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Intramolecular Electron-Transfer Reactions in Bridged Binuclear Ru(II)–Co(III) Molecules

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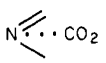
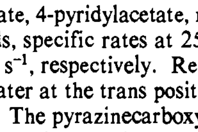
Abstract: Intramolecular electron transfer in Ru(II)–Co(III) binuclear complexes containing pyrazine, 4,4′-bipyridine, and selected pyridinecarboxylate anions as bridging ligands has been studied. For the series $(H_2O)Ru^{II}(NH_3)_4(R)Co^{III}(NH_3)_5{}^{4+}$, where R equals



with 3-pyridylacetate, 4-pyridylacetate, nicotinate, isonicotinate, 3-cinchomeronate, 4-cinchomeronate, and pyrazinecarboxylate as bridging ligands, specific rates at 25 °C are 0.566×10^{-3}, 7.83×10^{-3}, 1.80×10^{-3}, 12.4×10^{-3}, 1.1×10^{-3}, 42×10^{-3}, and $\leq 0.13 \times 10^{-3}$ s^{-1}, respectively. Related complexes with 4-cinchomeronate as bridging ligand but with iodide or sulfate substituting for water at the trans position of the ruthenium undergo electron transfer with specific rates at 25 °C of 0.5 and 5 s^{-1}, respectively. The pyrazinecarboxylate-bridged species undergoes facile photoinduced electron transfer, and its spectrum exhibits a shoulder at 390 nm ($\epsilon = 400 \pm 50$) which is absent from the spectra of both constituent mononuclear complexes. For the complexes $(O_3S)Ru^{II}(NH_3)_4(L)Co^{III}(NH_3)_5{}^{3+}$ where L = pyrazine and 4,4′-bipyridine, specific rates for electron transfer at 25 °C are 0.128 and 4×10^{-4} s^{-1}, respectively. These results indicate that electron transfer in the pyridinecarboxylato complexes approaches the adiabatic regime. The surprisingly low rate for the 4,4′-bipyridine-bridged complex, especially in comparison to the rate for the pyrazine complex, raises the possibility that electron transfer in this species is strongly nonadiabatic.

The work to be reported is a refinement and extension of the earlier preliminary results of Isied and Taube[1a] on the rates of intramolecular electron transfer based on the Co(III)–Ru(II) redox system. Activation parameters have now been determined, and an important correction on the rate constant for the isonicotinate-bridged species is reported. The work has been extended to related bridging groups, and the effect on the rate of electron transfer attending substitution on Ru(II) in the position trans to the bridging group has been examined.

A glossary of abbreviations used in the paper follows. 3-cinH represents the form in which the residue $Co(NH_3)_5$ replaces a proton on the meta-carboxyl of cinchomeronic acid



and 4-cinH implies that $Co(NH_3)_5$ is in the trans position; pz represents pyrazine, bpy, 4,4′-bipyridine, MES, morpholineethanesulfonic acid (used here as a buffer because of its very low affinity for metal ions),[2] HTFMS, trifluoromethanesulfonic acid, HTFA, trifluoroacetic acid; HTos, *p*-toluenesulfonic acid, and NaTos, sodium *p*-toluenesulfonate.

Experimental Section

Preparation of Cobalt(III) Complexes. Complexes of the type $[Co(NH_3)_5(L)](ClO_4)_2$, where L = nicotinate, 3-pyridylacetate, 4-pyridylacetate, isonicotinate, and pyrazinecarboxylate, were prepared by the method of Taube and Gould,[3] as modified by Isied.[1b] The complexes $[Co(NH_3)_5(3\text{-cinH})](ClO_4)_2$ and $[Co(NH_3)_5(4\text{-cinH})](ClO_4)_2$ were prepared by a method modified slightly from that used for the other carboxylate complexes. To obtain a maximum yield of the 3-cinH complex, we dissolved 20 mmol (3.4 g) of cinchomeronic acid (Aldrich) in 10 mL of 3.5 M NaOH at 50 °C, 1.0 g of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ was added, and the solution was maintained at 50–60 °C with stirring for 2 h. The solution was cooled slowly to room temperature, and the $[Co(NH_3)_5(3\text{-cinH})](ClO_4)_2$ was collected by filtration, washed with dilute aqueous $NaClO_4$ solution, ethanol, and ether, and dried under vacuum. Yield: 0.6–0.8 g of the 3-cinH complex. To enhance the yield of the 4-cinH, we followed the procedure to be outlined. Forty millimoles (6.8 g) of cinchomeronic acid was dissolved in 23 mL of 1.75 M NaOH at 75 °C, 2.0 g of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ was added, and the solution was maintained at 75 °C with stirring for 2 h. The solution was allowed to cool slowly to room temperature and to stand for 2–3 h, whereupon the relatively insoluble $[Co(NH_3)_5(3\text{-cinH})](ClO_4)_2$ was removed by filtration. Solid $NaClO_4$ was then added to the filtrate to precipitate $[Co(NH_3)_5(4\text{-cinH})](ClO_4)_2$, which was collected by filtration, washed with saturated $NaClO_4$ solution, ethanol, and ether, and dried under vacuum. Yield: ca. 0.8 g of the 4-cin complex.

The complexes $[Co(NH_3)_5(pz)]Cl_3{\cdot}2H_2O$ and $[Co(NH_3)_5(bpyH)]Cl_4{\cdot}H_2O$ were prepared as described by Gould, Morland, and Johnson[4] and isolated as chloride salts following purification by gel filtration chromatography with use of Bio-Gel P-2 (Bio-Rad Laboratories) with 0.1 M HCl or 0.5 M LiCl and 0.01 M HCl as eluant.

Ruthenium Compounds. Samples of $[Ru(NH_3)_6]Cl_3$ used to prepare solutions of $Ru(NH_3)_6{}^{2+}$ were recrystallized by the method of Armor.[5] The compound *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ was prepared by the method of Vogt, Katz, and Wiberley[6] according to Armor's procedure.[5]

Preparation of Ru(III)–Co(III) Binuclear Complexes. Binuclear complexes of the form $[(SO_4)Ru^{III}(NH_3)_4(L)Co(NH_3)_5]Cl_3{\cdot}2H_2O$, where L = nicotinate, 3- and 4-pyridylacetate, isonicotinate, 3-cinH, and 4-cinH, were prepared according to the method of Isied and Taube[1] and then purified by gel chromatography with use of Bio-Gel P-2 with 0.05–0.10 M HCl as eluant. The complex $[(SO_4)Ru^{III}(NH_3)_4(\text{pyrazinecarboxylate})Co^{III}(NH_3)_5]Cl_3{\cdot}2H_2O$ was prepared by a modification of this method. A 150-mg sample of *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ was combined with ca. 100 mg of $NaHCO_3$ and 190 mg of $[Co(NH_3)_5(\text{pyraziniumcarboxylate})]Cl_3$ in 8–10 mL of water under argon, and the solution was allowed to react for 1–2 min. One milliliter of 5 M HCl was then added with stirring, followed quickly by 6–8 drops of 30% H_2O_2. The resulting orange solution was mixed with ca. 75 mL of 1 M HCl, and acetone was added with stirring until the solution was just turbid (100–150 mL), when it was set to chill in an ice bath or refrigerator to induce precipitation of the product. Yield: ca. 50%. Attempts to purify the complex either by ion exchange or gel filtration were unsuccessful, owing to disproportionation of the complex on the column. It was purified by redissolving it in a minimum volume of 1 M HCl and either repeating the original precipitation procedure or adding solid NH_4PF_6 to precipitate the hexafluorophosphate salt.

It was desired to replace coordinated sulfate by another ligand in certain of the Ru(III)–Co(III) ions. The sulfato form of the iso-

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[1] (a) Isied, S. S.; Taube H. *J. Am. Chem. Soc.* **1973**, *95*, 8198. (b) Isied, S. S. Ph.D. Thesis, Stanford University, 1974.

[2] Good, N. F.; Winget, G. D.; Winter, W.; Connolly, T. N.; Izawa, S.; Singh, R. M. M. *Biochemistry* **1966**, *5*, 467.

[3] Taube, H.; Gould, E. S. *J. Am. Chem. Soc.* **1964**, *86*, 1318.

[4] Gould, E. S.; Morland, R. B.; Johnson, N. A. *Inorg. Chem.* **1976**, *15*, 1929.

[5] Armor, J. N. Ph.D. Thesis, Stanford University, 1970.

[6] Vogt, L. H.; Katz, J. L.; Wiberley, S. E. *Inorg. Chem.* **1965**, *4*, 1157.

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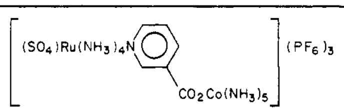
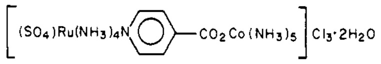
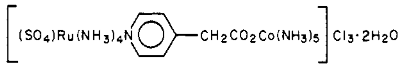
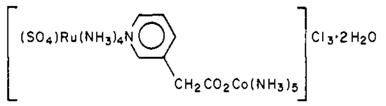
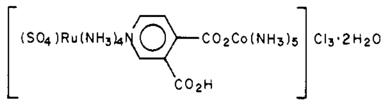
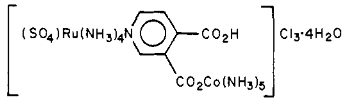
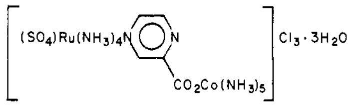
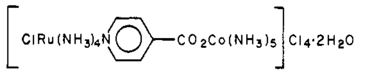
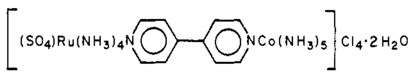
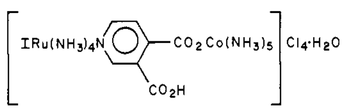
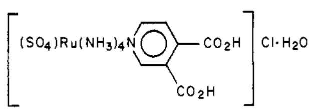
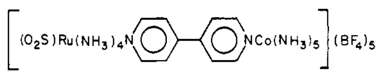
Table I. Microanalysis for Ru(III)–Co(III) Binuclear Complexes

compd		C	H	N	Ru	Co	Cl
	calcd	7.2	3.5	14.0			
	obsd	7.45	3.52	14.18			
	calcd	10.7	5.2	20.8			
	obsd	10.30	4.90	20.71			
	calcd	12.2	5.4	20.3			
	obsd	12.39	4.96	20.20			
	calcd	12.2	5.4	20.4			
	obsd	11.4	5.24	19.35			
	calcd	11.7	4.92	19.5	14.1	8.2	
	obsd	12.01	4.92	19.79	14.3	8.18	
	calcd	11.1	5.20	18.68			13.9
	obsd	11.09	4.85	18.42			13.19
	calcd	8.66	5.38	22.21	14.57	8.49	
	obsd	8.76	4.97	22.36	14.48	8.26	
	calcd	11.1	5.47	21.65	15.6	9.08	27.4
	obsd	11.15	5.35	21.82	15.65	9.05	28.81
	calcd	16.2	5.3	20.7			
	obsd	17.01	5.23	20.39			
	calcd	11.0	4.35	18.3	13.2	7.7	
	obsd	11.46	4.91	18.41	13.3	7.50	
	calcd	17.3	3.9	14.5			
	obsd	17.30	3.90	14.44			
	calcd	12.4	3.65	15.9	10.5	6.1	
	obsd	11.59	3.55	14.41	10.0	5.5	

nicotinate-bridged binuclear complex was converted to $[ClRu(NH_3)_4(isonicotinate)Co(NH_3)_5]Cl_4 \cdot 2H_2O$ by dissolving the original compound in a minimum of 1 M HCl at 10 °C, adding excess $Ru(NH_3)_6^{2+}$ or ascorbic acid, and then reoxidizing the binuclear after ca. 30 s by adding aqueous bromine solution until the red color of the Ru(II) species was discharged; the chloro species was then precipitated by using 8–10 volumes of acetone and purified by gel filtration. The sulfato form of the 4-cinH-bridged binuclear was converted to $[IRu(NH_3)_4(4\text{-}cinH)Co(NH_3)_5]Cl_4 \cdot 2H_2O$ by a slightly different procedure. A 200-mg sample of $[(SO_4)Ru(NH_3)_4(4\text{-}cinH)Co(NH_3)_5]Cl_3 \cdot 2H_2O$ was dissolved in a minimum volume of 0.05 M HTFMS, and chloride ion was removed from solution by gel filtration with 0.02 M HTFMS as eluant. The eluate (ca. 20 mL) was cooled to 10 °C, and 10 mL of a solution 0.3 M in NaI and 0.1 M in I_2 was added with stirring. After ca. 10 min, the solution was extracted with ether to remove I_2 and loaded onto a column of AG 50W-X2 resin, from which $IRu(NH_3)_4(4cinH)Co(NH_3)_5^{4+}$ was eluted with 5 M HCl and precipitated as the chloride salt by adding acetone.

The complex $[(O_2S)Ru(NH_3)_4(bpy)Co(NH_3)_5](BF_4)_5$ was prepared by the method of Isied.[1] Because the compound is light-sensitive and decomposes to a brown powder in about 24 h even when stored in a desiccator in the dark, it was protected from light as much as possible during preparation and kinetic experiments and used within 4 h of synthesis.

Microanalyses for the binuclear species are summarized in Table I.

Procedure for Kinetic Experiments. In most cases, a solution of the Ru(III)–Co(III) binuclear complex was treated with a reducing agent ($Ru(NH_3)_6^{2+}$ or ascorbate) to generate the Ru(II)–Co(III) ion, following Isied's procedure.[1] In principle, the intramolecular electron-transfer reaction in the Ru(II)–Co(III) complex, which yields Co^{2+} and the Ru(III)-bridged complex, can be followed by monitoring the disappearance of the Ru(II) absorption during the reaction, but in practice the reaction between the Ru(II)–Co(III) binuclear and the Ru(III) product (reaction 1) interferes with that of interest, resulting in curvature in first-order rate

$$\mathrm{Ru^{II}LCo^{III} + Ru^{III}L = Ru^{III}LCo^{III} + Ru^{II}L} \tag{1}$$

plots. This complication can be avoided by exploiting small but significant differences in the $\pi \rightarrow \pi^*$ absorptions of the $Ru^{II}LCo^{III}$ species and the corresponding $Ru^{II}L$ complex and using an excess of the external reducing agent so that the ruthenium remains in the reduced state following the intramolecular electron transfer. Under these conditions, the net changes observed is given by eq 2. Gould and Fan[7] have shown that

$$\mathrm{Ru^{II}LCo^{III} + reductant \rightarrow Ru^{II}L + Co^{2+} + oxidized\ product} \tag{2}$$

$Ru(NH_3)_6^{2+}$ reduces most (pentaamminecarboxylate)cobalt(III) complexes with a specific rate of 0.1 $M^{-1}\ s^{-1}$ or less, and ascorbate reduces Co(III) complexes even more slowly[8] so that with use of low ($<10^{-3}$ M) reactant concentrations, direct reduction of the Co(III) center by the external reductant can be avoided.

Reactions were initiated by injecting 0.15–0.25-mL reductant solution into 15–25 mL of degassed and thermostated solution of the $Ru^{III}LCo^{III}$ complex and were followed spectrophotometrically for 10 half-lives. Temperature measurements were made by inserting a thermometer directly into the cell at the end of the reaction.

Measurements for the faster reactions were performed with a stopped-flow apparatus which has been previously described.[9]

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[7] Gould, E. S.; Fan, F.-R. F. *Inorg. Chem.* **1974**, *13*, 2647.

[8] Zawacky, S., unpublished results.

The complex $[(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$ was generated in situ by combining *trans*-$Ru(NH_3)_4(H_2O)(SO_3)$ and $[Co(NH_3)_5(pz)]^{3+}$ in solution to from the binuclear according to eq 3. Isied and Taube[10] have

$$(O_3S)Ru(NH_3)_4(H_2O) + [Co(NH_3)_5(pz)]^{3+} \rightleftharpoons [(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+} \quad (3)$$

shown that for the analogous substitution of free pz into $(O_3S)Ru(NH_3)_4(H_2O)$ the rate for the forward reaction and the equilibrium constant are 13 M^{-1} s^{-1} and 2.9×10^3 M^{-1}, respectively. Corresponding values for the substitution by the cobalt complex will be lower by a factor of 2–5 because of the tripositive charge, but reaction 3 may be rapidly driven to completion by using $Co(NH_3)_5(pz)^{3+}$ in excess at high concentration (0.05 M). In the presence of an external reductant, formation of the binuclear complex is followed by two other reactions.

$$[(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+} \xrightarrow{k_{et}} [(O_3S)Ru(NH_3)_4(pz)] + Co^{2+} \quad (4)$$

$$(O_3S)Ru(NH_3)_4(pz) \xrightarrow{4.5 \times 10^{-3}\ s^{-1}} (O_3S)Ru(NH_3)_4(H_2O) + pz \quad (5)$$

(Reaction 4 as written implies that Ru(III) as produced is rapidly reduced by the external reductant.)

Reactions were initiated by injecting ca. 0.05 mL of a solution containing *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ (1–2 mg/mL of solution) and either $Ru(NH_3)_6^{2+}$ or ascorbic acid (0.03–0.04 M) into 2.5 mL of an argon-purged and thermostated solution of $[Co(NH_3)_5(pz)]X_3$, where X = Cl or ClO_4. Reaction progress was monitored spectrophotometrically for 5–6 half-lives, and to avoid complications from the slow aquation of $(O_3S)Ru(NH_3)_4(pz)$, we determined rate constants by Guggenheim's method.[11]

Because electron transfer in $[(O_3S)Ru(NH_3)_4(bpy)Co(NH_3)_5]^{3+}$ is much slower than in the pz-bridged complex, the method of Jwo and Haim[12] for monitoring electron transfer in a system in which aquation of the bridging ligand competes with and follows the redox step was used in this case. In the presence of ascorbate and a large excess of a ligand (nicotinamide) which substitutes rapidly at the ruthenium center following release of the bridging ligand, reaction 6–9 (Scheme I) take place.

Scheme I

$$\begin{tikzcd}
\text{I} \arrow[rr, "k_{et}"] \arrow[dr, "k_d"'] & & \text{II} \arrow[dl, "k_{-B}"] \\
& \text{IV} &
\end{tikzcd}$$

$$\text{I} \xrightarrow{k_{et}} \text{II} + \text{CO}^{2+} \quad (6)$$

$$\text{I} \xrightarrow{k_d} \text{III} + \text{Co(NH) (bpy)}^{3+} \quad (7)$$

$$\text{II} \xrightarrow{k_{-B}} \text{III} + \text{bpy} \quad (8)$$

$$\text{L} + \text{III} \xrightarrow{\text{fast}} \text{IV} \quad (9)$$

I = $[(O_3S)Ru(NH_3)_4(bpy)Co(NH_3)_5]^{3+}$, II = *trans*-$Ru(NH_3)_4(bpy)(SO_3)$, III = *trans*-$Ru(NH_3)_4(H_2O)(SO_3)$, IV = *trans*-$Ru(NH_3)_4$(nicotinamide)$(SO_3)$, L = nicotinamide

The absorbance at any time during the reaction sequence is given by eq 10. The value of k_{et} can be calculated by using eq 11. A_{II} and A_{IV} are

$$A_t = A_\infty + f \exp[-(k_d + k_{et})t] + g \exp(-k_{-B}t) \quad (10)$$

$$g = (A_{II} - A_{IV})k_{et}/(k_d + k_{et} - k_{-B}) \quad (11)$$

the absorbances of II and IV, respectively, at concentrations equal to the initial concentration of I; A_t is the measured absorbance at time t, and A_∞ is the measured absorbance at infinite time; and f, g, k_{-B}, and $(k_d + k_{et})$ are parameters for which values can be obtained from a nonlinear least-squares treatment of the A_t vs. t data.

Reaction was initiated by injecting 0.15 mL of a solution of freshly prepared $[(O_2S)Ru(NH_3)_4(bpy)Co(NH_3)_5](BF_4)_5$ into an argon-purged and thermostated solution of ascorbate (0.002 M) and nicotinamide (0.05 M) in the appropriate buffer; the progress of the reaction was monitored spectrophotometrically for 10 half-lives, and the A_t vs. t data were analyzed by a nonlinear least-squares treatment to determine values for f, g, k_{-B}, and $(k_d + k_{et})$ as described above.

The method of generating the complex in situ by mixing *trans*-$Ru(NH_3)_4(H_2O)(SO_3)$ and a large excess of the mononuclear cobalt complex was also used as a check on the result obtained from the computer treatment. To avoid complications from bridging ligand aquation, we only measured the initial rate, and to permit correction for outer-sphere reduction of Co(III) by Ru(II) in *trans*-$Ru(NH_3)_4(H_2O)(SO_3)$ and/or the binuclear complex, we performed experiments at two different Co(III) concentrations (0.025 and 0.050 M).

Cyclic Voltammetry. The apparatus used for these measurements has been previously described.[9]

Results

A. Electron Transfer in Binuclear Species Derived from $Ru^{III}(R)Co^{III}$ Complexes. The immediate product of the 1-e$^-$ reduction of a complex of the form $[(SO_4)Ru^{III}(NH_3)_4(L)Co^{III}(NH_3)_5]^{n+}$ is the corresponding Ru(II)–Co(III) species, which can undergo two reactions: aquation of coordinated sulfate and intramolecular electron transfer. The rate of sulfate aquation in any binuclear of this series will be close to that reported[1b] (k = 2.3 s^{-1}) for the related complex *trans*-$Ru(NH_3)_4$(isonicotinamide)(SO_4); and consequently, only if the rate of electron transfer exceeds this rate does the intramolecular redox reaction precede aquation. From the measured rates of electron transfer summarized in Table II it is plain that only in the 4-cinH-bridged complex does electron transfer occur faster than loss of sulfate, and therefore the reacting ion in each other case is $[(H_2O)Ru^{II}(NH_3)_4(L)Co^{III}(NH_3)_5]$. In particular, the present work shows that electron transfer in the isonicotinate-bridged species occurs about 2 orders of magnitude less rapidly than sulfate aquation; moreover, the measured rate is independent of whether $[ClRu(NH_3)_4(\text{isonicotinate})Co(NH_3)_5]^{4+}$ or $[(SO_4)Ru(NH_3)_4(\text{isonicotinate})Co(NH_3)_5]^{3+}$ is the source of the binuclear reactant.

In several cases, it was shown that the rate is independent of the concentration and nature of the external reducing agent. Thus in the isonicotinate-bridged case, the concentration of $Ru(NH_3)_6^{2+}$ changed by a factor of 2 with no effect on k_{et}. Moreover, the rate with Eu^{2+} as external reductant in this case is only slightly greater than for $Ru(NH_3)_6^{2+}$. The direct reaction of Eu^{2+} with Co(III) makes a significant contribution to the rate and this accounts for the larger value obtained for Eu^{2+}. In the case of $[(SO_3Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$, to be dealt with in more detail later, k_{et} at 15 °C using $Ru(NH_3)_6^{2+}$ was measured as 2.63×10^{-2} s^{-1}, while with ascorbic acid as external reductant, k_{et} was found to be 2.52×10^{-2} and 2.65×10^{-2} s^{-1}.

Structures of the two isomeric cinchomeronate-bridged complexes were assigned on the basis of the position of the $\pi \rightarrow \pi^*$ charge-transfer band as a function of pH and the rate of the electron-transfer reaction. For the Ru(II)–Co(III) ion prepared from the less soluble $[Co(NH_3)_5(cinH)]^{2+}$ complex, the charge-transfer transition appears at 443 nm at pH 5 but at 500 nm in 1 M acid; the magnitude of this shift indicates that the 4-carboxylate is the site of protonation and that the cobalt is bound to the carboxylate at the 3-position. Moreover, the rate of electron transfer in this ion is close to that observed for the nicotinate-bridged complex. For the Ru(II)–Co(III) species prepared from the other Co(III) complex, the charge-transfer band appears at ca. 475 nm at pH 5 and at ca. 500 nm in 1 M acid, and the rate of intramolecular electron transfer in the trans-aquo form is close to the rate for the isonicotinate complex; these observations indicate that in this complex the cobalt is attached to the carboxylate at the 4-position.

As expected, the rate of electron transfer in these complexes varies with pH. With decreasing pH, the rate of electron transfer in the 3-cin complex first decreases, reaching a minimum at about pH 1.4, and then increases slightly as the pH decreases still further (see Table II). Part of this pH dependence is attributable to protonation of the carboxylate function in the 4-position of the bridging ligand (pK_a as determined by electrochemical titration in 0.4 M benzoic acid–sodium benzoate is 1.8 ± 0.1). At pH 1.73 and 1.37 the observed rate is composite and includes contributions from the reaction of both the protonated and deprotonated forms of the complex. With use of the rate for the deprotonated form, 2.48×10^{-3} s^{-1} (corrected to 24.7 °C), the measured pK_a of 1.8, and the observed rates at pH 1.73 and 1.37, 1.79×10^{-3} and 1.41×10^{-3} s^{-1}, respectively, a value of $(1.08 \pm 0.1) \times 10^{-3}$ s^{-1} is calculated for the rate of electron transfer in the protonated form

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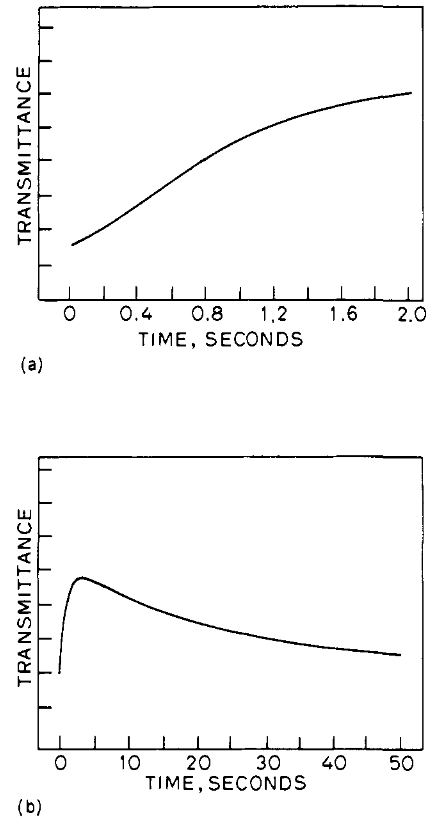


Figure 1. Stopped-flow traces for reaction following reduction of Ru(III) to Ru(II) in $[(SO_4)Ru(NH_3)_4(4\text{-cinH})Co(NH_3)_5]^{3+}$: (a) initial phase; (b) extended time period. See G and H of Table II for conditions.

of this complex at 24.7 °C. The small increase in rate at pH <1 may be due to a pathway involving still further protonation of the species, but it is also possible that it arises from reduction of the bridging ligand by $Ru(NH_3)_6^{2+}$ in strongly acidic solution.

In parts a and b of Figure 1 are shown the stopped-flow traces for the reduction of $[(SO_4)Ru^{III}(NH_3)_4(4\text{-cinH})Co^{III}(NH_3)_5]^{3+}$ in the presence of excess reducing agent on two different time scales. The reactions which need to be taken into account are represented by eq 12–15. Excess reducing agent ensures that

$$[(SO_4)Ru(NH_3)_4(4\text{-cinH})Co(NH_3)_5]^{2+} \xrightarrow{k_{12}} [(SO_4)Ru(NH_3)_4(cinH_n)]^{(n-2)+} + Co^{2+} \quad (12)$$

$$[(SO_4)Ru(NH_3)_4(4\text{-cinH})Co(NH_3)_5]^{2+} \xrightarrow{k_{13}} [(H_2O)Ru(NH_3)_4(4\text{-cinH})Co(NH_3)_5]^{4+} + SO_4^{2-} \quad (13)$$

$$[(SO_4)Ru(NH_3)_4(cinH_n)]^{(n-2)+} \xrightarrow{k_{14}} [(H_2O)Ru(NH_3)_4(cinH_n)]^{n+} + SO_4^{2-} \quad (14)$$

$$[(H_2O)Ru(NH_3)_4(4\text{-cinH})Co(NH_3)_5]^{4+} \xrightarrow{k_{15}} [(H_2O)Ru(NH_3)_4(cinH_n)]^{n+} + Co^{2+} \quad (15)$$

the ruthenium in the product of reaction 12 is in the 2+ state. It is also to be noted that further protonation of the ligand may ensue after cobalt is lost from it so that n in the product of reaction 15 may be 1 or 2.

In the first trace shown in Figure 1a, the effects mainly of reactions 12 to 14 are seen. Sulfate aquation (reactions 13 and 14) causes a transmittance increase; intramolecular electron transfer in the sulfato form of the binuclear is shown as a transmittance decrease which manifests itself only as a sigmoid distortion in the early part of the trace. Intramolecular transfer for the aquoruthenium(II) is much slower than for the sulfato form, and this reaction accounts for the decrease in transmittance observed over a long time span (Figure 1b).

If it is assumed that the rate of aquation of SO_4^{2-} is the same on Ru(II) in the binuclear as in the mononuclear form, i.e., $k_{13} = k_{14}$, the three specific rates k_{12}, $k_{13} = k_{14}$, and k_{15} can be obtained. The specific rate k_{15} is directly obtainable from the data comprising the descending portion of the trace in Figure 1b. The data early in the course of the reaction were treated by a computer program developed by Mr. Craig Cornelius to yield the other two specific rates.

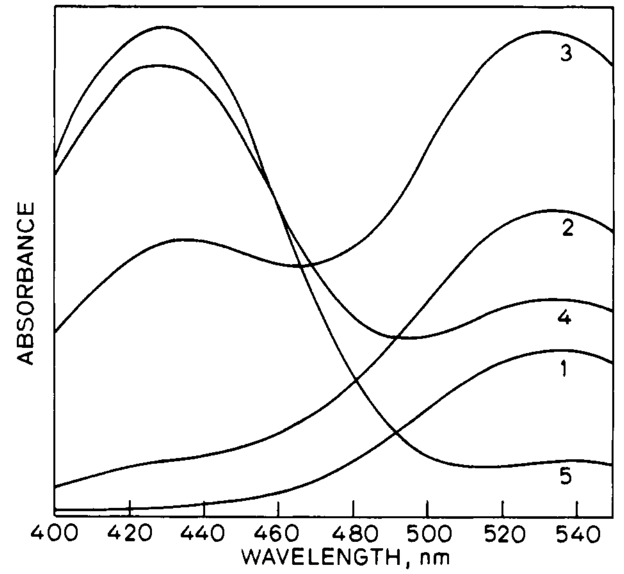


Figure 2. The formation and disappearance of $[(SO_3)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$ ([Co(III)] = 0.025 M; pH 5.9, 7 °C). Scans are at approximately 45-s intervals. Vertical scale = 0–1 in absorbance.

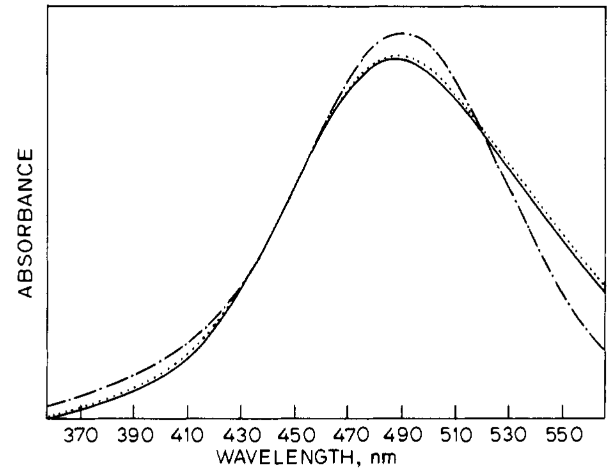


Figure 3. Visible spectra of $(H_2O)Ru(NH_3)_4$(pyrazinecarboxylate)$Co(NH_3)_5^{4+}$ (-·-) and $(H_2O)Ru(NH_3)_4$(pyrazinecarboxylate)$^+$ (—) in 0.0012 M HTFMS. Both ions are at a concentration of 1.4×10^{-5} M. The dotted line represents the spectrum of the solution containing 1.4×10^{-5} M $(H_2O)Ru(NH_3)_4$(pyrazinecarboxylate)$^+$ 30 min after formation. Vertical scale = 0–1.5 in absorbance.

B. Electron Transfer in $[(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$. When *trans*-$Ru(NH_3)_4(H_2O)(SO_3)$ is combined with excess $[Co(NH_3)_5(pz)]^{3+}$ and ascorbate under argon at pH 5–6, an absorption peak first appears at 530 nm. This then fades as a new peak appears at 425–430 nm, which then fades only slowly (see Figure 2). The peak at 425–430 nm identifies the final product of the reaction under these conditions as *trans*-$Ru(NH_3)_4(pz)(SO_3)$, which absorbs at 433 nm in 0.1 M $NaHCO_3$.[10] The discrepancy between the observed and reported positions arises because at the pH of the experiments a small percentage of the complex is in the form $Ru(NH_3)_4(pz)(HSO_3)^+$ (pK = 4.6[10]), which absorbs at higher energy. When $Ru(NH_3)_4(H_2O)(SO_3)$ and $[Co(NH_3)_5(pz)]^{3+}$ are mixed without an external reductant, the solution first becomes deep violet as before and then turns a turbid reddish brown characteristic of $[Ru(NH_3)_4(H_2O)(SO_3)]^+$. Because of the very rapid (k = 0.3 s^{-1}[9]) aquation of $[Ru(NH_3)_4$-

Table II. Data on Electron Transfer in the $Ru^{II}(R)Co^{III}$ Series

A. $[(H_2O)Ru(NH_3)_4(\text{4-pyridylacetate})Co(NH_3)_4]^{4+}$ [a]

	T, °C			
	15.0	19.8	24.4	30.2
10^3k_{et}, s^{-1}	2.46, 2.46	4.35, 4.52	7.35, 7.37	14.0, 13.8[b]

B. $[(H_2O)Ru(NH_3)_4(\text{3-pyridylacetate})Co(NH_3)_5]^{4+}$ [c]

λ	[Ru(III)···Co(III)], M	T, °C	10^3k_{et}, s^{-1} [d]
450	9.7×10^{-5}	24.9	0.563
450	1.0×10^{-4}	24.9	0.569
450	9.6×10^{-5}	30.0	0.968
450	9.6×10^{-5}	30.0	0.950
475	1.5×10^{-4}	34.9	1.67
450	0.8×10^{-4}	34.9	1.60
450	8.2×10^{-5}	40.6	2.77
450	7.5×10^{-5}	40.6	2.90

C. $[(H_2O)Ru(NH_3)_4(\text{nicotinate})Co(NH_3)_5]^{4+}$ [e]

	T, °C			
	35.3	30.8	24.7	19.3
10^3k_{et}, s^{-1}	5.79, 5.84	3.52, 3.54	1.76, 1.85	0.902, 0.895[f]

D. $[(H_2O)Ru(NH_3)_4(\text{isonicotinate})Co(NH_3)_5]^{4+}$ [g]

T, °C	10^3k_{et}, s^{-1} [h]	T, °C	10^3k_{et}, s^{-1} [h]
7.9	1.56, 1.53, 1.51	24.8[k]	12.1, 12.1, 12.0,[i] 15.3[i,j]
14.1	3.44, 3.46, 3.37	29.7	22.8, 22.5

E. $[(H_2O)Ru(NH_3)_4(\text{3-cin})Co(NH_3)_5]^{3+}$ (charge is 4+ for 3-cinH)[l]

medium	λ, nm	T, °C	10^3k_{et}, s^{-1}
0.38 M NaTos, 0.02 M MES (pH 5.5)	530	19.9	1.48, 1.46[m]
	530	25.2	2.70, 2.62[m]
	530	30.2	4.86, 4.80[m]
	530	34.4	8.02, 8.04[m]
0.02 M HTos, 0.38 M NaTos (pH 1.73)	420	24.7	1.75
	570	24.7	1.83
0.05 M HTos, 0.38 M NaTos (pH 1.37)	420	24.7	1.44
	420	24.7	1.37
0.10 M HTos, 0.30 M NaTos	550	24.7	1.84
0.4 M HTos	590	24.7	1.82

F. $[(H_2O)Ru(NH_3)_4(\text{4-cin})Co(NH_3)_5]^{3+}$ [n]

	T, °C		
	16.3	17.9	25.0
10^3k_{et}, s^{-1}	12.8	15.2, 15.5	33.6, 34.7, 33.9

G. $[(H_2O)Ru(NH_3)_4(\text{4-cinH})Co(NH_3)_5]^{4+}$ [o]

	T, °C	
	16.3	24.9
10^3k_{et}, s^{-1}	14.6, 14.9	43.0, 41.1, 39.9, 41.3

H. $[(SO_4)Ru(NH_3)_4(\text{4-cinH})Co(NH_3)_5]^{2+}$ [p]

for 8 experiments at 24.9 °C, $k_{et} = 5.0 \pm 1.6$ s^{-1} and $k(\text{aquation}) = 1.18 \pm 0.16$ s^{-1}

I. $[IRu(NH_3)_4(\text{cinH})Co(NH_3)_5]^{3+}$ [q]

at 24.9 °C, $k_{et} = 0.504$ and 0.495 s^{-1}

[a] 0.38 M NaTos and 0.02 M MES (pH 5.3); $[Ru(NH_3)_6{}^{2+}] = 4.0 \times 10^{-4}$ M and [Ru(II)···Co(III)] = 1.5 or 1.6×10^{-4} M, at λ = 475 nm. [b] $\Delta H^{\ddagger} = 19.1 \pm 0.2$ kcal/mol; $\Delta S^{\ddagger} = -4.0 \pm 0.7$ cal/(mol K). [c] In 0.38 M NaTos and 0.02 M MES (pH 5.3). $Ru(NH_3)_6{}^{2+}$ at 4.0×10^{-4} M except in 6th and 8th experiments where it was 3.0×10^{-4} M. [d] $\Delta H^{\ddagger} = 18.5 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -11.2 \pm 0.9$ cal/(mol K). [e] In 0.38 M NaTos and 0.02 M MES (pH 5.3); Ru(III)···Co(III) = $(1.8\text{-}2.6) \times 10^{-4}$ M and $[Ru(NH_3)_6{}^{2+}] = 6.0 \times 10^{-4}$ M, at λ = 500 nm. [f] $\Delta H^{\ddagger} = 20.2 \pm 0.17$ kcal/mol; $\Delta S^{\ddagger} = -3.0 \pm 0.6$ cal/(mol K). [g] In 0.01 M HTos and 0.39 M NaTos; complex in range $(0.65\text{-}1.34) \times 10^{-4}$ M (except in footnote *c* $[ClRu(NH_3)_4(\text{isonicotinate})Co(NH_3)_5]Cl_4$ used) and $Ru(NH_3)_6{}^{2+}$ at 3.0×10^{-4} M as external reductant except in footnote *d*, and λ at 560 nm except in footnote *e*. [h] $\Delta H^{\ddagger} = 19.7 \pm 0.16$ kcal/mol; $\Delta S^{\ddagger} = -1.0 \pm 0.5$ kcal/(mol K). [i] $[(SO_4)Ru(NH_3)_4(\text{isonicotinate})Co(NH_3)_5Cl_3$. [j] Eu^{2+} at 1.6×10^{-4} M as external reductant. Result based on initial rate. [k] λ at 550 nm. [l] [Ru(III)···Co(III)] = $(1.0\text{-}2.0) \times 10^{-4}$ M and $Ru(NH_3)_6{}^{2+}$ in 2.5-fold excess. [m] $\Delta H^{\ddagger} = 20.4 \pm 0.6$ kcal/mol; $\Delta S^{\ddagger} = -1.9 \pm 1.9$ cal/(mol K). [n] 0.38 M NaTos and 0.02 M MES (pH 5.2); Ru(III)-Co(III) = $(0.62\text{-}1.0) \times 10^{-4}$ M and $Ru(NH_3)_6{}^{2+}$ in 3-fold excess, at λ = 550 nm. [o] 0.05 M HTos and 0.35 M NaTos; Ru(III)-Co(III) = $(2.0\text{-}2.8) \times 10^{-4}$ M and $Ru(NH_3)_6{}^{2+}$ in 2.5-3-fold excess, at λ = 590 nm. [p] 0.05 M HTos and 0.35 M NaTos; Ru(III)-Co(III) = 2.0×10^{-4} and $Ru(NH_3)_6{}^{2+} = 6.5 \times 10^{-4}$, at λ = 580 nm. [q] 0.05 M HTos and 0.35 M NaTos; Ru(III)-Co(III) = 1.9×10^{-4} M and $Ru(NH_3)_6{}^{2+} = 6.5 \times 10^{-4}$ M, at λ = 625 nm.

Table III. Electron Transfer in $(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5{}^{3+}$ [c]

λ, nm	pH	$[Co(NH_3)_5\text{-}(pz)X_3]$, M	X	$[Ru(NH_3)_4\text{-}(H_2O)(SO_3)]$, M	[ext red], M	T, °C	10^2k, s^{-1}
550	5.5	0.050	ClO_4^-	1.0×10^{-4}	5.4×10^{-4} [a]	10.2	1.76 1.74
540	5.5	0.050	ClO_4^-	1.0×10^{-4}	5.4×10^{-4} [a]	15.3	3.70 3.62
540	5.5	0.050	ClO_4^-	1.0×10^{-4}	5.4×10^{-4} [a]	19.8	6.60 6.39
540	5.5	0.050	ClO_4^-	8.0×10^{-5}	4.0×10^{-4} [a]	25.4	13.4 13.6 13.3
540	5.9	0.10	Cl^-	1.0×10^{-4}	5.4×10^{-4} [a]	15.1	2.63
540	5.9	0.05	Cl^-	1.2×10^{-4}	7.2×10^{-4} [a]	10.5	1.25
540	5.9	0.10	Cl^-	8.0×10^{-5}	4.0×10^{-4} [b]	15.2	2.52
540	5.9	0.05	Cl^-	8.0×10^{-5}	4.0×10^{-4} [b]	15.2	2.65
540	5.9	0.025	Cl^-	8.0×10^{-5}	4.0×10^{-4} [b]	15.2	2.47
540	2.99	0.10	Cl^-	1.0×10^{-4}	7.2×10^{-4} [a]	15.1	1.7

[a] $Ru(NH)_6{}^{2+}$ as external reductant. [b] Ascorbate as external reductant. [c] $\Delta H^{\ddagger} = 21.8 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = +10.4 \pm 1.0$ cal/(mol K).

$(pz)(SO_3)]^+$, this is the expected final product. These observations therefore indicate that intramolecular electron transfer occurs rapidly in this binuclear ion despite the stabilization of Ru(II) relative to Ru(III) by the sulfite group.

In Table III are reported the rates of electron transfer in this binuclear ion as measured at various temperatures and Co(III) concentrations. Within experimental error, the rate of intramolecular electron transfer is independent of $[Co(NH_3)_5(pz)]^{3+}$ concentration in the range 0.025–0.10 M. The rate does show an anion dependence; electron transfer proceeds about 40% faster in perchlorate medium than in chloride medium. The enhancement of rate by the perchlorate medium was observed in experiments with samples of the cobalt complex isolated originally as a perchlorate and in experiments with samples of the cobalt complex isolated originally as the chloride and reprecipitated as the perchlorate.

Table IV. Electron Transfer in $(O_3S)Ru(NH_3)_4(bpy)Co(NH_3)_5{}^{3+}$ [a]

A. Results Using Haim's Method[b,c]

λ, nm	$10^5 \times$ [Ru(II)···Co(III)], M	A_{IV}	$10^3 \times (k_{et} + k_d)$	$10^3 \times k_{-B}$	g	$10^4 \times k_{et}$, s^{-1}
440	1.3	0.068	2.80	2.21	0.221	4.1
440	2.0	0.101	2.80	2.31	0.313	3.2
440	2.0	0.099	3.00	2.18	0.304	5.4
440	3.5	0.173	3.13	2.05	0.338	4.5
440	1.5	0.097	2.88	2.20	0.267	4.0
440	1.5	0.075	2.79	2.28	0.279	4.1

B. Results Using Isied's Method[d]

λ, nm	$[Co(NH_3)_5(bpy)^{3+}]$, M	$10^5[Ru(II)]_{total}$, M	$10^4 k_{obsd}$, s^{-1}	$10^4 k_{is}$, s^{-1}
430	0.025	6.0	5.6	3.4
430	0.050	6.0	7.8	

[a] All measurements at 24.8 °C. [b] Medium is a solution containing 0.20 M NaCl, 0.05 M nicotinamide, 0.001 M ascorbate, and 0.05 M MES, with pH 6.5. [c] Parameters are defined in Experimental Section. [d] Medium is a solution containing Cl^- at 4 times the concentration of Co(III) and 0.03 M MES, with pH 6.5.

The experiments were done with sufficient external reducing agent so that even when, as in the case of $Ru(NH_3)_6{}^{2+}$, reaction of this reagent with $[Co(NH_3)_5(pz)]^{3+}$ is significant, the reducing agent persists throughout the course of the reaction. Only after the experimental phase of the research was ended was it appreciated that the complication which obliged us to resort to the present method in the case of the tetraammineaquoruthenium(II) systems is not serious for tetraammine(sulfito)ruthenium(II) as reducing agent. There is a large difference in the potentials for the 3+/2+ couples in $[(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$ and in $(O_3S)Ru(NH_3)_4(pz)$ (0.64 and 0.51 V, respectively),[9] favoring the 3+ state in the mononuclear product so that the accumulation of $[(O_3S)Ru(NH_3)_4(pz)]^+$ does not produce a significant drain on the concentration Ru(II)···Co(III) reactant

$$[(O_3S)Ru(NH_3)_4pzCo(NH_3)_5]^{3+} + [(O_3S)Ru(NH_3)_4(pz)]^+ = [O_3SRu(NH_3)_4(pz)Co(NH_3)_5]^{4+} + (O_3S)Ru(NH_3)_4(pz) \tag{16}$$

(the equilibrium quotient for the reaction is 6.7×10^{-3}). In retrospect, the experiments on this system might well have been done without using an external reducing agent. The important point however is that the rates we measured were the same regardless of whether $Ru(NH_3)_6{}^{2+}$ or ascorbic acid was the external reductant.

C. Electron Transfer in $[(O_3S)Ru(NH_3)_4(bpy)Co(NH_3)_5]^{3+}$. The results of measurements of the rate of electron transfer in this complex are presented in Table IV. Calculations of k_{et} in the experiments in which the computer treatment was used required the extinction coefficients for $(O_3S)Ru(NH_3)_4(bpy)$ and $(O_3S)Ru(NH_3)_4$(nicotinamide) at 440 nm to be known. The values were found in separate experiments to be ε 5490 ± 30 and 960 ± 2, respectively. The results obtained by using Isied's method of initial slopes and correcting for bimolecular reduction of $[Co(NH_3)_5(bpy)]^{3+}$ are in reasonable agreement with those obtained from the computer treatment.

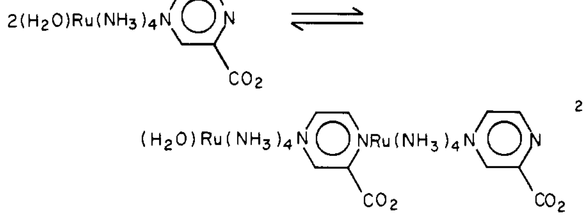
D. Structure, Reactivity, and Spectrum of $[(H_2O)Ru^{II}(NH_3)_4(pyrazinecarboxylate)Co^{III}(NH_3)_5]^{4+}$. Although $Ru(NH_3)_5(H_2O)^{2+}$ can substitute at either or both of the nitrogens in the pyrazinecarboxylate ion,[13] apparently substitution by *trans*-$Ru(NH_3)_4(H_2O)(SO_3)$ occurs only at the nitrogen remote from the carboxylate function. In support of this conclusion is the observation that when *trans*-$Ru(NH_3)_4(H_2O)(SO_3)$ and $Co(NH_3)_5(2\text{-chloronicotinate})^{2+}$ (note that Co(III) is on the carboxylate function) are mixed in solution, no color change, and hence no substitution, occurs. The pyrazinecarboxylate-bridged complex used in this work is the structural analogue of the nicotinate-bridged ion in which the ruthenium is bound to the nitrogen two carbons away from the position carrying the carboxylate group.

Only an upper limit for the rate of electron transfer in $(H_2O)Ru(NH_3)_4(pyrazinecarboxylate)Co(NH_3)_5{}^{4+}$ was obtained. Plots of absorbance vs. time for kinetic runs performed without external reductant were sigmoid in shape, suggesting complications from autocatalysis.[14] Moreover, during these runs the absorbance maximum shifted from 492 nm, the maximum for this binuclear ion, toward higher wavelengths, sometimes as high as 510 nm, and then returned to 492–495 nm. Attempts to follow electron transfer by using $Ru(NH_3)_6{}^{2+}$ as external reductant gave variable, but higher, apparent rates. (Preliminary experiments showed that at 25 °C the specific rate for the reduction of $Co(NH_3)_5(pyrazinecarboxylate)^{2+}$ by $Ru(NH_3)_6{}^{2+}$ is less than 0.1 $M^{-1}\,s^{-1}$). The apparent half-life for disappearance of the Ru(II)–Co(III) species, in experiments in 0.4 M citrate buffer, pH 2.9, in which its concentration was 6×10^{-6} M and the Ru(III)–Co(III) species was present at a 10-fold excess, was 5400 s, giving $k \leq 1.3 \times 10^{-4}$ s^{-1} at 25 °C.

Attempts to measure the rate of electron transfer in this binuclear species under conditions where the remote nitrogen is protonated showed that electron transfer in the protonated form is even slower. A solution containing 2×10^{-5} M Ru(II)–Co(III) complex and 4×10^{-4} M Ru(III)–Co(III) complex in 1 M HCl registered a 10% absorbance increase in 12 h.

When solutions containing $(H_2O)Ru(NH_3)_4(pyrazinecarboxylate)Co(NH_3)_5{}^{4+}$ (~10^{-4} M) at pH 3 or higher were exposed to room light, the color of the Ru(II)–Co(III) ion faded completely in less than 10 min. Solutions of the Ru(II)–Co(III) ion in 1 M HCl or 2 M HTFA were stable in room light for days; however, when a 5×10^{-4} M solution of the Ru(III)–Co(III) ion in 2 M HTFA was irradiated for 5 min by using a medium pressure mercury vapor lamp and a Pyrex filter to screen out light of wavelength below 310 nm, the absorption intensity diminished by 80%.

Spectra for $(H_2O)Ru^{II}(NH_3)_4(pyrazinecarboxylate)Co^{III}(NH_3)_5{}^{4+}$ and $(H_2O)Ru(NH_3)_4(pyrazinecarboxylate)^+$ are compared in Figure 2. The most striking feature of the spectrum for this complex is a small shoulder on the high-energy side of the metal-to-ligand charge-transfer band. This shoulder is absent from the spectrum of the mononuclear Ru(II) complex and occurs in a region of the spectrum where $Co(NH_3)_5(pyrazinecarboxylate)^{2+}$ absorbs extremely weakly. The spectra for the binuclear and mononuclear Ru(II) complexes were obtained from the same solution by the following procedure. With the room lights off, excess ascorbic acid solution was injected into an argon-purged solution of $(SO_4)Ru^{III}(NH_3)_4(pyrazinecarboxylate)Co^{III}(NH_3)_5{}^{3+}$ ($(1–6) \times 10^{-5}$ M at pH 3) in a spectrophotometer cell. After the spectrum of the Ru(II)–Co(III) ion was recorded the sample cell was removed from the cell compartment and exposed to room light for 10 min; the sample was then returned to the cell compartment, and the spectrum of the mononuclear Ru(II) ion was recorded. The spectrum of $(H_2O)Ru(NH_3)_4(pyrazinecarboxylate)^+$ showed slowly increasing absorbance with time above 470 nm and below 430 nm (see Figure 2). This complication, most likely caused by condensation of the Ru(II) ions (cf. eq 17), was minimized by



(17)

using very low complex concentrations. The difference in extinction coefficient is largest for the Ru(II)–Co(III) and Ru(II)

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(13) Clarke, M., M. S. Thesis, Stanford University, 1970.

(14) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; p 19.

Table V. Half-Wave Potentials for Ru(III)/Ru(II) Couples in Ru(II)···Co(III) Binuclear and Related Species

species	medium[b]	$E_{1/2}$,[c] V	λ_{max},[a] nm (ϵ)
$(H_2O)Ru(NH_3)_4$(3-pyridylacetic acid)$^{3+/2+}$	A	+0.33	410
$(H_2O)Ru(NH_3)_4$(4-pyridylacetic acid)$^{3+/2+}$	A	+0.33	407
$(H_2O)Ru(NH_3)_4$(nicotinic acid)$^{3+/2+}$	A	+0.38	420
$(H_2O)Ru(NH_3)_4$(isonicotinic acid)$^{3+/2+}$	A	+0.42	490
$(H_2O)Ru(NH_3)_4$(nicotinate)$Co(NH_3)_5{}^{5+/4+}$	B	+0.35	418
$(H_2O)Ru(NH_3)_4$(isonicotinate)$Co(NH_3)_5{}^{5+/4+}$	B	+0.39	475
$(H_2O)Ru(NH_3)_4$(3-cinH)$Co(NH_3)_5{}^{5+/4+}$	B	+0.41	500
$(H_2O)Ru(NH_3)_4$(3-cin)$Co(NH_3)_5{}^{4+/3+}$	C	+0.37	443
$(H_2O)Ru(NH_3)_4$(4-cin)$Co(NH_3)_5{}^{4+/3+}$	C	+0.40	
$(H_2O)Ru(NH_3)_4$(4-cinH)$Co(NH_3)_5{}^{5+/4+}$	B	+0.43	
$(SO_4)Ru(NH_3)_4$(4-cinH)$Co(NH_3)_5{}^{3+/2+}$	B	+0.28	
$IRu(NH_3)_4$(4-cinH)$Co(NH_3)_5{}^{4+/3+}$	B	+0.295	
$(O_3S)Ru(NH_3)_4(bpy)Co(NH_3)_5{}^{4+/3+}$	D	+0.45	450 ($\sim 1 \times 10^4$)
$(O_3S)Ru(NH_3)_4(bpy)^{+/0}$	D		410 (7.4×10^3)
$(H_2O)Ru(NH_3)_4(bpy)Co(NH_3)_5{}^{6+/5+}$	E	+0.42	555[d] (1.6×10^4)
$(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5{}^{4+/3+}$	F	+0.64	530 (3.7×10^4)
$(O_3S)Ru(NH_3)_4(pz)^{+/0}$	G	+0.51[e]	433[f] (5.7×10^3)
$(H_2O)Ru(NH_3)_4$(pyrazinecarboxylate)$Co(NH_3)_5{}^{5+/4+}$	H	+0.51	492
$(H_2O)Ru(NH_3)_4$(pyraziniumcarboxylate)$Co(NH_3)_5{}^{6+/5+}$	I	+0.62	530

[a] Band maximum for charge-transfer band of Ru^{II} species. [b] A = 0.039 M NaTos and 0.01 M HTos; B = 0.1 M HTos and 0.3 M NaTos; C = 0.38 M NaTos and 0.02 M MES (pH 5); D = 0.20 M NaCl and 0.05 M MES (pH 6.5); E = 0.4 M HTFA; F = 0.05 M phthalate and 0.10 M NaCl (pH 5.9) at 5 °C; G = unspecified, $\mu = 0.1$; H = 0.4 M acetate buffer (pH 4); I = 2 M HTFA. [c] vs. NHE. [d] From ref 16. [e] From ref 9. [f] From ref 10.

Table VI. Summary of Rate Parameters

reductant	$E_{1/2}$ (Ru(III)/ Ru(II)), V	10^3k,[a] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, kcal/(mol k)
$(H_2O)Ru^{II}$(3-pyridylacetate)	0.33	0.566	18.5 ± 0.3	−11.2 ± 0.9
$(H_2O)Ru^{II}$(4-pyridylacetate)	0.33	7.83	19.1 ± 0.2	−4.0 ± 0.7
$(H_2O)Ru^{II}$(nicotinate)	0.35	1.80	20.2 ± 0.17	−3.0 ± 0.6
$(H_2O)Ru^{II}$(isonicotinate)	0.39	12.4	19.7 ± 0.16	−1.0 ± 0.5
$(H_2O)Ru^{II}$(3-cin)	0.37	2.57	20.4 ± 0.6	−1.9 ± 1.9
$(H_2O)Ru^{II}$(3-cinH)	0.41	1.1		
$(H_2O)Ru^{II}$(4-cin)	0.40	34		
$(H_2O)Ru^{II}$(4-cinH)	0.43	42		
$(SO_4)Ru^{II}$(4-cinH)	0.28	5×10^3		
IRu^{II}(4-cinH)	0.30	0.5×10^3		
$(SO_3)Ru^{II}(bpy)$	0.45	0.4		
$(SO_3)Ru^{II}$(pyrazine)	0.64	128	22 ± 0.3	10.4 ± 1

[a] At 25 °C.

ions at 390 nm, where it is $\epsilon = 400 \pm 50$. The extinction coefficient for $Co(NH_3)_5(pyrazinecarboxylate)^{2+}$ is $\epsilon = 13$ at 390 nm. The band maxima for the mononuclear Ru(II) complex and the binuclear are very nearly identical at pH 3, but the band for the mononuclear is significantly broader on the low-energy side. This is an expected consequence of the difference in pK_a for the uncomplexed nitrogen for the two complexes; a significant amount of the less acidic mononuclear complex is present in the protonated form at pH 3, while the binuclear complex is completely deprotonated at this pH.

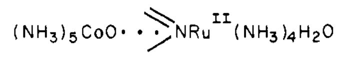
E. Formal Potentials for Ru(III)/Ru(II) Couples in Binuclear Species. Potentials measured by cyclic voltammetry are summarized in Table V. The observed peak-to-peak separation was in all cases 55–60 mV. To minimize complications due to intramolecular electron transfer, we recorded voltammograms at fast scan rates (5 V/s).

Discussion

For convenience in reference, the rate data accumulated in this work have been summarized in Table VI.

The rates reported here for the nicotinate, 3-pyridylacetate, and 4-pyridylacetate complexes are in good agreement with the earlier results,[1] but the value we report for the isonicotinate complex is almost 4 orders of magnitude lower than the value in the literature. (Isied, coauthor with H.T. of the earlier publication, has reinvestigated the isonicotinate-bridged systems and has obtained results in agreement with those reported here). The error in the first measurements apparently was caused by impurities in the sample of the binuclear complex which was used. In the course of the present work, irreproducible and high rates were also observed but only in experiments using material which had not been purified chromatographically. In the Isied–Taube work,[1] the reaction was followed by monitoring the disappearance of Ru(II), and the spurious rate enhancement must have been caused by an oxidizing impurity. Trimeric acetone peroxide[15] can be produced under the conditions obtaining for the preparation of the binuclear species and may be the impurity responsible for the rapid consumption of Ru(II) in material not rigorously purified.

With the revised value for the isonicotinate-bridged species, the rate pattern which emerges for the series based on



$(NH_3)_5CoO\cdot\cdot NRu^{II}(NH_3)_4H_2O$

is much like that observed for the bipyridine-bridged complex,[16,17] namely, that the rate is rather insensitive to the nature of the bridging group. We conclude for this series as well that the reactions approach the adiabatic regime. Excluding the molecule bridged by 3-pyridylacetate, where it is likely as already noted,[1] that electron transfer does not involve the bridging group, the entropies of activation are much the same within this series as are the energies of activation. None of the reactions is, however, cleanly in the adiabatic regime. This is indicated by the fact that the specific rate for the 4-cinH system is higher than that for the isonicotinate, despite the less favorable driving force, at least as measured by the Ru(III)/Ru(II) couple (the proviso is

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(15) Tobolsky, A. V.; Mesrobian, R. B. "Organic Peroxides: Their Chemistry, Decomposition and Role in Polmyerization"; Interscience: New York, 1954; p 49.

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necessary—Co(III) may be a stronger oxidant in the 4-cinH case because here the carboxylate is less basic than it is in the 3 position), and by the fact that adding carboxylate to the pyridine has a smaller effect when the two metals are disposed meta rather than para on the pyridine ring. These effects seem to reflect the influences of changes in electronic coupling. The difference between the nicotinate and isonicotinate system also may be taken to reflect a difference in electronic coupling, although in this case the issue is obscured by the fact that the charge distribution for the two molecules is different and thus the solvation barrier to electron transfer may be different.

It is remarkable that the rates for the 4-pyridylacetate annd isonicotinate systems differ by such a small factor. There is of course a difference in driving force but even when this is allowed for (by assuming that k_{et} varies with $K_{eq}^{1/2}$ the rate ratio is only a factor of 5.[18a] It still seems reasonable, as suggested earlier,[1] that in the 4-pyridylacetate system, because the bridge can fold so that the carbonyl oxygen comes very close to the ring, the CH_2 linkage is bypassed. It also seems reasonable that the greater adverse effect on the rate and on the entropy of activation of inserting a CH_2 group in the bipyridine systems[17] arises because the latter cannot fold to compensate as effectively for the insertion of the saturated unit as is the case for the carboxylate–pyridine systems.

The data obtained for the 4-cin-bridged systems bear on a basic issue raised by Rieder and Taube:[17] is the insensitivity of rate to nature of the bridging group simply a reflection of the fact the reactant is in labile equilibrium with a Ru(III)–Co(II) intermediate, which then in a slow step decays by substitution and/or spin change to Co(II)? In this event, when $E_{1/2}$ for the Co(III)/Co(II) couples remains constant, as is likely the case in the present series, the rates are expected to reflect directly the effect of changes in $E_{1/2}$ for the Ru(III)/Ru(II) couple on the pre-equilibrium. On this basis the rate for $[IRu(NH_3)_4(\text{4-cinH})Co(NH_3)_5]^{3+}$ would be expected to be 160-fold greater than for the species with H_2O in place of SO_4^{2-}. The actual rate ratio is about 11, and this result supports the conclusion reached earlier that the rate of intramolecular electron transfer is in fact rate determining. It would be of interest to apply the Marcus correlation[18] to the data, but the self exchange rates for the (iodo)- and (sulfato)tetraammineruthenium(III)/(iodo)- and (sulfata)tetraammineruthenium(II) couples are lacking.

We turn now to a consideration of the systems in which SO_3^{2-} occupies a position in the Ru(II) coordination sphere trans to the bridging group in the act of electron transfer. As a point of departure we take the result for the bpy-bridged species, $k_{et} = 4 \times 10^{-4}\ s^{-1}$, in relation to that obtained by Fischer et al.,[16] for H_2O in place of SO_3^{2-}, 4.4×10^{-2}. The corresponding values of $E_{1/2}$ for the Ru(III)/Ru(II) couples as measured in the present work are 0.45 and 0.42, respectively. It is clear that the decrease in rate registered on replacing H_2O by SO_3^{2-} on Ru(II) trans to the bridging group is much larger than can be accounted for by the modest difference in driving force. Furthermore, the comparison of $(SO_4)(NH_3)_4Ru^{II}$ and $(H_2O)(NH_3)_4Ru^{II}$ acting through 4-cinH as bridging group suggests that the rate difference for $(SO_3)(NH_3)_4Ru^{II}$ and $(H_2O)(NH_3)_4Ru^{II}$ cannot be attributed simply to differences in charge distribution—SO_4^{2-} replacing H_2O enhances the rate. There is left then the possibility that SO_3^{2-}, because it is a π acid, decreases the rate by decreasing the electronic coupling between the metal centers. This is tantamount to admitting that intramolecular electron transfer in $(SO_3)(NH_3)_4Ru(bpy)Co^{III}$ is strongly nonadiabatic. While it is possible that some of the rate difference is attributable to changes is rates of self-exchange for the two Ru(III)/Ru(II) couples, it is highly unlikely that they can be accounted for solely in this way.

The conclusion that nonadiabaticity affects the rates is supported by the comparison of k_{et} for $[(SO_3)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$ with that for the same complex but with bpy now as the bridging group: replacing pz by bpy leads to a rate decrease by a factor of nearly 300, despite the fact that the driving force is more favorable in the bpy-bridged system by 0.19 V. Correcting for this difference by assuming that k_{et} varies with $K_{eq}^{1/2}$ yields then a factor of ca. 10^4 to be taken into account. Part of this can be ascribed to the greater solvent reorganization barrier in the bpy system arising from the greater metal to metal separation in this case. This can be estimated by comparing the energies of the intervalence transitions $[(Cl(L\text{–}L)_2Ru)_2(pz)]^{3+}$ [19] and $[(Cl(L\text{–}L)_2Ru)_2(bpy)]^{3+}$ [20] (L–L represents 2,2′-bipyridine), that for the latter being greater by 7.5 kcal. (It needs to be pointed out that the analogous pentaammineruthenium systems are unsuitable for this comparison because $[((NH_3)_5Ru)_2(pz)]^{5+}$ is rather strongly delocalized.[21]) It it is assumed that the thermal barrier to electron transfer is one-fourth the energy of the intervalence band, a decrease in the rate of electron transfer by a factor of 30 is expected attributable to the greater solvent reorganization energy which attends replacing pz by bpy as bridging group. Because the first coordination spheres of the $(L\text{–}L)_2Ru$ species we have used to estimate the effect of distance on k_{et} are somewhat larger than in the metal species we have dealt with in our experiments, this factor is probably a lower limit to the effect produced by increasing the metal–metal distance in our systems. But it is highly unlikely that a factor of 10^4 can be accounted for on this basis. In fact in the analogous comparison using $Fe(CN)_5^{3-}$ as reducing agent the rate decrease resulting from replacing pz by bpy is a factor of 21 (k_{et} for the pz-bridged species is reported[22a,b] as $5.5 \times 10^{-2}\ s^{-1}$ while for the bpy bridged it is $2.6 \times 10^{-3}\ s^{-1}$ [23]). Allowance must be made in this case also for differences in driving force, but in all likelihood the distance factor alone can account for most of the rate differences observed with $Fe(CN)_5^{3-}$. In any event, the much greater rate difference in the (sulfito)ruthenium(II) comparison suggests that there is an additional factor at work there.

It has been suggested[17] that with $[(H_2O)Ru(NH_3)_4]^{2+}$ as reducing agent and with bpy as bridging group intramolecular electron transfer to $Co(NH_3)_5^{3+}$ is adiabatic. When $[(SO)_3Ru(NH_3)_4]$ is the reducing agent but the good π acid pz is the bridging group, electron transfer is quite likely also adiabatic. If so, then the rate difference between $[(SO_3)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$ and $[(H_2O)Ru(NH_3)_4(bpy)Co(NH_3)_5]^{5+}$, a factor of 3 favoring the former, can be accounted for by Franck–Condon factors. This in fact seems to be the case. The factor of 3 becomes 10^2 when the solvent reorientation is taken into account; i.e., because of the shorter metal to metal separation in the former species, the rate is expected to be higher by a factor of about 30. The difference in driving forces then needs to be taken into account. According to the measurements summarized in Table V, this is less favorable for $(SO_3)Ru(NH_3)_4$ than for $[(H_2O)Ru(NH_3)_4]^{3+}$ by 0.22 V. With the assumption that k_{et} varies with $K_{eq}^{1/2}$, the factor of 100 is satisfactorily taken into account. The observations are in harmony with the suggestion that both reactions are adiabatic. Something needs to be said in defense of using the relation $k_{et} \approx K_{eq}^{1/2}$ for the inner-sphere reactions dealt with here. It has been shown that with bpy[24] as bridging group and $Ru(NH_3)_5$ as the metal radical, the stabilization resulting from electron delocalization in the activated complex is quite small, and thus these inner-sphere reactions correspond to the weak overlap case of Marcus.[18c]

Still to be considered is the result, $k_{et} = 0.30\ s^{-1}$, obtained[25] when an external reducing agent acts on $(SO_4)Ru^{III}(NH_3)_4(pz)Co^{III}(NH_3)_5$. If electron transfer for this and the corre-

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sponding sulfito species, which we studied, are both adiabatic, we might hope to rationalize the rate differences by making use of the Marcus correlation, taking account of the differences in E_f and the self-exchange rates of the pertinent Ru(III)/Ru(II) couples. There is an ambiguity in Isied's observations because it is not certain whether aquation of sulfate ion precedes internal electron transfer. As reported by Isied, k_{et} is about 4 times smaller than the specific rate we have recorded for aquation of SO_4^{2-} from Ru(II) when 4-cinH is the bridging group. This would suggest that electron transfer from $(H_2O)Ru(NH_3)_4^{2+}$ to Co(III) was being studied by Isied. The value of the Ru(III)/Ru(II) couple is expected[26,27] to be much the same in $[(H_2O)Ru(NH_3)_4(pz)Co(NH_3)_5]^{6+/5+}$ as in $[(NH_3)_5Ru(pz)Rh(NH_3)_5]^{6+/5+}$ (both Co(III) and Rh(III) are πd^6 systems), namely, 0.71 V;[21] for $[(O_3S)Ru(NH_3)_4(pz)Co(NH_3)_5]^{4+/3+}$ it is 0.64 V. Isied's reported rate is greater than ours by a factor of 2.5 despite a less favorable driving force which alone would call for a rate smaller by a factor of about 4. If the self-exchange rate for the sulfato complex were greater than that of the sulfito by a factor of 100, Isied's measurement and ours would be in accord. A difference in self-exchange rates this large is possible, but it is also possible that because pyrazine is a stronger π acid than 4-cinH, aquation of sulfate in Isied's complex is slower than we measured for $(SO_4)Ru^{II}(4\text{-cinH})$ and that he was observing electron transfer from a (sulfato)ruthenium(II) species to Co(III). The value of E_f for the sulfato Ru(III)/Ru(II) couple in question is not known, but by making the assumption that, as is rather common for 3+/2+ couples, the affinity of SO_4^{2-} for Ru(III) is 10^2 greater than for Ru(II), we estimate it as 0.61 V. On this basis, k_{et} measured for $[(SO_3)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$, a factor of 2.5 lower than Isied's value, would without invoking differences in self-exchange rates agree with his because the driving force in our system is 0.03 V less.

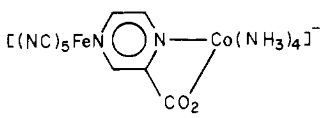
Even though the high rate observed for $[(SO_3)Ru(NH_3)_4(pz)Co(NH_3)_5]^{3+}$ seems to be accounted for by taking account of solvent reorganization, the issue cannot be taken as settled. The high rate relative to others for which $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been measured is in spite of higher value of $\Delta H^{\ddagger}$, because $\Delta S^{\ddagger}$ is much more positive than for the other systems. It is not at all clear that the differences in solvent reorganization should manifest themselves in this way, and further work on systems amenable to accurate measurements of k_{et} as a function of temperature is called for, especially for those in which the metal to metal distance is short. Tacit in the kind of analysis we have made is the assumption that the reaction coordinate for the systems being compared is the same. It is possible that some specific effect for pz such as a change of shape of the bridging ligand in the activated complex is at play, thus vitiating the attempts we have made to compare rates quantitatively.

Table VII. Intervalence Transfer Bands in Binuclear Complexes Containing Co(III)

complex	λ_{max}[a]	ref
$(NC)_5RuCNCo(NH_3)_5^-$	375 (690)	33a
$(NC)_5RuCNCo(CN)_5^{6-}$	312 (460)	33b
$(NC)_5FeCNCo(CN)_5^{6-}$	385 (630)	33b
$(NC)_5FeCNCo(histidinate)_2^{3-}$	500	34

[a] λ is in nm.

Electron transfer in $[(H_2O)Ru(NH_3)_4(\text{pyrazinecarboxylate})Co(NH_3)_5]^{4+}$ presents two features of interest. First the deprotonated form of this complex undergoes photoinduced electron transfer extremely rapidly upon exposure to ordinary room light. Intramolecular electron transfer following irradiation at wavelengths corresponding to the metal-to-ligand charge-transfer transition for the reducing metal ion has been observed previously in a number of binuclear complexes,[28-30] including



but among Ru(II)–Co(III) complexes bridged by pyridinecarboxylate ions, the distorted form of the pyrazinecarboxylate complex is unusually photosensitive; even the protonated form of the same complex is stable to room light. The high efficiency of photoinduced electron transfer in this ion may result from the stability of the configuration in which the Co(III) coordination sphere approaches the uncomplexed nitrogen in the bridging ligand closely in the plane of the ring. The complex $[Ru(NH_3)_5(pz)]^{2+}$ is known to coordinate to positive ions even more readily than free pz,[32] due to stabilization of positive charge at the remote nitrogen due to back donation from Ru(II). Therefore it is reasonable to expect that Ru(II) backbonding would stabilize the configuration described above for the ion $(H_2O)Ru(NH_3)_4(\text{pyrazinecarboxylate})Co(NH_3)_5^{4+}$, and this configuration would also be favorable for electron transfer from the ring π system to Co(III) following excitation of the metal-to-ligand transition. Protonation of the uncomplexed nitrogen would block this reaction pathway, sharply reducing the efficiency of the photoinduced redox reaction, as observed.

A second feature of interest for this binuclear complex is the absorption shoulder at 390 nm which is absent from the spectra of both $[(H_2O)Ru(NH_3)_4(\text{pyrazinecarboxylate})]^+$ and $[Co(NH_3)_5(\text{pyrazinecarboxylate})]^{2+}$. This shoulder may represent a Ru(II)–Co(III) intervalence transition; this band is in fact quite similar in both position and intensity to IT bands reported for binuclear complexes featuring Co(III) as the oxidizing metal, as shown in Table VII.

Acknowledgment. Support of this work by the National Science Foundation Grant No. CHE79-08633 is gratefully acknowledged, as is the help of Mr. Craig Cornelius in analyzing the more complex kinetic data.

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