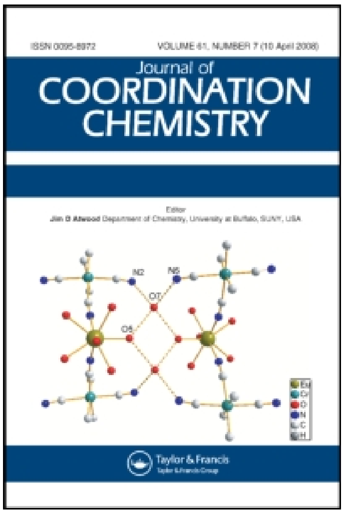

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Jay Sung[a]; Wan-Ting Hsu[a]; Andrew Yeh[a]; Yuan-Jang Chen[b]
[a] Department of Chemistry, Tunghai Christian University, Taichung, Taiwan, ROC [b] Department of Chemistry, Fu Jen Catholic University, Taipei, Taiwan, ROC

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Stabilities and reactivities of the cyano-bridged binuclear complexes of *trans*-isonicotinamidetetraammineruthenium and hexacyanoferrate

JAY SUNG†, WAN-TING HSU†, ANDREW YEH*† and YUAN-JANG CHEN‡

†Department of Chemistry, Tunghai Christian University, Taichung, Taiwan, ROC
‡Department of Chemistry, Fu Jen Catholic University, Taipei, Taiwan, ROC

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The binuclear complexes, *trans*-(isn)$(NH_3)_4RuNCFe(CN)_5^n$ ($n = 2-, 1-, 0$), were prepared both in aqueous solutions and as isolated salts. Their properties, particularly that of the mixed-valence species (**M**), were characterized by UV-Vis, infrared, electrochemical and kinetic studies. The results suggested that Ru(III)–Fe(II) was both thermodynamically and kinetically stable oxidation states. The extent of delocalization of **M** was estimated by analysis of the intervalence band on the basis of Hush's theory. The stabilization of **M** with respect to its oxidation state isomer (**M′**) was investigated and it was found that the electrostatic effect associated with the net charges of metal moieties constituted the dominant factor governing the stability of **M**.

Keywords: Mixed-valence; Intervalence band; Charge effect; Electron transfer

1. Introduction

There have been numerous studies on binuclear complexes of pentacyanoferrate(II, III) and pentaammineruthenium(II, III) [1–9]. In addition to the investigation of the spectra and electrochemical aspects which are usually emphasized in the diruthenium system [10, 11], work on this system has also been extended to the reactivity of mixed-valence compounds. Nevertheless, most of the previous work on the binuclear complexes of this kind were focused on using *N*-heterocyclic aromatic compounds as bridging ligands, and little effort has been devoted to the investigation of other types of ligands as mediating bridge. Haim *et al.* [2], prepared the mixed-valence $(CN)_5Fe(CN)Ru(NH_3)_5^-$ binuclear complex by kinetic study of the outer-sphere electron transfer reaction of $Ru(NH_3)_5(H_2O)^{3+}$ and $Fe(CN)_6^{4-}$. They further studied this mixed valence ion by characterizing the intervalence band and suggested that it belonged to the valence-trapped species containing Fe(II)/Ru(III) oxidation states. Hupp *et al.* [12–15] also investigated this ion later with emphasis on the electronic coupling between metal

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*Corresponding author. Email: adyeh@thu.edu.tw

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centers of the mixed-valence state, including the theoretical treatment of their electrochemical results [15].

In view of our long standing interest in binuclear complexes of $Fe(CN)_5^{3-/2-}$ and $Ru(NH_3)_5^{2+/3+}$ moieties [1, 2, 5, 6, 9], we have taken up the study of the binuclear complexes of the form *trans*-$[(isn)(NH_3)_4RuNCFe(CN)_5]^n$ ($n = 2-, 1-, 0$, isn = isonicotinamide). Unlike $Ru(NH)_5^{2+/3+}$, the Ru(II) metal center of the present system carries a π-acceptor ligand which will facilitate characterization of the binuclear complexes due to strong $d\pi$-to-$\pi_{isn}{}^*$ charge transfer absorption of the Ru(II) complex. Moreover, the air sensitivity of *trans*-$Ru(NH_3)_4(isn)(H_2O)^{2+}$ being less than $Ru(NH_3)_5(H_2O)^{2+}$ will facilitate the direct preparation of the binuclear complex in its reduced form. In addition to the investigation of the properties of the mixed-valence molecule, we also report the reactivities of the binuclear complexes toward substitution and redox reactions.

2. Experimental

2.1. *Materials*

$Ru(NH_3)_5Cl_3$ [16] and *trans*-$[Ru(NH_3)_4(isn)(SO_4)]Cl$ [17] were prepared according to literature methods. Solutions of *trans*-$Ru(NH_3)_4(isn)(H_2O)^{2+}$ complex were prepared by dissolving *trans*-$[Ru(NH_3)_4(isn)(SO_4)]Cl$ in water and then reducing with zinc amalgam under argon for 20 min. The complex ion also could be precipitated upon the addition of ammonium hexafluorophosphate [18]. Doubly-distilled deionized water was obtained by passing house-line distilled water through a Barnstead NANO water purification system. All chemicals were reagent grade and used without further purification.

2.2. *Syntheses of binuclear complexes*

To avoid interference of air in the preparation, all syntheses were carried out in a glove box with nitrogen gas.

2.2.1. K_2[*trans*-$(isn)(NH_3)_4RuNCFe(CN)_5] \cdot 5H_2O$. 90 mg $K_4Fe(CN)_6 \cdot 3H_2O$ (0.22 mmol) was dissolved in 20 mL H_2O and 120 mg *trans*-$[Ru(NH_3)_4(isn)(H_2O)](PF_6)_2$ (0.20 mmol) was added. The resulting solution was stirred for 20 min to allow the reaction to be complete. A methanol/ether (1 : 10) mixed solvent was then gradually added to the solution until permanent turbidity was observed. Upon cooling to 0°C, the solid that formed was filtered and washed with methanol and ether. Yield: 114 mg (85%).

2.2.2. K[*trans*-$(isn)(NH_3)_4RuNCFe(CN)_5] \cdot 6H_2O$. A solution containing 1.0×10^{-2} M *trans*-$(isn)(NH_3)_4RuNCFe(CN)_5^{2-}$ (20 mL) was treated with one equivalent of $Na_2S_2O_8$ under stirring. After 10 min an acetone/ether (1 : 10) mixed solvent was added gradually until permanent turbidity was formed. After cooling the solution to 0°C for 30 min, the solid formed was filtered and washed with acetone and ether. Yield: 84 mg (70%).

2.2.3. *trans*-(isn)$(NH_3)_4$RuNCFe$(CN)_5$ • $7H_2O$. A 20 mL solution of 1.0×10^{-2} M *trans*-(isn)$(NH_3)_4$RuNCFe$(CN)_5^{2-}$ was oxidized with equimolar $Na_2S_2O_8$ and the solution was stirred for 20 min. A methanol/ether (1 : 10) mixed solvent was added gradually until permanent turbidity was formed. After cooling the solution to 0°C for 30 min, the solid formed was filtered and washed with methanol and ether. Yield: 86 mg (70%).

2.2.4. K[*trans*-(isn)$(NH_3)_4$RuNCCo$(CN)_5$] • $4H_2O$. 73 mg $K_3Co(CN)_6$ (0.22 mmol) was dissolved in 20 mL H_2O, and 120 mg *trans*-[Ru$(NH_3)_4$(isn)(H_2O)]$(PF_6)_2$ was added. The mixture was stirred for 20 min to allow the reaction to be complete. A methanol/ether (1 : 10) mixed solvent was added gradually until permanent turbidity was formed. After cooling to 0°C for 30 min, the solid was filtered and washed with methanol and ether. Yield: 90 mg (73%).

The results of elemental analysis of the binuclear complexes are listed in table 1.

2.3. *Instrumentation*

Ultraviolet and visible spectra were measured on a Hewlett-Packard HP 8453 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1725X FT-IR spectrophotometer in KBr pellets. The intervalence band was measured on a Shimadzu 3101 PC UV-Vis-NIR spectrophotometer. Electrochemistry was performed on a PAR model 273A potentiostat/galvanostat system as described previously [19].

2.4. *Kinetic measurements*

Rates of formation of the binuclear complexes, *trans*-(isn)$(NH_3)_4$RuNCFe$(CN)_5^{n}$ ($n = 2-$ for Fe(II), $n = 1-$ for Co(III)) were measured by mixing freshly prepared solutions of *trans*-Ru$(NH_3)_4$(isn)$(H_2O)^{2+}$ with an excess of $Fe(CN)_6^{4-}$ or $Co(CN)_6^{3-}$, and the measurements were carried out by following the formation of the binuclear complexes at or near their band maxima. The kinetics of the oxidation of mono- and binuclear complexes of *trans*-Ru$(NH_3)_4$(isn)L^{2+} were also measured under pseudo-first-order conditions with peroxydisulfate in excess. The measurements were performed by following the disappearance of the MLCT absorptions of Ru(II) complexes or the intervalence band (mixed-valence compound only). All kinetic runs were carried out on the Hi-Tech CU61 stopped-flow apparatus at $\mu = 0.1$ M LiCl and

Table 1. Elemental analysis of binuclear complexes.

Complex		C%	H%	N%
K_2[*trans*-(isn)$(NH_3)_4$RuNCFe$(CN)_5$] · $5H_2O$ (**R**)	Anal. Calcd	21.46	4.20	25.03
	Found	21.89	4.29	25.58
K[*trans*-(isn)$(NH_3)_4$RuNCFe$(CN)_5$] · $6H_2O$ (**M**)	Anal. Calcd	22.16	4.65	25.84
	Found	22.12	4.77	25.04
trans-(isn)$(NH_3)_4$RuNCFe$(CN)_5$ · $7H_2O$ (**O**)	Anal. Calcd	22.90	5.12	26.71
	Found	22.70	5.16	26.26
K[*trans*-(isn)$(NH_3)_4$RuNCCo$(CN)_5$] · $4H_2O$	Anal. Calcd	23.34	4.24	27.22
	Found	23.00	3.95	27.15

pH = 5.0 (acetate). The pseudo-first-order rate constants were obtained from the slopes of the linear least square fits of $\ln|A_\infty - A_t|$ *versus* time plots.

3. Results and discussion

3.1. *Characterization of the binuclear complexes*

When solution of *trans*-$Ru(NH_3)_4(isn)(H_2O)^{2+}$ was mixed with an equimolar solution of $Fe(CN)_6^{4-}$, an absorption at $\lambda_{max} = 510\,nm$ ($\varepsilon_{max} = 1.50 \times 10^4\,M^{-1}\,cm^{-1}$) was observed, suggesting formation of the binuclear complex in its reduced form (**R**). As shown in table 2, there is a bathochromatic shift in the spectrum for the binuclear complexes compared to that of the mononuclear Ru(II) complex. The shift arises from charge transfer of $Fe(CN)_5^{3-}$ rather than the electron withdrawing effect of the Fe(II) since the λ_{max} for the *trans*-$(isn)(NH_3)_4RuNCCo(CN)_5^-$ binuclear complex, in which $Co(CN)_5^{2-}$ acts as a σ acid center, remains the same as the mononuclear Ru(II) complex. The coupling of the $d\pi$ orbitals between Fe(II) (3d) and Ru(II) (4d) may destabilize the $d\pi$ orbital of Ru(II) and lower the energy of $d\pi$-to-$\pi_{isn}{}^*$ charge transfer. When **R** was oxidized with one equivalent of peroxydisulfate to the mixed-valence species (**M**), the MLCT absorption disappeared, indicating that the Ru(II) center was oxidized. Moreover, a lack of 420 nm band which was characteristic of ligand field splitting of cyanoferrate(III) complexes [20–22] implied that the iron center was Fe(II). The spectral results therefore favor assignment as Ru(III) and Fe(II) oxidation states. The infrared spectral measurements of the solid samples with $\upsilon_{CN} = 2049\,cm^{-1}$ and $\delta(NH_3)_{sym} = 1322\,cm^{-1}$ for **M** species, as shown in table 2, also confirm the above assignment of oxidation states. When **M** was further oxidized to the oxidized binuclear complex (**O**), the solution turned blue with an absorption at $\lambda_{max} = 550\,nm$ in addition to the expected 415 nm band. Both absorptions disappeared immediately when the solution was reduced with excess ascorbic acid, and correspondingly, the reduced form (**R**) formed stoichiometrically as evidenced from the absorption at 510 nm. Since the solution did not turn blue for the mixed-valence species (**M**), we prefer to think that the color might arise from the $\pi_{CN} \rightarrow Fe(III)$ charge transfer from the bridged cyanide.

Table 2. UV-Vis and IR absorption spectra for Fe(II, III) and Ru(II, III) complexes.

Complex	λ_{max} (nm)	$10^{-3}\ \varepsilon_{max}$ ($M^{-1}\,cm^{-1}$)	υ_{CN} (cm^{-1})	$\delta(NH_3)_{sym}$ (cm^{-1})
$Fe(CN)_6^{4-}$			2044	
$Fe(CN)_6^{3-}$	420[a]	1.04	2125	
trans-$Ru(NH_3)_4(isn)(H_2O)^{2+}$	475[b]	12.0		1259
trans-$Ru(NH_3)_4(isn)(H_2O)^{3+}$	320	5.50		1322
trans-$(isn)(NH_3)_4RuNCFe(CN)_5^{2-}$ (**R**)	510	15.0	2041	1271
trans-$(isn)(NH_3)_4RuNCFe(CN)_5^-$ (**M**)	320 (sh)		2049	1322
trans-$(isn)(NH_3)_4RuNCFe(CN)_5$ (**O**)	320 (sh)		2117	1320
	415	1.47		
	550	1.29		
trans-$(isn)(NH_3)_4RuNCCo(CN)_5^-$	475	14.7	2117	1274

[a] Ref. [20].
[b] Ref. [18].

Additional evidence in favor of localized Ru(III) and Fe(II) oxidation states for **M** comes from reduction potentials of the various couples, as shown in table 3. The cyclic voltammogram of the $Ru^{II}NCFe^{II}$ exhibited two consecutive reversible waves at $E_f = 0.23$ and 0.66 V, respectively, as shown in figure 1.

Owing to the similarity in reduction potentials for mononuclear Fe(II) and Ru(II) complexes, the E_f of the first step of oxidation of the binuclear complex, from **R** to **M**, is hard to distinguish which metal center is oxidized. However, since $Fe(CN)_5^{2-}$ and $Co(CN)_5^{2-}$ moieties both behave as σ acid centers, the E_f of the second step of oxidation will be close to that of the $Ru^{II}NCCo^{III}$ binuclear complex if **M** features Ru(II)–Fe(III) oxidation states. The 0.19 V higher potential for the **O**/**M** couple implies that oxidation of **M** actually goes to Fe(II).

Table 3. Reduction potentials for Ru(III) and Fe(III) complexes.[a]

Complex	E_f, V *vs.* NHE
$Fe(CN)_6^{3-/4-}$	0.43[b]
trans-$Ru(NH_3)_4(isn)(H_2O)^{3+/2+}$	0.44[c]
trans-$(isn)(NH_3)_4RuNCFe(CN)_5^{2-/1-}$	0.23
trans-$(isn)(NH_3)_4RuNCFe(CN)_5^{1-/0}$	0.66
trans-$(isn)(NH_3)_4RuNCCo(CN)_5^{1-/0}$	0.47
$(NH_3)_5RuNCFe(CN)_5^{2-/1-}$	−0.071 (−0.083)[d]
$(NH_3)_5RuNCFe(CN)_5^{1-/0}$	0.65 (0.62)[d]
$(NH_3)_5RuNCCo(CN)_5^{1-/0}$	0.18

[a] $\mu = 0.10$ M LiCl, pH = 5.0 (acetate), $T = 25°C$.
[b] Ref. [3].
[c] Ref. [18].
[d] Ref. [15].

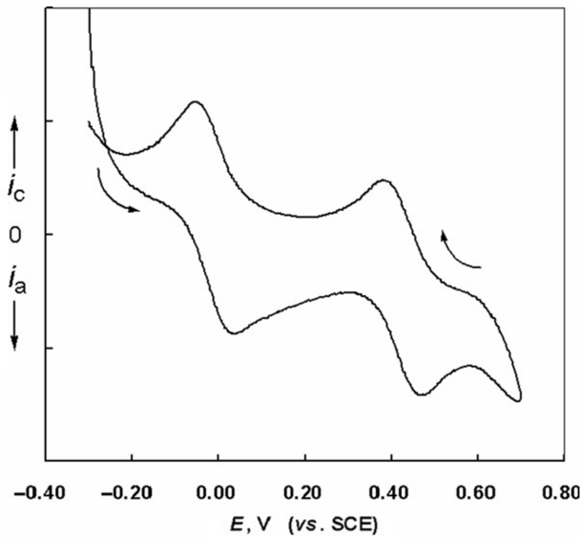

Figure 1. CV diagram for *trans*-$(isn)(NH_3)_4RuNCFe(CN)_5^{2-}$ [bin] = 3.0×10^{-4} M, $\mu = 0.10$ M LiCl, pH = 5.0.

3.2. *Kinetics of formation of binuclear complexes*

Pseudo-first-order rate constants for formation of the binuclear complexes *trans*-$\mathrm{Ru(NH_3)_4(isn)L^n}$ ($n = 2-$ for $\mathrm{L = Fe(CN)_6^{4-}}$ and $n = 1-$ for $\mathrm{L = Co(CN)_6^{3-}}$) according to equation (1) varied linearly with concentration of the cyanocomplexes, as shown in figure 2. Specific rate constants are obtained from slopes of one-parameter linear least square fits of k_{obs} *versus* $\mathrm{M(CN)_6^{n-}}$ plots. The results are listed in table 4.

$$trans\text{-}\mathrm{Ru(NH_3)_4(isn)(H_2O)^{2+} + L} \underset{k_\mathrm{d}}{\overset{k_\mathrm{f}}{\rightleftharpoons}} trans\text{-}\mathrm{Ru(NH_3)_4(isn)L^n + H_2O} \qquad (1)$$

Plots of $\ln(k_\mathrm{f}/T)$ *versus* $1/T$ are linear, yielding $\Delta H^{\neq} = 15.0 \pm 0.4$ and $16.4 \pm 0.1\,\mathrm{kcal\,mol^{-1}}$, $\Delta S^{\neq} = 0.99 \pm 0.01$ and $1.4 \pm 0.1\,\mathrm{cal\,mol^{-1}\,K^{-1}}$, for $\mathrm{L = Fe(CN)_6^{4-}}$ and $\mathrm{Co(CN)_6^{3-}}$, respectively, at $\mu = 0.1\,\mathrm{M}$ LiCl and pH = 5.0 (acetate). Since the activation parameters were comparable for both complexes, the difference in rate constants may simply arise from charge effects rather than the intrinsic reactivity of complexes. We have tried to measure the rate of dissociation for the binuclear complex **R** using isonicotinamide as the scavenger, however, less than 10% change in absorbance for **R** was observed in two weeks, and the formation of *trans*-$\mathrm{Ru(NH_3)_4(isn)_2^{2+}}$ complex was not observed. Taking this as the lower limit for the half-life for dissociation of **R**, the rate constant of dissociation would be $k_\mathrm{d} \approx 5.7 \times 10^{-7}\,\mathrm{s^{-1}}$. The values of k_f and k_d

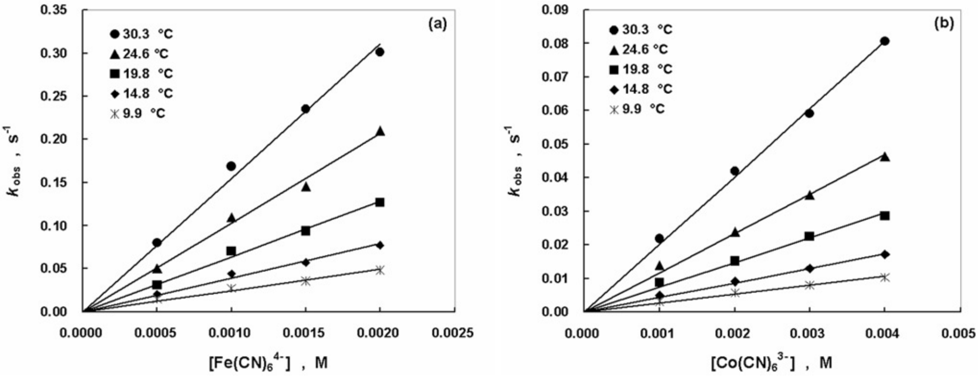

Figure 2. k_{obs} *vs.* [L] plots for formation of *trans*-$\mathrm{Ru(NH_3)_4(isn)L^n}$ complexes (a) $\mathrm{L = Fe(CN)_6{}^{4-}}$; (b) $\mathrm{L = Co(CN)_6{}^{3-}}$, $\mu = 0.10\,\mathrm{M}$ LiCl, pH = 5.0.

Table 4. Rate constants, k_f, for formation of *trans*-$\mathrm{Ru(NH_3)_4(isn)L^n}$.[a]

	k_f ($\mathrm{M^{-1}\,s^{-1}}$)	
T (°C)	$\mathrm{L = Fe(CN)_6^{4-}}$	$\mathrm{L = Co(CN)_6^{3-}}$
9.9	24.7 ± 0.08	2.66 ± 0.07
14.8	39.4 ± 0.09	4.35 ± 0.09
19.8	64.0 ± 0.09	7.38 ± 0.08
24.6	103 ± 0.05	11.7 ± 0.2
30.3	155 ± 0.04	20.2 ± 0.3

[a] $\mu = 0.10\,\mathrm{M}$ LiCl, pH = 5.0 (acetate).

yielded the affinity for the formation of **R** as K_R $(k_f/k_d) = 1.8 \times 10^8\,\mathrm{M}^{-1}$ at $\mu = 0.1\,\mathrm{M}$ LiCl, pH = 5.0 (acetate) and $T = 25°\mathrm{C}$. From the results of reduction potentials and K_R, the equilibrium constant for formation of **M**, K_M, can be estimated by utilizing the following cycle and equation (2), and the value is $K_M = 7.3 \times 10^{11}\,\mathrm{M}^{-1}$.

$$\begin{tikzcd}
\textit{trans}\text{-Ru(NH}_3)_4(\text{isn})(\text{H}_2\text{O})^{3+} + \text{Fe(CN)}_6^{4-} \arrow[r, shift left, "K_M"] \arrow[d, shift left, "E^o_1"] \arrow[d, phantom, shift right=6, "-e"] & \textit{trans}\text{-(isn)(NH}_3)_4\text{RuNCFe(CN)}_5^{-} + \text{H}_2\text{O} \arrow[l, shift left] \arrow[d, shift left, "+e"] \arrow[d, phantom, shift right=6, "E^o_2"] \\
\textit{trans}\text{-Ru(NH}_3)_4(\text{isn})(\text{H}_2\text{O})^{2+} + \text{Fe(CN)}_6^{4-} \arrow[r, shift left, "K_R"] \arrow[u, shift left] & \textit{trans}\text{-(isn)(NH}_3)_4\text{RuNCFe(CN)}_5^{2-} + \text{H}_2\text{O} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

$$\left(\frac{RT}{F}\right)\ln K_M = E_1^\circ + \left(\frac{RT}{F}\right)\ln K_R + E_2^\circ \tag{2}$$

3.3. *Kinetics of the oxidation of mono- and binuclear complexes*

The rate constants of oxidation, k_{ox}, for the oxidation of Ru(II) complexes, as obtained from the slopes of the linear plots of k_{obs} *versus* $[S_2O_8^{2-}]$(figure 3) are listed in table 5.

$$trans\text{-Ru(NH}_3)_4(\text{isn})\text{L}^n + S_2O_8^{2-} \xrightarrow{k_{ox}} 2trans\text{-Ru(NH}_3)_4(\text{isn})\text{L}^{n+1} + 2\text{So}_4^{2-} \tag{3}$$

$$k_{obs} = 2k_{ox}\left[S_2O_8^{2-}\right] \tag{4}$$

With the exception of **M**, the values of k_{ox} $(10^3 - 10^4\,\mathrm{M}^{-1}\,\mathrm{s}^{-1})$ fall in the range expected for oxidation of Ru(II) complexes [19, 23]. The result for oxidation of **R** indicate Fe(II)–Ru(III) formulation also was the kinetically stable isomer of **M**.

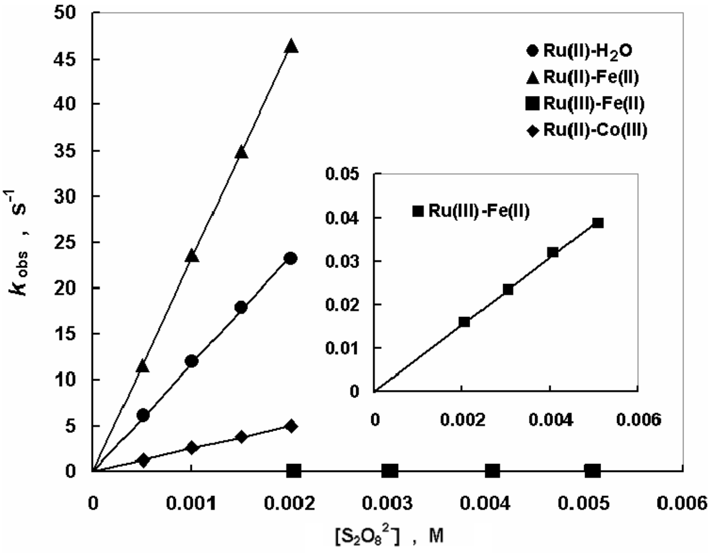

Figure 3. k_{obs} *vs.* $[S_2O_8^{2-}]$ plots for the oxidation of ruthenium complexes, $\mu = 0.10\,\mathrm{M}$ LiCl, pH = 5.0.

Table 5. k_{ox} for the oxidation of Ru(II) and Fe(II) complexes.[a]

Complex	k_{ox} ($M^{-1}\,s^{-1}$)
$Fe(CN)_6^{4-}$	$(4.3 \pm 0.1) \times 10^{-2}$
trans-$Ru(NH_3)_4(isn)(H_2O)^{2+}$	$(5.85 \pm 0.06) \times 10^3$
trans-$(isn)(NH_3)_4RuNCFe(CN)_5^{2-}$	$(1.16 \pm 0.01) \times 10^4$
trans-$(isn)(NH_3)_4RuNCFe(CN)_5^{-}$	3.88 ± 0.03
trans-$(isn)(NH_3)_4RuNCCo(CN)_5^{-}$	$(1.24 \pm 0.01) \times 10^3$

[a] $\mu = 0.10$ M LiCl, pH = 5.0 (acetate), $T = 25°C$.

The difference in rate constants of oxidation between **M** and $Fe(CN)_6^{4-}$ by two orders of magnitude indicates direct oxidation of the Fe(II) center on **M** is not likely. Rather, it proceeds first through rapid equilibrium of **M** with its oxidation state isomer **M′**, followed by oxidation of **M′** to **O** (equations (5) and (6)), as previously proposed [4, 7, 8].

$$\underset{(M)}{trans\text{-}(isn)(NH_3)_4Ru^{III}NCFe^{II}(CN)_5} \xrightleftharpoons{K} \underset{(M')}{trans\text{-}(isn)(NH_3)_4Ru^{II}NCFe^{III}(CN)_5} \tag{5}$$

$$2M' + S_2O_8^{2-} \xrightarrow{k'_{ox}} 2O + 2SO_4^{2-} \tag{6}$$

According to this mechanism, $k_{ox} = k_{ox}'\,K$. Taking $E_f = 0.47$ V for the **O**/**M′** couple, the same as the reduction potential of $Ru^{III}NCCo^{III}$, the calculated value of K was 6.0×10^{-4}. This yielded $k_{ox}' = 6.4 \times 10^3\,M^{-1}\,s^{-1}$, as expected for oxidation of the Ru(II) center.

3.4. *Intervalence (IT) band*

The D_2O solution of **M** exhibited an intervalence band (figure 4) at $\lambda_{max} = 1335$ nm ($7490\,cm^{-1}$) with $\varepsilon_{max} = 4.36 \times 10^3\,M^{-1}\,cm^{-1}$ and $\Delta\upsilon_{1/2} = 4.12 \times 10^3\,cm^{-1}$. The extent of delocalization can be assessed by calculation of the delocalization parameter α^2 and the electronic coupling H_{AB} from equations (7) and (8) [24]. Taking the internuclear distance $d = 5.2$ Å [3], we have $\alpha^2 = 3.8 \times 10^{-2}$ and $H_{AB} = 1.5 \times 10^3\,cm^{-1}$.

$$\alpha^2 = 4.24 \times 10^{-4} \varepsilon_{max} \frac{(\Delta\upsilon_{1/2})}{\upsilon_{max} d^2} \tag{7}$$

$$H_{AB} = \upsilon_{max}\alpha \tag{8}$$

These values are comparable to the other cyanide bridged binuclear complexes [3], but are considerably greater than values for the aromatic *N*-heterocyclic bridged complexes [2, 4–10]. As noted, before the better coupling between metals may result from the availability of a pair of perpendicular π_{CN}* orbitals and possible direct $d\pi$–$d\pi$ overlap due to the short bridge ligand [3].

Recently, Hupp [14, 15] and Boxer [25] in their studies of cyanide–bridged mixed valence binuclear complexes have found that the effective charge transfer distances, as obtained from electroabsorption (Stark) spectra, could be significantly smaller than the geometric separation between the donor and the acceptor. As a result, the coupling

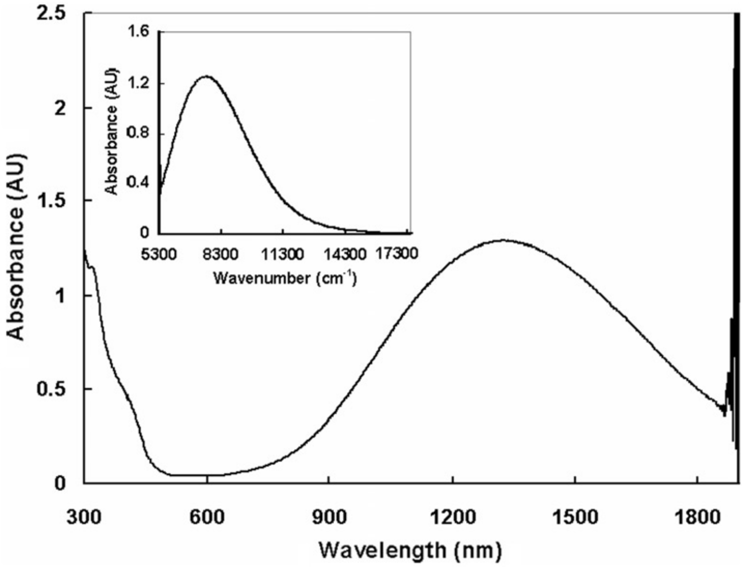

Figure 4. Intervalence band of *trans*-(isn)(NH$_3$)RuNCFe(CN)$_5^-$.

between metal centers may be much higher than that observed when simple geometric distances are used. Thus the evaluated α^2 is 8.0×10^{-2} for (CN)$_5$Fe^{II}(CN)Ru^{III}(NH$_3$)$_5^-$, as compared to the value of 2.2×10^{-2} when $d = 5.0$ Å was used [3]. On the basis of this approach, and assuming $|\Delta\mu_{1/2}| = 4.5\,\mathrm{e\,Å}$, taken to be equal to that of the (CN)$_5$Fe^{II}(CN)Ru^{III}(NH$_3$)$_4$(py)$^-$ [15], we calculated $\alpha^2 = 4.4 \times 10^{-2}$, and $H_{AB} = 1.6 \times 10^3\,\mathrm{cm}^{-1}$ for our system, only slightly higher than values predicted by Hush's theory. As was previously discussed [15], the small difference might be rationalized as the longer effective charge transfer distance arising from the presence of a π–acceptor in the Ru(III) metal center of the mixed valence complex. When **M** is excited to **M**′*, the Ru(II) in the excited state enhances its ability to donate electron density to the isonicotinamide ligand. The effect of the electron donation to the *trans* isonicotinamide would place the transferred charge in the electronic excited state of **M**′ further from the ground state electron donor of **M** (Fe^{II}(CN)$_5$) than would be the case if the saturated ligand such as NH$_3$ is used.

The thermal electron barrier ΔG^* for equation (5) can be approximated by equation (9) [10] where λ is the Franck–Condon barrier which can be considered as the contribution of the solvent and the inner-coordination sphere distortions to the reorganization barrier [24]

$$\Delta G* = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} \tag{9}$$

The rate constant of the intramolecular electron transfer can be calculated from equation (10);

$$k_{\mathrm{et}} = \upsilon_{\mathrm{et}} \exp\left(\frac{-\Delta G^*}{\mathrm{RT}}\right) \tag{10}$$

υ_{et}, the hopping frequency, is taken as $5 \times 10^{12}\,s^{-1}$ [10]. With measured υ_{max} and K for equation (5), we calculate $k_{et} = 5.7 \times 10^7\,s^{-1}$. The k_{et} of $\mathbf{M} \rightarrow \mathbf{M}'$ for the pentaammineruthenium system [3] can also be calculated the same way and the value is $1.5 \times 10^4\,s^{-1}$. The difference in rates may arise from the difference in the equilibrium barrier (ΔG°) between the two systems. If we correct the contribution of the equilibrium barrier, then the rate constant will be

$$k'_{et} = \upsilon_{et} \exp\left(\frac{-\lambda}{4RT}\right) \tag{11}$$

The value of k_{et}' are 3.8×10^9 and $2.2 \times 10^9\,s^{-1}$ for our system and the other, respectively. The agreement in k_{et}' is expected since the coupling constants for the two systems are the same ($1.5 \times 10^3\,cm^{-1}$). The relative stability of *trans*-$Ru(NH_3)_4(isn)^{2+}$ with respect to that of $Ru(NH_3)_5{}^{2+}$ may account for the difference in equilibrium barrier of equation (5) of the two systems (0.28 V) as is reflected from their difference in the reduction potentials of M/R couple (0.30 V).

3.5. *Stability of the binuclear complexes*

The comproportionation constant according to equation (12), as calculated from the reduction potentials, is $K_c = 1.9 \times 10^7$.

$$[Ru(II), CN^-, Fe(II)] + [Ru(III), CN^-, Fe(III)] \overset{K_c}{\rightleftharpoons} 2[Ru(III), CN^-, Fe(III)] \tag{12}$$

This leads to $5.0\,kcal\,mol^{-1}$ additional stability of **M** with respect to its isovalent states. As previously described [2, 26], the possible factors that contribute to the stabilization of the binuclear complexes include electronic delocalization associated with the mixed-valence species, electrostatic effects associated with the net charge of the metal moieties that make up the binuclear complexes, and the metal to ligand backbonding charge transfer. Unlike other Fe(II)–Ru(III) systems where the stability of the mixed-valence species mainly comes from the MLCT contribution [2, 6], the charge effect becomes the dominant factor that governs the stability of **M** *versus* **R** and **O** for the present system. The stability arises from the interaction between metal centers, $\alpha^2\upsilon_{max}$ [27], is $0.8\,kcal\,mol^{-1}$ if $\alpha^2 = 3.8 \times 10^{-2}$ or $0.9\,kcal\,mol^{-1}$ if $\alpha^2 = 4.4 \times 10^{-2}$. The electrostatic factor in the mixed-valence state contains 3+ and 4− moieties that lead to an electrostatic attraction of 24 ($3 \times 4 \times 2$ for 2 moles), whereas the isovalent states contain 2+, 4− and 3+, 3− that amount to an attraction of 17. Thus the contribution calculated from the ion-pair formation constants [23] is $1.9\,kcal\,mol^{-1}$ in favor of **M**. The backbonding stabilization contributes no more than the remaining 2.3 (or 2.2) $kcal\,mol^{-1}$. Unlike the binuclear complexes with *N*-heterocyclic aromatic bridges where the backbonding stabilization is the dominant factor in affecting the stability of **M** [1, 6], the contribution of the charge effect is comparable with that of the backbonding effect in the present system.

The charge effect also accounts for the stability of **M** with respect to **M′** ($4.4\,kcal\,mol^{-1}$). The electrostatic contribution (3+, 4− *vs.* 2+, 3− moieties) yields $3.2\,kcal\,mol^{-1}$. Another factor which may also favor **M** over **M′** is the saturation effect of Ru(II) due to its larger radial extension of *d* electrons (4d) compared to that of Fe(II)

(3d) [28]. Thus the coordination of $Co(CN)_5^{3-}$ on the remote nitrogen of $Ru(NH_3)_5(pyr)^{2+}$ (pyr = pyrazine) causes only a small bathochromatic shift from 474 to 520 nm, whereas a shift from 452 to 576 nm is observed when $Rh(NH_3)_5^{3+}$ is coordinated to $Fe(CN)_5(pyr)^{3-}$ complex [2]. The saturation effect of the Ru(II) center may also explain the fact that the λ_{max} is the same for *trans*-$(isn)(NH_3)_4RuNCCo(CN)_5^-$ and mononuclear Ru(II) complex, as shown in table 2.

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