

## Molecular Co<sup>III</sup>/Fe<sup>II</sup> Cyano-Bridged Mixed-Valence Compounds with High Nuclearities and Diversity of Co<sup>III</sup> Coordination Environments: Preparative and Mechanistic Aspects

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The kinetic-mechanistic study of the formation of discrete tri- and tetranuclear mixed-valence cyano-bridged (Co<sup>III</sup>)<sub>2</sub>/Fe<sup>II</sup> and (Co<sup>III</sup>)<sub>3</sub>/Fe<sup>II</sup> complexes has been carried out from their already described parent dinuclear Co<sup>III</sup>/Fe<sup>II</sup> and mononuclear Co<sup>III</sup> complexes. Different Co<sup>III</sup> encapsulating units have been used in order to tune both the redox potential on the mono- and dinuclear complexes and the lability of the mononuclear building blocks. The importance of outer-sphere precursor complex formation involving the oppositely charged reactants has been established by experiments conducted at high ionic strength where electrostatic effects are nullified. The influence of the pH is also crucial, and this has been linked to the pH dependence of the precursor Co<sup>III/II</sup> redox potentials in terms of enabling a redox-assisted association (at low pH) between the ferricyanide analogue and the labile Co<sup>II</sup> partner. A new asymmetric Co<sup>III</sup>L/Fe<sup>II</sup>/Co<sup>III</sup>L' complex has been fully characterized, and a series of putative (Co<sup>III</sup>L)<sub>2</sub>/Fe<sup>II</sup>/Co<sup>III</sup>L' and (Co<sup>III</sup>L)<sub>3</sub>/Fe<sup>II</sup> forms have been spectroscopically detected. A comparison with the mechanistic reaction pathways established for the formation of the parent dinuclear Co<sup>III</sup>/Fe<sup>II</sup> complexes indicates that an important tuning of the direct substitution and redox-catalyzed mechanism is applicable. For the formation of the trinuclear complexes, only in the most favorable conditions is a redox-assisted sequence observed. The rate and activation parameters for the reactions have been determined and are indicative of an essential outer-sphere precursor formation. Similarly, for reactions where redox-assisted mechanisms are unfavorable, only direct substitution processes have been found to be applicable, with their rate coefficients and activation parameters also agreeing with the expectations, once an outer-sphere precursor complex is formed. Formation of the tetranuclear (Co<sup>III</sup>L)<sub>3</sub>/Fe<sup>II</sup> complexes has only been detected on decomposition of the parent trinuclear (Co<sup>III</sup>L)<sub>2</sub>/Fe<sup>II</sup> complexes following reduction to their Co<sup>II</sup> form. The overall processes seem to be based on the outer-sphere association between the respective building blocks in such a way that both unfavorable redox potentials and Lewis basicities are overcome.

### Introduction

Mixed-valence transition-metal compounds have been intensively studied, with those involving cyano-bridged polymeric motifs being the first known examples.<sup>1,2</sup> The theoretical basis of their electronic structure and properties has emerged in parallel with electron-transfer and spectroscopic investigations.<sup>3–6</sup> A general feature of so-called Class II

mixed-valence complexes<sup>5</sup> is the existence of a metal-to-metal charge-transfer (MMCT) electronic transition. These complexes can be used in different ways: as general multielectron donor/acceptor systems;<sup>7</sup> as compounds with useful macroscopic properties (such as magnetism);<sup>8,9</sup> as photoinduced electron-transfer devices (involving the MMCT band to give a charge-separated species),<sup>10</sup> and from a fundamental standpoint for understanding electronic delocalization between metal centers.<sup>4</sup> In this respect, the careful determination and control of the mechanism of assembly as well as the characterization of polynuclear mixed-valence complexes

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underpin all theoretical and spectroscopic studies of these compounds.

In recent years, we have been involved in the preparation of a series of discrete Class II mixed-valence cyanide-bridged complexes of the type  $[\text{LCo}^{\text{III}}\text{NCFe}^{\text{II}}(\text{CN})_5]^-$  (where L represents a neutral pentadentate  $\text{N}_5$ - or  $\text{N}_3\text{S}_2$ -donor macrocyclic ligand), as well as in their formation mechanism and redox reactivity.<sup>11–15</sup> Compounds of this type have been anchored on  $\text{TiO}_2$  surfaces in order to check their possible use as dye-sensitized solar cell sensitizers.<sup>16</sup> Following these studies, the formation of trimetallic species of the type  $[\{\text{LCo}^{\text{III}}\text{NC}\}_2\text{Fe}^{\text{II}}(\text{CN})_4]^{2+}$  has also been achieved, and some of the complexes have been fully characterized.<sup>17</sup> Their redox reactivity has also been studied for comparison with their parent dinuclear species; furthermore, their encapsulation in silica matrixes has been achieved, and their reactivity was found to parallel that seen in solution.<sup>18</sup>

The reaction sequence for the formation of dinuclear complexes has already been established and that for trinuclear complexes has been assumed to be the same.<sup>17,19</sup> Nevertheless, no systematic kinetic-mechanistic study of the assembly of trinuclear mixed-valence complexes of this type has been carried out. This is important because the rational “bottom-up” assembly of more sophisticated mixed-valence polynuclear complexes demands control over both reactivity and stereoselectivity in order to avoid intractable mixtures of products. We have utilized the hexacyanoferrate(II) anion (and its trivalent analogue) extensively as the “core” reactive center, where the terminal N atoms of the cyano ligands coordinate to a different metal center (typically  $\text{Co}^{\text{III}}$ ). In principle, between one and six Co ions may be taken up by each ferrocyanide moiety (and all combinations in between including isomeric *cis/trans* and *mer/fac* forms).

The mechanism for the assembly of dinuclear  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}$  complexes involves the formation of an outer-sphere  $[\text{Co}^{\text{III}}\text{L}(\text{OH}_2)]^{3+}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  complex, which then undergoes an electron-transfer cross reaction to generate a labile  $\text{Co}^{\text{II}}$  complex (and ferricyanide). The  $\text{Co}^{\text{II}}$  complex undergoes rapid ligand exchange with a terminal N atom of ferricyanide, with inner-sphere electron transfer ( $\text{Co}^{\text{II}}$  to  $\text{Fe}^{\text{III}}$ ) generating the inert  $\text{Co}^{\text{III}}\text{—NC—Fe}^{\text{II}}$  final product.

However, the introduction of successive tripositive  $\text{Co}^{\text{III}}$  moieties raises the  $\text{Fe}^{\text{III/II}}$  redox potential by about 200 mV for each  $\text{Co}^{\text{III}}$  ion.<sup>17</sup> Ultimately, this will disfavor the initial outer-sphere reduction of the monomeric  $\text{Co}^{\text{III}}$  complex by the polynuclear  $\{\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}(\text{CN})_6\}$  assembly. The result will be that a redox-assisted mechanism becomes unfavorable relative to a direct substitution process on the inert  $\text{Co}^{\text{III}}$

center without reduction. This alternative process is bound to produce much slower and less predictable reactions. We have reported that raising the redox potential of the polycyanoiron complex may be achieved by the introduction of bipyridyl ligands (i.e.,  $[\text{Fe}^{\text{II}}(\text{bpy})(\text{CN})_4]^{2-}$ ), and this has the same effect as disabling any redox-assisted mechanism for the assembly of mixed-valence complexes.<sup>15</sup> Scheme 1 illustrates the diversity of processes inherent to these studies ( $n = 0$ , trinuclear complexes;  $n > 0$  higher-nuclearity complexes). The key point should be determining which mechanism operates for the different “building block” components, as well as which combinations can be obtained under specific conditions. Furthermore, the possible simultaneous parallel direct substitution and redox-assisted substitution mechanisms in some cases have to be considered. The final goal is the establishment of a rational and controllable preparative method that is often lacking for the assembly of many of the related polynuclear aggregates.<sup>9,20,21</sup>

In this paper, we present a kinetic-mechanistic study of the formation of trinuclear mixed-valence  $\{\{\text{LCo}^{\text{III}}\text{NC}\}\{\text{L}'\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_4\}^{2+}$  complexes with a range of  $\text{N}_5$  and  $\text{N}_3\text{S}_2$  pentadentate ligands<sup>22</sup> (Scheme 1). The complex with  $\text{L} = \text{L}_{14}$  and  $\text{L}' = \text{L}_{14\text{S}}$  has been prepared and characterized for the first time following the preparative mechanistic procedure determined and represents the first example in a series of complexes having nonequivalent acceptor centers showing distinct redox potentials. The formation of the tetranuclear mixed-valence species  $[\{\text{L}_{14}\text{Co}^{\text{III}}\text{NC}\}_3\text{Fe}^{\text{II}}(\text{CN})_3]^{5+}$  has also been studied by use of the already known *cis-* and *trans-* $\{\{\text{L}_{14}\text{Co}^{\text{III}}\text{NC}\}_2\text{Fe}^{\text{II}}(\text{CN})_4\}^{2+}$  precursor building blocks plus the mononuclear  $\{\text{Co}^{\text{III}}\text{L}_{14}\}$  unit. The results obtained indicate that a fine-tuning of the preparative mechanistic reactivity exists in these processes, highlighting the challenges of this chemistry in previous attempts. The redox potentials of both the Fe and Co centers play a crucial role in determining the alternative activation of direct substitution versus redox-assisted processes (Scheme 1). Furthermore, the effect of the ionic strength of the reaction medium has also been studied, given the importance of the formation of specific precursor outer-sphere complexes.<sup>19</sup>

## Experimental Section

**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 while in the solid state.

**Syntheses.** All of the  $\{\text{Co}^{\text{III}}\text{L}\}$  building block mononuclear complexes (Scheme 1) have been prepared by well-established procedures<sup>23–26</sup>

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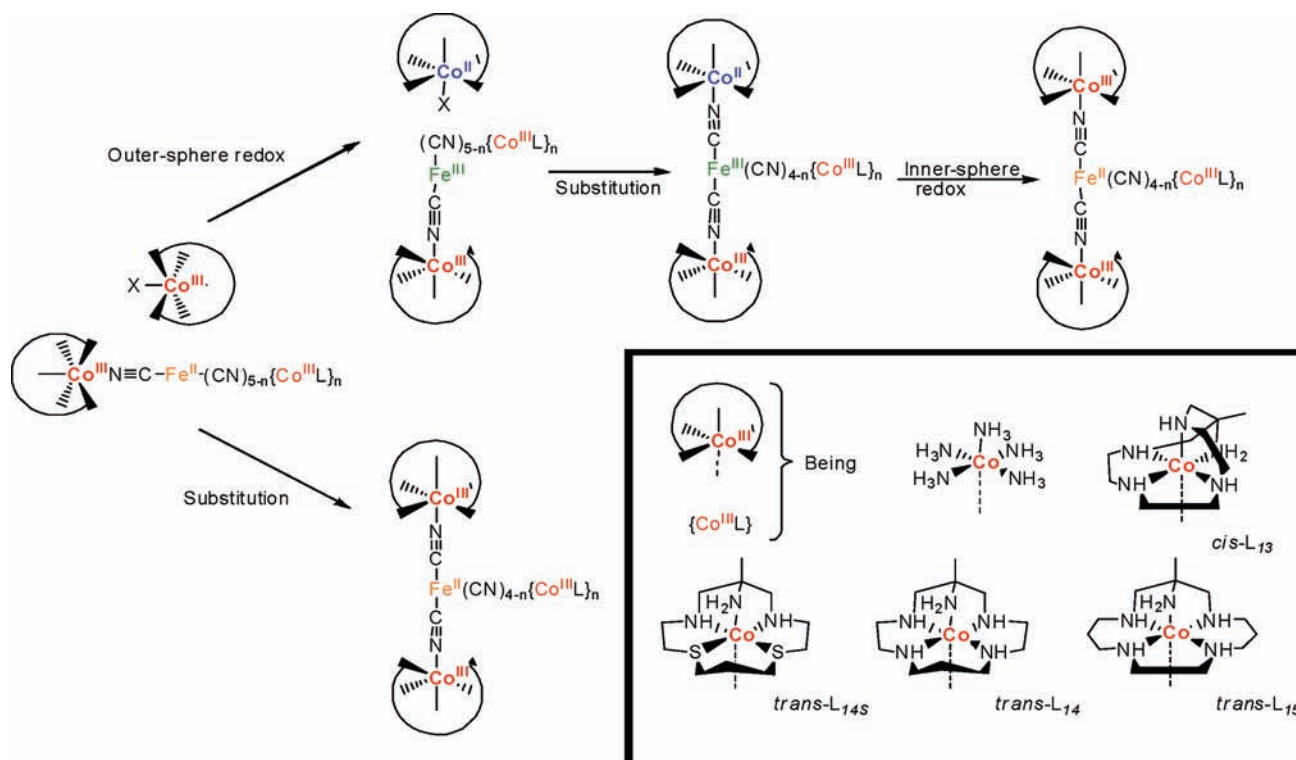
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Scheme 1



The trinuclear complex  $[\{trans-I-L_{14}Co^{III}NC\}\{trans-III-L_{14S}Co^{III}NC\}Fe^{II}(CN)_4]^{2+}$  was obtained for the first time in this work by the reaction of equimolar quantities of the dinuclear mixed-valence complex<sup>26</sup>  $[\{trans-I-L_{14}Co^{III}NC\}Fe^{II}(CN)_5]^-$  and the corresponding  $trans-III-[CoCIL_{14S}]^{2+}$  mononuclear building block cobalt complex. An aqueous solution  $8 \times 10^{-3}$  M in both complexes ( $50 \text{ cm}^3$ ) at a resulting pH of 4.5 was reacted at room temperature for 3 h; the mixture was diluted 8-fold and loaded on a Sephadex C-25 cation-exchange column. Under these conditions, only two cationic species eluted separately with 0.1 M  $NaClO_4$ . They were each concentrated to a small volume (ca.  $5 \text{ cm}^3$ ) at room temperature on a rotary evaporator; the addition of ethanol (ca.  $150 \text{ cm}^3$ ) yielded two solids in equal amounts.

The solid from the first band (40% yield) was characterized as  $trans-\{[trans-I-L_{14}Co^{III}NC]\{trans-III-L_{14S}Co^{III}NC\}Fe^{II}(CN)_4\}^{2+}$ .  $^{13}C$  NMR ( $D_2O$ ):  $trans-I-L_{14}$ , 21.0, 30.8, 52.9, 54.9, 55.1, 62.1, 68.5 ppm;  $trans-III-L_{14S}$ , 21.8, 28.1, 34.5, 44.0, 58.4, 64.1, 71.6 ppm; cyanides, 174.0 ( $\times 4$ ), 189.9, 191.0 ppm. The peaks indicate the presence of both  $trans-I-L_{14}$  and  $trans-III-L_{14S}$  ligands,<sup>13,26,27</sup> as well as three cyanide carbon signals (Figure S1a in the Supporting Information) indicative of its  $trans$  geometry and mirror-plane symmetry. Anal. Calcd (found) for  $[\{L_{14}Co^{III}NC\}\{L_{14S}Co^{III}NC\}Fe^{II}(CN)_4](ClO_4)_2 \cdot 8H_2O$ : C, 28.85 (29.13); N, 16.82 (16.50); H, 5.88 (5.49); S, 5.50 (5.34). Electrochemistry (mV vs NHE): 820 ( $Fe^{III/II}$ ), -210 and -490 ( $Co^{III/II}$ ). Electronic spectrum in water [ $\lambda_{max}/nm$  ( $\epsilon/M^{-1} \text{ cm}^{-1}$ ): 456 (1102), 515 (1025). IR ( $\nu_{CN}/\text{cm}^{-1}$ ): 2126, 2093, 2050.

The solid from the second band was also dissolved in  $D_2O$  and its  $^{13}C$  NMR spectrum recorded. The signals of the  $trans-I-L_{14}$  and  $trans-III-L_{14S}$  ligands were the only ones present in the saturated carbon region ( $trans-I-L_{14}$ , 21.0, 30.8, 52.9, 54.9, 55.1, 62.1, 68.5 ppm;  $trans-III-L_{14S}$ , 21.8, 28.1, 34.5, 44.0, 58.4, 64.1, 71.6 ppm),<sup>13,26,27</sup> but in the cyanide carbon region, the

spectrum shows five predominant signals at 171.9 ( $\times 2$ ), 172.3, 172.4, 189.0, and 189.4 ppm plus some other minor signals (Figure S1b in the Supporting Information). The solution eluted from the column before workup exhibited UV-vis spectral maxima at 455 and 510 nm ( $\epsilon_{455}/\epsilon_{510} = 1.03$ ) and redox potentials (mV vs NHE): 845 ( $Fe^{III/II}$ ), -240 and -510 ( $Co^{III/II}$ ).

The solid was consequently dissolved and reloaded on a Sephadex C-25 cation-exchange column. Elution with 0.1 M  $NaClO_4$  produced again two distinct bands, the first having the electronic spectrum of the  $trans-\{[trans-I-L_{14}Co^{III}NC]\{trans-III-L_{14S}Co^{III}NC\}Fe^{II}(CN)_4\}^{2+}$  isomer. Again the second band was precipitated following the same workup procedure as before and rechromatographed. A series of minor bands appeared on elution, indicating decomposition of the probable  $cis-\{[trans-I-L_{14}Co^{III}NC]\{trans-III-L_{14S}Co^{III}NC\}Fe^{II}(CN)_4\}^{2+}$  isomeric form of the desired complex (see the Results and Discussion section). No further characterization was carried out given the inherent instability of this isomeric form.

**Physical Methods.** NMR spectra were recorded on a Varian Mercury-400 ( $^1H$  400 MHz or  $^{13}C$  100.6 MHz) instrument in  $D_2O/H_2O$  (8/2 to 2/8) using NaTSP as the external standard at Serveis Científico-Tècnics, Universitat de Barcelona. Elemental analyses, as well as inductively coupled plasma optical emission (ICP-OES), were also carried out by Serveis Científico-Tècnics, Universitat de Barcelona. UV-vis spectra were recorded on HP5482A, Cary 50, or J&M TIDAS instruments depending on the circumstances, as indicated. Cyclic voltammetry and differential pulse voltammetry (DPV) experiments were carried out on 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  $1 \times 10^{-3}$  M solutions of the sample and using 0.1 M  $NaClO_4$  as the supporting electrolyte unless stated. For the processes that were found to be irreversible on such a working electrode, polarography on a mercury drop working electrode was used on a Metrohm 757VA Computrace instrument. All potential values are given versus NHE once corrected for the reference electrode used.

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**Kinetics.** All reactions were followed by UV–vis spectroscopy in the full 800–300 nm range. Observed rate constants were derived from the absorbance versus time traces at wavelengths where a maximum increase and/or decrease of the absorbance was observed.<sup>28</sup> No dependence of the observed rate constant values on the selected wavelengths was detected, as was expected for reactions where a good retention of isobestic points is observed. The general kinetic technique is that previously described,<sup>19,29,30</sup> both pseudo-first-order and second-order conditions were used for the studies (see the Results and Discussion section).<sup>31</sup> For pseudo-first-order conditions, the concentration of the complex in deficit was kept in the  $(3\text{--}5) \times 10^{-3}$  M margin, and rate constants were found to be independent of its concentration. For second-order conditions, the concentrations of both reactants were kept equal and within the  $(3\text{--}5) \times 10^{-3}$  M margin. In both cases, the rate constants were determined by the use of Specfit.<sup>32</sup> Acetate and borax buffer solutions were prepared with  $I = 0.2$  M for pH 5 and 9, respectively;  $I = 1.0$  M was achieved with NaClO<sub>4</sub>.<sup>33</sup>

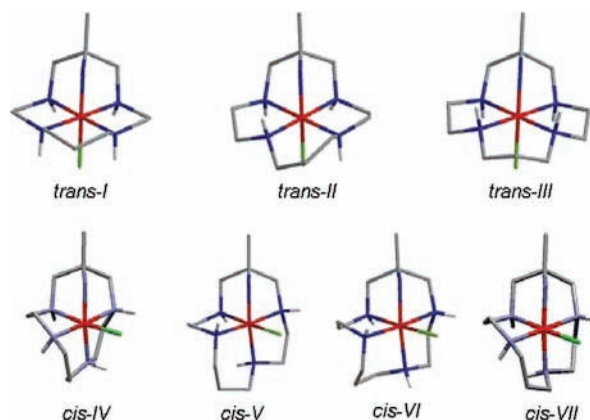
Atmospheric pressure runs were recorded on a Cary 50 or a HP8452A instrument, equipped with a thermostatted multicell transport. For runs carried out at elevated pressures, an already described pressurizing cell system setup was used connected to a TIDAS instrument.<sup>34,35</sup> All of the values obtained for the first- and second-order rate constants as a function of the metal complex, temperature, pressure, and different reactant concentrations are collected in Table S1 (Supporting Information).

Thermal activation parameters ( $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) have been determined by the standard Eyring plots of  $\ln(k/T)$  vs  $1/T$ , while the volumes of activation have been calculated from the slopes of the established  $\ln k$  vs  $P$  plots.<sup>28,31</sup>

## Results and Discussion

**Precursor Complexes.** The simple [CoCl(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub> mononuclear complex only required recrystallization for purification, while the macrocyclic complexes [CoClL](ClO<sub>4</sub>)<sub>2</sub> (L = L<sub>13</sub>, L<sub>14</sub>, L<sub>15</sub>, L<sub>14S</sub>) demanded cation-exchange chromatography in order to separate both their *cis* and *trans* isomers and various N-based isomers depending on the ring size.<sup>13,27</sup> Only the final thermodynamically stable isomeric forms of all of these complexes in different media have been used for this study in order to avoid complications from isomerization during the assembly reaction. These most stable forms are (according to the trivial nomenclature now well established for the N-based isomers of cyclam complexes),<sup>27,36</sup> *cis-V*-[CoClL<sub>13</sub>]<sup>2+</sup>, *trans-I*-[CoClL<sub>14</sub>]<sup>2+</sup>, and *trans-III*-[CoClL<sub>14S</sub>Cl]<sup>2+</sup> (see Chart 1 as an example for L<sub>14</sub>). The hydroxo derivatives of the complexes were obtained in solution by base hydrolysis of the corresponding chloro compounds<sup>23</sup> to produce thermo-

Chart 1



dynamically and kinetically stable forms. These are *trans-I*-[CoOHL<sub>14</sub>]<sup>2+</sup> (from *trans-I*-[CoClL<sub>14</sub>]<sup>2+</sup>) and *trans-II*-[CoOHL<sub>14S</sub>]<sup>2+</sup> (from *trans-III*-[CoClL<sub>14S</sub>Cl]<sup>2+</sup>), which were used for further reactivity.<sup>27</sup> The isomeric form and purity of all of the different species have been determined by <sup>13</sup>C NMR in D<sub>2</sub>O/H<sub>2</sub>O.

The {[LCo<sup>III</sup>NC]Fe<sup>II</sup>(CN)<sub>5</sub>]<sup>-</sup> (L = *cis-V*-L<sub>13</sub>, *trans-I*-L<sub>14</sub>, *trans-III*-L<sub>15</sub>, and *trans-III*-L<sub>14S</sub>) dinuclear building blocks used in this study have also been prepared via the procedures already described.<sup>13–15,26,37</sup> The *cis*- and *trans*-[*trans-I*-L<sub>14</sub>Co<sup>III</sup>NC]<sub>2</sub>Fe<sup>II</sup>(CN)<sub>4</sub>]<sup>2+</sup> precursor building blocks have also been prepared by published procedures.<sup>17,18</sup> The isomeric purity of the di- and trinuclear complexes has also been established by <sup>13</sup>C NMR in D<sub>2</sub>O/H<sub>2</sub>O.<sup>27</sup>

### Mechanistically Driven Preparation of the Complexes.

Although some trinuclear complexes of the family of mixed-valence Co<sup>III</sup>/Fe<sup>II</sup> cyano-bridged complexes shown in Scheme 1 have already been prepared and characterized (structurally and spectroscopically),<sup>17</sup> the mechanism leading to their formation was uncertain. In some cases, trinuclear complexes were obtained (accidentally) as byproducts in the preparation of the parent dinuclear Co<sup>III</sup>/Fe<sup>II</sup> compounds.<sup>17,18,38</sup> In this respect, the cyclic voltammogram signature of the trinuclear Co<sup>III</sup>/Fe<sup>II</sup> complexes (an anodically shifted Fe<sup>III</sup>/Fe<sup>II</sup> redox couple relative to the dinuclear precursor) is always observed on repetitive redox cycling of the dinuclear Co<sup>III</sup>/Fe<sup>II</sup> complexes, inferring that the redox mechanism operating for the formation of the dinuclear complexes also applied (Scheme 1).<sup>39</sup> Nevertheless, the increasing redox potential of the iron center upon attachment of successive mononuclear {Co<sup>III</sup>L} units to the bridging cyano ligands must ultimately preclude the redox-assisted process; i.e., the Fe<sup>II</sup> center can no longer act as a reductant to trigger a redox-assisted reaction.<sup>15</sup> Moreover, the formation of a {3+/1-} ([CoL(OH<sub>2</sub>)]<sup>3+</sup>/[LCoNCFe(CN)<sub>5</sub>]<sup>-</sup>) or a {2+/1-} ([CoLX]<sup>2+</sup>/[LCoNCFe(CN)<sub>5</sub>]<sup>-</sup>) (X = OH<sup>-</sup> or Cl<sup>-</sup>) outer-sphere complex is less favorable than the more attractive {3+/4-} or {2+/4-} association in the synthesis of

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the parent dinuclear species from  $[\text{Co}^{\text{III}}\text{L}(\text{OH}_2)]^{3+}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  or  $[\text{Co}^{\text{III}}\text{LX}]^{2+}/[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ .<sup>29,40</sup>

The first step taken in order to investigate which of the two mechanisms indicated in Scheme 1 is dominant (redox-assisted or direct substitution) in the formation of species with nuclearities higher than 2 ( $n \geq 0$ ) was a simple study of the reaction of  $[\{\text{trans-III-L}_{15}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  or  $[\{\text{cis-V-L}_{13}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  with  $[\text{Co}^{\text{III}}\text{X}(\text{NH}_3)_5]^{2+}$  at a pH adjusted to 5 ( $\text{X} = \text{Cl}$ ) and 9 ( $\text{X} = \text{OH}$ ) with and without the presence of ethylenediaminetetraacetic acid (EDTA). The reduction of  $[\text{Co}^{\text{III}}\text{Cl}(\text{NH}_3)_5]^{2+}$  in water leads to immediate dissociation of all ammine ligands so that EDTA acts as a scavenger of the resulting  $\text{Co}_{\text{aq}}^{2+}$ . At pH 5 in the presence of EDTA, the reactions between  $[\text{Co}^{\text{III}}\text{Cl}(\text{NH}_3)_5]^{2+}$  and the dinuclear  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}$  complexes proceed rapidly (in minutes) at 298 K with a resulting significant increase in the intensity of the MMCT band around 500–550 nm, characteristic of the formation of a new mixed-valence species of higher nuclearity, i.e.,  $\{\{\text{LCo}^{\text{III}}\text{NC}\}\{\text{EDTA}\}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_4\}$ .<sup>41</sup> When EDTA was omitted (at pH 5), the mixture produced an immediate precipitate attributed to the  $\text{Co}^{\text{II}}$  salt of the anionic mixed-valence dinuclear precursor, as found in other  $[\text{Co}^{\text{III}}\text{X}(\text{NH}_3)_5]^{2+}$  reactions.<sup>42</sup> It is thus clear that the reaction between  $[\text{Co}^{\text{III}}\text{Cl}(\text{NH}_3)_5]^{2+}$  and dinuclear  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}$  complexes proceeds via an outer-sphere redox-assisted mechanism involving a rapid reduction of the pentaammine complex by the  $\text{Fe}^{\text{II}}$  center of the dinuclear mixed-valence complex (Scheme 1, top). The kinetic information related to these experiments is collected in the Kinetic Studies section.

When the reaction was carried out in the same way as that at pH 9, the process is found to be much slower (reaction times of 10–20 h at 333 K), and the presence or absence of EDTA had no influence on the outcome. In this case, the production of a mixed-valence complex of higher nuclearity seems to be produced by a simple slow substitution process (Scheme 1, bottom) of the hydroxo ligand on  $[\text{Co}^{\text{III}}(\text{OH})(\text{NH}_3)_5]^{2+}$  (the only mononuclear species present at pH 9) by one of the cyanide N atoms of  $[\{\text{LCo}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  with no formation of  $\text{Co}^{\text{II}}$  at any stage. The kinetic information related to the experiments carried out with  $[\{\text{cis-V-L}_{13}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  is also collected in the Kinetic Studies section. Given the fact that the redox potentials for all of the dinuclear  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}$  complexes are pH-independent within the range  $5 < \text{pH} < 9$ <sup>11</sup> and that the charges of both mononuclear pentaammine  $\text{Co}^{\text{III}}$  complexes are the same, the differences in the apparent mechanism have to be related to the redox potentials of the  $[\text{Co}^{\text{III}}\text{X}(\text{NH}_3)_5]^{2+}$  units. Although these redox reactions are totally irreversible, the  $\text{Co}^{\text{III/II}}$  redox potentials of  $[\text{Co}^{\text{III}}\text{Cl}(\text{NH}_3)_5]^{2+/+}$  (+320 mV vs NHE) and  $[\text{Co}^{\text{III}}(\text{OH})(\text{NH}_3)_5]^{2+/+}$  (–220 mV vs NHE) have been determined polarographically.<sup>43</sup> Clearly, the large difference between the  $\text{Co}^{\text{III/II}}$  redox potentials of the mononuclear precursors accounts qualitatively for the redox-assisted reaction of the chloro complex being

favored while direct substitution on the hydroxocobalt (III) analogue is preferred.

The next step was elucidating the mechanism for formation of the known, and well-characterized,<sup>17</sup> trinuclear *cis*- and *trans*- $[\{\text{trans-I-L}_{14}\text{Co}^{\text{III}}\text{NC}\}_2\text{Fe}^{\text{II}}(\text{CN})_4]^{2+}$  species from their common dinuclear  $[\{\text{trans-I-L}_{14}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  parent in a reaction with the mononuclear *trans-I*- $[\text{Co}^{\text{III}}\text{XL}_{14}]^{2+}$  ( $\text{X} = \text{Cl}$  or  $\text{OH}$ ) building blocks. The redox potentials of these mononuclear species have been determined as –157 mV ( $\text{X} = \text{Cl}$ ) and –450 mV ( $\text{X} = \text{OH}$ ) both versus NHE.<sup>26</sup> When the process was conducted at  $I = 1.0$  M ( $\text{NaClO}_4$ ), no reaction with *trans-I*- $[\text{Co}^{\text{III}}\text{Cl}_{14}]^{2+}$  was evident at either pH 5 or 9 after 1 day (before aquation of the chloro ligand takes place). Only when the ionic strength was lowered to 0.2 M at pH 9 was any reactivity observed. It appears that the outer-sphere precursor association<sup>28,44</sup> is crucial, and inhibition at high ionic strength prevents actuation of any of the mechanisms indicated in Scheme 1. Under these conditions (pH 9,  $I = 0.2$  M), some kinetic experiments were conducted (see the Kinetic Studies section) and the reaction rate and activation parameters indicated that formation of the known  $[\{\text{trans-I-L}_{14}\text{Co}^{\text{III}}\text{NC}\}_2\text{Fe}^{\text{II}}(\text{CN})_4]^{2+}$  complexes takes place by a simple very slow substitution process.

In a further attempt to tune this reactivity, the redox potentials of *trans-III*- $[\text{Co}^{\text{III}}\text{CIL}_{14\text{S}}]^{2+/+}$  (–105 mV vs NHE) and *trans-II*- $[\text{Co}^{\text{III}}(\text{OH})\text{L}_{14\text{S}}]^{2+}$  (–200 mV) were determined. A much smaller difference between the chloro and hydroxo complexes is apparent (noting also that the macrocycles have different N-based configurations, as were found in other complexes of this system).<sup>26</sup> From there, the reactions of dinuclear core complexes  $[\{\text{trans-I-L}_{14}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  and  $[\{\text{trans-III-L}_{14\text{S}}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  with the mononuclear  $[\text{Co}^{\text{III}}\text{XL}_{14\text{S}}]^{2+}$  ( $\text{X} = \text{Cl}$  or  $\text{OH}$ ) complexes were investigated at 0.2 and 1.0 M ionic strengths. In all cases, the reaction with *trans-III*- $[\text{Co}^{\text{III}}\text{CIL}_{14\text{S}}]^{2+}$  occurs within minutes with an increase in the absorbance of around 520 nm at room temperature, indicating that the trinuclear mixed-valence complexes are formed via the redox-triggered sequence indicated in Scheme 1. Contrarily, the reactions of both dinuclear compounds with *trans-II*- $[\text{Co}^{\text{III}}(\text{OH})\text{L}_{14\text{S}}]^{2+}$  occur in the hours/days time scale at any ionic strength, indicating that a simple slow substitution process is taking place under these conditions. It is clear that the value of –105 mV is still accessible for the redox process to take place once the outer-sphere precursor complex,  $\{\{\text{LCo}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5\}^-; [\text{CoCIL}_{14\text{S}}]^{2+}\}$  ( $\text{L} = \text{L}_{14}$  or  $\text{L}_{14\text{S}}$ ) forms. The  $\text{Fe}^{\text{III/II}}$  redox potential for the isolated dinuclear complex is +630 mV (Table S2 in the Supporting Information), but this value is not necessarily directly comparable with that of the mononuclear cobalt complex (–105 mV) in terms of the thermodynamics of the outer-sphere electron-transfer reaction. When ion-pair formation occurs, leading to the outer-sphere complex  $\{\{\text{LCo}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5\}^-; [\text{CoCIL}_{14\text{S}}]^{2+}\}$ , the actual  $\text{Fe}^{\text{III/II}}$  and  $\text{Co}^{\text{III/II}}$  redox potentials within the assembly are likely to be very different from those of the individual precursors because of electrostatics and

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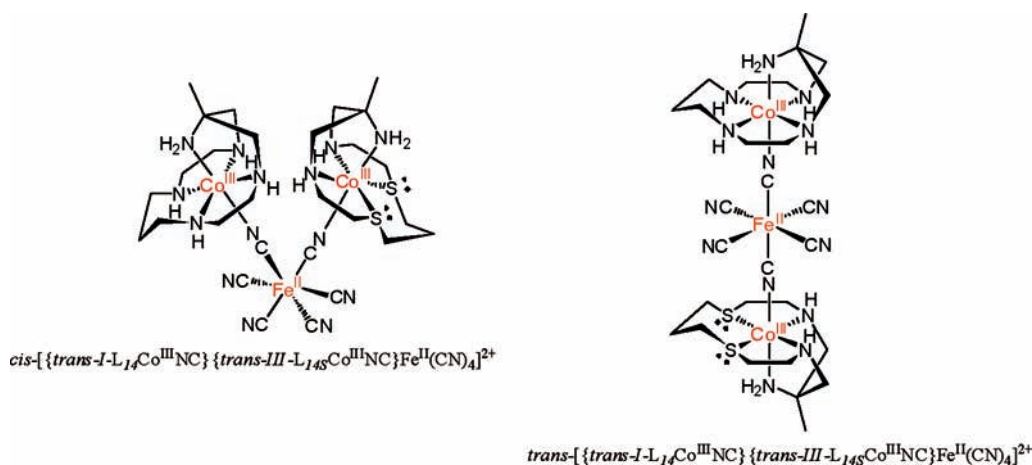
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Scheme 2



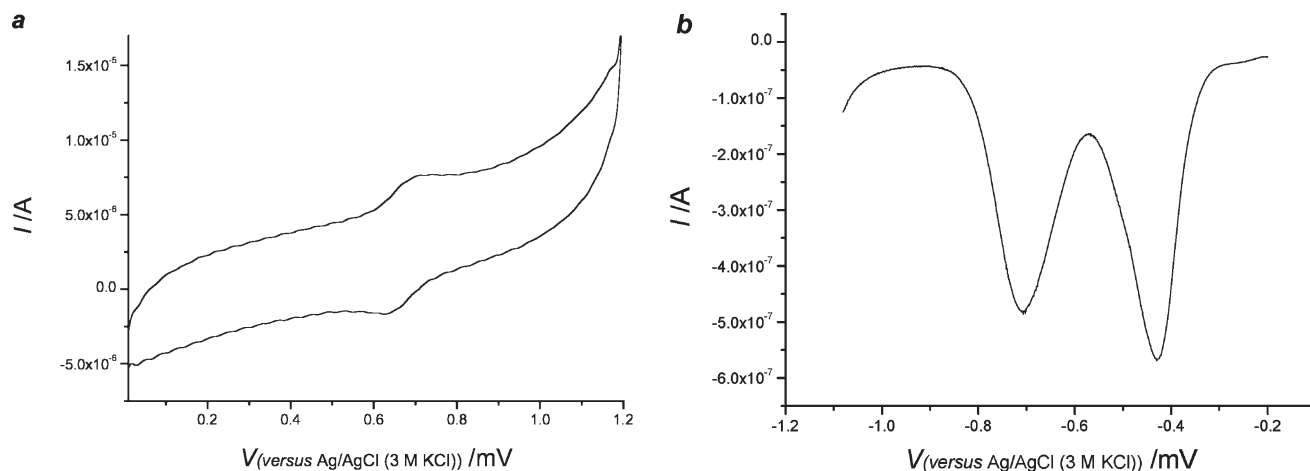
hydrogen-bonding influences within the outer-sphere complex. Once the redox potential of the mononuclear building block is decreased to  $-200$  mV and the precursor becomes  $\{[LCo^{III}NC]Fe^{II}(CN)_5\}^-; [Co^{III}(OH)L_{14S}]^{2+}\}$  ( $L = L_{14}$  or  $L_{14S}$ ), the redox reactivity indicated in Scheme 1 (top) is lost and a slow direct ( $Co^{III}$ ) substitution process operates, as for the  $[Co^{III}(OH)(NH_3)_5]^{2+}$  reactions. In the Kinetics Studies section, the kinetic experiments carried out to corroborate this mechanism are collected.

Once the mechanistic pathways leading to trinuclear complexes were established, the study of the possible formation of tetranuclear  $(Co^{III})_3/Fe^{II}$  was envisaged. It is clear from the reactivity indicated above that the activation of a redox-driven mechanism is improbable. Indeed, the reaction of trinuclear  $[{\{L_{14}Co^{III}NC\}_2Fe^{II}(CN)_4}]^{2+}$  with  $[Co^{III}X(NH_3)_5]^{2+}$  in acid ( $X = Cl$ ) and alkaline ( $X = OH$ ) pH in the absence of EDTA gave no precipitation of  $Co^{II}$  species in any case. That is, the redox mechanism indicated in Scheme 1 (top) was not operative for this model reaction. Consequently, the slower substitutionally directed mechanism was monitored, via UV-vis spectroscopy, with  $[Co^{III}(NH_3)_5(OH_2)]^{3+}$  (pH 5) and  $[Co^{III}(OH)(NH_3)_5]^{2+}$  (pH 9) and at high ionic strength to offset the electrostatic repulsion of the  $3+/2+$  and  $2+/2+$  charged reactants. In the alkaline pH regime, no reproducible reaction was observed for 1 day at  $70$  °C before decomposition of the solution mixture took place, even with a 10-fold excess of the mononuclear hydroxo complex. Similarly, at pH 5 and using a noncoordinating buffer,<sup>45,46</sup> no increase of the absorbance in the  $500-520$  nm region was observed after 1 day at  $80$  °C, indicative of no formation of a new mixed-valence complex. Nevertheless, when  $0.04 \times 10^{-3}$  mol of  $trans-[{\{trans-I-L_{14}Co^{III}NC\}_2Fe^{II}(CN)_4}]^{2+}$  was dissolved in  $50$  cm<sup>3</sup> of a pH 5 ( $I = 0.4$  M) buffer with a 5-fold excess of  $trans-I-[Co^{III}(H_2O)L_{14}]^{3+}$  and left at  $70-80$  °C for 3 days, only 70–75% of the starting trinuclear complex was recovered by chromatography workup. Elution with  $0.5$  M  $NaClO_4$  of a dark-brown band, which was left on top of the column after workup, produced a solution

(ca. 10% yield) showing the expected electrochemistry and UV-vis spectrum for a tetranuclear  $[{\{L_{14}Co^{III}NC\}_3Fe^{II}(CN)_3}]^{5+}$  species (Figure S2 in the Supporting Information;  $E^\circ(Fe^{III/II}) = 1040$  mV,  $E^\circ(Co^{III/II}) = -315$  mV,  $\lambda = 490$  nm ( $2000$  M<sup>-1</sup> cm<sup>-1</sup>), and  $430$  nm ( $2300$  M<sup>-1</sup> cm<sup>-1</sup>). ICP-OES analyses for iron and cobalt from these chromatographed solutions showed a Co/Fe ratio of 2.90 (i.e., 3:1), indicating the validity of the tetranuclear assignment. That is, although no substitution could be monitored reproducibly, applying forcing conditions led putatively to the expected tetranuclear mixed-valence complex. A redox-driven process (Scheme 1, top) from a partially decomposed reaction mixture following an MMCT excitation can explain these results, as discussed in the following section.

**Mixed-Valence Complexes.** The complexes *cis*- and *trans*- $[{\{trans-I-L_{14}Co^{III}NC\}{\{trans-III-L_{14}SCo^{III}NC\}Fe^{II}(CN)_4}]^{2+}$  (Scheme 2) have been prepared for the first time following the redox-facilitated mechanism indicated above. The complexes show <sup>13</sup>C NMR spectra expected for this family of complexes; the *trans-I-L<sub>14</sub>* and *trans-III-L<sub>14S</sub>* geometrical isomeric forms have been confirmed from the <sup>13</sup>C NMR data in the aliphatic carbon region when compared with published data on similar compounds of known stereochemistry.<sup>27</sup> The signals for the cyanide carbons at 171.9, 172.3, 172.4, 189.0, and 189.4 ppm and at 174.0, 189.9, and 191.0 ppm are as expected for the *cis* and *trans* isomers.<sup>17,18</sup> The values of the more intense signals at 171.9 and 174.0 ppm are assigned to the two and four equivalent terminal *cis*-CN groups, respectively, while the signals at 189.0 and 189.9 ppm have been assigned to the  $Fe^{II}-CN-Co^{III}L_{14}$  ligands and those at 189.4 and 191.0 ppm to the bridging  $Fe^{II}-CN-Co^{III}L_{14S}$  ligands, according to the trend observed for the dinuclear complexes of this family. The electrochemistry of the species on a glassy carbon electrode shows a reversible  $Fe^{III/II}$  response around 800 mV (vs NHE) (Figures 1a and S3a in the Supporting Information) and a rather broad irreversible response for the  $Co^{III}$  units. When the cobalt signal was studied by DPV on a mercury drop electrode, two clearly resolved couples were identified at  $-200$  and  $-500$  mV (vs NHE) corresponding to the  $\{Co^{III}(trans-III-L_{14S})\}$

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**Figure 1.** (a) Cyclic voltammogram of the *cis*-[*trans*-*I*-L<sub>14</sub>Co<sup>III</sup>NC]{*trans*-*III*-L<sub>14S</sub>Co<sup>III</sup>NC}Fe<sup>II</sup>(CN)<sub>4</sub>]<sup>2+</sup> complex (as eluted from the column) on a glassy carbon electrode (100 mV s<sup>-1</sup>). (b) Cathodic differential pulse polarography (step 1 mV, 0.4 s; amplitude 50 mV, 0.04 s) of *trans*-[*trans*-*I*-L<sub>14</sub>Co<sup>III</sup>NC]{*trans*-*III*-L<sub>14S</sub>Co<sup>III</sup>NC}Fe<sup>II</sup>(CN)<sub>4</sub>]<sup>2+</sup> on a mercury drop electrode.

**Table 1.** Characterization Data for the New Mixed-Valence Asymmetric Trinuclear Complexes<sup>a</sup>

Compound	$\lambda_{\text{MMCT}} (\epsilon)/\text{nm} (\text{M}^{-1}\text{cm}^{-1})$	$E^\circ(\text{Fe}^{\text{III/II}})/\text{mV}^b$	$E^\circ(\text{Co}^{\text{III/II}})/\text{mV}^b$
<i>trans</i> -[ <i>trans</i> - <i>I</i> -L <sub>14</sub> Co <sup>III</sup> NC]{ <i>trans</i> - <i>III</i> -L <sub>14S</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>4</sub> ] <sup>2+</sup> <sup>c</sup>	515 (1025)	820	-490, -210
<i>cis</i> -[ <i>trans</i> - <i>I</i> -L <sub>14</sub> Co <sup>III</sup> NC]{ <i>trans</i> - <i>III</i> -L <sub>14S</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>4</sub> ] <sup>2+</sup> <sup>c</sup>	510 <sup>d</sup>	845	-510, -240
<i>trans</i> -[ <i>trans</i> - <i>I</i> -L <sub>14</sub> Co <sup>III</sup> NC] <sub>2</sub> Fe <sup>II</sup> (CN) <sub>4</sub> ] <sup>2+</sup> <sup>17</sup>	490 (950)	844	-530
<i>cis</i> -[ <i>trans</i> - <i>I</i> -L <sub>14</sub> Co <sup>III</sup> NC] <sub>2</sub> Fe <sup>II</sup> (CN) <sub>4</sub> ] <sup>2+</sup> <sup>17</sup>	475 (1060)	842	-528
<i>trans</i> -[ <i>trans</i> - <i>III</i> -L <sub>15</sub> Co <sup>III</sup> NC] <sub>2</sub> Fe <sup>II</sup> (CN) <sub>4</sub> ] <sup>2+</sup> <sup>17</sup>	515 (930)	804	-533
<i>cis</i> -[ <i>trans</i> - <i>III</i> -L <sub>15</sub> Co <sup>III</sup> NC] <sub>2</sub> Fe <sup>II</sup> (CN) <sub>4</sub> ] <sup>2+</sup> <sup>17</sup>	515 (950)	790	-530
<i>cis</i> -[ <i>trans</i> - <i>III</i> -L <sub>14S</sub> Co <sup>III</sup> NC] <sub>2</sub> Fe <sup>II</sup> (CN) <sub>4</sub> ] <sup>2+</sup> <sup>38</sup>	547 (1060)	884	-269
[ <i>trans</i> - <i>I</i> -L <sub>14</sub> Co <sup>III</sup> NC]Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-14</sup>	510 (510)	630	-600
[ <i>trans</i> - <i>III</i> -L <sub>14S</sub> Co <sup>III</sup> NC]Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-14</sup>	566 (515)	640	-350
<i>trans</i> - <i>I</i> -[Co <sup>III</sup> ClL <sub>14</sub> ] <sup>2+</sup> <sup>26</sup>			-157
<i>trans</i> - <i>I</i> -[Co <sup>III</sup> (OH)L <sub>14</sub> ] <sup>2+</sup> <sup>26</sup>			-450
<i>cis</i> - <i>III</i> -[Co <sup>III</sup> ClL <sub>14S</sub> ] <sup>2+</sup>			-105
<i>cis</i> - <i>II</i> -[Co <sup>III</sup> (OH)L <sub>14S</sub> ] <sup>2+</sup>			-200
[Fe <sup>II</sup> (CN) <sub>6</sub> ] <sup>4-</sup> <sup>44</sup>		465	

<sup>a</sup> Relevant literature data from other tri-, di-, and mononuclear complexes of the same family are included for comparison. <sup>b</sup> Versus NHE.

<sup>c</sup> This work. <sup>d</sup>  $\epsilon$  not determined.

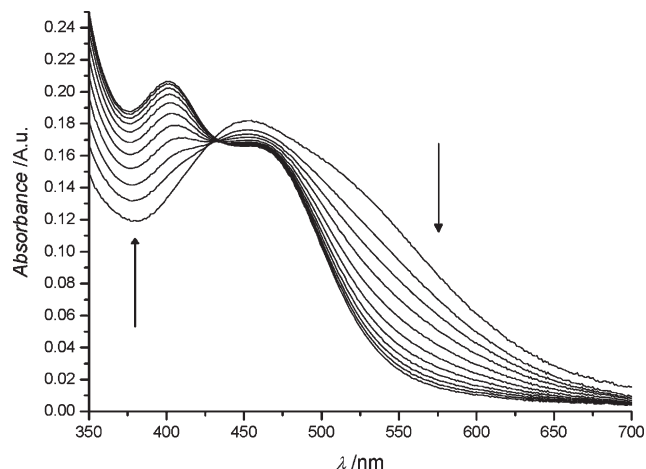
and {Co<sup>III</sup>(*trans*-*I*-L<sub>14</sub>)} units according to the donor character of the macrocyclic ligand (Figures 1b and S3b in the Supporting Information).<sup>13</sup>

The values found for all of these redox potentials follow the expected trend and are collected in Table 1 together with other relevant data for these and other complexes of the family. The iron center shows a positive shift of ca. 200 mV upon attachment of a tripositive {Co<sup>III</sup>L} unit to the dinuclear parent; similarly, the {Co<sup>III</sup>L} units show shifts of ca. +100 mV (L = L<sub>14</sub>) and +150 mV (L = L<sub>14S</sub>) upon modification of the {Fe<sup>II</sup>(CN)<sub>6</sub>} attached unit. The influence of the other metal centers on the redox couples of groups within the “unsymmetrical” multinuclear complexes appears to be greater than within that of their “symmetrical” counterparts. In this respect, the energy of the MMCT transition ( $E_{\text{op}}$ ; Table 1) for complexes at 515 and 510 nm, which vanished upon S<sub>2</sub>O<sub>8</sub><sup>2-</sup> oxidation of the Fe<sup>II</sup> moiety (Figure 2),<sup>11,18</sup> can be related to the thermodynamic driving force of the photoinduced intramolecular Fe<sup>II</sup>-to-Co<sup>III</sup> electron-transfer reaction of the trinuclear unit as well as the reorganizational energy,  $\lambda$ , of the charge transfer according to eq 1.<sup>6</sup> The appearance of the band at ca. 400 nm is related to the formation of the

{Fe<sup>III</sup>(CN)<sub>6</sub>} moiety on the oxidized {Co<sup>III</sup>L<sub>14</sub>}/Fe<sup>III</sup>/ {Co<sup>III</sup>L<sub>14S</sub>} complex.

$$E_{\text{op}} = \Delta G^\circ + \lambda \quad (1)$$

In each complex, the value of  $E_{\text{op}}$  appears to be the same for both Fe<sup>II</sup>-to-Co<sup>III</sup> transitions (no splitting of the MMCT band is apparent);  $E_{\text{op}} = 19\,420$  and  $19\,610 \text{ cm}^{-1}$  for the *trans* and *cis* isomers, respectively. Values for  $\Delta G^\circ$ , calculated from the difference between the redox potentials,<sup>6</sup> are  $10\,350 \text{ cm}^{-1}$  (Fe<sup>II</sup>CNCo<sup>III</sup>L<sub>14</sub>) and  $8140 \text{ cm}^{-1}$  (Fe<sup>II</sup>CNCo<sup>III</sup>L<sub>14S</sub>) for the *trans* isomer and  $10\,705 \text{ cm}^{-1}$  (Fe<sup>II</sup>CNCo<sup>III</sup>L<sub>14</sub>) and  $8570 \text{ cm}^{-1}$  (Fe<sup>II</sup>CNCo<sup>III</sup>L<sub>14S</sub>) for the *cis* form. These data produced for the *trans* isomer values of  $\lambda$  of  $9070$  and  $11\,280 \text{ cm}^{-1}$  for the Fe<sup>II</sup>CN-Co<sup>III</sup>L<sub>14</sub> and Fe<sup>II</sup>CNCo<sup>III</sup>L<sub>14S</sub> units, respectively, and  $8905$  and  $11\,040 \text{ cm}^{-1}$  for the equivalent units on the *cis* form, which are quite different from the reorganizational energy found for the parent units in the dinuclear species ( $9800$  and  $9600 \text{ cm}^{-1}$ , respectively).<sup>14</sup> Although a decrease from  $9800$  to  $9500 \text{ cm}^{-1}$  has already been observed for the Fe<sup>II</sup>CNCo<sup>III</sup>L<sub>14</sub> unit on going from di- to trinuclear complexes,<sup>17</sup> the significant increase from



**Figure 2.** Spectral changes upon  $S_2O_8^{2-}$  oxidation of the mixed-valence trinuclear complex  $trans\text{-}\{[trans\text{-}I\text{-}L_{14}Co^{III}NC]\{trans\text{-}III\text{-}L_{14S}Co^{III}NC\}Fe^{II}(CN)_4\}^{2+}$  prepared in this work. Total time 30 min,  $[S_2O_8^{2-}] = 0.1$  M,  $[H^+] = 0.01$  M,  $30^\circ C$ .

9600 to 11 100–11 200  $cm^{-1}$  for  $Fe^{II}CNCo^{III}L_{14S}$  is remarkable. In this case, the appearance of the MMCT band at the wavelength observed is related to an increase in the reorganizational energy,  $\lambda$ . The solvent hydrogen-bonded cages surrounding these types of complexes,<sup>11,12,47</sup> combined with the diverse nature of the stereochemistry of the donors on the  $Co^{III}$  centers, four NH (hydrogen-bonded donor) groups pointing toward the iron-bonded cyano ligands ( $trans\text{-}I\text{-}L_{14}$ ) versus two NH groups pointing to the iron-bonded cyano ligands in the  $trans\text{-}III\text{-}L_{14S}$  Co moiety (Scheme 2), seem to play a role in the differences observed.

The relative instability of the  $cis\text{-}\{[trans\text{-}I\text{-}L_{14}Co^{III}NC]\{trans\text{-}III\text{-}L_{14S}Co^{III}NC\}Fe^{II}(CN)_4\}^{2+}$  species merits further comment and can be related to the reorganizational energy observed for the  $Fe^{II}CNCo^{III}L_{14S}$  unit upon MMCT excitation coupled with steric hindrance. Although the complex is evidently formed during preparative procedures (as seen from the  $^{13}C$  NMR signals in the cyanide region), workup of the complex produces inevitably the more stable  $trans$  isomer in addition to all of the possible mono- and dinuclear components, i.e.,  $trans\text{-}III\text{-}[Co^{III}L_{14S}(OH_2)]^{3+}$ ,  $trans\text{-}I\text{-}[Co^{III}L_{14}(OH_2)]^{3+}$ ,  $[\{trans\text{-}III\text{-}L_{14S}Co^{III}NC\}Fe^{II}(CN)_5]^-$ , and  $[\{trans\text{-}I\text{-}L_{14}Co^{III}NC\}Fe^{II}(CN)_5]^-$ , as found from the UV-vis spectra of species separated by cation chromatography of mixtures that had been allowed to stand for extended periods. The presence of nonstatistical quantities of  $cis\text{-}\{[LCo^{III}NC]_2Fe^{II}(CN)_4\}^{2+}$  species had already been noticed before, with  $L_{14}$  and  $L_{15}$ ,<sup>17</sup> but it was attributed to steric factors. No evolution from the solution of any of the isomeric forms was observed at reasonable times, but a rather different response is seen here. It is clear that the instability of the system is driven by a fast redox reaction (see above), while activation of a slower substitutionally driven mechanism is relevant for the  $L_{14}$  and  $L_{15}$  compounds (reverse steps of Scheme 1).

Interestingly, ion-exchange chromatography of solutions of  $trans\text{-}$  and  $cis\text{-}\{[trans\text{-}I\text{-}L_{14}Co^{III}NC]\{trans\text{-}III\text{-}L_{14S}Co^{III}NC\}Fe^{II}(CN)_4\}^{2+}$  that had been standing for

extended periods showed also a number of positively charged bands eluting with 0.5 M  $NaClO_4$  after the purified trinuclear complexes. The UV-vis spectrum of the most intense band (Figure S4a in the Supporting Information) has a very broad band in the 425–550 nm region (460 nm ( $2200\text{ M}^{-1}\text{ cm}^{-1}$ ); 515 nm ( $1800\text{ M}^{-1}\text{ cm}^{-1}$ )), and its electrochemistry shows one redox response at 1060 mV and two at  $-195$  and  $-100$  mV (Figure S4b, c in the Supporting Information), which were assigned to the  $Fe^{III/II}$  and  $\{Co^{III/II}L_{14}\}$  and  $\{Co^{III/II}L_{14S}\}$  centers, according to the trend observed for this family of complexes (Table 1). ICP-OES analyses for iron and cobalt from these chromatographed solutions showed a Co/Fe ratio of 2.95 (i.e., 3:1), indicating the validity of a tetranuclear assignment. Table 2 collects these data together with those observed in the decomposition of the  $trans\text{-}\{[trans\text{-}I\text{-}L_{14}Co^{III}NC]_2Fe^{II}(CN)_4\}^{2+}$  indicated above.

**Kinetic Studies.** As indicated in the previous sections, the preliminary kinetic studies carried out with  $[Co^{III}X(NH_3)_5]^{2+}$  ( $X = Cl$  or  $OH$ ) and  $[\{LCo^{III}NC\}Fe^{II}(CN)_5]^-$  ( $L = cis\text{-}V\text{-}L_{13}$  and  $trans\text{-}III\text{-}L_{15}$ ) proved to be very revealing. Figure 3 indicates the typical limiting kinetics trend<sup>28,44</sup> of the observed pseudo-first-order rate constants of the reaction of  $[Co^{III}Cl(NH_3)_5]^{2+}$  (redox process, see above) and  $[Co^{III}(OH)(NH_3)_5]^{2+}$  (substitution process, see above) with the concentration of excess  $Co^{III}/Fe^{II}$  mixed-valence complexes (Scheme 3 and eq 2). The values extracted for the redox processes of  $[Co^{III}Cl(NH_3)_5]^{2+}$  at pH 5.0 and  $I = 1.0$  M are  $^{298}k_{lim} = 5.4 \times 10^{-4}$  and  $2.0 \times 10^{-4}\text{ s}^{-1}$  (for the reaction with  $[\{cis\text{-}V\text{-}L_{13}Co^{III}NC\}Fe^{II}(CN)_5]^-$  and  $[\{trans\text{-}III\text{-}L_{15}Co^{III}NC\}Fe^{II}(CN)_5]^-$ ) with respect to precursor formation equilibrium constants,  $K_{OS}$ , of 590 and  $530\text{ M}^{-1}$ . For the substitution reaction of  $[Co^{III}(OH)(NH_3)_5]^{2+}$  at pH 9.0 and  $I = 1.0$  M with  $[\{trans\text{-}III\text{-}L_{15}Co^{III}NC\}Fe^{II}(CN)_5]^-$ , the relevant values are  $^{333}k_{lim} = 1.6 \times 10^{-3}\text{ s}^{-1}$  and  $K_{OS} = 340\text{ M}^{-1}$ .

$$k_{obs} = \frac{k_{lim}K_{OS}[\text{reactant excess}]}{1 + K_{OS}[\text{reactant excess}]} \quad (2)$$

The data collected for the redox processes on  $[Co^{III}Cl(NH_3)_5]^{2+}$  show interesting differences from the values in the literature for the reduction of the same complex with  $[Fe^{II}(CN)_6]^{4-}$ .<sup>19,29</sup> In that case, the values of  $^{298}k_{lim}$  and  $K_{OS}$  have been found to be  $2.7 \times 10^{-2}\text{ s}^{-1}$  and  $40\text{ M}^{-1}$ , respectively. Although, according to the Marcus theory,<sup>48,49</sup> the difference in  $k_{lim}$  ( $=k_{electron\ transfer}$ ) can be related to the 200 mV positive shift of the redox potential of the  $Fe^{II}$  center in the dinuclear mixed-valence complex, the difference in the value of  $K_{OS}$  is much more difficult to rationalize. The importance of specific hydrogen-bonding interactions with these dinuclear complexes has already been established, and the values of  $K_{OS}$  were found to be not solely based on charge factors.<sup>30,50</sup>

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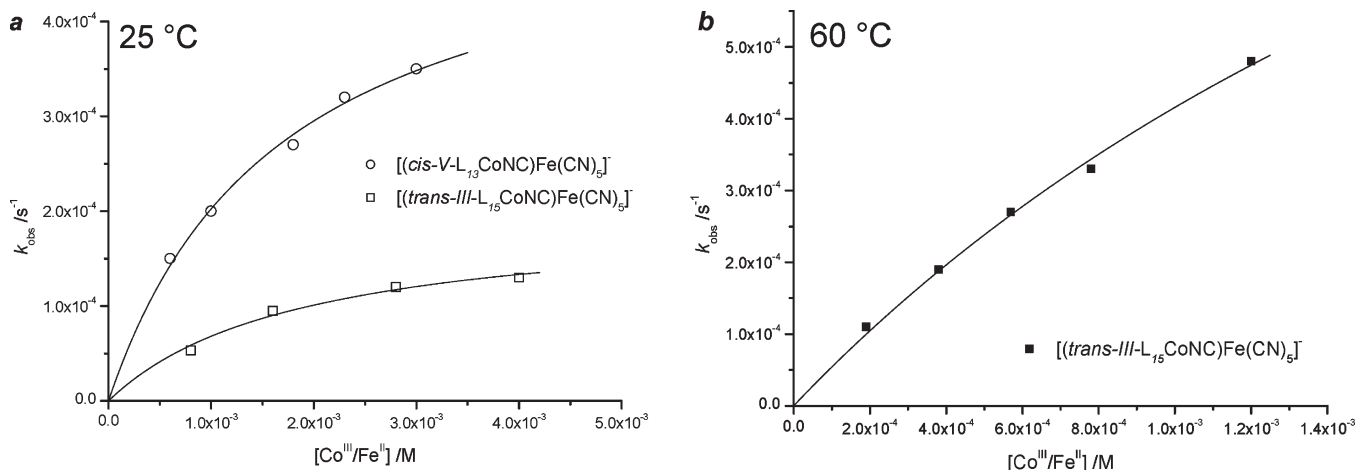
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**Table 2.** Characterization Data for the Mixed-Valence Tetranuclear Complexes<sup>a</sup>

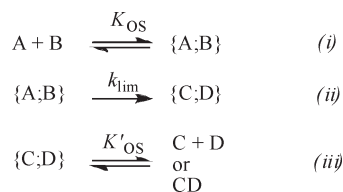
Compound	$\lambda_{\text{MMCT}}/\text{nm}$	$E^\circ(\text{Fe}^{\text{III/II}})/\text{mV}$	$E^\circ(\text{Co}^{\text{III/II}})/\text{mV}$
$[\{\text{L}_{14}\text{Co}^{\text{III}}\text{NC}\}_3\text{Fe}^{\text{II}}(\text{CN})_3]^{5+}$	490	1040	-315
$[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}_2\{\text{trans-III-L}_{14}\text{S}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_3]^{5+ b}$	515	1060	-195, -100
$\text{trans-}[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}\{\text{trans-III-L}_{14}\text{S}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_4]^{2+}$	515	820	-490, -210
$\text{cis-}[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}\{\text{trans-III-L}_{14}\text{S}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_4]^{2+}$	510	845	-510, -240
$\text{trans-}[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}_2\text{Fe}^{\text{II}}(\text{CN})_4]^{2+ 17}$	490	844	-530
$\text{cis-}[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}_2\text{Fe}^{\text{II}}(\text{CN})_4]^{2+ 17}$	475	842	-528
$\text{cis-}[\{\text{trans-III-L}_{14}\text{S}\text{Co}^{\text{III}}\text{NC}\}_2\text{Fe}^{\text{II}}(\text{CN})_4]^{2+ 38}$	547	884	-269
$[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^{-14}$	510	630	-600
$[\{\text{trans-III-L}_{14}\text{S}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^{-14}$	566	640	-350

<sup>a</sup> Relevant data from other tri- and dinuclear complexes of the same family are included for comparison (Table 1). <sup>b</sup> Assigned from the relative intensity of the -195 and -100 mV signals (see the text).



**Figure 3.** Observed pseudo-first-order rate constants for the reaction of (a)  $[\text{Co}^{\text{III}}\text{Cl}(\text{NH}_3)_5]^{2+}$  (pH 5.0, 0.2 M acetate buffer) and (b)  $[\text{Co}^{\text{III}}(\text{OH})(\text{NH}_3)_5]^{2+}$  (pH 9.0, 0.2 M borate buffer) as a function of the concentration of excesses of the  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}$  mixed-valence complexes indicated,  $I = 1.0 \text{ M}$ .

### Scheme 3<sup>a</sup>



<sup>a</sup>  $k_{\text{lim}}$  represents the electron-transfer rate constant or the substitution rate constant. B is the reactant in excess. The final products are C + D or CD, depending on whether the mixed-valence compounds are formed.

In this respect, the substitution process on  $[\text{Co}^{\text{III}}(\text{OH})(\text{NH}_3)_5]^{2+}$  at 60 °C is ca. 1 order of magnitude faster than any of the anation reactions studied on aquapentamminecobalt(III) centers, while the value of  $K_{\text{OS}}$  is 2 orders of magnitude larger.<sup>51,52</sup> This is extremely interesting, given the  $I_d$  mechanism operating for the substitution of pentamminecobalt(III) complexes<sup>53,54</sup> and the Lewis basicity of the hydroxo group. If the high value of  $K_{\text{OS}}$  obtained is accepted to involve an element of molecular

recognition for association,<sup>12,18,30</sup> as indicated above, the value of  $k_{\text{lim}}$  for the substitution process does not have to be related to a simple dissociative interchange mechanism of the hydroxo ligand, so explaining the results obtained for this system.

The kinetics of the processes leading to some of the characterized discrete trinuclear mixed-valence complexes was also monitored; Table 3 collects the relevant data for the reactions studied. In all cases, only 1:1 second-order rate constants could be obtained; the high absorption coefficient of the dinuclear complex<sup>14</sup> prevents its use as a reactant in excess under conditions producing high enough absorbance changes. Similarly, the use of an excess of the mononuclear cobalt complex had to be avoided in order to prevent the formation of complexes of higher nuclearity (see before). Consequently, the possible values of  $K_{\text{OS}}$  for association of the precursor complexes could not be determined.<sup>44</sup>

From the data collected in Table 3, it is clear that an important difference exists between the reaction occurring at low pH (substitutionally inert mononuclear chloro derivatives) and high pH (substitutionally inert mononuclear hydroxo derivatives). From the data determined for the pentammine derivatives, it is clear that only the processes involving the more easily reduced *trans-III*- $[\text{Co}^{\text{III}}\text{ClL}_{14}\text{S}]^{2+}$  complexes occur via the redox-triggered substitution mechanisms indicated in Scheme 1, bottom. The reaction rate constant is too large and the process too simple (Figure 4) for a chloride aquation reaction

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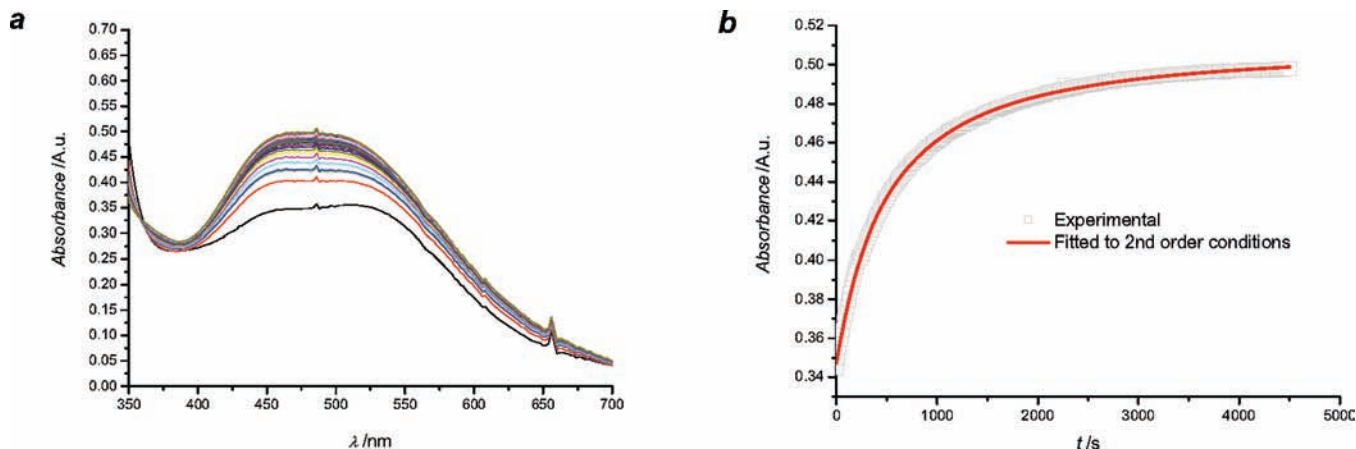
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**Table 3.** Kinetic and Activation Parameters for the Formation of the Trinuclear Mixed-Valence Complexes  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}/\text{Co}^{\text{III}}$  Studied<sup>a</sup>

Reaction of mononuclear complex + dinuclear mixed-valence complex	<i>I</i> /M	<sup>333</sup> <i>k</i> /M <sup>-1</sup> s <sup>-1</sup>	$\Delta H^\ddagger$ /kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ /J K <sup>-1</sup> mol <sup>-1</sup>
<i>trans</i> -I-[CoClL <sub>14</sub> ] <sup>2+</sup> + [{ <i>trans</i> -I-L <sub>14</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	not detected		
<i>trans</i> -III-[CoClL <sub>14S</sub> ] <sup>2+</sup> + [{ <i>trans</i> -I-L <sub>14</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	5.9	97 ± 5	46 ± 8
	1.0	1.5	104 ± 3	55 ± 10 <sup>b</sup>
<i>trans</i> -I-[CoClL <sub>14</sub> ] <sup>2+</sup> + [{ <i>trans</i> -III-L <sub>14S</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	not detected		
<i>trans</i> -III-[CoClL <sub>14S</sub> ] <sup>2+</sup> + [{ <i>trans</i> -III-L <sub>14S</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	5.2	96 ± 6	41 ± 21
	1.0	1.4	105 ± 5	57 ± 17
<i>trans</i> -I-[Co(OH)L <sub>14</sub> ] <sup>2+</sup> + [{ <i>trans</i> -I-L <sub>14</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	0.060	145 ± 8	160 ± 15
<i>trans</i> -II-[Co(OH)L <sub>14S</sub> ] <sup>2+</sup> + [{ <i>trans</i> -I-L <sub>14</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	0.31	138 ± 11	143 ± 30
	1.0	0.18	131 ± 8	120 ± 17
<i>trans</i> -I-[Co(OH)L <sub>14</sub> ] <sup>2+</sup> + [{ <i>trans</i> -III-L <sub>14S</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	0.045	123 ± 11	80 ± 20
<i>trans</i> -II-[Co(OH)L <sub>14S</sub> ] <sup>2+</sup> + [{ <i>trans</i> -III-L <sub>14S</sub> Co <sup>III</sup> NC}Fe <sup>II</sup> (CN) <sub>5</sub> ] <sup>-</sup>	0.2	0.26	124 ± 8	100 ± 24
	1.0	0.16	124 ± 6	97 ± 5

<sup>a</sup> Chloro complexes at pH 5 (0.2 M acetate buffer) and hydroxo complexes at pH 9 (0.2 M borate buffer). <sup>b</sup>  $\Delta V^\ddagger = 38 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$ .



**Figure 4.** (a) Spectral changes observed for the reaction of *trans*-III-[CoClL<sub>14S</sub>]<sup>2+</sup> with [{*trans*-I-L<sub>14</sub>Co<sup>III</sup>NC}Fe<sup>II</sup>(CN)<sub>5</sub>]<sup>-</sup> at *I* = 0.2 M (NaClO<sub>4</sub>) and 60 °C. (b) Extracted absorbance vs time trace at 405 nm showing the *SPECFIT* software fit to second-order conditions under equal  $4 \times 10^{-4}$  M concentrations of the reactants.

followed by an anation by the dinuclear mixed-valence complex.<sup>55</sup> Surprisingly, the values found for the thermal activation parameters are of the same magnitude as those found for the reactions of the same cobalt complexes with [Fe<sup>II</sup>(CN)<sub>6</sub>]<sup>4-</sup>, despite the less favorable redox potential in the present case. However, the activation parameters are derived from the second-order rate constants, and any contribution of the outer-sphere association constant is included in the values. In fact, the overall process becomes enthalpically more favorable at lower ionic strength, as expected,<sup>56</sup> while keeping similar values for  $\Delta S^\ddagger$ , which should have both outer-sphere and electrostriction contributions. In this respect, the value of the  $\Delta V^\ddagger$  determined (*trans*-III-[Co<sup>III</sup>ClL<sub>14S</sub>]<sup>2+</sup> + [{*trans*-I-L<sub>14</sub>Co<sup>III</sup>NC}Fe<sup>II</sup>(CN)<sub>5</sub>]<sup>-</sup> at *I* = 1.0 M) is on the same order as those obtained for the formation of the parent dinuclear complexes, indicating again that the differences expected are probably compensated for between outer-sphere association and electrostriction factors.

At high pH, all of the values found for the reaction rate constants are more than 1 order of magnitude smaller, and the thermal activation parameters are indicative of a large degree of disorder en route to the transition state. In agreement with the preliminary kinetic experiments

carried out on [Co<sup>III</sup>(OH)(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>, the process seems directed by a simple dissociatively activated substitution process of the hydroxo ligand at the mononuclear Co<sup>III</sup> complex by one of the cyanide N atoms of the dinuclear mixed-valence complex. Taking into account that the outer-sphere association constant has been determined as 340 M<sup>-1</sup> for the similar pentaammine system, the values of *k* appear in the 10<sup>-4</sup> s<sup>-1</sup> region, as expected for substitution on a [Co<sup>III</sup>X(RNH<sub>2</sub>)<sub>5</sub>]<sup>2+</sup> center. The trend found for the substitution rate constants agrees very well with the strength of the Co<sup>III</sup>-OH bond, expected to be weaker for complexes with the ligand having a better donor character, i.e., L<sub>14S</sub>.<sup>13</sup> The values found for the enthalpy of activation agree with the dissociation of a hydroxo ligand under these conditions. The activation entropies are extraordinarily large and, in contrast to the reactions carried out on the chloro derivatives, none of the parameters indicated in Table 3 are affected significantly by the ionic strength of the medium. Considering that the solvent and medium effects on *K*<sub>OS</sub> have to be included in these two observations, it is clear,<sup>47</sup> as seen for the reaction with [Co<sup>III</sup>(OH)(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>, that the outer-sphere association is important with consequent liberation of solvent, while electrostriction is at its minimum, given the lack of charge transfer in the process.

Finally, under these reaction conditions, long times and high temperatures, secondary processes are observed

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for systems where the  $\{\text{Co}^{\text{III}}\text{L}_{14\text{S}}\}$  building block is present. As indicated in the previous section, the trinuclear complexes with this unit seem to show a certain instability from the kinetically formed isomeric mixture. Light excitation of these complexes over long times leads to photochemical decomposition of their component units, and these react further until the thermodynamically stable isomeric mixture is achieved. The detection of mixtures of  $[\text{Co}^{\text{III}}\text{L}_{14\text{S}}(\text{OH}_2)]^{3+}$ ,  $[\text{Co}^{\text{III}}\text{L}_{14}(\text{OH}_2)]^{3+}$ ,  $[\{\text{L}_{14\text{S}}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$ , and  $[\{\text{L}_{14}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_5]^-$  (plus putative  $[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}_2\{\text{trans-III-L}_{14\text{S}}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_4]^{5+}$ ) in aged solutions of *cis*- $[\{\text{trans-}I\text{-L}_{14}\text{Co}^{\text{III}}\text{NC}\}\{\text{trans-III-L}_{14\text{S}}\text{Co}^{\text{III}}\text{NC}\}\text{Fe}^{\text{II}}(\text{CN})_4]^{2+}$  (see above) corroborates this reactivity not detected in other complexes of this family.

### Conclusions

The reactivity for the formation of mixed-valence cyano-bridged  $\text{Co}^{\text{III}}/\text{Fe}^{\text{II}}$  complexes of nuclearities higher than 2 has been found to be very finely tuned between a redox- and a substitution-driven mechanism of the sixth ligand in the mononuclear macrocycle-encapsulated  $\text{Co}^{\text{III}}$  building blocks. For the more redox-accessible chloro derivatives of the  $\text{Co}^{\text{III}}$  building blocks, only the already established redox-driven mechanism has been found to be operative for the formation of trinuclear complexes, while for the hydroxo derivatives of the same building blocks, the process has been found to be substitutionally driven. Even though the reactivity behavior could also be initially associated with simple redox potential factors (Table S2 in the Supporting Information), a careful analysis on nonencapsulated  $[\text{Co}^{\text{III}}\text{X}(\text{NH}_3)_5]^{2+}$  complexes

clearly indicates the preferred substitution reactivity of the hydroxo derivatives. As a whole, the processes indicated in Scheme 1 seem to be directed by an outer-sphere complex capable of tuning the process by either overriding the redox potential influence, in the case of some of the chloro derivatives, or following the substitution process expected from a redox-inactive system.

Nevertheless, the observed reactivities leading to complexes with even higher reactivities are not directed by the substitutionally driven mechanism. The formation of  $\text{Co}^{\text{II}}$  complexes capable of reacting with mixed-valence complexes of lower nuclearity is needed in all cases. This  $\{\text{Co}^{\text{II}}\text{L}\}$  species has been found to be produced by partial decomposition of the parent building blocks, as found in previously studied electrochemical processes. The improvement of the reaction conditions for the formation of these compounds with higher nuclearities will be studied consequently.

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**Supporting Information Available:** Values of  $k_{\text{obs}}$  determined in this work, reaction potentials for the processes studied,  $^{13}\text{C}$  NMR spectrum of the new asymmetric complexes prepared, UV-vis spectra and electrochemical experiments of the tetranuclear  $5+$  species observed, and UV-vis spectral changes for one of the reactions studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.