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The Influence of Ligand Substitution at the Electron Donor Center in Molecular Cyano-Bridged Mixed-Valent Co^{III}/Fe^{II} and Co^{III}/Ru^{II} Complexes

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In this paper we report a new variety of dinuclear cyano-bridged Co^{III}/M^{II} (M = Fe or Ru) mixed-valent complexes of the general formula $[L_nCo^{III}(\mu\text{-NC})M^{II}(CN)_x(bpy)_y]^{z+}$ (where L_n represents a pentaamine macrocycle and M = Fe or Ru with x = 4, y = 1 and z = 1 or x = 2, y = 2 and z = 3)]. The incorporation of the bpy ligand in place of cyano ligands within the coordination sphere raises the $M^{III/II}$ redox potential significantly relative to the hexacyanometalate analogs we have reported previously. However, the metal-to-metal (M^{II} to Co^{III}) charge-transfer transitions are shifted to lower energies in accordance with Hush theory as a result of a decreased reorganizational energy component, which result in them overlapping with more intense MLCT (M^{II} to bpy) transitions.

Introduction

In recent years we have reported on synthetic strategies leading to *molecular*, cyano-bridged, dinuclear[1–4] and trinuclear[5] d^6–d^6 heterometallic complexes; this work has been reviewed.[6] These Co^{III}/Fe^{II} and Co^{III}/Ru^{II} complexes each display characteristics of a *Class II* Robin and Day asymmetric, low-spin d^6–d^6 mixed-valent complex,[7] exhibiting metal-to-metal charge-transfer (MMCT, Fe^{II} to Co^{III} or Ru^{II} to Co^{III}) transitions in the visible region, in addition to the transitions characteristic of the two isolated metal-complex moieties.

According to Hush theory [Equation (1)],[8] the energy of the MMCT transition (E_{op}) is directly related to the free energy difference (ΔG°) between the Co^{III}–NC–M^{II} and Co^{II}–NC–M^{III} (M = Fe, Ru) forms. The Co^{II}–NC–M^{III} form cannot be isolated as it is inherently unstable with respect to the Co^{III}–NC–M^{II} complex so this free energy difference cannot be measured directly. However, if the two redox centers do not interact strongly then this free energy difference may be estimated from the difference between the $Co^{III/II}$ and $M^{III/II}$ redox potentials. The reorganizational energy (λ) associated with the MMCT process is also important and includes both inner sphere (bond length/angle changes) and outer sphere (solvation) terms.

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

In previous publications we have demonstrated how the MMCT energy of the Co^{III}–NC–M^{II} chromophore is very sensitive to variations at both metal centers. Specifically, the ring size of the pentadentate macrocyclic ligand bound to the Co^{III} ion (e.g. L_{14} or L_{15}),[2] its geometric isomeric form (*cis* or *trans*),[3] and the donor set of the macrocycle (N_5 or N_3S_2)[4] all have an effect on the $Co^{III/II}$ redox potential, which in turn is reflected in variations in the MMCT transition energy in accordance with Hush theory. Alternatively, protonation of the terminal cyanide ligands in the hexacyanoferrate(II) moiety[9] or the substitution of the metal (Ru for Fe)[4] raises the $M^{III/II}$ (M = Fe or Ru) redox potential of the donor and the energy of the MMCT transition accordingly.

In this paper we have explored a new MMCT energy tuning strategy by replacing the hexacyanometalate(II) unit by various combinations of *cis*-$[M(CN)_4(bpy)]^{2-}$ and *cis*-$[M(CN)_2(bpy)_2]$ (M = Fe and Ru, bpy = 2,2′-bipyridyl). This change brings additional complexity to the optical properties of the system, as metal-to-ligand charge transfer (MLCT, M^{II} to bpy) transitions are also possible and inherently more intense than the MMCT transitions.[10] The identification of the MMCT (M^{II} to Co^{III}) transitions in these new mixed-valent complexes is consequently not straightforward. Nevertheless, this can be overcome when their intense electronic spectra are compared with that of the mononuclear cyano complexes of M^{II} (Fe or Ru in com-

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bination with one or two bpy ligands). This analysis brings additional information regarding the energetics of MMCT in these molecular systems.

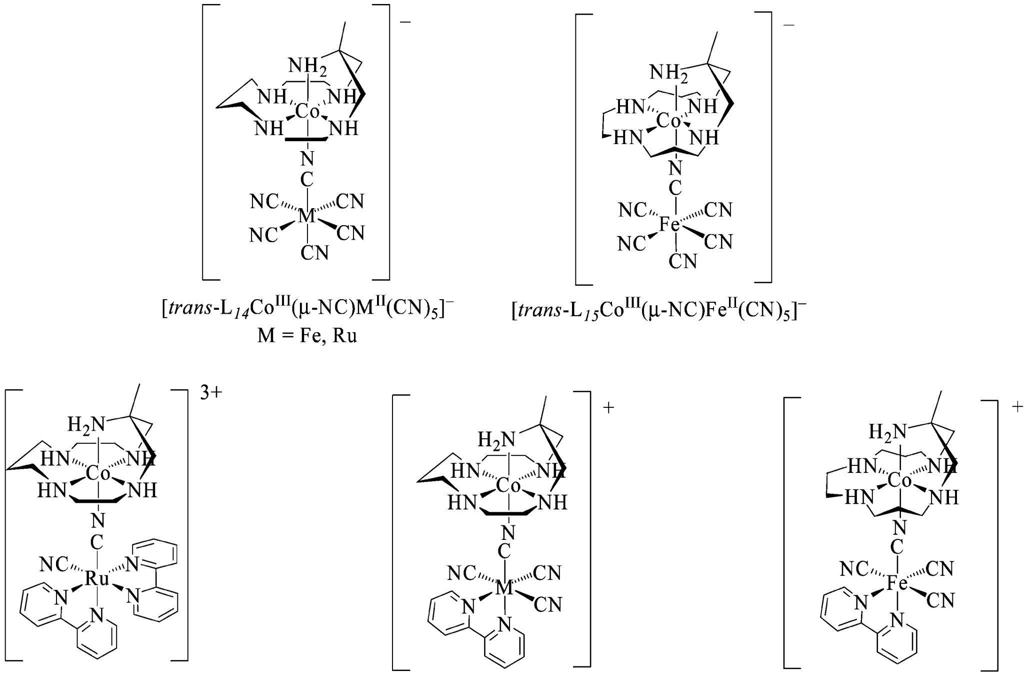
Results and Discussion

Synthesis

All complexes were prepared by direct substitution of the aqua ligand on the appropriate *trans*-$[CoL_n(OH_2)]^{3+}$ complex by a single bridging cyano ligand of the Fe^{II} or Ru^{II} precursor. In previous papers[2,11] we have exploited a redox-catalyzed substitution reaction whereby the hexacyanoferrate(II) complex undergoes an outer sphere electron transfer cross reaction with the Co^{III} partner to generate a labile Co^{II} intermediate. However, given the much higher $Fe^{III/II}$ and $Ru^{III/II}$ redox potentials involved, this protocol could not be used. Despite this fact, the careful choice of stoichiometry and reaction conditions allowed the isolation of each desired complex after purification by cation chromatography. In this case the reactions are merely ligand substitutions on the Co^{III} center unassisted by reduction. A detailed mechanistic study of these "uncatalyzed" processes, also applicable in some cases for the preparation of trinuclear complexes of this family, is currently underway.

Spectroscopic Characterization

The ^1H NMR resonances of all the complexes of L_{14} in the high-field region are indicative of retention of the so-called *trans-I* form of the $\{Co^{III}L_{14}\}$ moiety (all NH protons *syn*, see Scheme 1) which has mirror plane symmetry and hence exhibits only five chemically distinct methylene groups.[3] The ^1H NMR in the same region for the $\{Co^{III}L_{15}\}$ unit in the corresponding complex is consistent with the *trans-III* form (two NH protons up and two down) which has been identified in other related dinuclear complexes.[1] The low-field region of each spectrum is dominated by the aromatic bpy protons and is useful in assigning the isomeric form involving the bpy ligands for each complex. The ^1H NMR spectra of both [*trans*-$L_{14}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ and [*trans*-$L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)_3(bpy)_{eq,ax}]^+$ (see Figures S1a and S1b in the electronic supporting information) are virtually identical as expected from the structures shown in Figures 1 and 2. Only the two protons in 6- and 6′-positions (equivalent in the free bpy ligand) are clearly separated in the NMR spectrum and appear downfield (>9 ppm) of all other peaks because of the inductive effect of the adjacent coordinated N-atoms. The ^1H NMR resonances of the other bpy protons (3/3′, 4/4′ and 5/5′) overlap, despite being chemically inequivalent. The low symmetry is consistent with the *equatorial*,*axial* geometric isomeric form where one bpy N-donor (equatorial) is *trans* to a terminal cyano ligand while the other (axial) is *trans* to the unique bridging cyano ligand. The ^1H NMR spectrum of [*trans*-$L_{15}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ (Figure S1c, supporting information) in this low-field region is found indistinguishable from that of [*trans*-$L_{14}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ and thus the same *eq*,*ax* isomeric can be assigned. A minor band was



[*trans*-$L_{14}Co^{III}(\mu\text{-}NC)M^{II}(CN)_5]^-$
M = Fe, Ru

[*trans*-$L_{15}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_5]^-$

[*trans*-$L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)(bipy)_{2,cis}]^{3+}$

[*trans*-$L_{14}Co^{III}(\mu\text{-}NC)M(CN)_3(bipy)_{eq,ax}]^+$
M = Fe, Ru

[*trans*-$L_{15}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_3(bipy)_{eq,ax}]^+$

Scheme 1.

seen in the chromatographic purification of this complex and this is likely to be the more symmetrical *eq,eq* isomer but it was not present in sufficient quantities to characterize fully.

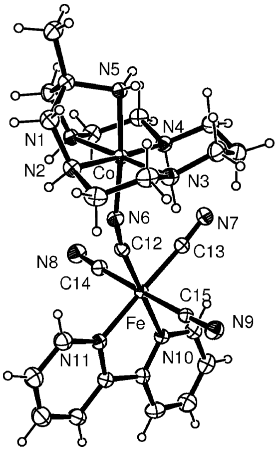


Figure 1. ORTEP drawing of the [*trans*-$L_{14}Co^{III}$(μ-NC)$Fe^{II}(CN)_3$-$(bpy)_{eq,ax}]^+$ cation (30% ellipsoids shown). Relevant bond lengths [Å] and angles [°]: Co–N(5) 1.951(2); Co–N(1) 1.958(3); Co–N(2) 1.952(3); Co–N(3) 1.960(3); Co–N(4) 1.965(3); Co–N(6) 1.897(3); Fe–N(11) 1.986(2); Fe–N(10) 1.994(2); Fe–C(12) 1.870(3); Fe–C(12)–N(6) 170.1(2); Co–N(6)–C(12) 157.5(2).

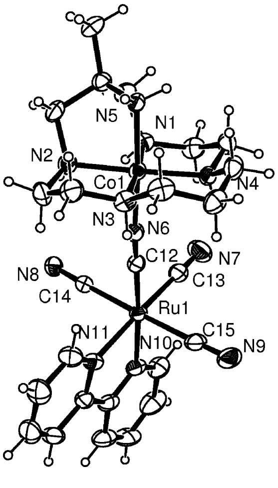


Figure 2. ORTEP drawing of the [*trans*-$L_{14}Co^{III}$(μ-NC)$Ru^{II}(CN)_3$-$(bpy)_{eq-ax}]^+$ cation (30% ellipsoids shown). Relevant bond lengths [Å] and angles [°]: Co–N(5) 1.960(5); Co–N(1) 1.940(5); Co–N(2) 1.953(5); Co–N(3) 1.945(5); Co–N(4) 1.950(6); Co–N(6) 1.906(6); Ru–N(11) 2.108(6); Ru–N(10) 2.116(5); Ru–C(12) 1.958(7); Ru–C(12)–N(6) 177.3(6); Co–N(6)–C(12) 166.7(6).

The ^1H NMR spectrum of [*trans*-$L_{14}Co^{III}$(μ-NC)Ru^{II}-$(CN)(bpy)_{2,cis}]^{3+}$ (Figure S1d, supporting information) is more complex because of the presence of 4 chemically inequivalent pyridyl rings. Interestingly, a pair of high-field protons at the 6-position (from different bpy ligands) is also present, but the other two protons at the 6-position appear well upfield (7.2–7.4 ppm). This effect has also been noted previously for *cis*-$Ru(CN)_2(bpy)_2$ and $[Ru(bpy)_3]^{2+}$, and has been assigned to the shielding effect of the adjacent aromatic ring current.[12]

The IR spectra of all [*trans*-L_nCo^{III}(μ-NC)$M^{II}(CN)_3$-$(bpy)_{eq,ax}]^+$ ($n = 14$ or 15, M = Fe; $n = 14$, M = Ru) complexes are very similar in the $\tilde{\nu}_{C\equiv N}$ region, exhibiting three bands around 2060, 2080 and 2100 cm^{-1}. On the basis of our previous studies,[1,2,4] and those on other related cyano-bridged complexes,[13,14] the highest frequency vibration is invariably due to the bridging cyano ligand. The lowest frequency vibration is twice the intensity of the intermediate frequency band and thus is most likely due to the two equivalent (mutually *trans*) cyano ligands. The intermediate frequency band is consequently assigned to the single cyano ligand *trans* to a bpy N-donor. The IR spectrum of [*trans*-$L_{14}Co^{III}$(μ-NC)$Ru^{II}(CN)(bpy)_{2,cis}]^{3+}$ exhibits only two $\tilde{\nu}_{C\equiv N}$ bands of similar intensity. Again, the higher frequency band is assigned to the bridging cyano ligand by reference to the published IR spectrum of *cis*-$Ru(CN)_2$-$(bpy)_2$ where both ligands are terminal.[14]

Structural Characterization

The crystal structure of [*trans*-$L_{14}Co^{III}$(μ-NC)$Fe^{II}(CN)_3$-$(bpy)_{eq,ax}]^+$ (Figure 1) shows the typical *trans-I* form of the macrocyclic L_{14} ligand,[2–4] already found in the [*trans*-$L_{14}Co^{III}$(μ-NC)$Fe^{II}(CN)_5]^-$ as well as in the precursor *trans*-*I*-$[CoClL_{14}]^{2+}$ complexes. The bond angles and distances for the cobalt moiety on the complex do not show any significant deviation with respect to previously characterized structural analogs, and the shortest distance of the cobalt environment is, as usual, that to the cyano ligand. As for the iron $\{Fe^{II}(CN)_4(bpy)\}$ unit in the dinuclear complex, its geometry is close to octahedral with the bpy ligand in an *equatorial*,*axial* disposition, forcing the $\{Co^{III}L_{14}\}$ group to tilt severely producing a Co–N≡C angle of only 157.5°. Only for the oxidized complex [*trans*-$L_{14}Co^{III}$(μ-NC)Fe^{III}-$(CN)_5]$ has a tilting of this degree been observed before;[3] as a consequence the Co^{III}–Fe^{II} distance becomes effectively shorter than in the rest of Co^{III}/Fe^{II} complexes of this family.[6]

The crystal structure of [{*trans*-$L_{14}Co^{III}$(μ-NC)}Ru^{II}-$(CN)_3(bpy)_{eq,ax}](ClO_4)_{1/2}\cdot Cl_{1/2}\cdot 4H_2O$ was also determined. The cation geometry (Figure 2) is very similar to that of the iron analog and the only notable differences are the longer Ru coordinate bonds. There is considerable disorder in the anions both translational and over different orientations. Apart from this feature the salient features of the structure mirror those of the Fe analog.

Electrochemistry

Electrochemistry of the four dinuclear complexes in aqueous solution identified redox couples from both metal centers. The $Co^{III/II}$ couples for [*trans*-L_nCo^{III}(μ-NC)M^{II}-$(CN)_3(bpy)_{eq,ax}]^+$ ($n = 14$ or 15, M = Fe; $n = 14$, M = Ru) are rather similar (Table 1) and lower than seen in [*trans*-$L_{14}Co^{III}$(μ-NC)$Ru^{II}(CN)(bpy)_{2,cis}]^{3+}$. This fact can be attributed to the electrostatic effects of the dinegatively charged $\{M(CN)_4(bpy)\}^{2-}$ moiety in the [*trans*-L_nCo^{III}(μ-

Table 1. Redox potentials and spectroscopic data for new cyano-bridged dinuclear complexes prepared. Literature values for relevant compounds of the same family have also been included.

	E^o (Ag/AgCl) / mV $Ru/Fe^{III/II}$	 $Co^{III/II}$	ΔG^o / cm^{-1}	E_{op} / cm^{-1}	λ / cm^{-1}
$[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)(bpy)_{2,cis}]^{3+}$	1196	–492	13600	≈21000[a]	7400
$[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)_3(bpy)_{eq,ax}]^{+}$	1079	–642	13900	≈21000[a]	7100
$[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_3(bpy)_{eq,ax}]^{+}$	584	–701	10400	[b]	[c]
$[trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_3(bpy)_{eq,ax}]^{+}$	579	–734	10600	[b]	[c]
$[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_5]^{-}$	434	–796	9900	19600[d]	9800
$[trans\text{-}L_{15}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_5]^{-}$	404	–776	9500	18400[e]	9000
$[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)_5]^{-}$	954	–733	13600	26300[f]	12700

[a] Partially obscured by MLCT band. [b] Totally obscured. [c] Could not be determined. [d] Ref.[2]. [e] Ref.[1]. [f] ref.[4].

$NC)M^{II}(CN)_3(bpy)_{eq,ax}]^+$ analogs which lowers the $Co^{III/II}$ couple relative to that seen in $[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)(bpy)_{2,cis}]^{3+}$ while the charge neutral $\{Ru^{II}(CN)_2(bpy)_2\}$ moiety exerts no electrostatic influence. The cyclic voltammograms of the Ru complexes are shown in Figure 3. As reported before, the $Co^{III/II}$ redox processes are fully reversible on an Hg working electrode but only quasireversible, or even irreversible, on glassy carbon surfaces. That is, the best responses for the $Co^{III/II}$ were obtained on Hg while the high-potential $Fe^{III/II}$ and $Ru^{III/II}$ couples (inaccessible on Hg) had to be measured with a glassy carbon electrode. Also of note are the lower $Co^{III/II}$ couples of the dinuclear hexacyanometalate complexes because of the greater (tetranegative) charge of the anionic cyano $\{Fe^{II}(CN)_6\}$ moiety.

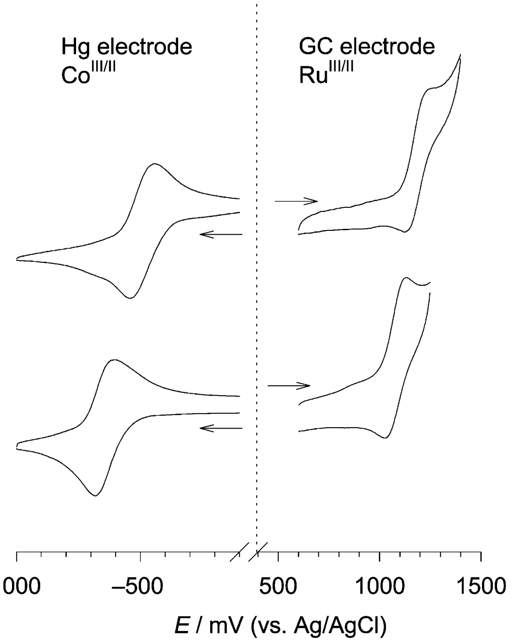


Figure 3. Cyclic voltammograms (500 $mV\,s^{-1}$) of $[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)(bpy)_{2,cis}]^{3+}$ (top) and $[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)_3(bpy)_{eq,ax}]^+$ (bottom) measured with a glassy carbon (GC) working electrode (right) or a Hg drop electrode (left). The currents have been scaled to compensate for the different electrode areas.

The $Ru^{III/II}$ and $Fe^{III/II}$ couples are both clearly influenced by the tripositively charged $\{Co^{III}L_n\}^{3+}$ moiety. Comparison with the mononuclear redox potentials of $[Fe(CN)_4(bpy)]^{-/2-}$ (380 mV),[15] $[Ru(CN)_4(bpy)]^{-/2-}$ (890 mV)[16] and $cis\text{-}[Ru(CN)_2(bpy)_2]^{+/0}$ (940 mV)[17] (all vs. Ag/AgCl) illustrates this point. A ca. 200 mV anodic shift is found in each case on going from the mononuclear complex to the cyano-bridged Co^{III}/M^{II} complex, as for the previously studied hexacyano complexes.[1–5] Further comparisons can be made with these redox potentials of the hexacyanometalate analogs that we have already reported (Table 1). Clearly the bpy ligand destabilizes the trivalent Fe and Ru forms relative to a pair of terminal cyano ligands.

Apart from these thermodynamic measurements, there also appears to be a labilizing effect upon oxidation of the Ru^{II} center. As illustrated in Figure 4, the $Ru^{III/II}$ couple of $[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)_3(bpy)_{eq,ax}]^+$ is irreversible at a sweep rate of 100 $mV\,s^{-1}$ (no cathodic peak is observed), while reversibility is restored at sweep rates higher than

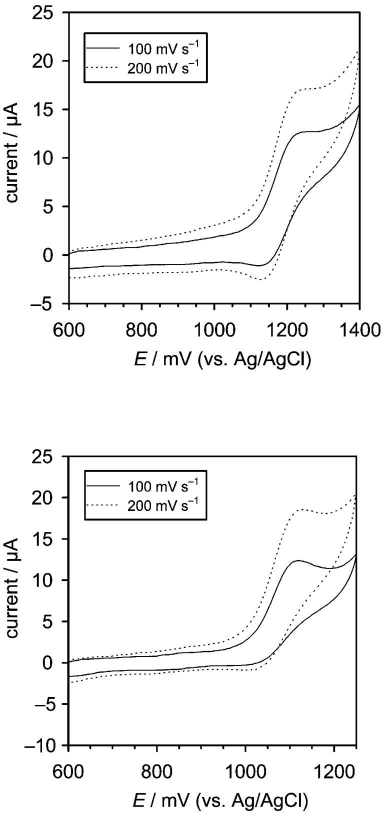


Figure 4. Sweep-rate dependence of the $Ru^{III/II}$ couple potentials for $[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)(bpy)_{2,cis}]^{3+}$ (top) and $[trans\text{-}L_{14}Co^{III}(\mu\text{-}NC)Ru^{II}(CN)_3(bpy)_{eq,ax}]^+$ (bottom).

500 mV s^{-1}. This fact is indicative of a chemical reaction, of uncertain nature, following oxidation. The Ru$^{III/II}$ redox couple in [*trans*-L$_{14}$Co^{III}(μ-NC)Ru^{II}(CN)(bpy)$_{2,cis}$]$^{3+}$ appears at even higher potential yet it is reversible at all sweep rates, which rules out catalytic water oxidation as the reason for the loss of the cathodic peak in [*trans*-L$_{14}$Co^{III}(μ-NC)-Ru^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$ (the higher potential Ru$^{III/II}$ couple should result in a greater rate of water oxidation). It seems that the chemical reaction that follows oxidation has to be related to ligand dissociation at the Ru^{III} center with a first-order rate constant of ca. 15 s^{-1}, as determined by examination of the scan-rate dependence of the cathodic/anodic currents.[18] Electrochemical experiments run in dmf (data not shown) revealed a similar result, indicating the chemical irreversibility of the oxidation of the ruthenium center in the complex despite the absence of water. Interestingly the electrochemistry of [Ru(CN)$_4$(bpy)]$^{2-}$ performed under the same conditions is facile and totally reversible at sweep rates of 100 mV s^{-1}, which suggests a destabilizing influence of the attached Co^{III} moiety. Earlier studies[19] on the bromine oxidation of [Ru(CN)$_6$]$^{4-}$ showed that the product is [Ru(CN)$_5$(OH$_2$)]$^{3-}$ which indicates that the intermediate [Ru(CN)$_6$]$^{3-}$ is unstable with respect to ligand substitution in water. Indeed the [Ru(CN)$_6$]$^{3-}$ ion has only recently been characterized structurally[20] and, once isolated, it decomposes rapidly upon dissolution.

Electronic Spectroscopy

The energy of the MMCT transition is of interest, given the wide separation of the redox couples of the two metal centers relative to other systems we have investigated (see Table 1). The electronic spectra of [*trans*-L$_{14}$Co^{III}(μ-NC)-Ru^{II}(CN)$_3$(bpy)$_{eq,ax}$]$^+$ and [*trans*-L$_{14}$Co^{III}(μ-NC)Ru^{II}(CN)-(bpy)$_{2,cis}$]$^{3+}$ in aqueous solution show an intense MLCT (Ru^{II} to bpy) peak around 400 nm which exhibits a distinct shoulder at its low-energy side (Figure 5); this shoulder is totally absent in the parent [Ru^{II}(CN)$_4$(bpy)]$^{2-}$ and only the MLCT band is apparent (Figure 5, dashed line). These shoulders then appear to be due to the MMCT (Ru^{II} to Co^{III}) transitions both around 500 nm. In other systems we have already studied, such as [*trans*-L$_{14}$Co^{III}(μ-NC)M^{II}-(CN)$_5$]$^-$ (M = Fe and Ru),[2,4] the MMCT transition is dominant, as only much weaker Co^{III} d–d transitions ($\varepsilon \approx 100$ M^{-1} cm^{-1}) are seen in the visible region. Equation (1) enables the reorganization energies for each Ru^{II}/Co^{III} complex to be calculated. These values are collected in Table 1.

For both Fe^{II} complexes, the UV/Vis spectra show a rather broad and featureless band at 460–470 nm that may be attributed to the corresponding MLCT (Fe^{II} to bpy) transition (the value being 482 nm, 2400 M^{-1} cm^{-1} for [Fe^{II}-(CN)$_4$(bpy)]$^{2-}$).[21] This band diminishes in intensity on addition of the oxidant Na$_2$S$_2$O$_8$ as a result of the oxidation of the iron center and two new bands (506 nm, 110 M^{-1} cm^{-1} and 416 nm, 940 M^{-1} cm^{-1}) corresponding to the [Fe^{III}(CN)$_4$-(bpy)]$^-$ chromophore are evident (Figure S2, supporting information). Also, oxidation of the Fe^{II} center must result in loss of the MMCT (Fe^{II} to Co^{III}) band, but this was completely obscured by the more intense Fe^{II} to bpy MLCT band so its energy is unknown.

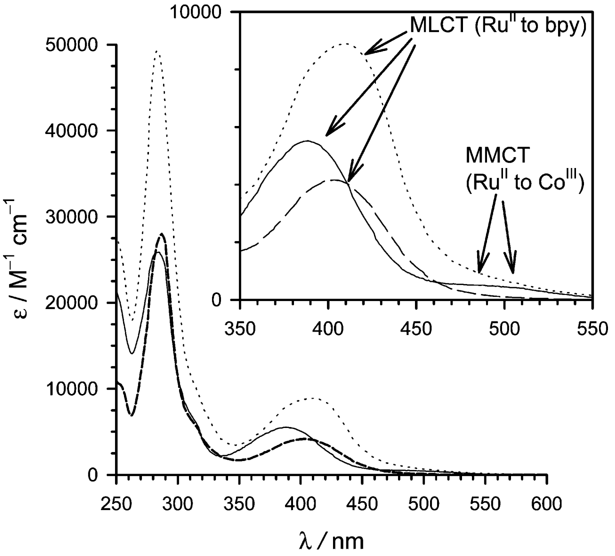


Figure 5. UV/Vis spectra of [*trans*-L$_{14}$Co^{III}(μ-NC)Ru^{II}(CN)-(bpy)$_{2,cis}$]$^{3+}$ (dotted line), [*trans*-L$_{14}$Co^{III}(μ-NC)Ru^{II}(CN)$_3$-(bpy)$_{eq,ax}$]$^+$ (grey solid line) and [Ru^{II}(CN)$_4$(bpy)]$^{2-}$ (dashed line). MLCT and MMCT bands are indicated.

Bulk electrolysis oxidation of the Ru^{II}–CN–Co^{III} complexes was unsuccessful with decomposition occurring during the experiment. It is likely that loss of one or more cyano ligands from the Ru^{III} center is the origin of this decomposition reaction by analogy with the known instability of [Ru(CN)$_6$]$^{3-}$.[19,20]

Conclusions

The present study has illustrated new ways in which the MMCT energy of this extended series of molecular *Class II* mixed-valent Co^{III}/M^{II} complexes can be modified through ligand exchange on the M^{II} electron donor. Although partially obscured by the more intense Ru^{II} to bpy MLCT transitions, the Ru^{II} to Co^{III} MMCT bands have been determined, while in the case of the Fe^{II}–CN–Co^{III} systems we were unable to resolve the Fe^{II} to Co^{III} transitions because of their complete overlap with the more intense Fe^{II} to bpy MLCT bands. In each case the substitution of a pair of *cis* cyano ligands with a single bidentate bpy ligand raises the redox potential of the M^{II} donor relative to its hexacyanometalate(II) analog. Interestingly the Co$^{III/II}$ couple is inductively raised by a similar amount, leaving the free energy changes barely affected. The MMCT energy of the Ru^{II}–CN–Co^{III} complexes is smaller because of a significant (ca. 60 %) decrease in the reorganizational energy of the bpy complexes relative to the hexacyanoruthenate parent, although the variations in charge may also be a factor in addition to specific H-bonding with the number of terminal cyano ligands. We are currently exploring further synthetic routes to novel di- and trinuclear mixed-valent complexes with a view to further being able to tune their optical and electrochemical properties.

Experimental Section

Physical Methods: Proton NMR spectra at 400 MHz were recorded with either a Varian Mercury-400 (Serveis Científico-Tècnics de la Universitat de Barcelona) or Bruker AV400 instrument. All chemical shifts are cited relative to TMS. Cyclic voltammetry employed a BAS100B/W or EG&G 263A potentiostat and using either a glassy carbon disc working electrode, or a PAR Model 303 static Hg drop working electrode. The reference electrode was Ag/AgCl (3 м KCl) and a platinum wire counter electrode was employed. The background electrolyte was either 0.1 м $NaClO_4$ or 0.1 $NaNO_3$ as indicated. All solutions were purged with N_2 prior to measurement. UV/Vis spectra were measured with Analytik Jena Specord 210, HP5482A, Cary5, Cary50 and J&M TIDAS spectrophotometers. IR spectra were carried out in an FT-IR Impact 400 Nicolet spectrometer employing KBr disks or a Perkin–Elmer 1600 series spectrophotometer using an ATR assembly.

Syntheses

Caution: All reactions must be carried out in a well-ventilated fume hood as liberation of HCN may occur in some of the preparations if solutions are acidified. Perchlorate salts are potentially explosive and should only be handled in small quantities, never heated in the solid state not scraped from sintered glass frits.

The precursor complexes *trans-I*-$[CoClL_{14}](ClO_4)_2$,[2] *trans-II*-$[CoClL_{15}](ClO_4)_2$,[22] $K_2[Fe(CN)_4(bpy)]\cdot 3H_2O$,[21] $K_4[Ru(CN)_6]$,[23] $K_2[Ru(CN)_4(bpy)]$[24] were prepared using published procedures. The complex *cis*-$Ru(CN)_2(bpy)_2$ was prepared by refluxing *cis*-$Ru(bpy)_2Cl_2$[25] (0.3 g) and excess KCN (0.241 g) in 50% aqueous EtOH (100 cm^3) for 5 h; the initial purple color changed to orange during this period. After this time the solvent was removed in vacuo (**caution** – excess cyanide present) and the resultant red/orange powder was dissolved in MeOH and purified on a Sephadex LH-20 size-exclusion column and recrystallized from $MeOH/Et_2O$. All other reagents and solvents were obtained commercially.

[*trans*-$L_{14}Co^{III}$(μ-NC)$Fe^{II}(CN)_3(bpy)_{eq,ax}$]($ClO_4$)·$4H_2O$: A solution of *trans-I*- $[CoClL_{14}](ClO_4)_2$ (0.20 g) in water (20 cm^3) was adjusted to pH = 10 with NaOH and then stirred for 10 min to give the hydroxo derivative after hydrolysis of the chloro ligand. After addition of a solution of $K_2[Fe(CN)_4(bpy)]\cdot 3H_2O$ (0.22 g) in water (20 cm^3), the pH was raised to 6.2 with 1 м NaOH solution; any $KClO_4$ precipitate was filtered off and stirring was continued for 72 h. at 40 °C. The final solution was diluted to 1000 cm^3 and loaded to a 30 × 2 cm column of Sephadex C-25 cation-exchange resin (Na^+ form). Elution with 0.1 м $NaClO_4$ produced two diffuse red bands. The major second band was collected, diluted to 5 L, and reloaded onto another column of the same type. This time elution with 0.05 м $NaClO_4$ produced a narrow major band that was collected and evaporated at reduced pressure to ca. 15 cm^3. Standing for a few days at 5 °C produced the desired product in crystalline form (15% yield) suitable for X-ray work. $C_{25}H_{43}ClCoFeN_{11}O_8$ (775.92): calcd. C 38.7, H 5.6, N 19.8; found C 39.1, H 5.7, N 19.2. ^1H NMR (D_2O): δ = 1.35 (s, 3 H, CH_3), 1.80–3.70 (m, 18 H, CH_2), 7.50 (m, 2 H, 5/5′-pyr), 7.98 (t, 2 H, 4/4′-pyr), 8.23 (d, 2 H, 3/3′-pyr), 9.01 (d, 1 H, 6-pyr), 9.28 (d, 1 H, 6′-pyr) ppm. IR: $\tilde{\nu}_{CN}$ = 2061, 2074, 2096 cm^{-1}. UV/Vis (H_2O): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 458 (3380), 332 (3330) nm.

[*trans*-$L_{15}Co^{III}$(μ-NC)$Fe^{II}(CN)_3(bpy)_{eq,ax}$]($ClO_4$)·$3H_2O$: The procedure for the preparation of the dinuclear complex is the same one as above except *trans-II*-$[CoClL_{15}](ClO_4)_2$ was used as the precursor. Elution with 0.1 м $NaClO_4$ produced two diffuse red bands. The major second one was collected, diluted to 5 L, and reloaded on another Sephadex C-25 column (Na^+ form). Elution with 0.05 м $NaClO_4$ produced an initial major band that was collected and evaporated at reduced pressure to ca. 15 cm^3. Standing in a refrigerator for a few days produced the desired product in crystalline form in a 10% yield. $C_{26}H_{43}ClCoFe_{11}O_7$ (1176.32): calcd. C 40.5, H 5.6, N 20.0; found C 40.8, H 5.9, N 21.0. ^1H NMR (D_2O): δ = 1.40 (s, 3 H, CH_3), 1.90–3.50 (m, 20 H, CH_2), 7.52 (m, 2 H, 5/5′-pyr), 8.02 (t, 2 H, 4/4′-pyr), 8.28 (d, 2 H, 3/3′-pyr), 9.10 (d, 1 H, 6-pyr), 9.32 (d, 1 H, 6′-pyr) ppm. IR: $\tilde{\nu}_{CN}$ 2052, 2080, 2106. UV/Vis (H_2O): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 470 (2500), 338 (2160) nm.

[*trans*-$L_{14}Co^{III}$(μ-NC)$Ru^{II}(CN)_3(bpy)_{eq,ax}$]($ClO_4$)·$6H_2O$: *trans-I*-$[CoClL_{14}](ClO_4)_2$ (0.26 g) and $K_2[Ru(bpy)(CN)_4]$ (0.25 g) were refluxed in 50% aqueous MeOH (100 cm^3) at pH = 8. The color of the orange solution quickly darkened and developed into a brownish orange. After 6 h the solution was cooled and diluted with water to 5 L and loaded onto a Sephadex C-25 (Na^+ form) column and the desired product eluted with 0.1 м $NaClO_4$. Upon concentration of the eluate on a rotary evaporator an orange powder precipitated on standing. This was filtered off and then further purified via size exclusion chromatography (Sephadex LH-20, MeOH) to remove contamination by co-precipitated $NaClO_4$. The orange fraction collected from the Sephadex LH-20 column was left to slowly concentrate and the complex precipitated in a 43% yield. $C_{25}H_{45}ClCoN_{11}O_{10}Ru$ (855.15): calcd. C 35.0, H 5.5, N 18.0; found C 35.1, H 5.7, N 17.9. ^1H NMR ([D_4]MeOH): δ = 1.28 (s, 3 H, -CH_3), 2–3.55 (m, 16 H, -CH_2-), 7.052 (quint, 2 H, 5/5′-pyr), 7.97–8.03, (t, 2 H, 4/4′ pyr), 8.383–8.356 (d, 2 H, 3/3′ pyr), 9.12–9.13 (d, 1 H, 6 pyr), 9.32–9.34 (d, 1 H, 6′ pyr) ppm. IR: $\tilde{\nu}_{CN}$ 2050, 2071, 2105. UV/Vis (H_2O): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 470 (sh, 550), 389 (5500) 284 (25800) nm. Crystals of the mixed salt [*trans*-$L_{14}Co^{III}$(μ-NC)-$Fe^{II}(CN)_3(bpy)_{eq,ax}$]$(ClO_4)_{1/2}\cdot Cl_{1/2}\cdot 6H_2O$ were grown from a solution of the complex in a mixture of $NaClO_4$ and NaCl.

[*trans*-$L_{14}Co^{III}$(μ-NC)$Ru^{II}(CN)(bpy)_{2,cis}$]$(ClO_4)_3$: *trans-I*-$[CoClL_{14}]$-$(ClO_4)_2$ (0.25 g) and *cis*-$[Ru(CN)_2(bpy)_2]$ (0.3 g) were refluxed in 50% aqueous MeOH (100 cm^3) at pH = 8. The color of the orange solution quickly developed in intensity. After 6 h the solution was cooled, diluted with water to 5 dm^3 and loaded onto a Sephadex C-25 column (Na^+ from). The desired product eluted as the major orange band with 0.3 м $NaClO_4$. Upon concentration of the eluate, an orange powder precipitated and was filtered off. Further purification was achieved with size exclusion chromatography (Sephadex LH-20, MeOH) to remove excess $NaClO_4$. Yield 36%. $C_{33}H_{47}Cl_3CoN_{11}O_{14}Ru$ (1088.16): calcd. C 37.04, H 4.24, N 14.40; found C 36.58, H 4.22, N 14.35. ^1H NMR ([D_3]MeCN): δ = 1.20 (s, 3H-CH_3), 1.4–3.5 (m, 16H-CH_2-), 7.26 (quintd, 2 H), 7.42 (d, 1 H), 7.61 (m, 2 H), 7.72 (td, 1 H), 7.95 (qd, 2 H), 8.11 (tquint, 2 H), 8.33 (dd, 2 H), 8.42 (t, 2 H), 9.30 (d, 1 H), 9.54 (d, 1 H) ppm. IR: $\tilde{\nu}_{CN}$ 2048, 2089. UV/Vis (H_2O): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 490 (sh, 800), 411 (8900) 283 (49300) nm.

Crystallography

Cell constants for [{*trans*-$L_{14}Co^{III}$(μ-NC)}$Fe^{II}(CN)_3(bpy)_{eq,ax}$]-($ClO_4$)·$4H_2O$ and [{*trans*-$L_{14}Co^{III}$(μ-NC)}$Ru^{II}(CN)_3(bpy)_{eq,ax}$]-$(ClO_4)_{1/2}Cl_{1/2}\cdot 6H_2O$ were determined by a least-squares fit to the setting parameters of 25 independent reflections measured with an Enraf–Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo-K_α radiation (0.71073 Å).

Data reduction was performed with the WINGX[26] suite of programs. Structures were solved by direct methods with SHELXS and refined by full-matrix least-squares analysis with SHELXL-97.[27] All non-H atoms were refined with anisotropic thermal parameters. Aryl, alkyl and amino H-atoms were included at estimated positions using a riding model. Water H-atoms (if any) were not located. Molecular structure diagrams were produced with ORTEP3.[28] Crystal and refinement data are summarized in Table 2, and selected bond lengths and angles appear in the captions of Figures 1 and 2.

Table 2. Crystal data.

Formula	$C_{25}H_{43}ClCoFeN_{11}O_8$	$C_{25}H_{47}ClCoN_{11}O_8Ru$
Empirical formula	775.93	825.19
Crystal system	monoclinic	trigonal
Space group	$P2_1/c$	$R\bar{3}$
a [Å]	12.473(13)	22.786(3)
b [Å]	15.579(8)	
c [Å]	17.929(3)	37.01(1)
β [°]	97.53(4)	
V [Å^3]	3454(4)	16641(5)
Z	4	18
T [K]	293	293
D_c [g cm^{-3}]	1.492	1.482
μ [mm^{-1}]	1.039	0.987
R_1 (obsd. data)	0.0532	0.0555
wR_2 (all data)	0.1053	0.1725

CCDC-653712 and -653713 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Four ^{1}H NMR spectra (aromatic regions) of complexes and UV-Vis spectral changes on addition of solid $Na_2S_2O_8$ to a solution of complex [*trans*-$L_{15}Co^{III}(\mu\text{-}NC)Fe^{II}(CN)_3(bpy)_{eq,ax}]^+$ in water.

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