Inorg. Chem. 2006, 45, 74–82

Inorganic Chemistry Article

Dinuclear Cyano-Bridged Co^{III}–Fe^{II} Complexes as Precursors for Molecular Mixed-Valence Complexes of Higher Nuclearity

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Received July 11, 2005

The preparation and characterization of a series of trinuclear mixed-valence cyano-bridged Co^{III}–Fe^{II}–Co^{III} compounds derived from known dinuclear $[\{L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ complexes ($L_n = N_5$ or N_3S_2 *n*-membered pendant amine macrocycle) are presented. All of the new trinuclear complexes were fully characterized spectroscopically (UV–vis, IR, and ^{13}C NMR). Complexes exhibiting a trans and cis arrangement of the Co–Fe–Co units around the $[Fe(CN)_6]^{4-}$ center are described (i.e., *cis/trans*-$[\{L_nCo^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$), and some of their structures are determined by X-ray crystallography. Electrochemical experiments revealed an expected anodic shift of the $Fe^{III/II}$ redox potential upon addition of a tripositively charged $\{Co^{III}L_n\}$ moiety. The $Co^{III/II}$ redox potentials do not change greatly from the di- to the trinuclear complex, but rather behave in a fully independent and noncooperative way. In this respect, the energies and extinction coefficients of the MMCT bands agree with the formal existence of two mixed-valence Fe^{II}–CN–Co^{III} units per molecule. Solvatochromic experiments also indicated that the MMCT band of these compounds behaves as expected for a class II mixed-valence complex. Nevertheless, its extinction coefficient is dramatically increased upon increasing the solvent donor number.

Introduction

The polymeric cyano-bridged complex Prussian Blue (iron(III) hexacyanoferrate(II)) is the oldest known example of a mixed-valence complex. Many mixed-metal analogues of this compound have been studied featuring a similar M−CN−M′−NC structural core that propagates in all three dimensions.[1,2] In addition to their use as electrochromic materials,[3,4] certain Prussian Blue analogues have shown extraordinary magnetic properties that are activated by excitation of their metal-to-metal charge transfer (MMCT) transition.[5−7] The electronic configuration of these complexes has been found to be a crucial determinant of their physical properties.[8−10] These are intimately related to their structures, and careful control of preparative procedures seems to be a crucial element in obtaining complexes with the desired structural and physical properties.[11,12] The study of the electronic properties of this type of complex is important from a fundamental standpoint, given the fact that it adds to our understanding of electronic delocalization within mod-

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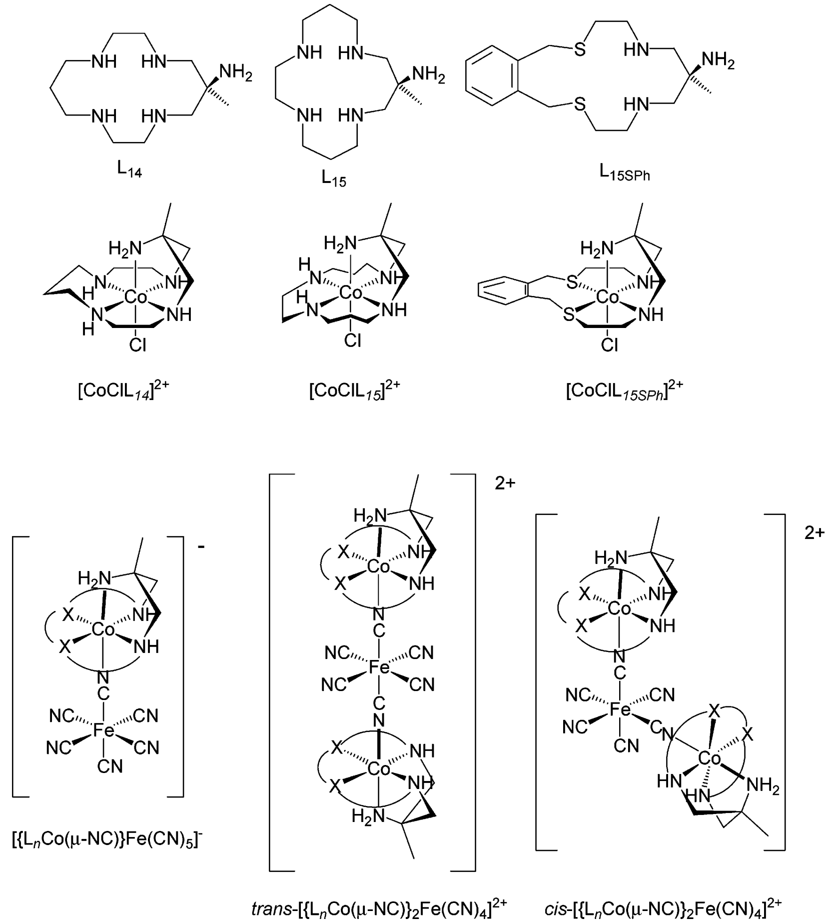
10.1021/ic0511423 CCC: $33.50

Published on Web 12/08/2005

Chart 1



erately coupled class II mixed-valence metal complexes.[13−15] The study of their redox properties can also assess their use as multielectron donors and acceptors.[9,15,16]

In recent years, we have investigated a number of discrete dinuclear cyano-bridged mixed-valence compounds, and we have been successful in tuning the energy of the (visible) MMCT transition through deliberate structural changes made at each metal center.[17−22] These complexes comprise $\{Fe^{II}(CN)_6\}^{4-}$ or $\{Ru^{II}(CN)_6\}^{4-}$ moieties bound as monodentate ligands (through a single bridging cyano ligand) to the Co^{III} complexes of known pentadentate macrocyclic ligands (see Chart 1).[23−26] When coupled with hexacyanometalate(II) ions, the resulting dinuclear complexes exhibit different MMCT transition energies. These can be explained on the basis of the macrocyclic ring size (13, 14, or 15), the donor atoms (N_5 or N_3S_2), and the conformation of the macrocyclic ring (either planar (trans) or folded (cis)).

During the electrochemical characterization of these complexes, partial decomposition to $[Fe^{II}(CN)_6]^{4-}$ and presumed trinuclear Co^{III}−Fe^{II}−Co^{III} compounds has been observed.[20,27] The process is associated with the reduction of the Co^{III} macrocyclic center (during the cathodic voltammetric sweep). This creates a labile Co^{II} species that dissociates from its ferrocyanide partner; it then associates with one of the five terminal cyano ligands of a {L$_n$Co−NC−Fe(CN)$_5$} dinuclear complex, forming a trinuclear Co−NC−Fe−CN−Co species. Equilibrium between trinuclear, dinuclear, and mononuclear complexes is established within the diffusion layer, as the successive sweeps upon repeated cyclic voltammetry are identical. This reaction is paralleled

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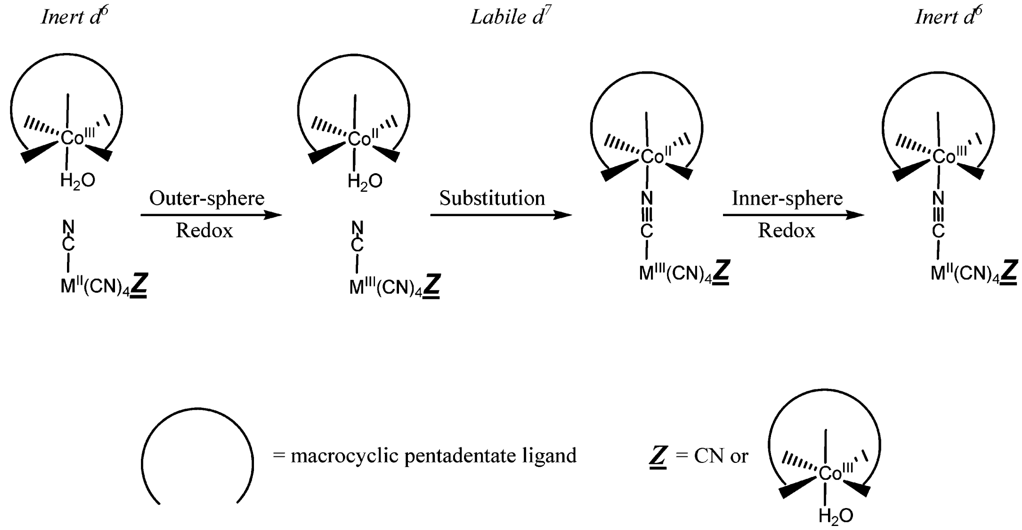
Scheme 1



by a redox process on the Co center, the mechanism by which the corresponding dinuclear complexes are formed in the first place.[28]

We present herein the preparation and characterization of a new series of symmetrical trinuclear mixed-valence Co^{III}_2-Fe^{II} complexes derived from the analogous dinuclear Co^{III}−Fe^{II} compounds of the type indicated in Chart 1. Interestingly, complexes derived from trans (coaxial) or cis (equatorial) attachment of a $\{CoL_n\}$ moiety to $[\{L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ precursor were obtained in some cases, representing a novel example of geometric isomerism. Electrochemistry and optical spectroscopy studies have been undertaken with these trinuclear complexes, and the results are compared with data obtained for their dinuclear precursor analogues.

Results and Discussion

Synthesis and Characterization. A number of new trinuclear $[\{L_nCo^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ complexes have been prepared. For comparison, an isoelectronic $[\{L_nCo^{III}(\mu\text{-NC})\}_2Co^{III}(CN)_4]^{3+}$ analogue was also prepared. In all cases, the macrocyclic ligand is coordinated in a trans configuration, with the four secondary donors coplanar and the bridging cyano ligand trans to the pendant amine (Chart I). However, novel isomeric forms of the trinuclear complexes were isolated that differed in the relative disposition of the two $\{Co^{III}L_n\}$ moieties. Specifically, the compounds prepared were *cis*-$[\{L_{14}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$, *trans*-$[\{L_{14}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$, *cis*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$, *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$, and *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ where the cis/trans nomenclature refers to the relative position of the two $\{CoL_n\}$ moieties around the Fe coordination sphere. These complexes have been formed via the outer-sphere redox reaction[28] between $[Co^{III}L_nCl]^{2+}$ and $[\{L_nCo^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$.[27] The redox-catalyzed reactions leading to the trinuclear Co^{III}−Fe^{II}−Co^{III} systems have the same origin as those leading to the formation of the starting dinuclear precursors, which indicates the versatility of the mechanistically designed preparative procedure for these mixed-valence species (Scheme 1).[27,28]

It can be seen that this redox-catalyzed mechanism could, potentially, occur sequentially, generating complexes of increasingly higher nuclearity. A likely exception is the tricobalt complex *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Co^{III}(CN)_4]^{3+}$. This complex was formed directly by reacting 2 equiv of the macrocyclic complex with 1 equiv of hexacyanocobaltate(III). Unlike the complexes containing a ferrocyanide group, the precursors *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}Co^{III}(CN)_5]$ and $[Co(CN)_6]^{3-}$ cannot act as reductants, and therefore the only possible mechanism by which *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Co^{III}(CN)_4]^{3+}$ can be formed is base-catalyzed ligand substitution by an incoming N-bound cyano ligand on the inert $[Co^{III}L_{15}(OH_2)]^{3+}$ complex.

The relative amounts of cis and trans {Co−NC−Fe−CN−Co} isomers obtained in this work merit some discussion. These isomers are obtained in essentially equal quantities during the preparative processes involving the $\{CoL_{14}\}$ and $\{CoL_{15}\}$ moieties. There is a statistical factor of 4 favoring formation of the *cis*-Co_2Fe complex over the *trans*-Co_2Fe isomer, but this is counterbalanced by the steric hindrance associated with two $\{CoL_n\}$ moieties being placed in adjacent positions about the Fe coordination sphere. We have not observed any cis-to-trans isomerization under the preparative conditions used, and the two pairs of isolated *cis*- and *trans*-Co_2Fe isomers appear to be noninterconvertible. In this respect, the presence of only the trans isomeric form of $[\{L_{15SPh}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ is revealing and, given the larger size of the $\{Co^{III}L_{15SPh}\}$ unit, suggests that this selectivity is steric in origin. Furthermore, recent DFT calculations on the dinuclear complexes indicate that the cyanide nitrogen attached in the trans position to the cobalt center carries the larger electron density, thus also favoring the formation of the trans isomer of the trinuclear complex for electronic reasons.[29]

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The mononuclear $[Co^{III}L_nCl]^{2+}$ building blocks have been described with different N-based geometric isomers, their relative stability being determined both by the size of the macrocyclic ring and by the nature of the ligand in the sixth coordination site of the Co^{III} center.[20,23,24,30,31] The so-called *trans*-I(RSRS) form for complexes $[CoL_{14}Cl]^{2+}$ is dominant (all secondary amine H-atoms on the same side of the macrocycle), whereas the *trans*-II(RSRR) (three up, one down) and *trans*-III(RSSR) (two up and two down) forms are more common, but not exclusive, for $[CoL_{15}Cl]^{3+}$. The fact that the latter complex has been structurally characterized in various N-based isomeric forms is consistent with our observation of multiple isomeric forms of both *trans*- and *cis*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ in solution and in the solid state. A study on the stability of the different isomeric forms of the mononuclear Co complexes and their pH-dependent interconversion is currently underway, indicating that on intensive workup or on long standing all these species convert to a unique thermodynamically stable form.[32] In this respect, all final trinuclear complexes crystallized and studied in this work have been found to be isomerically pure species. For the L_{15} complexes, the *trans*-III(RSSR) form is the only one present in all cases, as proved by X-ray crystal analysis and a comparison of the ^{13}C NMR spectrum with that of the equivalent dinuclear characterized complex.[31] For L_{14} complexes, the uniqueness of the *trans*-I(RSRS) isomeric form is proved by the comparison of the signal of the ^{13}C NMR spectrum with those of the known dinuclear parent complexes.[18] Finally, for the L_{15SPh} trinuclear complex, only one set of signals in the ^{13}C NMR spectrum is evident, indicating that only a single isomeric form is present in the prepared complex and corresponding to a fully symmetrical trans form.

The trinuclear complexes all show spectroscopic characteristics similar to those of their dinuclear precursors. In particular, although the IR cyano stretching bands were found to be sensitive to the isomeric form of the complex[21] (see Experimental Section), the ^{13}C NMR spectra in the 170−200 ppm (CN) region provided the best indication of the isomeric form of the Co_2Fe complex. To a first approximation, ignoring the local symmetry of each $\{CoL_n\}$ moiety, the *trans*-Co_2Fe complexes have effective D_{4h} symmetry, and exhibit two distinct ^{13}C cyanide resonances (terminal and bridging). In contrast, the *cis*-Co_2Fe complexes have 2-fold rotational symmetry; three ^{13}C cyanide resonances (bridging, trans to bridging CN, and mutually trans) are anticipated, and are indeed found. The signals corresponding to bridging CN are always found at 190−195 ppm, whereas the groups having a terminal arrangement appear in the 170−180 ppm region, with a clear differentiation between those being trans or cis to the μ-CN group.

Crystallography. The crystal structure of *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ is shown in Figure 1. The complex has no crystallographically imposed symmetry, but the

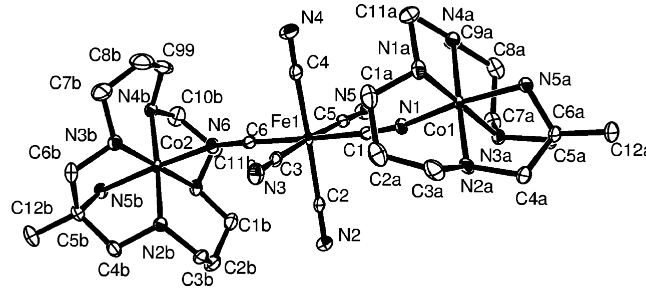

Figure 1. ORTEP drawing of *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ (30% probability level ellipsoids, H-atoms omitted). Selected bond lengths (Å): Fe(1)−C(1) 1.894(4); Fe(1)−C(2) 1.925(5); Fe(1)−C(3) 1.908(5); Fe(1)−C(4) 1.917(5); Fe(1)−C(5) 1.928(5); Fe(1)−C(6) 1.894(4); Co(1)−N(1) 1.889(3); Co(1)−N(1A−5A) 1.955(3)−1.971(4); Co(2)−N(6) 1.899(4); Co(2)−(N1B−N5B) 1.937(3)−1.987(4).

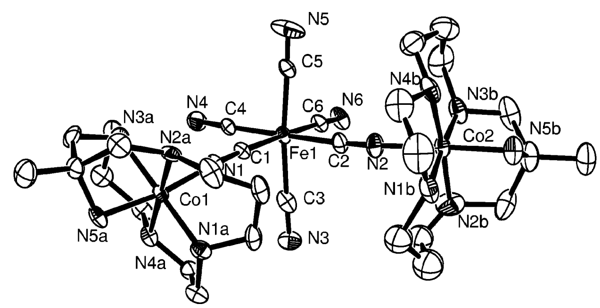

Figure 2. ORTEP drawing of *cis*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ (30% probability level ellipsoids, H-atoms omitted). Selected bond lengths (Å): Fe(1)−C(1) 1.90(1); Fe(1)−C(2) 1.88(2); Fe(1)−C(3) 1.94(2); Fe(1)−C(4) 1.92(2); Fe(1)−C(5) 1.93(1); Fe(1)−C(6) 1.90(1); Co(1)−N(1) 1.91(1); Co(1)−N(1A−5A) 1.95(1)−1.98(1); Co(2)−N(2) 1.91(1); Co(2)−N(1B−5B) 1.92(1)−1.99(1).

coordinate bond lengths and angles about the two Co centers are essentially the same. Each $\{CoL_{15}\}$ unit exhibits a *trans*-III N-based configurationally isomeric form, as that shown for the mononuclear precursor in the chart. An interesting feature that emerges from this high-resolution structure is the fact that the Fe−CN coordinate bonds are sensitive to whether the CN ligand is terminal or bridging. The two independent bridging Fe−CN coordinate bonds are significantly shorter than those of the four terminally coordinated cyano ligands. Apart from this feature, the coordinate bonds are as expected for the ferrocyanide[33] and pentaaminecobalt(III)[34] moieties. The bridging cyano ligands also form the shortest bonds to each Co center, as seen previously in all structurally characterized dinuclear analogues.[18,20,21]

The crystal structure of the isomer *cis*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4](ClO_4)_2\cdot 9H_2O$ was also determined (Figure 2). The precision of the structure was not as high as that of the trans isomer, so no meaningful comparisons between the bond lengths of the trans and cis isomeric forms of the complex can be made. All molecules are on general sites, and there is disorder in one of the perchlorate anions and in two of the nine water molecules in the asymmetric unit; also, a six-membered chelate ring bound to Co(2) is disordered between a chair and twist-boat conformation. The N-based isomeric form of each Co moiety is again *trans*-III. Although the

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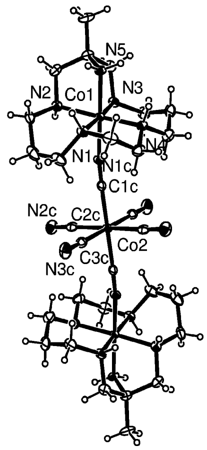

Figure 3. ORTEP drawing of one of the independent cations *trans*-[{L_{15}-Co^{III}(μ-NC)}$_2$$Co^{III}$$(CN)_4$]$^{3+}$ (30% probability level ellipsoids, H-atoms omitted). Selected bond lengths (Å): Co(2)−C(1C) 1.861(7); Co(2)−C(2C) 1.916(8); Co(2)−C(3C) 1.905(8); Co(1)−N(1C) 1.899(6); Co(1)−N(2−5) 1.934(5)−1.978(5).

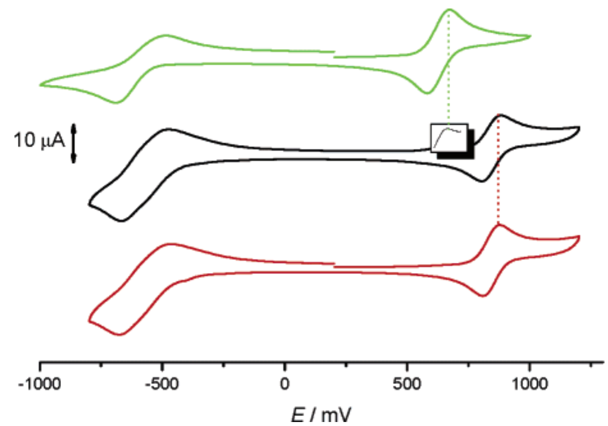

Figure 4. Cyclic voltammograms of *trans*-[{$Co^{III}L_{14}$(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]$^-$ (first cycle, bottom), *trans*-[{$Co^{III}L_{14}$(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]$^-$ (second cycle, center), and [{$Co^{III}L_{14}$(μ-NC)}$Fe^{II}$$(CN)_5$]$^{2+}$ (top). Glassy carbon working electrode, NHE reference, 1.0 M $NaClO_4$, 25 °C.

coordinate angles around the Fe atom deviate significantly from an ideal octahedral geometry, similar angular distortions were seen in the crystal structure of *trans*-[{$L_{15}Co^{III}$(μ-NC)}$_2$-$Fe^{II}$$(CN)_4$]$^{2+}$. Thus steric repulsion between the two adjacent {CoL_{15}} groups in *cis*-[{$L_{15}Co^{III}$(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]$^{2+}$ cannot be solely responsible for the angular distortions seen in this structure. In earlier papers, we have noted that angular distortions, particularly about the hexacyanometalate group, are most likely associated with packing forces rather than with any intrinsic electronic or steric effects within the mixed-valence complex.[21]

The crystal structure of the isoelectronic analogue *trans*-[{$L_{15}Co^{III}$(μ-NC)}$_2$$Co^{III}$$(CN)_4$]$Cl_3$·7$H_2O$ has also been determined. The structure comprises two independent complex cations each on a center of symmetry. There are no obvious differences between the two complex cations. Once again a significant (ca. 0.04 Å) shortening of the bridging Co−CN coordinate bonds, relative to the terminal Co−CN bonds, is a feature of this high-resolution crystal structure. As expected, the Co−CN bonds are somewhat shorter than the corresponding Fe−CN bonds as a consequence of the higher oxidation state of the cobalt ion. The coordinate bonds in the macrocyclic {CoL_{15}} moiety match those found in the analogue *trans*-[{$L_{15}Co^{III}$(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]$^{2+}$.

Electrochemistry. Trinuclear complexes of the type isolated here have been proposed to be present during the electrochemistry of their dinuclear precursors.[20] For example, in the cyclic voltammetry of [{$L_{14}Co^{III}$(μ-NC)}$Fe^{II}$$(CN)_5$]$^-$ (which exhibits an $Fe^{III/II}$ potential of ca. 600 mV vs NHE), a higher-potential $Fe^{III/II}$ redox couple at ca. 800 mV emerges after the first complete cycle in addition to a wave of equal intensity at ca. 400 mV, which is characteristic of the [$Fe(CN)_6$]$^{3-/4-}$ couple. The highest-potential couple was assigned to a trinuclear complex, although the isomeric form could not be assigned. The reverse of this di/trinuclear equilibrium feature is also observed in the cyclic voltammetry of the trinuclear complexes (Figure 4, center and bottom) isolated here. Upon repeated cycling, an $Fe^{III/II}$ wave corresponding to the dinuclear analogue appears in the voltammograms, indicating that an equilibrium between di- and trinuclear complexes is established. On the basis of the results reported here (Table 1), the electrochemical properties of *trans*- and *cis*-[{$L_{15}Co^{III}$(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]$^{2+}$ cannot be differentiated, so it is possible that the putative trinuclear complexes formed in the electrochemistry of the dinuclear analogues reported previously[18,20,21] are cis/trans isomeric mixtures.

Table 1. Redox Potentials (vs NHE) of the Two Metal Centers in the Di- and Trinuclear Mixed-Valence Complexes Studied As Determined by Cyclic Voltammetry (1.0 M $NaClO_4$, 25 °C)

complex	E^0 (mV) $Fe^{III/II}$	$Co^{III/II}$	ref
[$Fe^{II}(CN)_6$]$^{4-}$	420		40
trans-[$Co^{III}(OH)L_{14}$]$^{2+}$		−200	20
[{$Co^{III}L_{14}$(μ-NC)}$Fe^{II}(CN)_5$]$^-$	630	−595	20
cis-[{$Co^{III}L_{14}$(μ-NC)}$_2$$Fe^{II}(CN)_4$]$^{2+}$	842	−528	this work
trans-[{$Co^{III}L_{14}$(μ-NC)}$_2$$Fe^{II}(CN)_4$]$^{2+}$	844	−530	this work
[{$Co^{III}L_{15}$(μ-NC)}$Fe^{II}(CN)_5$]$^-$	600	−580	18
cis-[{$Co^{III}L_{15}$(μ-NC)}$_2$$Fe^{II}(CN)_4$]$^{2+}$	790	−530	this work
trans-[{$Co^{III}L_{15}$(μ-NC)}$_2$$Fe^{II}(CN)_4$]$^{2+}$	804	−533	this work
trans-[{$Co^{III}L_{15SPh}$(μ-NC)}$_2$$Fe^{II}(CN)_4$]$^{2+}$	871	−190	this work
trans-[{$Co^{III}L_{15}$(μ-NC)}$_2$$Co^{III}(CN)_4$]$^{3+}$		−376	this work

In contrast to the electrochemistry of the dinuclear [{L_n-Co^{III}(μ-NC)}$Fe^{II}$$(CN)_5$]$^-$ complexes (where complexes of higher nuclearity, i.e., trinuclear, were formed), no tetranuclear complexes were identified in the voltammetry of the prepared trinuclear [{L_nCo^{III}(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]$^{2+}$ analogues. The formation of these trinuclear complexes occurred in the diffusion layer of the electrochemical experiment because of the dissociation of the labile {$Co^{II}L_n$}$^{2+}$ unit from the electrochemically generated reduced dinuclear [{L_nCo^{II}(μ-NC)}$Fe^{II}$$(CN)_5$]$^{2-}$ complex. Further reaction of the putative [$Co^{II}L_n(OH_2)$]$^{2+}$ (or five-coordinate analogues) with some undissociated reduced dinuclear complex produces the final fully reduced neutral trinuclear [{L_nCo^{II}(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]^0 compound. For the formation of tetranuclear $Co_3^{III}Fe^{II}$ complexes of general formula [{L_nCo^{III}(μ-NC)}$_3$$Fe^{II}$$(CN)_4$]$^{5+}$, a reaction has to occur between an electrochemically generated neutral trinuclear [{L_nCo^{II}(μ-NC)}$_2$$Fe^{II}$$(CN)_4$]^0 complex and some dissociated [$Co^{II}L_n(H_2O)$]$^{2+}$, but this is not observed. Electrostatics is probably a plausible cause of this lack of reactivity. The approach of two units of [2+]

and [0] charge is unassisted by electrostatic attraction, in contrast to the association of [2+] and [2−] moieties in the electrochemical generation of Co_2Fe complexes from $[LCo^{II}Fe^{II}]^{2-}$ and $[CoL]^{2+}$ precursors. Steric congestion around the iron center may also be related to this lack of reactivity.

In all cases, even with the use of high-resolution techniques such as square-wave and differential-pulse voltammetry, the two $Co^{III/II}$ couples of the trinuclear complex could not be resolved. Attachment of each tripositively charged $\{CoL_n\}$ unit to ferrocyanide produces a successive ca. +200 mV shift in the $Fe^{III/II}$ redox potential. However, there is a more modest increase of ca. 60 mV on the $Co^{III/II}$ redox potential(s) upon introduction of an additional $\{CoL_n\}$ group to the dinuclear parent. The redox potentials of *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ merit special mention. Although the $Fe^{III/II}$ potential is similar to those found in the trinuclear analogues bearing $\{CoL_{14}\}$ and $\{CoL_{15}\}$ moieties, the $Co^{III/II}$ potentials of *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ are anodically shifted by 350 mV relative to the other compounds, and are essentially the same as those of the aqua complexes of pentaamine precursors $[CoL_n(OH_2)]^{3+}$. These differences are consistent with that observed previously going from $[\{L_{14}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ (bearing a CoN_6 coordination sphere) to $[\{L_{14S}Co^{III}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$ (with a CoN_4S_2 coordination sphere), where the S-donors stabilize the Co^{II} oxidation state relative to the amino N-donors.[35] Finally, the tricobalt complex *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Co^{III}(CN)_4]^{3+}$ exhibits a single $Co^{III/II}$ couple from the peripheral $\{CoL_{15}\}$ moieties at ca. 200 mV more positive than *trans*- and *cis*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$. Cyclic voltammetry found this response to be totally irreversible at slow scan rates (<100 mV s^{-1}) but quasi-reversible at fast scan rates (>1000 mV s^{-1}). This behavior is typical of an irreversible chemical reaction (in this case dissociation) following reduction of the complex. The anodic shift in the $\{Co^{III/II}L_{15}\}$ potential is a consequence of the less-negative charge of the central $\{Co(CN)_6{}^{3-}\}$ unit facilitating the reduction of the attached macrocyclic cobalt ions. No redox response from the $\{Co(CN)_6{}^{3-}\}$ moiety was obtained within the potential window set by aqueous solution.

Spectroscopy. The visible absorption spectrum changes upon oxidation with $S_2O_8{}^{2-}$ of *trans*-$[\{L_{15SPh}Co^{III}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ are shown in Figure 5. The more prominent maximum at ca. 550 nm vanishes. In analogy to our previous work, this feature is indicative of oxidation of the ferrocyanide group, which is accompanied by a loss of the MMCT transition.[18,20,21] The maximum that remains around 460 nm is due to the macrocyclic Co^{III} chromophore, and is unaffected by the Fe-centered oxidation reaction. Further evidence in support of this assignment comes from the relatively simple spectrum of the tricobalt complex *trans*-$[\{L_{15}Co^{III}(\mu\text{-NC})\}_2Co^{III}(CN)_4]^{3+}$, which is devoid of any bands at wavelengths longer than 470 nm, i.e., no MMCT transitions are present in this complex.

The energies of the MMCT transitions for all of the new trinuclear complexes and other relevant analogues are collected in Table 2. Although the MMCT band maximum appears as the most intense band in each spectrum, it partially overlaps with other d−d maxima anticipated to emerge from the $\{Co^{III}N_6\}$ and $\{Fe^{II}(CN)_6\}$ chromophores. Nevertheless, we can take the apparent MMCT maximum as a good estimate of the energy of the transition without resorting to spectral deconvolution methods. Application of eq 1

$$E_{op} = \Delta G^0 + \lambda \qquad (1)$$

leads to reorganizational energy λ, which is also collected in Table 2.[36,37] ΔG^0 is taken from the difference between the redox potentials of the two couples (i.e., $Co^{III}{}_2Fe^{II}$ vs $Co^{II}{}_2Fe^{III}$), expressed in cm^{-1}. Hush theory, in its simplest form, describes a single donor−acceptor pair; in our case, the independence of the two Co^{III} centers indicated in the voltammetry experiments enables the trinuclear mixed-valence complexes to be treated similarly.

It is evident that there is little variation in the reorganizational energies λ across this series (Table 2). In other words, the only significant variable affecting E_{op} is the difference between the $Co^{III/II}$ and $Fe^{III/II}$ redox potentials (ΔG^0). Only the Fe center feels the full force of the introduction of an additional tripositive center, producing a positive shift that results in an increased separation between the two couples of about 150 mV. This equates to a hipsochromic shift of ca. 1200 cm^{-1} in the MMCT energy

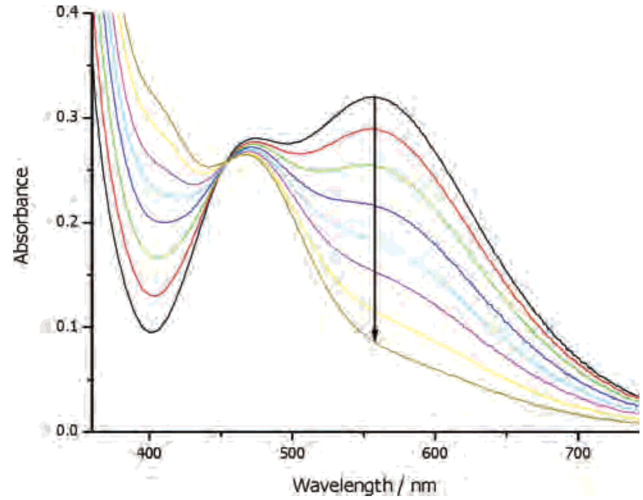

Figure 5. UV−vis spectral changes obtained during ca. 2 h for the MMCT band of the complex *trans*-$[\{Co^{III}L_{15SPh}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ (ca. 3 × 10^{-4} M) on addition of $Na_2S_2O_8$ in 0.01 M $HClO_4$ at 25 °C.

Table 2. Metal-to-Metal Charge Transfer Band Energies for the Series of Complexes Studied in Aqueous Solution in the 3−6 × 10^{-4} M Region

complex	E_{op} (cm^{-1}) (ϵ (M^{-1} cm^{-1}))	λ (cm^{-1})	ref
$[\{Co^{III}L_{14}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$	19 600 (610)	9800	20
cis-$[\{Co^{III}L_{14}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$	20 100 (1060)	9200	this work
trans-$[\{Co^{III}L_{14}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$	20 400 (950)	9500	this work
$[\{Co^{III}L_{15}(\mu\text{-NC})\}Fe^{II}(CN)_5]^-$	18 400 (420)	9000	18
cis-$[\{Co^{III}L_{15}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$	19 500 (950)	8600	this work
trans-$[\{Co^{III}L_{15}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$	19 500 (930)	8800	this work
trans-$[\{Co^{III}L_{15SPh}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$	18 100 (1010)	9600	this work

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Table 3. MMCT Data for the Complex *trans*-$[\{Co^{III}L_{14}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ in Different Solvents (25 °C, [complex] in the $1-3 \times 10^{-4}$ M region)

solvent	E_{op} (cm^{-1})	ϵ (M^{-1} cm^{-1})
H_2O	20 400	950
MeOH	19 100	1700
DMF	18 200	2800
DMSO	17 100	3900

(from di- to trinuclear complex) according to Hush theory; the experimental data in Table 2 concur with this prediction. The intensity of the MMCT band for the trinuclear complexes is approximately double that seen for the dinuclear complexes. In other words, the extinction coefficients report on the effective concentration of $\{Co^{III}-NC-Fe^{II}\}$ chromophores within the complex. It is interesting to note that the existence of up to six units should be, in principle, possible for these type of compounds, which would make them attractive targets for electrochromic applications.[38,39]

Table 3 collects the differences observed for the energy and intensity of the MMCT band for the *trans*-$[\{Co^{III}L_{14}(\mu\text{-NC})\}_2Fe^{II}(CN)_4]^{2+}$ species in different solvents and at low concentrations to avoid undesirable ionic-strength effects. The trend of the MMCT energy is in excellent agreement with the predicted shift (Figure S1a) because of changes in the static and optical dielectric constants of the solvent for a MMCT band. That is, the class II Robin−Day mixed-valence complex character is reinforced, and only the solvent-related reorganizational energy is affected.[40,41] As for the differences in value of the extinction coefficient, those are extremely important. The application of eq 2, and taking into account that $\lambda_{max} = (\Delta\nu_{1/2})^2/2295$ at 298 K, produces very large changes in the values of the electronic coupling term, H_{ab}.[42]

$$H_{ab} \propto \{\epsilon_{max}\lambda_{max}\Delta\nu_{1/2}\}^{1/2} \quad (2)$$

This is surprising, taking into account that only solvent external effects have to be considered, and that changes in the electronic coupling matrix element are related to internal coupling. The trend, on the other hand, is related directly to donor solvent numbers and inversely to Reichardt's acceptor strength.[41,43] That is, the greater the interaction of the solvent with the amine protons of the cobalt environment, the larger the degree of coupling between the Co^{III} and Fe^{II} centers. This is in line with that found for related studies in dinuclear complexes, where the importance of ion-pairing vs ionic cloud[44] and specific nonpolar interactions[22] has been investigated. Furthermore, specific interactions between the complexes and solvents have also been established in their redox and substitution reactivity.[17,19,30,45]

Conclusions

The use of dinuclear cyano-bridged $Co^{III}-Fe^{II}$ complexes as precursors for mixed-valence compounds of higher nuclearity has been demonstrated. Interestingly, all the redox centers behave electrochemically in a fully independent way. Furthermore, an additive effect in the MMCT extinction coefficients is observed. The solvatochromism of these charge transfer bands is remarkable. Not only is the expected shift in the MMCT energy observed as a function of the solvent but the intensity of the transition is also affected; we are not aware of such an effect being reported previously. These results pave the way for the preparation of complexes with dissimilar terminal electron acceptor groups that should exhibit distinct MMCT transitions from a common ferrocyanide donor core. Studies of the outer-sphere redox processes leading to the fully oxidized species, which in turn have proven to be active in water oxidation, are also currently under way.

Experimental Section

Physical Methods. All NMR spectra were recorded at the facilities of the Serveis Científico Tècnics de la Universitat de Barcelona on a Varian Mercury-400 (^{1}H, ^{13}C 100.6 MHz) spectrometer in D_2O and using the sodium salt of deuterated trimethylsilylpropionate as an internal standard. IR spectra were recorded on a Nicolet 520 FT-IR instrument. Characterization UV−vis spectra were recorded on an HP8452A instrument at a concentration of ca. 5×10^{-4} M in water. Electrochemical experiments were carried out with an EG&G PAR 263A instrument with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode; solutions were degassed prior to the cyclic (100 mV s^{-1}), square-wave (25 mV s^{-1}), or differential-pulse (60 mV pulse) voltammetry experiments. The values given for the potential are always corrected to those referred to the NHE electrode. Characterization voltammograms of the complexes were recorded at a ca. 1×10^{-3} M complex concentration in 1.0 M $NaClO_4$.

Crystallography. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four circle diffractometer employing graphite monochromated Mo Kα radiation (0.71073 Å) and operating in the $\omega-2\theta$ scan mode. Data reduction and empirical absorption corrections (ø-scans) were performed with the WINGX package.[46] Structures were solved by direct methods with SHELXS-86, and were refined by full-matrix least-squares analysis against F^2 with SHELXL-97.[47] H-atoms were included at estimated positions. Drawings of molecules were produced with ORTEP3.[48] Crystal data are summarized in Table 4.

Materials and Reagents. ***Safety note**: Perchlorate salts are potentially explosive, and should never be heated in the solid state or scraped from sintered glass frits.*

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Table 4. Crystal Data for the Structures Determined by X-ray Analysis

	Na_2\{*trans*-[\{$L_{15}Co^{III}$(μ-NC)\}$_2$ $Fe^{II}(CN)_4$] (citrate)·Cl·13H_2O\}	*cis*-[\{$L_{15}Co^{III}$(μ-NC)\}$_2Fe^{II}(CN)_4$] $(ClO_4)_2$·9H_2O	*trans*-[\{$L_{15}Co$(μ-NC)\}$_2$ $Co(CN)_4$]Cl_3·7H_2O
formula	$C_{36}H_{89}ClCo_2FeN_{16}O_{20}$	$C_{30}H_{76}Cl_2Co_2FeN_{16}O_{17}$	$C_{30}H_{70}Cl_3C_3N_{16}O_6$
fw	1275.39	1177.68	1034.16
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	9.9350(10)	15.273(2)	9.2247(9)
b (Å)	17.133(2)	11.297(1)	14.478(2)
c (Å)	17.882(2)	30.747(6)	19.651(2)
α (deg)	71.471(8)	90.14(2)	74.08(1)
β (deg)	76.752(9)	90.14(2)	76.329(1)
γ (deg)	85.14(1)	90.14(2)	72.79(1)
V (Å^3)	2809.0(5)	5305(1)	2376.2(5)
Z	2	4	2
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
μ (cm^{-1})	9.70	10.65	12.59
ρ_{calc}	1.508	1.475	1.445
R(obs data)[a]	0.0463	0.1102	0.0556
wR^2(all data)[b]	0.1509	0.3854	0.1783

[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^2]^{1/2}$.

The [CoL_nCl]$^{2+}$ complexes, as well as the dinuclear mixed-valence complexes [\{$L_{14}Co^{III}$(μ-NC)\}$Fe^{II}(CN)_5$]$^-$ and [\{$L_{15}Co^{III}$-(μ-NC)\}$Fe^{II}(CN)_5$]$^-$, have been prepared according to published procedures.[20,21,23−25,31]

The precursor *trans*-[CoL_{15SPh}Cl]$(ClO_4)_2$ was obtained from a complexation reaction of the known[49] ligand L_{15SPh} with Co^{II}, following the same standard preparative procedure described for this family of complexes.[24−26] A 20% excess of $CoCl_2$·6H_2O (0.49 g) was added with stirring to an aqueous solution of the hydrochloride (L_{15SPh}·3HCl) of 8-methyl-6,10-diaza-3,13-dithia-1,15,16,-17,18,19-dehydrobicyclo[13.4.0]nonadecan-8-amine (0.75 g) in water (150 cm^3), and the pH was adjusted to ca. 7. The solution was aerated for 2 h at room temperature to give a dark brown solution, to which were added concentrated HCl (20 cm^3) and activated charcoal (3 g). The suspension was stirred overnight at room temperature and filtered; the filtrate was diluted to ca. 2 dm^3, and was absorbed onto a column of Dowex 50WH2 cation-exchange resin. After we washed the solution with 0.5 M HCl to remove unreacted Co^{II}, a single red band was eluted with 5 M HCl. The eluate was reduced in volume to 20 cm^3, and concentrated $HClO_4$ (1 cm^3) was added. Red crystals were obtained after slow evaporation (yield 59%). *trans*-[CoL_{15SPh}Cl]$(ClO_4)_2$·$^3/_2$$H_2O$. Anal. Calcd: C, 30.07; N, 6.57; H, 4.68. Found: C, 29.76; N, 6.51; H, 4.83. Electronic spectrum (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 399 (shoulder, 500), 476 (170), 548 (230). SWV (mV vs NHE, 1.0 M NaCl): 127.

[\{L_nCo^{III}(μ-NC)\}$_2$Fe^{II}(CN)$_4$]$^{2+}$ (n = 14, 15). These complexes were obtained by reaction of equimolar ratios of the dinuclear mixed-valence core and the corresponding cobalt complex, as indicated above. An aqueous solution 3 × 10^{-3} M in both [CoL_n-Cl]$^{2+}$ and [\{L_nCo^{III}(μ-NC)\}$Fe^{II}(CN)_5$]$^-$ was adjusted to pH 7.5, and was left to react at 60 °C overnight. The resulting mixture was diluted 8-fold, and was loaded on a Sephadex C-25 cation-exchange column. Unreacted (anionic) dinuclear complex was not retained, and was eluted out by washing the column with water. Two cationic species eluted separately with 0.1 M $NaClO_4$. The unreacted mononuclear cobalt complex [CoL_n(OH_2)]$^{3+}$ can be eluted only with much higher concentrations of electrolyte.

n* = 14.** The two above mentioned bands were each concentrated to a small volume (ca. 5 cm^3) at room temperature under reduced pressure on a rotary evaporator. Addition of ethanol (ca. 150 cm^3) yielded the desired isomeric trinuclear complexes as their perchlorate salts (caution, see ***Safety note).

trans-[\{$L_{14}Co^{III}$(μ-NC)\}$_2Fe^{II}(CN)_4$]$(ClO_4)_2$·7H_2O (first band, 30% yield). Anal. Calcd: C, 28.63; N, 19.08; H, 5.83. Found: C, 28.87; N, 19.03; H, 5.83. Electrochemistry (mV vs NHE): 844 (Fe$^{III/II}$), −530 (Co$^{III/II}$). Electronic spectrum (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 324 (600), 434 (1050), 490 (950). IR (CN, cm^{-1}): 2090, 2065, 2032. ^{13}C NMR (δ, D_2O): 20.7, 30.7, 52.9, 54.9, 55.1, 62.0, 68.3, 175.9, 190.3.

cis-[\{$L_{14}Co^{III}$(μ-NC)\}$_2Fe^{II}(CN)_4$]$(ClO_4)_2$·6H_2O (second band, 25% yield). Anal. Calcd: C, 27.61; N, 18.40; H, 5.46. Found: C, 27.57; N, 18.11; H, 5.38. Electrochemistry (mV vs NHE): 842 (Fe$^{III/II}$), −528 (Co$^{III/II}$). Electronic spectrum (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 326 (570), 442 (1080), 498 (1060). IR (CN, cm^{-1}): 2124 (weak), 2052 (broad, strong). ^{13}C NMR (δ, D_2O): 20.7, 30.9, 52.8, 54.9, 5.1, 62.0, 68.4, 173.7, 176.4, 191.6.

n* = 15.** Cation-exchange chromatography again gave two bands that eluted with 0.1 M $NaClO_4$. However, ^{13}C NMR spectroscopy of fractions taken from each band as they eluted revealed mixtures of N-based isomeric forms of each complex. Nevertheless, as indicated by the number of ^{13}C NMR signals in the 170−195 ppm zone, the first band contained exclusively *trans*-Co_2Fe complexes, whereas the second well-separated band contained exclusively *cis*-Co_2Fe complexes. As expected for chromatography procedures carried out at neutral pH, we have been unable to separate these N-based isomers given their fast interconversion under these conditions. We had encountered similar complications in our investigations of other complexes of L_{15} such as *trans*-[Co^{III}ClL_{15}]$^{2+}$ and [\{$L_{15}Co^{III}$(μ-NC)Fe^{II}\}$(CN)_5$]$^-$, where at least three isomeric forms of the \{CoL_{15}\} moiety have been characterized crystallographically after cation-exchange chromatography in acidic conditions.[24,30,31] Thus, concentration of these bands at room temperature and precipitation by the addition of ethanol yielded solids that were mixtures of N-based isomers (caution, see ***Safety note).

Na_2\{trans-[\{$L_{15}Co^{III}$(μ-NC)\}$_2Fe^{II}(CN)_4$](citrate)Cl·13H_2O\} (first band). The sample mixture containing the *trans*-Co_2Fe isomers did not produce isomerically pure species on standing. The mixture was chromatographed on a Sephadex C-25 column again, and was eluted with a 0.2 M mixture of sodium citrate and chloride (2:1). On standing, crystals of the mixed citrate salt Na_2\{*trans*-[\{L_{15}-Co^{III}(μ-NC)\}$_2Fe^{II}(CN)_4$](citrate)Cl·13H_2O\} were obtained as an isomerically pure species. Anal. Calcd: C, 33.33; N, 16.81; H, 6.73.

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Found: C, 33.30; N, 16.75; H, 8.01. Electrochemistry (mV vs NHE): 804 ($Fe^{III/II}$), −533 ($Co^{III/II}$). Electronic spectrum (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 326 (580), 450 (930), 512 (930). IR (CN, cm^{-1}): 2097 (strong), 2059 (strong). ^{13}C NMR (δ, D_2O, after citrate-to-chloride exchange): 21.5, 26.4, 50.1, 51.2, 54.8, 61.6, 66.7, 175.0, 190.9.

cis-$[\{L_{15}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4](ClO_4)_2 \cdot 9H_2O$ *(second band)*. The mixture of *cis*-Co_2Fe N-based isomers was redissolved in water, and on standing for weeks and slow evaporation of the solution afforded X-ray quality crystals of isomerically pure *cis*-$[\{L_{15}Co^{III}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4](ClO_4)_2 \cdot 9H_2O$. Anal. Calcd: C, 30.60; N, 19.10; H, 6.50. Found: C, 30.72; N, 19.03; H, 6.39. Electrochemistry (mV vs NHE): 790 ($Fe^{III/II}$), −530 ($Co^{III/II}$). Electronic spectrum (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 328 (660), 454 (950), 514 (950). IR (CN, cm^{-1}): 2128 (weak), 2091 (strong), 2048 (strong). ^{13}C NMR (δ, D_2O): 21.5, 26.4, 50.1, 51.2, 54.8, 61.6, 66.7, 174.3, 174.5, 191.7.

***trans*-$[\{Co^{III}L_{15SPh}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4](ClO_4)_2 \cdot 14H_2O$.** The trinuclear complex *trans*-$[\{Co^{III}L_{15SPh}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4]^{2+}$ was obtained as a side product from the preparative procedure of the dinuclear $[\{Co^{III}L_{15SPh}(\mu\text{-}NC)\}Fe^{II}(CN)_5]^-$ complex. A solution of $[CoClL_{15SPh}](ClO_4)_2 \cdot {}^3/_2H_2O$ (8×10^{-4} mol) in water (100 cm^3) was adjusted to ca. pH 9 with NaOH, and 100 cm^3 of an aqueous solution of 9×10^{-4} mol of $Na_4[Fe(CN)_6] \cdot 10H_2O$ was added. The mixture darkened immediately, and the pH was readjusted to 9 with 1 M HCl. After being stirred overnight at ca. 60 °C, the resulting mixture was filtered, and the filtrate was diluted to 2 dm^3. The reaction mixture was loaded onto a DEAE-Sephadex anion-exchange column, and the cationic trinuclear complex was not retained. The eluate was loaded on a Sephadex C-25 cation exchanger, and a single blue-purple band was eluted with 0.1 M $NaClO_4$. Concentration of this band at room temperature and addition of ethanol yielded the desired isomerically pure *trans*-$[\{Co^{III}L_{15SPh}(\mu\text{-}NC)\}_2Fe^{II}(CN)_4](ClO_4)_2 \cdot 14H_2O$ (yield 15%) complex. Anal. Calcd: C, 31.87; N, 11.74; S, 8.96; H, 5.84. Found: C, 31.72; N, 11.48; S, 8.85; H, 5.86. Electrochemistry (mV vs NHE): 871 ($Fe^{III/II}$), −190 ($Co^{III/II}$). Electronic spectrum (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 469 (880), 554 (1010). IR (CN, cm^{-1}): 2088 (strong), 2051 (strong). ^{13}C NMR (δ, D_2O): 21.3, 40.8, 43.2, 57.8, 62.4, 70.9, 133.2, 135.2, 135.7, 172.5, 192.5.

***trans*-$[\{L_{15}Co(\mu\text{-}NC)\}_2Co(CN)_4]Cl_3 \cdot 7H_2O$.** This compound was prepared in the same way as the $\{L_{15SPh}Co_2Fe\}$ analogues above, from the reaction of $[CoL_{15}Cl]Cl_2$ (adjusted to pH 9 with NaOH) with $K_3[Co(CN)_6]$. Yellow crystals of the sparingly soluble isomerically pure trichloride salt, suitable for X-ray work, were deposited from the reaction mixture upon standing for weeks (yield 50%). Anal. Calcd: C, 34.25; N, 21.30; H, 6.90. Found: C, 34.10; N, 21.54; H, 6.66. Electrochemistry (mV vs NHE): −376 (macrocyclic $Co^{III/II}$). Electronic spectrum (λ_{max} (nm), ϵ (M^{-1} cm^{-1})): 322 (380), 471 (210). IR (CN, cm^{-1}): 2134 (strong), 2191 (strong).

Acknowledgment. We thank the Ministerio de Educación y Ciencia (Project CTQ2004-00954/BQU) and the Australian Research Council (Project 00/ARCL073G) for financial support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0511423