It seems, then, that the $Co(sep)^{3+/2+}$ and $Co([9]aneS_3)_2^{3+/2+}$ self-exchange reactions can be taken to represent the adiabatic "norm" for $Co^{III/II}$ couples and that $Co(en)_3^{3+/2+}$ is distinctly nonadiabatic. Endicott and co-workers[29,30] have considered the problem of the relative reactivities of $Co(sep)^{3+/2+}$ and $Co(en)_3^{3+/2+}$ in detail and calculate a difference of 15 kJ mol^{-1} in the contributions of internal reorganization to the free energies of activation for the two exchange reactions, taking into account the small but significant difference in Δd (17 vs 21 pm, respectively) and the greater relaxation of nonbonded repulsions in the former reaction. This would account for a factor of about 400 in k and so suggests an electronic transmission coefficient of perhaps 10^{-2} in the latter couple, since the complexes are otherwise similar in size and charge type.

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4- and 3-Cyanopyridine-Bridged Binuclear Complexes of Pentacyanoferrate and Pentaammineruthenium

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The binuclear complexes $(CN)_5Fe(PyCN)Ru(NH_3)_5^-$ (III) (4- and 3-isomers) were prepared by the substitution reactions of $Ru(NH_3)_5NCPy^{2+}$ on $Fe(CN)_5OH_2^{3-}$. Complexes III undergo nitrile hydrolysis to give mixed-valence species of the form $(CN)_5Fe(PyCONH)Ru(NH_3)_5^-$ (IV) (4- and 3-isomers) when they are subjected to chemical oxidations of 1 equiv of peroxydisulfate. The results of UV–vis, IR, and electrochemical data suggest that complexes IV belong to a valence-trapped formulation containing the localized oxidation states Fe(II) and Ru(III). Rate constants of formation and dissociation of III and IV were measured, and the values of k_f ($\sim 10^3$ M^{-1} s^{-1}) and k_d ($\sim 10^{-3}$ s^{-1}) were consistent with kinetic results expected for the substitution of $Fe(CN)_5OH_2^{3-}$ with the divalent ligands. The kinetics of the nitrile hydrolysis were investigated, and it was found that the oxidized binuclear complexes III hydrolyze at a faster rate than the corresponding mononuclear Ru(III) complexes. Cyclic voltammetry of IV shows that the oxidation proceeds in two one-electron steps corresponding to $[III,L,III] + e \rightleftharpoons [II,L,III]$ and $[II,L,III] + e \rightleftharpoons [II,L,II]$. The 4-isomer-bridged binuclear complex IV exhibits an intervalence band at 645 nm with molar absorbance 5.70×10^2 M^{-1} cm^{-1} and a half-width of 5100 cm^{-1}. The properties of the IT band are discussed on the basis of Hush's theory.

Since the preparation of the Creutz–Taube ion,[1] $[(NH_3)_5RuPzRu(NH_3)_5]^{5+}$ (I), the binuclear compounds based on the $[Ru(NH_3)_5^{3+/2+}]$ couple have played a central role in the study of mixed-valence chemistry.[2,3] Series of both localized[4-8] and delocalized[9-11] systems have been prepared and examined spectroscopically and electrochemically. The electronic structure of the Creutz–Taube ion is still a matter of controversy.[12-18] Taking advantage of the similarity between the $Ru(NH_3)_5^{2+/3+}$ and $Fe(CN)_5^{3-/2-}$ moieties, we have prepared and characterized the heterobinuclear complexes $[(CN)_5FePzRu(NH_3)_5]^n$ ($n = -1$, 0) (II).[19] The mixed-valence state of II contains valence-trapped Fe(II)/Ru(III) oxidation states. Recently, we have carried out some studies on binuclear complexes analogous to II, but using 4- and 3-cyanopyridines as bridging ligands, $[(CN)_5FePyCNRu(NH_3)_5]^n$ ($n = -1, 0$) (III). The mixed-valence states of III for both bridge ligands are unstable with respect to ligand hydrolysis, which gives the final species in the form $[(CN)_5Fe^{II}PyCONHRu^{III}(NH_3)_5]$ (4- and 3-isomers) (IV). We wish to report herein our studies of the spectroscopic, kinetic, and electrochemical properties of the binuclear complexes III and IV, with emphasis on the characterization of the mixed-valence species IV. A study of the binuclear complex III with the 4-cyanopyridine bridge ligand has recently been reported briefly.[20] However, the results are restricted to the solid-state form, and nothing has been reported concerning the mixed-valence species.

Experimental Section

Materials. Chloropentaammineruthenium(III) chloride[21] and sodium amminepentacyanoferrate(II) trihydrate[22,23] were prepared according to the cited literature methods. 4- and 3-cyanopyridines were purchased from Fluka and were recrystallized from ethanol before use. 4-Cyano-*N*-methylpyridinium iodide ($(4\text{-}NCPyCH_3)I$) was prepared by adding 3 g of 4-cyanopyridine to a solution containing 10 mL of neat methyl iodide and 50 mL of anhydrous diethyl ether. The resulting solution was mixed well and stored in the dark for 1 week to allow the reaction to proceed to completion. The orange-yellow precipitate thus formed was filtered out, washed with ethanol, and dried in a vacuum desiccator overnight. Yield: 5.9 g. Anal. Calcd for $C_7H_7N_2I$: C, 34.2; N, 11.4; H, 2.87.

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Found: C, 34.1; N, 11.3; H, 2.63. Solutions of binuclear complexes were obtained by mixing a solution of $Fe(CN)_5OH_2^{3-}$ ($\leq 1 \times 10^{-4}$ M) with solutions of equimolar corresponding mononuclear ruthenium complexes. The distilled water was purified by passing the houseline distilled water through a Kintech Model DI-S4 Ultra Pure Water System. All other chemicals were reagent grade and were used as received.

Synthesis of Complexes. $[Ru(NH_3)_5L](ClO_4)_3$ (L = 4- and 3-NCPyH, 4-NCPyCH_3) were prepared by the literature method.[24] During the preparation the solutions were kept at 1 M acid concentration in order to make sure that no pyridine-bound complexes were formed. The products were recrystallized twice from 1 M $HClO_4$ solution. Anal. Calcd for $RuC_6H_{20}N_7Cl_3O_{12}$ (cyanopyridine complexes): C, 12.2; N, 16.6; H, 3.42. Found: C, 13.4; N, 16.9; H, 3.63 (4-NCPyH); C, 12.3; N, 16.6; H, 3.35 (3-NCPyH). Calcd for $RuC_7H_{22}N_7Cl_3O_{12}$ (4-NCPyCH_3 complex): C, 13.9; N, 16.2; H, 3.67. Found: C, 14.3; N, 15.7; H, 3.11.

Caution! Ruthenium perchlorate salts, especially those of Ru(II) complexes, may detonate upon scratching or heating.

$[Ru(NH_3)_5L'](ClO_4)_3$ (L' = 4- and 3-NHCOPyH, 4-NHCOPyCH_3). A 0.12-g amount of $[Ru(NH_3)_5L](ClO_4)_3$ was dissolved in 1 M $HClO_4$ solution; 0.05 g of $Na_2S_2O_8$ was then added to the solutions, and the hydrolysis reaction was allowed to proceed to completion under an argon atmosphere (1 h for 4-cyanopyridine and 4-cyano-*N*-methylpyridinium; 5 h for 3-cyanopyridine). At this point saturated $NaClO_4$ solution was added dropwise until the precipitate began to form. The solution was cooled in an ice bath for 1 h. The solid that formed was filtered out and washed with ethanol and ether. The products were recrystallized from hot water (50 °C). Yield: 60 mg (4-NHCOPyH), 82 mg (3-NHCOPyH), and 80 mg (4-NHCOPyCH_3). Anal. Calcd for $RuC_6H_{21}N_7Cl_3O_{13}$ (pyridinecarboxamido complexes): C, 11.8; N, 16.3; H, 3.46. Found: C, 12.6; N, 15.7; H, 3.65 (4-NHCOPyH); C, 11.7; N, 15.9; H, 3.43 (3-NHCOPyH). Calcd for $RuC_7H_{23}N_7Cl_3O_{13}$ (4-NHCOPyCH_3 complex): C, 13.5; N, 15.8; H, 3.73. Found: C, 13.6; N, 15.7; H, 3.07.

$Na[(CN)_5Fe(4\text{-},3\text{-PyCN})Ru(NH_3)_5]\cdot xH_2O$. A 0.1-g amount of $[Ru(NH_3)_5(4\text{-},3\text{-CNPyH})](ClO_4)_3$ was dissolved in 5 mL of distilled water, and the solution was bubbled with argon for 5 min. An equimolar amount of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was added, and the mixture was kept under argon atmosphere for 20 min. A 0.6-g sample of NaI was added, and the solutions were cooled in an ice bath for 1 h. The precipitates that formed were filtered out and washed with ethanol and ether. Anal. Calcd for $Na[(CN)_5FeC_6H_4N_2Ru(NH_3)_5]\cdot xH_2O$: C, 22.4; N, 28.5; H, 4.92 (x = 5, 4-isomer); C, 25.5; N, 32.5; H, 4.06 (x = 1, 3-isomer). Found: C, 22.8; N, 27.9; H, 4.80 (4-isomer); C, 25.1; N, 31.6; H, 3.92 (3-isomer).

$Na[(CN)_5Fe(4\text{-},3\text{-PyCONH})Ru(NH_3)_5]\cdot 2.5H_2O$. A 0.05-g amount of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was added to a predeaerated aqueous solution containing 0.1 g of $[Ru(NH_3)_5(4\text{-},3\text{-NHCOPyH})](ClO_4)_3$. The resulting solutions were bubbled with argon for 10 min, and then 2 mL of ethanol that was saturated with NaI was added. The solution was cooled at 0 °C for 1 h. The orange precipitates thus formed were filtered out and washed with alcohol and ether. The binuclear complexes can also be prepared alternatively by the stoichiometric oxidation of the solutions of the reduced form of III, followed by the same process of precipitation. Anal. Calcd for $Na[(CN)_5FeC_6N_2OH_5Ru(NH_3)_5]\cdot 2.5H_2O$: C, 23.5; N, 29.9; H, 4.49. Found: C, 24.3; N, 29.2; H, 5.17 (4-isomer); C, 23.7; N, 29.0; H, 4.72 (3-isomer).

Analytical Methods. Ultraviolet and visible spectra were measured either on a Specord M40 spectrophotometer or on a Shimadzu Model UV 160 spectrophotometer. The infrared spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer in KBr pellets. pH measurements were carried out with a Suntex Model SJ-5 pH meter. Carbon, nitrogen, and hydrogen analyses were performed by the microanalytical laboratory of National Cheng Kung University.

Kinetic Measurements. Rates of formation of the binuclear complexes $[(CN)_5FeLRu(NH_3)_5]^-$ (L = 4- and 3-cyanopyridine and pyridinecarboxamido ligands) were measured by mixing freshly prepared solutions of $Fe(CN)_5OH_2^{3-}$[25,26] with an excess of $Ru(NH_3)_5L^{2+}$ on a Photal RA401 stopped-flow apparatus (Union Giken) that was interfaced with a NEC 9801VX microcomputer for data acquisition. The measurements were carried out by following the absorbance change at or near the maximum wavelength of absorption of the binuclear complexes. Rates of dissociation of the binuclear complexes were measured by adding an excess amount of *N*-methylpyrazinium[27] to a solution of the complex and following the slow absorbance increase at the λ_{max} (655 nm)[28] of the $[Fe(CN)_5PzCH_3]^{2-}$ complex. The measurements were carried out on a Specord M40 spectrophotometer. The kinetics of the nitrile ligand hydrolysis were measured by following the absorbance increase at maximum wavelength of the Ru(III)–amido complexes (380–390 nm) either on a Specord M40 spectrophotometer or on a Photal RA401 stopped-flow spectrophotometer, depending on the rate of hydrolysis. Temperatures of the experiments were controlled by a Hotech 360-D temperature bath. All kinetic measurements were carried out at ionic strength 0.10 M ($LiClO_4$) unless otherwise specified. Observed rate constants were obtained by linear least-squares fitting of ln ($A_t - A_\infty$) vs time plots.

Table I. Absorption Spectra of Iron(II) and Ruthenium(II) Complexes of Cyanopyridine (PyCN) and Pyridinecarboxamido ($PyCONH_2$)[a]

complex	λ_{max}, nm	$10^{-3}\epsilon_{max}$, $M^{-1}\ cm^{-1}$
$Ru(NH_3)_5(4\text{-NCPy})^{2+}$	424	10.2
	425	5.37[b]
$Ru(NH_3)_5(3\text{-NCPy})^{2+}$	401	9.56
	401	5.62[b]
$Ru(NH_3)_5(4\text{-NCPyH})^{3+}$[c]	534	13.9
	532	8.13[b]
$Ru(NH_3)_5(3\text{-NCPyH})^{3+}$[c]	458	7.08
	460	4.68[b]
$Ru(NH_3)_5(4\text{-NHCOPy})^{2+}$	386	3.24
$Ru(NH_3)_5(3\text{-NHCOPy})^{2+}$	387	3.68
$Ru(NH_3)_5(4\text{-NHCOPyH})^{3+}$[c]	358	4.71
$Ru(NH_3)_5(3\text{-NHCOPyH})^{3+}$[c]	357	2.85
$Ru(NH_3)_5(4\text{-NHCOPyCH}_3)^{3+}$[d]	358	3.01
$Fe(CN)_5(4\text{-PyCN})^{3-}$	476	6.40
	477	5.7[e]
$Fe(CN)_5(3\text{-PyCN})^{3-}$	415	3.29
	414	3.2[e]
$Fe(CN)_5(4\text{-PyCONH}_2)^{3-}$	435	4.65
	435	4.57[f]
$Fe(CN)_5(3\text{-PyCONH}_2)^{3-}$	398	3.29
$(CN)_5Fe^{II}(4\text{-PyCN})Ru^{II}(NH_3)_5^-$	480	15.9
	430 (sh)	
$(CN)_5Fe^{II}(3\text{-PyCN})Ru^{II}(NH_3)_5^-$	406	12.9
$(CN)_5Fe^{II}(4\text{-PyCONH})Ru^{III}(NH_3)_5^-$	398	6.86
$(CN)_5Fe^{II}(3\text{-PyCONH})Ru^{III}\ (NH_3)_5^-$	389	6.73

[a] All Fe complexes are pyridine bound, and all Ru complexes are either nitrile or amide bound. Measured at pH = 5 (acetate) unless otherwise specified. [b] Reference 24. [c] Measured in 1 M $HClO_4$. [d] Measured both in 1 M $HClO_4$ and at pH = 5. [e] Reference 25. [f] Reference 28.

Electrochemical Measurements. All electrochemical measurements were carried out at room temperature in aqueous solution with 0.10 M lithium perchlorate as supporting electrolyte. Experiments were performed on a PAR model 363 potentiostat and Model 175 universal programming system. A conventional three-electrode electrochemical cell was used for measurements. Cyclic voltammograms were obtained at a scan rate of 100 mV/s, using carbon paste as the working electrode and a platinum wire as the counter electrode. A saturated calomel electrode was used as the reference electrode.

Results and Discussion

UV–Vis Spectra. The electronic spectra in the UV–vis range of the binuclear complexes are summarized in Table I. For comparison, spectra of the corresponding mononuclear complexes are also included in the table. In Table I only charge-transfer bands are reported. The intensities of the MLCT bands of the reduced form of binuclear complex III are roughly the sum of that of the two corresponding mononuclear complexes. For the 3-cyanopyridine bridge ligand, the absorption spectrum of the binuclear complex is similar to the composite spectrum of the corresponding mononuclear complexes. When 4-cyanopyridine is the bridge ligand, the binuclear complex has a MLCT band at λ_{max} = 480 nm with a shoulder at 430 nm, suggesting that the spectrum is dominated by the Fe(II)–pyridyl interactions, an observation similar to that in the $(NH_3)_5Ru^{II}(4\text{-PyCN})Ru^{II}(NH_3)_5$ binuclear complex.[8] The shoulder may arise from the Ru(II)–nitrile MLCT, which has a band at 424 nm. When the mononuclear $Ru(NH_3)_5L^{2+}$ (L = 4-,3-PyCN) complexes were oxidized

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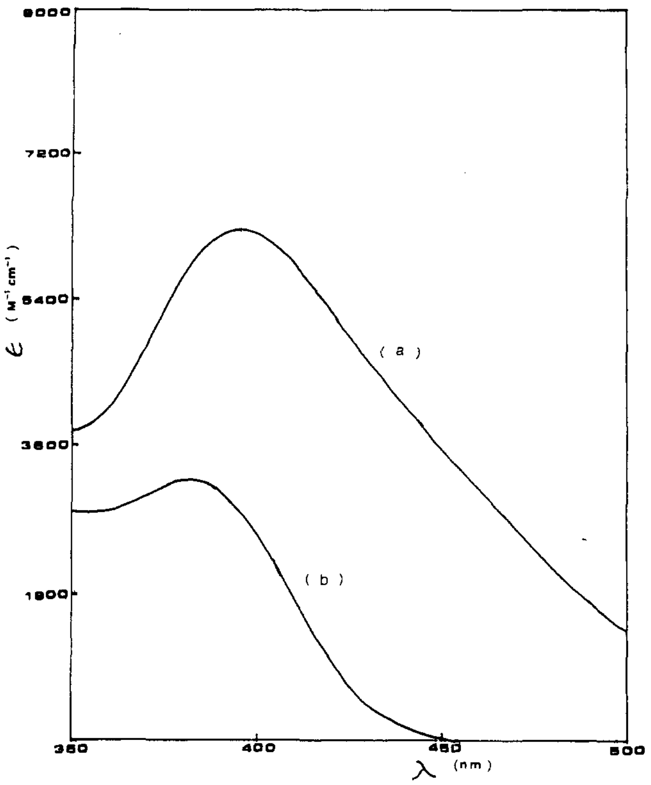

Figure 1. Absorption spectra of $(CN)_5Fe(4\text{-}PyCONH)Ru(NH_3)_5^-$ (a) and $Ru(NH_3)_5(4\text{-}NHCOPy)^{2+}$ (b).

to Ru(III), a new band at 386–387 nm was formed within 20 min of oxidation. This pronounced spectral change has been observed previously for a number of organic nitrile complexes of Ru(III)[29-31] and is characteristic of the conversion of the nitrile to the amide. By comparison with the absorption spectra of the Ru(III)–benzamide complex,[29] which shows an absorption at 322 nm for $Ru(NH_3)_5NH_2OCC_6H_5^{3+}$ and at 393 nm for $Ru(NH_3)_5NHOCC_6H_5^{2+}$, our spectral results seem to support the conclusion that our amido complexes are in the deprotonated form. When the oxidation reaction was carried out in 1 M $HClO_4$ solution, the absorption bands of the amido complexes shifted to shorter wavelength at 356–357 nm. The hypsochromic shift of the spectra apparently arises from the protonation of the ligand, which may be either on the amide nitrogen or on the pyridyl nitrogen. The similarity of the spectra with that of $Ru(NH_3)_5NHCOPyCH_3^{3+}$ suggests that the protonation site is on the pyridine nitrogen. The absorption spectrum of $Ru(NH_3)_5NHCOPyCH_3^{3+}$ does not change between pH = 5 and 1 M acid concentration.

When the reduced forms of III were oxidized with 1 equiv of peroxydisulfate ion, the spectra of the binuclear complexes underwent significant changes similar to that observed for the Ru(III) mononuclear complexes. The final spectral results gave λ_{max} = 389 nm (ϵ_{max} = 6.73 × 10^3 M^{-1} cm^{-1}) and 398 nm (ϵ_{max} = 6.86 × 10^3 M^{-1} cm^{-1}) for the 3- and 4-isomers, respectively. The spectra of both complexes are similar to those obtained for mononuclear Ru(III)–amido complexes except with larger extinction coefficients as shown in Table I. For the 4-isomer-bridged binuclear complex, the absorption band is shifted to longer wavelength compared to the corresponding Ru(III) mononuclear complex, indicating a greater metal–metal coupling than in the 3-isomer-bridged binuclear complex. Surprisingly, we do not observe the charge-transfer bands correspond to the Fe(II) → L transitions. However, the extinction coefficients of the binuclear complexes are almost the sum of those corresponding Ru(III)–L and Fe(II)–L mononuclear complexes. Moreover, the absorption spectra of the binuclear complexes are broader than the corresponding Ru(III)–L complexes, as shown in Figure 1. Iron, which has 3d orbitals, has less π character than ruthenium with 4d orbitals. In addition, the cyanide, which is also a good π acceptor, will reduce the π property of the iron in the $Fe(CN)_5^{3-}$ moiety. Therefore, the charge-transfer bands of the binuclear complexes can be dominated by the L → Ru(III) transitions and the dπ → π* MLCT of the $Fe(CN)_5L^{3-}$ complexes may only increase the electron density on the amido nitrogen of the ligands, which, in turn, will lower the energies of the transitions in the band maxima as are observed. Both the UV–vis spectral results and the elemental analyses of the isolated products of binuclear complexes suggest that the oxidation of III is at the ruthenium center, which further undergoes ligand hydrolysis to give the final mixed-valence binuclear complexes in the IV form.

Table II. Characteristic Infrared Bands of Pentacyanoferrate and Pentaammineruthenium Complexes[a]

complex	$\nu(CN)$, cm^{-1}	$\delta(NH_3)_{sym}$, cm^{-1}
$Ru(NH_3)_5(4\text{-}NCPy)^{2+}$	2180[c] (2179[b])	1260
$Ru(NH_3)_5(3\text{-}NCPy)^{2+}$	2179[c] (2181[b])	1269
$Ru(NH_3)_5(4\text{-}NHCOPyH)^{3+}$		1295
$Ru(NH_3)_5(3\text{-}NHCOPyH)^{3+}$		1308
$Ru(NH_3)_5(4\text{-}NHCOPyCH_3)^{3+}$		1287
$(CN)_5Fe(4\text{-}PyCN)Ru(NH_3)_5^-$	2045, 2192 (2179[b])	1279
$(CN)_5Fe(3\text{-}PyCN)Ru(NH_3)_5^-$	2045, 2186	1287
$(CN)_5Fe(4\text{-}PyCONH)Ru(NH_3)_5^-$	2044	1311
$(CN)_5Fe(3\text{-}PyCONH)Ru(NH_3)_5^-$	2043	1307

[a] In KBr pellets. [b] Reference 24. [c] Reference 20.

Infrared Spectra. The infrared bands representing the cyanide stretching frequencies of the cyanoferrate and the nitrile-bound ruthenium complexes and the symmetric ammonia deformation frequencies ($\delta(NH_3)_{sym}$) of the ruthenium ammine complexes are listed in Table II. All the mono- and binuclear complexes of Ru(II) under study exhibit a characteristic shift of CN stretching frequencies to lower energies compared to those of the corresponding free ligands (2232 cm^{-1} for both 4- and 3-PyCN[24]), as is expected for the nitrile-bound Ru(II) complexes. In the binuclear complexes III and IV, another strong cyanide stretching band at 2045 cm^{-1}, which is characteristic of Fe(II)–cyanide stretching,[32,33] is also observed. The nitrile stretching band disappears both in the hydrolysis products of Ru(III) mononuclear complexes and in the isolated mixed-valence binuclear complexes, indicating that the nitrile functional group has been converted to the amide. Unfortunately, the expected amide carbonyl stretching bands (~1650 cm^{-1}) are masked by the ammonia absorption of ruthenium ammines.[30] The symmetric ammonia deformation frequencies of the mixed-valence species and the mononuclear Ru(III)–amido complexes were shifted to lower frequencies (1297–1310 cm^{-1}) than the expected range of 1330–1360 cm^{-1} for ruthenium(III) ammine complexes.[32] This shift may arise from the increase in electron density of Ru(III) dπ orbitals due to the ligand to metal charge transfer. The observation of the Fe(II)–cyanide stretching band at 2043–2045 cm^{-1} for the mixed-valence compounds also suggests that the binuclear complexes belong to the valence-trapped localized system featuring Fe(II) and Ru(III) oxidation states.

Kinetics of Formation and Dissociation of Binuclear Complexes. The kinetics of formation and dissociation of binuclear complexes for reaction 1 were measured spectrophotometrically (L = 4- and

$$Fe(CN)_5OH_2^{3-} + Ru(NH_3)_5L^{2+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} (CN)_5FeLRu(NH_3)_5^- + H_2O \quad (1)$$

3-cyanopyridine and pyridinecarboxamido ligands). The results

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Table III. Pseudo-First-Order Rate Constants for the Reactions of $Ru(NH_3)_5L^{2+}$ with $Fe(CN)_5OH_2^{3-}$ [a]

ligand	10^4[ligand], M	k_{obs}, s^{-1}
$Ru(NH_3)_5(4\text{-}NCPy)^{2+}$	3.06	1.42
	4.67	2.17
	5.96	2.77
	7.38	3.41
	9.20	4.23
$Ru(NH_3)_5(3\text{-}NCPy)^{2+}$	3.16	1.58
	4.46	2.41
	5.94	3.46
	7.61	4.36
	9.01	5.27
$Ru(NH_3)_5(4\text{-}NHCOPy)^{2+}$	1.04	0.287
	2.04	0.450
	3.16	0.832
	3.87	0.967
	5.01	1.26
$Ru(NH_3)_5(3\text{-}NHCOPy)^{2+}$	1.12	0.403
	1.55	0.580
	2.69	0.920
	3.51	1.27
	4.22	1.37

[a] [Fe(II)] = (1–2) × 10^{-5} M. $\mu = 0.10$ M ($LiClO_4$), pH = 5.0 (acetate), and $T = 25$ °C.

Table IV. Rate Constants of Formation and Dissociation of Pentacyanoferrate(II)[a]

ligand	$10^{-3}k_f$, M^{-1} cm^{-1}	10^3k_d, s^{-1}	$10^{-6}K$, M^{-1}
4-PyCN[b] (Py bound)	0.383	1.02	0.375
3-PyCN[b] (Py bound)	0.413	2.80	0.148
$Ru(NH_3)_5(4\text{-}NCPy)^{2+}$	4.62 ± 0.02	2.96 ± 0.03	1.56
$Ru(NH_3)_5(3\text{-}NCPy)^{2+}$	5.73 ± 0.22	4.97 ± 0.07	1.15
$Ru(NH_3)_5(4\text{-}NHCOPy)^{2+}$	2.52 ± 0.05	2.56 ± 0.02	0.984
$Ru(NH_3)_5(3\text{-}NHCOPy)^{2+}$	3.41 ± 0.07	2.75 ± 0.05	1.42

[a] pH = 5.0 (acetate), $\mu = 0.10$ M ($LiClO_4$), and $T = 25$ °C. [b] Reference 25.

for the formation reaction are summarized in Table III. The second-order rate constants, as obtained from the slopes of the k_{obs} vs $[Ru(NH_3)_5L^{2+}]$ plots, are listed in column 2 of Table III. The increase in rate constants of formation for binuclear complexes by almost 1 order of magnitude compared to the corresponding mononuclear pentacyanoferrate(II) complexes may be attributed to the charge effect of the entering ligands.[19,34] In the measurements of the dissociation reaction, the first-order rate constants of dissociation were found to be independent of the *N*-methylpyrazinium concentration used (0.1–1 M). The values of k_d are shown in column 3 of Table IV. The equilibrium constants as obtained from k_f/k_d are listed in column 4 of Table IV. The high affinities of eq 1 for complexes under study indicate that the formation of binuclear complexes by a 1:1 stoichiometry is highly favorable.

Table V. Rate Constants of Hydrolysis of Ru(III)–Nitrile Complexes[a]

complex	10^3k_h, s^{-1}
$Ru(NH_3)_5(4\text{-}NCPy)^{3+}$	2.85 ± 0.02 1.78 ± 0.03[b]
$Ru(NH_3)_5(3\text{-}NCPy)^{3+}$	0.667 ± 0.007
$Ru(NH_3)_5(NCC_6H_5)^{3+}$	0.201 ± 0.007
$Ru(NH_3)_5(4\text{-}NCPyH)^{4+}$	10.4 ± 0.1[c]
$Ru(NH_3)_5(3\text{-}NCPyH)^{4+}$	3.41 ± 0.03[c]
$Ru(NH_3)_5(4\text{-}NCPyCH_3)^{4+}$	28.3 ± 0.8
$(CN)_5Fe(4\text{-}PyCN)Ru(NH_3)_5^-$	13.1 ± 0.1
$(CN)_5Fe(3\text{-}PyCN)Ru(NH_3)_5^-$	4.39 ± 0.06

[a] pH = 5.0, $\mu = 0.10$ M ($LiClO_4$), and $T = 25$ °C, unless otherwise specified. [b] $\mu = 1.0$ M $LiClO_4$. [c] In 1.0 M $HClO_4$.

Table VI. Rate Constants of Hydrolysis of the $(NH_3)_5Ru(NCPyCH_3)^{3+}$ Complex[a]

pH	k_h, s^{-1}	pH	k_h, s^{-1}
8.0	0.388 ± 0.008	2.0	0.210 ± 0.001
5.0	0.283 ± 0.001	1.3	0.190 ± 0.003
4.0	0.235 ± 0.001	1.0	0.193 ± 0.001

[a] $\mu = 0.10$ ($LiClO_4$–$HClO_4$) and $T = 25$ °C.

Table VII. Temperature Dependence of the Rate Constants of Nitrile Hydrolysis[a]

T, °C	10^3k_h, s^{-1}	
	$Ru(NH_3)_5(4\text{-}NCPy)^{3+}$	$(CN)_5Fe(4\text{-}NCPy)Ru(NH_3)_5$
10		4.01 ± 0.05
15	1.09 ± 0.01	6.27 ± 0.13
20	1.83 ± 0.01	8.92 ± 0.04
25	2.85 ± 0.02	13.1 ± 0.1
30	4.45 ± 0.03	18.4 ± 0.2
35	6.62 ± 0.04	21.5 ± 0.5
40	9.33 ± 0.07	30.3 ± 0.4
45	12.3 ± 0.1	39.9 ± 0.8

[a] pH = 5.0 (acetate) and $\mu = 0.10$ M ($LiClO_4$).

Kinetics of Nitrile Hydrolysis of Ru(III) Complexes. The kinetic measurements of hydrolysis reactions of the coordinated nitrile complexes were carried out by the oxidation of the mono- and binuclear complexes of $Ru^{II}(NH_3)_5L$ complexes with 1 equiv of peroxydisulfate ion, followed by monitoring the formation of the corresponding amido complexes. The results are given in Table V. The kinetics of the catalysis of the hydrolysis of organonitriles to amides by the $Ru(NH_3)_5^{3+}$ metal center has been reported both in basic[29] and in acidic[35,36] solutions. It is believed that the hydrolysis reaction proceeds by the direct attack of water at the carbon atom of the nitrile group.[29,37] As shown in Table V, the hydrolysis rate constants for $Ru(NH_3)_5(NCPy)^{3+}$ (both 4- and 3-isomers) complexes are greater than that of the benzonitrile complex under the same conditions. This is an expected result, since the nitrogen on the pyridine ring is more electronegative than the carbon on the benzene ring, which, in turn, will make the nitrile carbon more electropositive and more available for the nucleophilic attack. It is interesting to note that both 4- and 3-cyanopyridine complexes of Ru(III) hydrolyzed at a faster rate at 1 M acidic medium than at pH = 5. Previous kinetic measurements showed that the rate of hydrolysis was faster in basic medium due to the contribution of the OH^- catalytic path.[35] Thus, the rate constants of hydrolysis of $Ru(NH_3)_5(NCC_6H_5)^{3+}$ are 2.01 × 10^{-4} and 3.39 × 10^{-5} s^{-1} [35] at pH = 5 and 2.3, respectively. The increase in hydrolysis rate for the cyanopyridine complexes in the acidic medium may be attributed to the protonation of the pyridine nitrogen, which will act as an electron-withdrawing group and decrease the electron density on the nitrile carbon. The kinetics for the hydrolysis of the $Ru(NH_3)_5(4\text{-}NCPyCH_3)^{4+}$ complex, as shown in Table VI, further confirm this point. In this complex the protonation of the pyridine nitrogen is impossible, and the rate constant measured at 0.1 M $HClO_4$ is slower than that measured at pH = 8 by a factor of 2. The kinetic results of hydrolysis support the spectral argument that the protonation site of the Ru(III) complexes was on the pyridine nitrogen.

For the mixed-valence binuclear complexes III the hydrolysis rates were also found to be faster than the corresponding mononuclear Ru(III) complexes, as indicated in Table V. For the 3-cyanopyridine complex, this is easy to understand, since the electronic communication between two metal centers is so small that the Fe(II) moiety in the binuclear complex mainly behaves like an acid center. However, when 4-cyanopyridine is the bridge ligand, there is considerable interaction between the metals through the ligand, as is manifested in the spectroscopic results. Apparently, the increase in rate constant for the mixed-valence species

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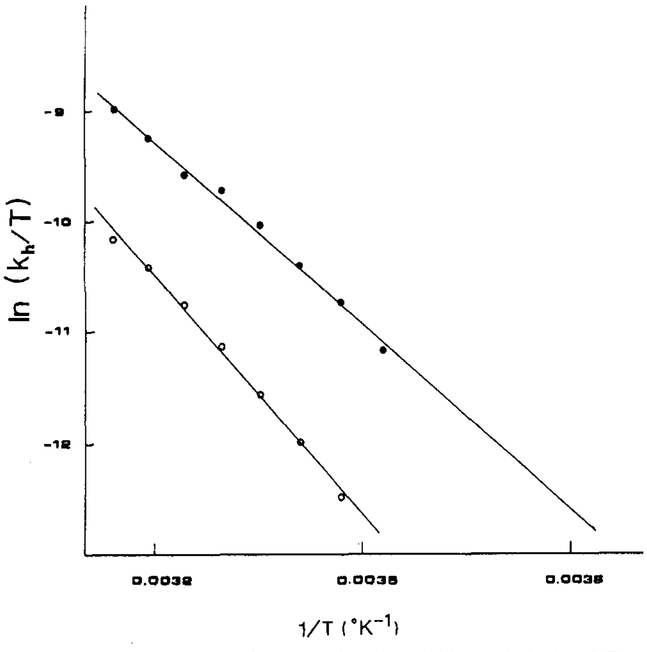

Figure 2. ln (k/T) vs $1/T$ plots for the nitrile hydrolysis of Ru(NH$_3$)$_5$(4-NCPy)$^{3+}$ (○) and (CN)$_5$Fe(4-PyCN)Ru(NH$_3$)$_5$ (●) (μ = 0.10 M (LiClO$_4$), pH = 5.0).

Table VIII. Reduction Potentials of Fe(CN)$_5$L$^{2-/3-}$ and Ru(NH$_3$)$_5$L$^{3+/2+}$ Complexes[a]

couple	$E_{1/2}$, V
Ru(NH$_3$)$_5$(4-NCPy)$^{3+/2+}$	0.592 0.56[b]
Ru(NH$_3$)$_5$(3-NCPy)$^{3+/2+}$	0.555
Fe(CN)$_5$(4-PyCN)$^{2-/3-}$	0.527 0.557[c]
Fe(CN)$_5$(3-PyCN)$^{2-/3-}$	0.527
Ru(NH$_3$)$_5$(4-NHCOPy)$^{2+/+}$	0.012
Ru(NH$_3$)$_5$(3-NHCOPy)$^{2+/+}$	0.002
Ru(NH$_3$)$_5$(4-NCPyH)$^{4+/3+}$[d]	0.637
Ru(NH$_3$)$_5$(3-NCPyH)$^{4+/3+}$[d]	0.575
Ru(NH$_3$)$_5$(4-NHCOPyH)$^{3+/2+}$[d]	−0.012
Ru(NH$_3$)$_5$(3-NHCOPyH)$^{3+/2+}$[d]	−0.020
Ru(NH$_3$)$_5$(4-NHCOPyCH$_3$)$^{3+/2+}$[e]	−0.023
Fe(CN)$_5$(4-PyCONH$_2$)$^{2-/3-}$	0.497 0.56[f]
Fe(CN)$_5$(3-PyCONH$_2$)$^{2-/3-}$	0.485
(CN)$_5$Fe^{II}(4-PyCN)Ru^{II}(NH$_3$)$_5^-$	~0.512, ~0.622
(CN)$_5$Fe^{II}(3-PyCN)Ru^{II}(NH$_3$)$_5^-$	0.557
(CN)$_5$Fe^{II}(4-PyCONH)Ru^{III}(NH$_3$)$_5^-$	−0.008, 0.502
(CN)$_5$Fe^{II}(3-PyCONH)Ru^{III}(NH$_3$)$_5^-$	−0.013, 0.507

[a] pH = 5.0 and μ = 0.10 M (LiClO$_4$), unless otherwise specified. [b] Reference 38. [c] Reference 39. [d] Measured in 1 M HClO$_4$. [e] Measured both in 1 M HClO$_4$ and at pH = 5. [f] Reference 40.

indicates that the inductive effect dominates over the electronic effect in affecting the rate of hydrolysis. The observations of ligand hydrolysis for the mixed-valence binuclear complexes III provide further evidence that the oxidation of their reduced forms is at the ruthenium center. The temperature dependence of the 4-cyanopyridine ligand hydrolysis has been studied for both mononuclear Ru(III) and mixed-valence binuclear complexes with 4-PyCN ligand, and the results are shown in Table VII. The plots of ln (k/T) vs $1/T$ are linear, as shown in Figure 2, yielding $\Delta H^* = 14.2 \pm 0.4$ and 10.9 ± 0.4 kcal/mol and $\Delta S^* = -22.7 \pm 0.2$ and -30.8 ± 0.3 cal deg^{-1} mol^{-1} for mono- and binuclear complexes, respectively, at pH = 5.0 and μ = 0.10 M LiClO$_4$.

Electrochemistry. Electrochemical data for the mono- and binuclear complexes under study are listed in Table VIII. The cyclic voltammograms for the 3-NCPy-bridged Fe^{II}-L-Ru^{II} binuclear complex gave a single wave at 0.557 V vs NHE with a large peak-to-peak separation (110 mV). The 4-NCPy-bridged binuclear complex III showed two overlapping waves, as shown in Figure 3. The binuclear complexes IV exhibited two anodic waves for both ligands, which correspond to the reduction potentials of two consecutive steps.

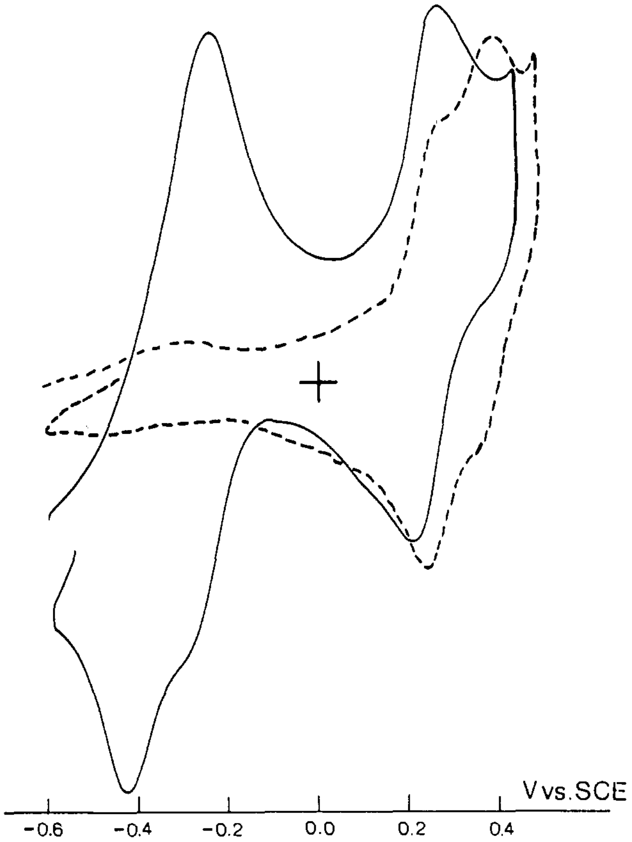

Figure 3. Cyclic voltammograms of (CN)$_5$Fe(4-PyCN)Ru(NH$_3$)$_5^-$ and its oxidized solution ([binuclear] = 5 × 10^{-4} M, 0.1 M LiClO$_4$, pH = 5.0). Key: (---) measured in reduced form; (—) measured in oxidized solution.

$$[\mathrm{III,L,II}] + e \overset{E^1_{1/2}}{\rightleftharpoons} [\mathrm{II,L,II}] \text{ and } [\mathrm{III,L,III}] + e \overset{E^2_{1/2}}{\rightleftharpoons} [\mathrm{III,L,II}]$$

When binuclear complexes III were oxidized by 1 equiv of peroxydisulfate ion, the cyclic voltammograms changed rapidly to the final wave forms, which gave reduction potentials of −0.008, 0.502 and −0.013, 0.507 V vs NHE, for the 4-PyCN- and 3-PyCN-bridged ligands, respectively. The cyclic voltammograms for the oxidized solution of the 4-isomer-bridged binuclear complex was also shown in Figure 3. The electrochemical results of the oxidized solutions are identical with those that were obtained by the direct mixing of Fe(CN)$_5$OH$_2^{3-}$ and Ru(NH$_3$)$_5$NHCOPy^{2+} (both 4- and 3-isomers) solutions, indicating that the change in wave forms in the oxidized solutions are results of the hydrolysis reactions of the nitrile ligands. By comparison with the reduction potentials of the corresponding mononuclear complexes, it is clear that the oxidation states of the mixed-valence species belong to the Fe(II)/Ru(III) valence-trapped localized system, confirming the spectral results discussed earlier. The closeness of the $E^2_{1/2}$ values in the mixed-valence molecules with that of the corresponding mononuclear Fe(CN)$_5$(PyCONH$_2$)$^{2-/3-}$ couple seems to suggest that the electronic coupling between the metal-metal centers in this system is rather weak. Note that in the pyrazine-bridged binuclear complex $E^2_{1/2}$ (0.71 V)[19] is 0.16 V greater than the $E_{1/2}$ for the Fe(CN)$_5$Pz$^{2-/3-}$ couple, while in this system the difference is less than 0.02 V.

The reduction potentials of binuclear complexes IV reflect the stability of the mixed-valence complexes with respect to the iso-

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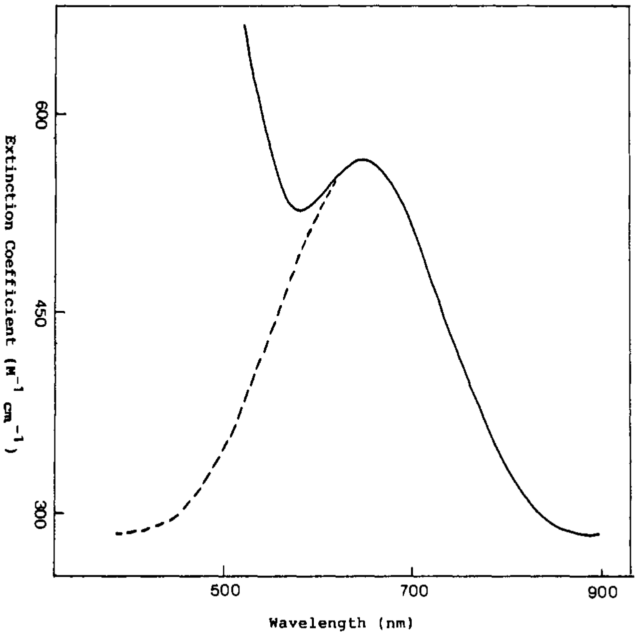

Figure 4. Intervalence band of $(CN)_5Fe(4\text{-}PyCONH)Ru(NH_3)_5^-$.

valent state in leading to the comproportionation constants according to eq 2.

$$[II,L,II] + [III,L,III] \rightleftharpoons 2[II,L,III] \quad K_{com} \qquad (2)$$

The comproportionation constants thus obtained are 4.26 × 10^8 and 6.29 × 10^8 for 4- and 3-pyridinecarboxamido-bridged binuclear complexes, respectively. The large values of K_{com} arise from the equilibrium barrier between the isomers of different oxidation states rather than a result of electronic coupling between the metal–metal centers.

Intervalence Band. Freshly prepared solutions of $(CN)_5Fe^{II}(4\text{-}PyCONH)Ru^{III}(NH_3)_5^-$ exhibit an intervalence band at 645 nm with a molar extinction coefficient 5.70 × 10^2 M^{-1} cm^{-1} and a half-width of 5100 cm^{-1}, as shown in Figure 4. The band is absent in the spectrum of the corresponding mononuclear complexes. According to Hush's theory, the bandwidth, $\Delta\bar{\nu}_{1/2}$, in the high-temperature limit is given by eq 3,[41,42] where E_{op} is the energy

$$\Delta\bar{\nu}_{1/2} = [16(\ln 2)k_BT(E_{op} - E_0)]^{1/2} \qquad (3)$$

of the optical transition maximum and E_0 the free energy barrier between the two oxidation states of the binuclear complex. At room temperature eq 3 yields

$$\Delta\bar{\nu}_{1/2} = [2310(E_{op} - E_0)]^{1/2} \qquad (4)$$

The value of E_0 can be obtained from the following cycle:

$$\begin{tikzcd}
(CN)_5Fe^{II}(4\text{-}PyCONH)Ru^{III}(NH_3)_5 \arrow[r, "E_0"] \arrow[d, "E_1^\circ"] & (CN)_5Fe^{III}(4\text{-}PyCONH)Ru^{II}(NH_3)_5 \\
(CN)_5Fe^{III}(4\text{-}PyCONH)Ru^{III}(NH_3)_5 \arrow[ur, "E_2^\circ"'] &
\end{tikzcd}$$

$E_1°$ was measured in the present work as −0.502 V. Assuming that the $Fe(CN)_5^{2-}$ center acts mainly as a σ acid, $E_2°$ be approximated by the reduction potential for the $Ru(NH_3)_5(4\text{-}NHCOPyCH_3)^{3+/2+}$ couple and was taken as −0.023 V. With the value of E_0 thus obtained, $\Delta\bar{\nu}_{1/2}$ can be calculated as 5100 cm^{-1}, in agreement with the experimentally measured value.

The extent of the delocalization can be obtained by a calculation of the delocalization parameter α^2 and electronic coupling H_{AB} from eqs 5 and 6. Taking d = 9.13 Å for the binuclear complex

$$\alpha^2 = 4.24 \times 10^{-4}\epsilon_{max}(\Delta\bar{\nu}_{1/2})/\bar{\nu}_{max}d^2 \qquad (5)$$

$$H_{AB} = \bar{\nu}_{max}\alpha \qquad (6)$$

of 4-cyanopyridine,[8] and substituting $\bar{\nu}_{max}$, ϵ_{max} and $\Delta\bar{\nu}_{1/2}$ into the equations, we have α^2 = 9.5 × 10^{-4} and H_{AB} = 4.8 × 10^2 cm^{-1}. This d value of 9.13 Å is surely a lower limit for the present amido-bridged complex, so the calculated value of α^2 = 9.5 × 10^{-4} represents an upper limit for this parameter. The small value of the delocalization parameter ($\alpha^2 \sim 0.1\%$) clearly supports the trapped-valence description of the binuclear complex. The α^2 and H_{AB} values in the present system are considerably smaller than values found for pyrazine-bridged (α^2 = 9.8 × 10^{-3}, H_{AB} = 6 × 10^2 cm^{-1})[19] and cyanide-bridged (α^2 = 2.2 × 10^{-2}, H_{AB} = 1.5 × 10^3 cm^{-1})[43] complexes. Such a trend is expected, since the coupling between sites is dominated by the metal centers–bridging ligand mixing.

Finally, the thermal electron barrier ΔG^* according to eq 7 can be approximated by eq 8,[2] where λ_{out} and λ_{in} are contributions

$$(CN)_5Fe^{II}(4\text{-}PyCONH)Ru^{III}(NH_3)_5 \xrightarrow{k_{et}} (CN)_5Fe^{III}(4\text{-}PyCONH)Ru^{II}(NH_3)_5 \qquad (7)$$

$$\Delta G^* = (\lambda + \Delta G°)^2/4\lambda \qquad (8)$$

$$\lambda = \lambda_{out} + \lambda_{in} \qquad (9)$$

$$\Delta G° \sim E° \qquad (10)$$

of the solvent and the inner-coordination sphere distortions to the reorganization barrier, respectively.[41] The rate constant of intramolecular electron transfer k_{et} can be calculated from eq 11,

$$k_{et} = \nu_{et} \exp(-\Delta G^*/RT) \qquad (11)$$

where ν_{et} is the hopping frequency. Since in our system

$$4.6 \times 10^{-3}H_{AB}{}^2(E_{op})^{-1/2} \text{ (in cm}^{-1}) > 1 \qquad (12)$$

the reaction should be considered as adiabatic.[2] Thus ν_{et} can be taken as 5 × 10^{12} s^{-1} at 25 °C, the same as in the case of pyrazine-bridged binuclear complex. On the basis of eq 11 and our measured values of E_{op} and E_0, we calculate k_{et} = 35 s^{-1}. With this value and the equilibrium constant of eq 7, the rate constant of electron transfer for the reverse reaction of eq 7 can also be calculated as 1.3 × 10^{10} s^{-1}.

In our previous work on the pyrazine-bridged binuclear complex,[19] we have calculated the rate constant of electron transfer for the E_0 = 0 process, or the rate constant according to eq 13.

$$k_{et}' = \nu_{et} \exp(-\lambda/4RT) \qquad (13)$$

In the same manner, we obtain a rate constant of 6.0 × 10^6 s^{-1} for the pyridinecarboxamido-bridged complex. This value is about 4 orders of magnitude smaller than that for the analogous pyrazine-bridged binuclear complex (2.7 × 10^{10} s^{-1}). The difference apparently arises from the reorganization parameter λ. λ_{out} and λ_{in} can be expressed by eqs 14 and 15, where n is the number of

$$\lambda_{out} = e^2(1/2a_2 + 1/2a_3 - 1/r)(1/D_{op} - 1/D_s) \qquad (14)$$

$$\lambda_{in} = n[2f_2f_3/(f_2 + f_3)](d_2° - d_3°) \qquad (15)$$

ligands per metal center, a_2, a_3 and f_2, f_3 are metal–ligand bond lengths and force constants for the metal in oxidation states II and III, respectively, r is the separation between the metal centers, ($d_2° - d_3°$) is the difference in the equilibrium bond distance between the two oxidation states of the metal ion, and D_{op} and D_s are the optical and static dielectric constants of the solvents.

When a_2 and a_3 remain basically unchanged, λ_{out} will increase as r increases according to eq 14. Thus, the rate constant of intramolecular electron transfer for $(CN)_5FeLCo(NH_3)_5$ changes from 5.5 × 10^{-2} to 1.4 × 10^{-3} s^{-1} when the internuclear distance changes from 6.9 (L = pyrazine[44]) to 13.2 Å (L = 4,4′-bipyridyl[45]).

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Similarly, an ~100-fold drop in rate constant was also found for the $(bpy)_2ClRuLRuCl(bpy)_2{}^{3+}$ binuclear series as *r* increases from 6.8 to 13.8 Å.[46] With the internuclear distance difference between the pyrazine-bridged and the 4-pyridinecarboxamido-bridged binuclear complexes in our system, a rate difference of 1 order of magnitude may therefore be expected from the λ_{out} contribution. Moreover, in the pyrazine case, the π-accepting ability of the ligand will make the configurations of the Ru(II)–L and the Ru(III)–L tend to become similar[47] in the binuclear complex. This, in turn, may lead to a low inner-shell reorganization energy according to eq 15. On the other hand, in the pyridinecarboxamido case, the $(d_2{}^{\circ} - d_3{}^{\circ})$ term in eq 15 may be significantly larger than the pyrazine species because of the σ character of the amido group. As a consequence, the inner-sphere reorganization energy also will be enhanced.

We were unable to observe any IT band for the binuclear complex IV with the 3-isomer as a bridge, probably due to the weak coupling arising from the meta position. However, for aged sample solutions, we observed a band at λ_{max} = 960 nm (ϵ_{max} = 710 M^{-1} cm^{-1}). Similar absorption at λ_{max} = 962 nm was also observed for the solution of the 4-isomer complex 30 min after its preparation. Since this 960-nm band was found only upon aging, we believe that the band is related to some decomposition compound rather than an intrinsic property of the binuclear complex itself. Similar observations were also found for a number of binuclear complexes containing the $Fe(CN)_5{}^{3-}$ moiety,[19,38] suggesting that the absorption may arise from some cyano-bridged binuclear cyanoferrate impurities.[19]

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Important Factors in Oxygen Atom Transfer to Metal Carbonyls. Rate of CO Substitution of $Cr(CO)_6$ and $Fe(CO)_5$ in the Presence of $(p\text{-}CH_3OC_6H_4)_2EO$ (E = Se, Te) and of $(C_6H_5)_3EO$ (E = As, Sb). Syntheses and X-ray Structure of $Cr(CO)_5E(p\text{-}CH_3OC_6H_4)_2$

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An attempt is made to obtain information on the various factors that contribute to the overall O atom transfer rates of reactions of metal carbonyls of the type M–CO + E–O → M + CO_2 + E. The metal carbonyls used were $Cr(CO)_6$ and $Fe(CO)_5$, and the O atom transfer reagents were $(p\text{-}CH_3OC_6H_4)_2EO$ (E = Se, Te), $(C_6H_5)_3EO$ (E = P, As, Sb), and $(C_6H_5)_2SO$. There was no reaction with either $(C_6H_5)_3PO$ or $(C_6H_5)_2SO$, under the experimental conditions used. The reagents that did react transfer their O atoms at the relative rates of TeO > SeO > SbO > AsO. These results, along with previously reported data, are discussed in terms of the various important factors believed to contribute to the energetics of these overall reactions. Syntheses are given of the new compounds $Cr(CO)_5E(p\text{-}CH_3OC_6H_4)_2$ (E = Se, Te), and the X-ray structure of the Te compound is reported. The Cr–Te distance in the present structure, 2.684 (1) Å, is the shortest known, and the Te atom is pyramidal.

Introduction

Although alkyl and aryl telluroxides and selenoxides are known[1] to be mild oxidizing reagents toward organic compounds, the reactions of these oxides as O atom transfer reagents toward inorganic complexes have not previously been reported. This paper is the first report of such a study, and it was prompted by our investigations[2] on the kinetics and mechanisms of O atom transfer from $(CH_3)_3NO$ to metal carbonyls.

Previous studies showed[2] that the rates for O atom transfer of $(CH_3)_3NO$ to metal carbonyls increased with increasing CO stretching frequencies of the metal carbonyls and with increasing basicities of the O atom of the amine oxides.[3] These results imply the rates of reaction are largely determined by a nucleophilic attack of the O atom of the amine oxides at a carbonyl carbon atom of the metal complexes. On this basis of viewing the rate-determining step as simply that of nucleophilic attack of the O atom on a CO carbon atom, we were surprised to find that $(CH_3)_3NO$ was as good a nucleophile as are CH_3Li[4a] and $C_6H_5CH_2MgBr$.[4b] This was initially explained in terms of "the high negative charge[5] on oxygen in $Me_3N^{\delta+} \rightarrow O^{\delta-}$".

More recently[3] the N–O bond strengths of the amine oxides were addressed in terms of their weaker bond strengths thermodynamically favoring their reaction to product. Holm[6] has tabulated thermodynamic data on available oxidation enthalpies of different O atom transfer reagents, and he has stressed the use of these data for predicting reactions in a manner analogous to the use made of values of standard redox potentials.

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