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Synthesis, Kinetics, and Physicochemical Studies of a New Mixed-Valent Heterobinuclear Cyano-Bridged Ruthenium(III)–Iron(II) Complex

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The synthesis and physicochemical properties (UV–vis, IR, EPR, cyclic voltammetry) of the complex $K_5[Ru^{III}(edta)(NC)Fe^{II}(CN)_5]$ (**2**) are described. Complex **2** shows an intervalence absorption maximum (E_{op}) at 940 nm in H_2O (at room temperature), and the position of the absorption maximum shifts with change in temperature (20–60 °C). The kinetics of the formation of complex **2** was studied spectrometrically by stopped-flow technique. The rate of formation of complex **2** was found to be first-order with respect to both $Ru(edta)(H_2O)^-$ and $Fe(CN)_6^{4-}$ concentrations and highly dependent on the ionic strength of the reaction medium. Rate and activation parameters (ΔH^* and ΔS^*) calculated for this reaction are in consistent with the proposed associative mechanism. The intervalence thermochromism for this ground-state mixed-valence complex **2** is discussed with reference to the data reported for the similar $[Ru^{III}(NH_3)_5(NC)Fe^{II}(CN)_5]^-$ complex.

Introduction

Besides the substitution mechanism for the aquo replacement reaction[1] of edta-type (edta = ethylenediaminetetracetate) complexes of ruthenium, the chemistry of polyamino–polycarboxylate complexes of ruthenium(III/II) is of continued interest due to their biochemical importance[2] and catalytic ability in oxidation[3] and reduction[4] reactions. We have been engaged in studying the kinetic and mechanistic behavior of $LRu^{III}H_2O$ (L = edta, pdta, hedtra) toward substitution reactions[5] and their possible catalytic role in the oxidation of organic substrates.[3] We have undertaken the present work for two principal reasons. First, to gain insight into the mechanism of substitution of $Ru^{III}(edta)(H_2O)^-$ with a complex molecule as a substituting ligand, which has not been reported so far, and, second, to synthesize a mixed-valence cyano-bridged coordination compound of ruthenium–edta. The chemistry of mixed-valence complexes of ruthenium (both homobinuclear and heterobinuclear) has been studied extensively;[6] however, the intramolecular electron-transfer process through the bridging ligand in itself is still interesting.[7] It can occur thermally or optically between the two metal centers through a bridging ligand. Studies of such reactions are important for developing our understanding of the electron-transfer process through a molecular bridge.

Hence, in the present study we have selected $Fe^{II}(CN)_6^{4-}$ as a substituting ligand which can serve the purpose of a potential nucleophile and be able to form the mixed-valence mixed-metal complex of our interest. In this paper, we report our experimental results on the synthesis, kinetics, and other physicochemical studies of the $[Ru^{III}(edta)(NC)Fe^{II}(CN)_5]^{5-}$ complex along with the thermochromic effect in this mixed-valence $[Ru^{III}(edta)(NC)Fe^{II}(CN)_5]^{5-}$ complex.

Experimental Section

Materials. $K[Ru^{III}(Hedta)Cl]\cdot 2H_2O$ was prepared by following the published procedure[8] and characterized. The $K[Ru^{III}(Hedta)Cl]$ complex rapidly gets aquated when dissolved in water,[9] and at pH 5–6 it exists predominantly as $Ru^{III}(edta)(H_2O)^-$ in solution. All other chemicals used were of AR grade. Double-distilled water was used throughout the experiments.

Synthesis of $K_5[Ru^{III}(edta)(NC)Fe^{II}(CN)_5]\cdot H_2O$ (2). The complex $K_5[Ru^{III}(edta)(NC)Fe^{II}(CN)_5]\cdot H_2O$ was prepared by reacting $K[Ru^{III}(Hedta)Cl]$ with $K_4[Fe(CN)_6]$ at pH 5.5. To a stirred solution (10 mL) of $K[Ru^{III}(Hedta)Cl]$ (1 mmol) (pH of solution was adjusted to 5.5 by NaOH) was slowly added $K_4[Fe(CN)_6]$ (1.1 mmol) dissolved in a minimum volume of water. The reaction mixture was allowed to stir for $^1/_2$ h at room temperature and then concentrated at room temperature under vacuum to 2–3 mL. On addition of acetone a green compound was precipitated, which was filtered off, washed with an acetone–water mixture (9:1) for several times, and dried under vacuum (yield 85%). Anal. Found (calcd): C, 23.50 (23.59); H, 1.76 (1.72); N, 13.69 (13.76).

Instrumentation and Techniques. Microanalyses were carried out by the use of a Carlo Erba elemental analyzer. Absorption spectra of complexes were recorded with a Schimadzu 160 UV–vis spectrophotometer

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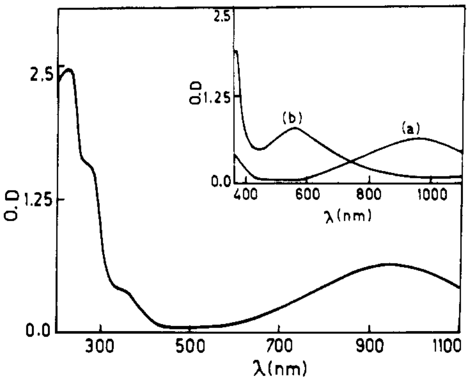

Figure 1. Spectrum of $K_5[Ru^{III}(edta)NCFe^{II}(CN)_5]$ (in H_2O) at room temperature. Inset: Spectra of (a) $K_5[Ru^{III}(edta)NCFe^{II}(CN)_5]$ and (b) $K_4[Ru^{III}(edta)NCFe^{III}(CN)_5)]$ in H_2O at room temperature.

equipped with a TCC 240A temperature controller. IR spectra were recorded on a Carl Zesis Specord M80 spectrometer, as KBr pellets. EPR studies were performed on a Bruker ESP 300 X-band spectrometer using a 100-kHz field modulation. Magnetic field calibrations were performed by using a built-in ERO 35 NMR gaussmeter. The EPR spectra of the complex were recorded in both powdered form (at 298 K) and frozen solution (at 77 K). The *g* values were determined with DPPH powder ($g = 2.0032$). Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were carried out with Princeton Applied Research (PAR) electrochemical instrument (Model 174A). Electrochemical studies (CV and DPV) were carried out in an aqueous medium using KCl as supporting electrolyte. A glassy-carbon working electrode and saturated calomel electrode (as reference) were used for this purpose. Variable-temperature electrochemical measurements were carried out by using a nonisothermal cell configuration[10] at which the reference electrode (SCE) was kept at constant temperature (room temperature). Coulometric experiments at controlled potential were carried out with a PAR-173 potentiostat equipped with a PAR 179 current integrator. A coulometric cell of three-electrode configuration consisting of a platinum gauge working electrode, a platinum wire counter electrode separated from the main solution by a glass frit, and an SCE as reference was used for this purpose.

Kinetic Studies. The kinetics of the substitution of $Ru^{III}(edta)(H_2O)^-$ with $Fe(CN)_6^{4-}$ was studied spectrophotometrically (at 900 nm) by using a HI-TECH stopped-flow spectrophotometer coupled with an Apple IIe data analyzer. The instrument was thermostated to ±0.1 °C. Rate constants were measured under pseudo-first-order conditions (excess $Fe(CN)_6^{4-}$), and the corresponding first-order plots were linear for a least 2–3 half-lives of the reaction. Rate constant data represented as an average of triplicate runs are reproducible within ±4%. Acetic acid–acetate buffers was used to maintain the pH of the kinetic solution, whereas KCl was used to control the ionic strength of the reaction medium. pH measurements were carried out with a Digisun pH meter.

Results and Discussion

In aqueous solution the $K[Ru^{III}(Hedta)Cl]$ complex hydrolyses rapidly to give the $Ru^{III}(Hedta)(H_2O)$ complex.[9] It had been reported that at pH 5.5 $Ru^{III}(Hedta)(H_2O)$ complex undergoes complete deprotonation of the uncoordinated –COOH group ($pK_1 = 2.4$) to give $Ru^{III}(edta)(H_2O)^-$ species **1**.[9] The spectrum of a solution of complex **1** (pale yellow) is almost featureless above 400 nm. Upon mixture of aqueous $K_4[Fe(CN)_6]$ (does not absorb above 400 nm) and complex **1** the solution immediately turned to green and the spectrum of the green solution displayed a new band at 940 nm ($\epsilon = 2.630$) as shown in Figure 1. On the basis of earlier reports for such mixed-valence cyano-bridged dimer complexes of ruthenium(III) and iron(II),[6] we assign this band (at 940 nm) to an intervalence-transfer (IT) band. The green complex, so obtained from the reaction of complex **1** and $Fe(CN)_6^{4-}$, was isolated, and elemental analysis of it confirmed the formula $K_5[Ru^{III}(edta)(NC)Fe^{II}(CN)_5]\cdot H_2O$ (**2**). The IR spectrum of complex **2** showed the usual ligational bonds of the edta ligand, a sharp band at 1600 cm^{-1} assigned to the uncoordinated COO^- group and a broad band at 1640 cm^{-1} for the coordinated COO^- group. In addition a broad strong band at 2080 cm^{-1} appeared in the spectrum of complex **2**. This band is assigned to cyanide stretching.[11] It may be noted here that the effect of bridging[11] through the cyano group was not prominently observed in the spectrum of complex **2**. In a similar observation, only one cyanide stretching band at 2060 cm^{-1} (broad and strong) was reported for the $[Ru^{III}(NH_3)_5(NC)Ru^{II}(CN)_5]^-$ complex.[6h] (Very recently, multiple CN vibrations were reported in published Raman data for the $[Ru^{III}(NH_3)_5NCRu^{II}(CN)_5]^-$ complex.)[6i] Interestingly two split bands at 2130 and 2090 cm^{-1} were observed in the cyanide stretching region of the spectrum of $[Ru^{III}(edta)(NC)Fe^{III}(CN)_5]^{4-}$ (**3**).[12] This may be explained in terms of an increase in the oxidation number of the iron center that causes a significant change in the bond order between bridging and terminal cyano groups.[11]

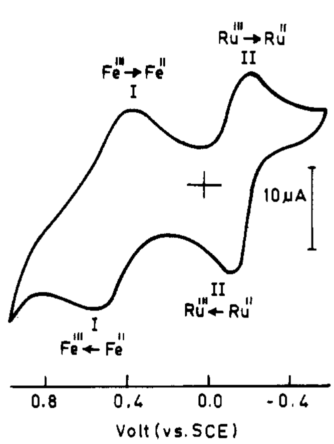

Figure 2. Cyclic voltammogram of $K_5[Ru^{III}(edta)NCFe^{II}(CN)_5]$ in aqueous 0.1 M KCl, scan rate 100 mV/s.

EPR spectra of complex **2** both in powder form and frozen solution (77 K) show a spectral pattern almost identical to that reported earlier for complex **1** ($g_1 = 2.393$, $g_2 = 2.345$, $g_3 = 1.765$).[3c] This is indicative of no apparent interaction (within the EPR time scale) between two metal orbitals in complex **2** in the ground state, and also there is no marked rearrangement in the geometry of the Ru–edta moiety in complex **2**.

A cyclic voltammogram of complex **2** is shown in Figure 2. Two pairs of reversible peaks indicated as I and II in Figure 2 are associated with Fe^{3+}/Fe^{2+}($E_{1/2}$ = 0.69 vs NHE) and Ru^{3+}/Ru^{2+}($E_{1/2}$ = 0.02 V vs NHE) redox couples, respectively. The linear dependency of peak currents on the square root of the potential scan rate confirmed the occurrence of a monoelectronic reversible electrochemical process at both of the redox sites as shown in Figure 2.

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(10) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131. (E_f was determined by cyclic voltammetry and equated to $E_{1/2}$ by assuming the diffusion coefficients of reduced and oxidized species are almost same; i.e., their ratio is close to unity.)

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(12) The complex $K_4[Ru^{III}(edta)NCFe^{III}(CN)_5]$ (**3**) was prepared by interacting complex **1** with $K_3[Fe(CN)_6]$ by following the same procedure as adopted for complex **2**. The preparation of complex **3** was required for comparison purposes. We found rate of substitution of complex **1** with $Fe(CN)_6^{3-}$ is slower ($k = 9.9$ M^{-1} s^{-1} at 30 °C, pH = 5, $\mu = 0.5$ M KCl) by 1 order of magnitude than that ($k = 99$ M^{-1} s^{-1} at 25 °C) obtained for $Fe(CN)_6^{4-}$ under same reaction conditions. Thus, $Fe^{II}(CN)_6^{4-}$ is a stronger nucleophile than $Fe^{III}(CN)^{3-}$ toward substitution of complex **1**. Further, no intervalence charge-transfer band was observed in the case of complex **3**. (See inset of Figure 1.) Controlled-potential oxidation of complex **2** (at 0.5 V) quantitatively produced complex **3** as confirmed by matching the spectra of an electrolyzed solution with the spectrum of complex **3**. The IT band (940 nm) completely disappeared after electrolysis (calculated *n* value of the coulometric experiment is 0.97) but reappeared upon addition of ascorbic acid or electrochemical reduction (at 0.3 V).

Table I. Values of k_{obs} at Different $[Fe(CN)_6^{4-}]^a$

$10^2[Fe(CN)_6^{4-}]$ (M)	k_{obs} (s^{-1})	$10^2[Fe(CN)_6^{4-}]$ (M)	k_{obs} (s^{-1})
0.5	0.49	2.0	1.98
1.0	0.99	2.5	2.47
1.25	1.24	4.0	3.96

[a] $[Ru^{III}]_T = 5 \times 10^{-4}$ M, pH = 5.5 (acetic acid–acetate), $\mu = 0.5$ M (KCl), and $t = 25$ °C.

Kinetics of Formation of Complex 2. The observed spectral changes at 900 nm associated with the formation of complex **2** (Figure 1) were employed to study the kinetics of the reaction. Preliminary kinetic experiments showed that the nucleophilicity of $Fe(CN)_6^{4-}$ is high enough so that the buffer components and Cl^- (used to control the ionic strength of solution) could not compete in the substitution of complex **1** when these were added to $Fe(CN)_6^{4-}$ solution prior to mixing with complex **1** in stopped-flow chamber. The kinetics of substitution of complex **1** with $Fe(CN)_6^{4-}$ was studied at pH 5.5, as it shows maximum reactivity[9] in the pH range 4–6 and the observed rate is practically independent of pH at $4 < pH < 6$.[9] The rate of reaction was found to be first order with respect to complex **1**. The observed rate constant (k_{obs}) increases with the increase of $Fe(CN)_6^{4-}$ concentration as shown in Table I. The plot of k_{obs} vs $[Fe(CN)_6^{4-}]$ gave a straight line (not shown) with a negligible intercept, which indicates the absence of a reverse aquation reaction under the specified conditions. Further, a few experiments were repeated under an inert atmosphere (Ar) and no marked change in the reaction rate was observed. On the basis of the above kinetic observations, the following mechanism is proposed for the substitution of complex **1** with $Fe(CN)_6^{4-}$:

$$Ru^{III}(edta)(H_2O)^- + Fe(CN)_6^{4-} \rightarrow [Ru^{III}(edta)(NC)Fe^{II}(CN)_5]^{5-} + H_2O \quad (1)$$

A rate expression is outlined in eq 2.

$$k_{obs} = k[Fe(CN)_6^{4-}] \quad (2)$$

In order to check the pertinence of our proposed mechanism (eq 1), we studied the ionic strength dependence of the rate constant, and we obtained the most convincing evidence in favor of the rate-determining step, as the plot of log k vs $\mu^{1/2}/(1 + \mu^{1/2})$ gave a straight line with a slope 4.23. According to the Bronsted equation[13] the slope represents the product of charges of the reacting ions. The value obtained (4.23) is indeed identical to the value expected for the mechanism outlined in eq 1.

The substitution reaction was studied at four different temperatures. The values of the rate constant (k) obtained are 99, 148, 188, and 215 $M^{-1}\,s^{-1}$ at 25, 33, 40, and 45 °C, respectively. The small ΔH^* value (28 ± 3 kJ mol^{-1}) and large negative ΔS^* value (−112 ± 8 J $deg^{-1}\,mol^{-1}$) are consistent with the operation of an associative mode of activation in the substitution process as reported for the other ligand substitution reaction with complex **1**.[1a,e,5a,c]

Thermochromic Effect on Intervalence Transfer. Complex **2** exhibits a metal–metal charge-transfer (MMCT) band at 940 nm (Figure 1), and the corresponding intervalence electron-transfer reaction is represented in eq 3.

$$[(edta)Ru^{III}(NC)Fe^{II}(CN)_5]^{5-} \rightleftarrows [(edta)Ru^{II}\text{–}NC\text{–}Fe^{III}(CN)_5]^{5-} \quad (3)$$

At room temperature, the intervalence absorption maximum (E_{op}) appears at 940 nm; however, the position of it changes with change in temperature (Figure 3). In the studied temperature range (20–60 °C), the value of E_{op} (cm^{-1}) decreases with an increase in temperature (K) as shown in the inset of Figure 3. The temperature-dependence term (dE_{op}/dT) for this thermal effect on the intervalence charge-transfer process (eq 3), obtained from the slope of the plot, is −5 ± 0.4 $cm^{-1}\,deg^{-1}$.

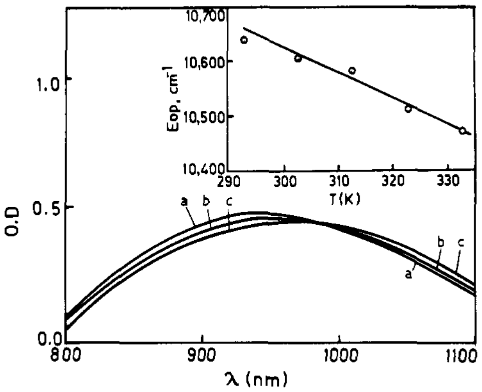

Figure 3. Intervalence absorption spectra for $[Ru^{III}(edta)NCFe^{II}(CN)_5]^{5-}$ in water at (a) 20, (b) 40, and (c) 60 °C. Inset: E_{op} versus temperature (K).

Very recently, Hupp and Dong[14] interpreted this above described thermochromic effect in terms of the thermodynamic parameter $\Delta S°_{rc}$ (reaction entropy) by simplifying the Hush treatment[15] of intervalence energies (E_{op}). According to the Hush treatment

$$E_{op} = \lambda_{vis} + \lambda_s + \Delta E + \Delta E' \quad (4)$$

where λ_{vib} and λ_s represent vibrational and solvent reorganization energies, respectively. ΔE represents the vibrationally relaxed initial-state/final-state separation energy, and $\Delta E'$ is an additional energy term for possible energy contributions due to spin–orbit coupling or ligand field asymmetry effects. If the above described energy components are reviewed as free energies,[16] the temperature dependence of E_{op} can be estimated by measuring the temperature dependence of any factor on the right-hand side of eq 4. Now, considering that some of the component energies (λ_s, $\Delta E'$) are negigibly temperature dependent[17] and the temperature dependence of λ_{vib} is difficult to envision, the Hush equation (eq 4) can be simplified as $E_{op} \approx \Delta E$. The ΔE component was proposed to be equal to the difference in the formal potentials (for the M(III) → M(II) electrochemical process) of two independent redox sites of the binuclear complex.[14] Under nonisothermal conditions, the temperature coefficient (dE_f/dT) of the individual formal potential (E_f) gives $\Delta S°_{rc}$ (reaction entropy).[10]

We have determined the temperature dependence of E_f for iron and ruthenium redox sites for the electrochemical processes in eqs 5 and 6 and found that E_f for the ruthenium center in complex **2** is practically immune to a temperature effect. The temperature dependance of E_f for the iron center is shown in Figure 4, and the value of $\Delta S°_{rc}$ (i.e. dE_f/dT) calculated from the slope of the plot (Figure 4) is −6 ± 1 $cm^{-1}\,deg^{-1}$. If we neglect the contribution from the ruthenium center of complex **2**, the temperature-dependence term (dE_{op}/dT) determined from cyclic

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(13) Espenson, J. H. *Chemical Kinetics and Reaction Mechanism*; McGraw-Hill: New York, 1981; p 172.

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(15) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(16) Marcus, R. A.; Sutin, N. A. *Comments Inorg. Chem.* **1986**, *5*, 119.

(17) The temperature dependence of λ_s can be estimated from the dielectric continuum theory for which temperature coefficients of static (ϵ_s) and optical-frequency (ϵ_{op}) dielectric constants are to be considered. For water as solvent the temperature coefficients are small and to some extent compensating. The overall temperature dependence of λ_s is reported to be in the order of 0.2 $cm^{-1}\,deg^{-1}$ or less (Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1984**, *88*, 1860). $\Delta E'$ is temperature independent. For λ_{vib} it is difficult to envision a significant temperature dependence unless the pertinent vibrational frequencies themselves show temperature dependence. Hence, the effect of temperature on λ_{vib} was not considered in this case.

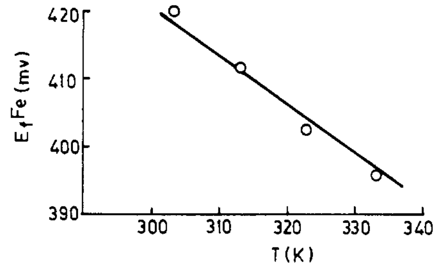

Figure 4. E_f versus temperature [nonisothermal cell configuration) for Fe^{III}/Fe^{II} (eq 5) in aqueous 0.1 M KCl.

$$[(edta)Ru^{III}(NC)Fe^{III}(CN)_5]^{4-} + e \rightarrow [(edta)Ru^{III}NCFe^{II}(CN)_5]^{5-} \quad (5)$$

$$[(edta)Ru^{III}NCFe^{II}(CN)_5]^{5-} + e \rightarrow [(edta)Ru^{II}NCFe^{II}(CN)_5]^{6-} \quad (6)$$

voltammetric studies at variable temperature using the nonisothermal technique is comparable to the value of dE_{op}/dT (−5 cm^{-1} deg^{-1}) obtained by spectral measurements at different temperatures. The effect of temperature on the intervalence charge transfer reported for the asymmetric $[Ru^{III}(NH_3)_5\text{–}NCFe^{II}(CN)_5]^-$ complex[14] is −13.5 cm^{-1} deg^{-1} (−9.2 ± 1.5 cm^{-1} deg^{-1} obtained from electrochemical measurements).[14] But for a symmetrical $[Fe^{III}(CN)_5(4,4'\text{-bipy})Fe^{II}(CN)_5]^{5-}$ system, the value of dE_{op}/dT observed by Hupp et al.[14] is almost negligible (0.1 ± 0.6 cm^{-1} deg^{-1}). They explained this phenomena in terms of the dependency of E_{op} on the other components (λ_{vib}, λ_s, and $\Delta E'$) on the Hush equation, but not on ΔE, which is necessarily zero. The observed variable-temperature effect on E_{op} clearly indicates the presence of a ΔE component in our case as expected for a asymmetric mixed-valence system. Interestingly, despite having asymmetry, the value of dE_{op}/dT observed in our case (−5 cm^{-1} deg^{-1}) is comparatively lower than that reported (−13.5 cm^{-1} deg^{-1}) for the $[Ru^{III}(NH_3)_5NCFe^{II}(CN)_5]^-$ complex (which is also an asymmetric system). This difference can possibly (at least at a qualitative level) be explained on the basis of earlier reports[18] on electrochemical thermodynamics of intervalence electron transfer between a pair of transition metals linked by an organic bridge. It was reported that in a given solvent the reaction enthalpies ΔS°_{rc} (i.e., dE_f/dT under nonisothermal condition) are largely dependent on the charge type of the redox couples and the chemical nature of the coordinated ligands.[18] Coordination of anionic ligands changes the cationic environment of the metal fragments and generally yields substantially smaller values of ΔS°_{rc}. Moreover, ΔS°_{rc} values for cyano Fe(III)/Fe(II) couples are known to be extremely sensitive to be cationic environment.[19] So, considering the above facts, it is understood that a change in charge type from +3/+2 (for $[Ru^{III}(NH_3)_5NCFe^{II}(CN)_5]^-$) to −1/−2 (for complex **2** in which anionic edta ligand is coordinated to the ruthenium center) on the ruthenium redox couples is probably the reason for the observed difference in dE_{op}/dT values between the two cyano-bridged mixed-valence complexes. However, it is to be noted here that, despite the above described charge effect on the observed thermochromism, other factors may remain present whose relative contributions to E_{op} are difficult to assess.

In conclusion, this study has clearly shown the ability of $Fe(CN)_6^{4-}$ to produce a stable cyano-bridged mixed-valence mixed-metal $[(edta)Ru^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^{5-}$ complex through a clean one-step substitution of complex **1**. There seems to be a fine balance between electrochemical and spectral observations on the thermochromic effect on the intervalence charge-transfer process in complex **2**, and the difference in the observed thermochromism in our complex **2** and $Ru^{III}(NH_3)_5NCFe^{II}(CN)_5^-$ is perhaps discriminated by the charge type effect on the Ru fragments. In addition, the perfectly reversible one-electron redox process which can take place at the iron center (see ref 12) of complex **2** seems to provide a good basis for redox reactions. Experiments pertinent to this matter are in progress.

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