CrIII/FeII complex. Treatment of the solution of the dinuclear complex with the oxidant S2O82− at pH = 4 results in depletion of the MMCT band at 350 nm, indicating that oxidation to the FeIII–CrIII complex has been achieved (ESI, Fig. S2).†

The values of $E^e$(FeIII/II) have a 200 mV or 300 mV positive increase for the attachment of the $[[[(HL_{15})(OH)Cr^{III}]^{3+}$ and $[[[(HL_{15})(H_2O)Cr^{III}]^{3+}$ positively charged units, respectively. For the $[[[(L_nCo^{III})]^{1+}$ units the increase has been established as 160–200 mV (for di-, tri-, and tetranuclear compounds), indicating than for this CrIII/FeII complexes the effect is more important. The value of $E^e$(CrIII/II) for the hydroxo derivative has been impossible to evaluate, leaving the definite value of $\Delta G^0$ unavailable in that case. Nevertheless, in 0.1 M HClO4 solution (aqua species) the value of $E^e$(CrIII/II) has been measured as −600 mV giving a $\Delta G^0$ value of 10 900 cm−1 and a reorganizational energy, $\lambda$, of 13 700 cm−1 according to eqn (2). The latter value is much higher than any of those observed for the similar CoIII analogue compounds (in the 900–1000 cm−1 range), which can be related with the very different arrangement of the macrocyclic ligand around the MIII centre.

Interestingly, the values determined for the extinction coefficient of the MMCT signals are 5–6 times larger than those observed for the CoIII analogues (Table 3), indicating that the value of the electronic coupling between the two metal centres is much greater (eqn (3)). Provided that the CrIII–FeII distance in the complex is similar to that for CoIII–FeII in the cobalt analogues, this has to be related with the fact that the t2g-to-eg MMCT transition for the CoIII/FeII systems now is a t2g-to-t2g transition for the CrIII/FeII complexes, both through a t2g* cyanide molecular orbital. It is interesting to note that the markedly increased values of $\epsilon$ allow the possibility of developing applications as electrochromic or pH sensor devices, which can be achieved by anchoring the complexes to solid supports through their exocyclic amine.

$$E^e = \Delta G^0 + \lambda$$

(2)
As for the final compound isolated after column work up of the mixture from the reaction of trans-\(\text{Cr}^{III}(L_{13})\text{(OH)}_{4}\)^+ with complex \(\{\text{cis-V-L}_{13}\text{Co}^{III}\text{(NC)}\text{Fe}^{III}\text{(CN)}_{4}\}\)

\(\{\text{cis-V-L}_{13}\text{Co}^{III}\text{(NC)}\text{Fe}^{III}\text{(CN)}_{4}\}\)^+ it corresponds to a mixture of the two possible cis- and trans-isomeric forms (Co to Cr units, see Experimental). Despite the fact that the trans-isomers have been previously found to be the non-statistically major components in the mixtures, probably due to steric reasons,\textsuperscript{14,17,19} this is case the cis-isomer has been found to be the major outcome of the preparative work. Possible hydrogen interactions between the two macrocycles (See Scheme 2) can be held responsible for this fact. The characterization of the final \(\{\text{cis-V-L}_{13}\text{Co}^{III}\text{(NC)}\text{Fe}^{III}\text{(CN)}_{4}\}\)^+ complex has only been carried out on the major cis-isomer, and the expected acid–base equilibrium of the coordinated aqua ligand has been observed (ESI, Fig. S33; Table 3). Furthermore, the spectra agree very well with that obtained from the final equilibrated solutions modelled (see below) with the Specfit software.\textsuperscript{31}

The electrochemistry of these solutions (Fig. 6b) shows the \(\text{Fe}^{II/III}\), \(\text{Cr}^{II/III}\) and \(\text{Cr}^{III/II}\) reduction peaks indicated in Table 3 that, as before, are dependent on the protonation of the coordinated water molecule. Furthermore, as in the dinuclear \(\text{Cr}^{III/II}\)/\(\text{Fe}^{III/II}\) complex, the reduction potential for the \(\text{Cr}^{III/II}\) unit is out of the electrochemical window used for the hydroxo derivative. The iron signal shows an additive positive shift that corresponds practically to the expected \((150 + 300)\) mV or \((150 + 200)\) mV (water or hydroxo ligand attached to the \(\text{Cr}^{III}\) centre) \(\text{Co}^{III/II}\)/\(\text{Cr}^{III/II}\) contributions, while the signal for the cobalt and chromium units corresponds to the expected di- to trinuclear shift observed for other systems.\textsuperscript{37} For the \(\text{L}^{cis}\{\text{cis-V-L}_{13}\text{Co}^{III}\text{(NC)}\text{Fe}^{III}\text{(CN)}_{4}\}\)^+ complex the value of \(\Delta G^0\) corresponding to each \(\text{M}^{II/III}\)/\(\text{Fe}^{III}\) unit can be extracted from the redox potentials. These are \(12500\) cm\(^{-1}\) for the \(\text{Cr}^{III}/\text{Fe}^{III}\) pair and \(11200\) cm\(^{-1}\) for the \(\text{Co}^{III}/\text{Fe}^{III}\) pair, which produce respective values of \(\lambda\) of \(12100\) cm\(^{-1}\) and \(9200\) cm\(^{-1}\) for the same pairs. In comparison with the already described trinuclear \(\text{Co}^{III/II}\)/\(\text{Fe}^{III/II}\) compounds,\textsuperscript{17} these values are much lower than for the parent \(\text{Cr}^{III}/\text{Fe}^{III}\) and \(\text{Co}^{III}/\text{Fe}^{III}\) dinuclear building block units, indicating some important differences in the character of the new \(\text{cis}\{\text{cis-V-L}_{13}\text{Co}^{III}\text{(NC)}\text{Fe}^{III}\text{(CN)}_{4}\}\)\(^+\) complex. Examination of the UV-vis spectra of the complex, particularly at alkaline pH is more revealing. In the spectrum the two independent signals of the \(\text{Fe}^{II/III}\)-to-\(\text{Cr}^{III}\) and \(\text{Fe}^{II/III}\)-to-\(\text{Co}^{III}\) units are visible \((340\) nm, \(4000\) M\(^{-1}\)cm\(^{-1}\) and \(490\) nm, \(500\) (sh) M\(^{-1}\)cm\(^{-1}\)). Despite the fact that these results agree with the lack of changes in the MMCT band position observed on going from di- to tri- or tetranuclear aggregates,\textsuperscript{14,17} and on other recently reported mixed valence complexes,\textsuperscript{99} the extinction coefficients have always been found to vary significantly with changes in nuclearity. For the \(\text{Co}^{III}/\text{Fe}^{III}\) aggregates the addition of each cobalt unit doubles the value of \(\epsilon\) from the parent species. Probably the high electronic coupling, \(H_{ab}\), indicated before for the \(\text{Cr}^{III}/\text{Fe}^{III}\) units prevents the coupling with the \(\text{Co}^{III}/\text{Fe}^{III}\) moiety, while for the \(\text{Co}^{III}/\text{Fe}^{III}\) aggregates is precisely the existence of more than one \(\text{Co}^{III}/\text{Fe}^{III}\) unit the responsible for the enhanced electronic coupling between the centres, with the consequent increase in the extinction coefficient of the MMCT signal observed.

**Conclusions**

The preparation of new discrete \(\{\text{LCr}^{III}\}/\text{Fe}^{III}\) and \(\{\text{LCr}^{III}\}/\text{Fe}^{III}\)/\(\text{L}^*\text{Co}^{III}\) (\(\text{L}^*\) and \(\text{L}^*\) represent pentadentate \(\text{N}_2\) macrocyclic ligands) cyanobridged mixed-valence complexes has been accomplished by application of the carefully kinetic and mechanistically designed procedures fully established for the analogous \(\{\text{LCr}^{III}\}/\text{Fe}^{III}\) derivatives also relevant differences are observed between the \(\text{Cr}^{III}\) and \(\text{Co}^{III}\) based systems. For the chromium systems described in this work, the process is envisaged as a simple base-hydrolysis substitution process on the macroyclic \(\{\text{LCr}^{III}\}\) complex by \(\text{Fe}^{III}(\text{CN})_{4}\)^\textsuperscript{2+}, the redox-assisted process operating for the assembly of dinuclear \(\{\text{LCo}^{III}\}/\text{Fe}^{III}\) complexes not being applicable in this case, given the unfavourable potential of the \(\{\text{LCr}^{III}\}\) building block precursor, as well as the enhanced lability of the \(\{\text{LCr}^{III}\}\) species generated. The study has also allowed the characterization of a new \(\text{N}\)-based isomer for the \(\{\text{LCr}^{III}\}\) building block, indicating that the isomerization reactivity observed for the analogous \(\{\text{LCr}^{III}\}\) derivatives also apply for other metal centres. Furthermore, an important difference has been established, for the \(\{\text{LCr}^{III}\}\) mononuclear building block complexes the alkaline \((\text{pH} 9)\) treatment for long periods of these units produce the decoordination of one of the amine groups generating a new series of \((\text{HL})(\text{OH})\text{Cr}^{III}\) (\(\text{HL}\) represents a tetradentate \(\text{HN}_2\) macrocycle) species that are responsible for the mixed-valence complex assembly.

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**References**
