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Intramolecular Electron-Transfer Reactions in Bridged Polynuclear Ru^{II}–Co^{III} Complexes Containing a (μ-Carboxylato)bis(μ-hydroxo)bis[(amine)cobalt(III)] (and a $Ru^{II}(NH_3)_5$) Structural Unit

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Abstract: Intramolecular electron transfer in Ru^{II}–L–$Co^{III}{}_n$ trinuclear and pentanuclear complexes containing nicotinate, isonicotinate, pyrimidine-4-carboxylate, pyridine-2,6-dicarboxylate, and pyrazine-2,6-dicarboxylate anions as bridging ligands and N-coordinated $Ru^{II}(NH_3)_5$ units as internal reductants and (μ-carboxylato)bis(μ-hydroxo)bis[(amine)cobalt(III)] moieties as oxidants has been studied. The nonbridging amines coordinated to cobalt(III) are three NH_3, diethylenetriamine, or 1,4,7-triazacyclononane, respectively. A linear correlation (slope 0.46) of ΔG^* vs. ΔG_0 has been established for the intramolecular electron-transfer reactions with $(NH_3)_6Co_2(\mu\text{-}OH)_2$ units as oxidants and $Ru^{II}(NH_3)_5L$ as internal reductants. Variation of nonbridging amine ligands at the Co(III) centers affects the rate of intramolecular rate constants markedly. Reactivity differences are accounted for by differing driving force due to varying redox potentials of Co(III)/Co(II) couples. The rates of electron transfer were found to be rather insensitive to changes of the bridging ligand, which is taken as an indication that the reactions approach the adiabatic regime, although strongly negative entropies of activation (−10 to −18 cal K^{-1} mol^{-1}) are observed for the series of complexes.

Intramolecular electron-transfer processes in binuclear Ru^{II}–L–Co^{III} complexes have been studied by Taube and co-workers and others in detail.[1-6] $(H_2O)(NH_3)_4Ru^{II}$, $(SO_3)(NH_3)_4Ru^{II}$, and $(SO_4)(NH_3)_4Ru^{II}$ moieties were N-coordinated to bridging ligands such as 4,4′-bipyridines (and derivatives thereof), pyrazine,[7] imidazolate,[8] and pyridinecarboxylates (nicotinate, isonicotinate, cinchomeronic acid) and pyrazinecarboxylate.[4] In most cases a $Co(NH_3)_5$ unit was attached to these organic bridging molecules via O- or N-coordination. Because of synthetic problems the reducing properties of the simpler $Ru^{II}(NH_3)_5$ unit have been exploited in such binuclear Ru^{II}–L–Co^{III} systems to a much lesser extent.[9,10]

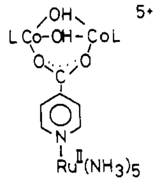
From these and other systematic studies of this kind using $(CN)_5Fe^{II}$ as internal reductant[11,12] it was hoped to establish criteria to unambiguously assign the mechanism of a given electron-transfer reaction to be adiabatic or nonadiabatic. This rather elusive electronic factor can only be hoped to be demonstrated when factors such as driving force and the role of the distance[9,13] between the redox-active transition-metal centers are taken into account.

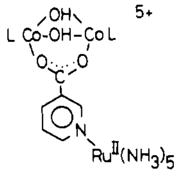
In order to understand reactivity differences of structurally similar systems, which are due to differences of driving force, a number of experimental facts have emerged which seem to indicate that if electron transfer, k_1, is rate determining in eq 1, a half-power dependence of the intramolecular rate constant, k_{et}, with respect to the equilibrium constant K_1 (k_1/k_{-1}) is observed.[2-4,11-13] In other words, a relation $\Delta G^* \approx 0.5\Delta G_0$ for this type of inner-sphere electron-transfer reactions has been proposed, and it is hoped to establish a formalism which is analogous to that developed by Marcus[14] for outer-sphere reactions.

$$Ru^{II}\text{–}L\text{–}Co^{III} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{III}\text{–}L\text{–}Co^{II} \tag{1}$$

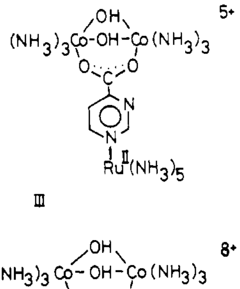
$$Ru^{III}\text{–}L\text{–}Co^{II} \xrightarrow{k_2} \text{products} \tag{2}$$

As Taube[5] has point out, "little of general significance is learned by measurements made with a single system". Therefore, we have synthesized a series of complexes, I–V, which allow the variation of reducing capacity of $Ru^{II}(NH_3)_5L$ (which can be measured by

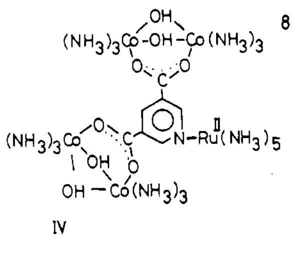




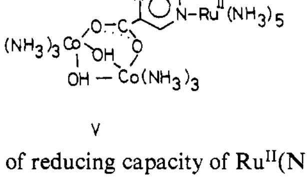
L:		
$3NH_3$	Ia	IIa
dien	Ib	IIb
[9]aneN$_3$	Ic	IIc



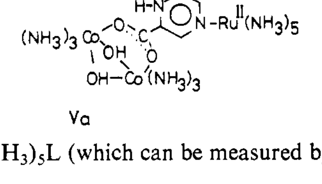
III



IV



V



Va

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Table I. Elemental Analyses of New Complexes (Calculated Values in Parentheses)

complex[a]	formula	C	H	N	Cl
Ia	$C_6H_{39}N_{12}O_{28}Cl_lRuCo_2\cdot 2H_2O$	6.0 (6.1)	4.3 (3.68)	13.0 (13.4)	
Ib	$C_{14}H_{47}N_{12}O_{28}Cl_6RuCo_2\cdot H_2O$	13.4 (13.1)	4.1 (3.82)	13.2 (13.1)	
Ic	$C_{18}H_{51}N_{12}O_{28}Cl_6RuCo_2\cdot 3H_2O$	15.8 (15.86)	3.9 (3.77)	12.6 (12.3)	
IIa	$C_6H_{39}N_{12}O_{28}Cl_6RuCo_2\cdot 3H_2O$	6.1 (5.94)	3.8 (3.74)	13.8 (13.85)	17.8 (17.53)
IIb	$C_{14}H_{47}N_{12}O_{28}Cl_6RuCo_2\cdot 4H_2O$	12.5 (12.60)	4.3 (4.12)	12.6 (12.30)	
IIc	$C_{18}H_{51}N_{12}O_{28}Cl_6RuCo_2$		explosive		
III	$C_5H_{38}N_{13}O_{28}Cl_6RuCo_2\cdot 2H_2O$	5.2 (5.18)	3.3 (3.30)	14.4 (15.7)	18.5 (18.34)
IV	$C_7H_{58}N_{18}O_{44}Cl_9RuCo_4\cdot 7H_2O$	4.6 (4.47)	3.7 (3.87)	13.2 (13.4)	16.1 (16.9)
V	$C_6H_{57}N_{19}O_{44}Cl_9RuCo_4\cdot 7H_2O$	4.3 (3.83)	3.8 (3.77)	13.6 (14.1)	
	$[Ru(NH_3)_5(pyr\text{-}3,5\text{-}H_2)](ClO_4)_3\cdot 3H_2O$	13.9 (13.89)	4.1 (4.16)	13.9 (13.88)	
	$[Ru(NH_3)_5(pym\text{-}4\text{-}H_2)](ClO_4)_3\cdot 4H_2O$	8.6 (8.8)	3.9 (3.96)	14.4 (14.40)	

[a] Roman numerals refer of the perchlorate salts of the complex cations of which the formula of the reduced forms (Ru(II)) are depicted in the text (the cationic charges are increased by one unit in the table (Ru(III)).

cyclic voltammetry) whereas the oxidizing ability of Co^{III} is kept very nearly constant upon variation of the bridging ligand L. Furthermore, replacement of nonbridging ligands coordinated to cobalt(III), e.g., substitution of three NH_3 groups by diethylenetriamine or 1,4,7-triazacyclononane, allows the variation of the oxidizing power of Co(III), keeping the reducing capacity of $Ru^{II}(NH_3)_5L$ unaffected. We report here an experimental verification of the relation $\Delta G^* \approx 0.5\Delta G_0$ for inner-sphere electron-transfer reactions where intramolecular rate constants have been measured.

Experimental Section.

Caution. The perchlorate salts are potentially dangerous; they may explode violently when heated.

Abbreviation of Ligands. dien = 2-(aminoethyl)-1,2-ethanediamine (diethylenetriamine); [9]aneN_3 = 1,4,7-triazacyclononane; pyr-4 and pyr-3 = pyridine-4-carboxylate (isonicotinate) and pyridine-3-carboxylate (nicotinate); pyr-4-H = pyridinecarboxylic acid; pyr-3-H = pyridine-3-carboxylic acid; pym-4 (pym-4-H) = pyrimdine-4-carboxylate (pyrimidine-4-carboxylic acid); dipic = dipicolinate (pyridine-2,6-dicarboxylate); pyraz-2,6 (pyraz-2,6-H_2) = pyrazine-2,6-dicarboxylate (pyrazine-2,6-dicarboxylic acid); pyr-3,5 (pyr-3,5-H_2) = pyridine-3,5-dicarboxylate (pyridine-3,5-dicarboxylic acid).

Preparation of Ligands. Pyrazine-2,6-dicarboxylic acid was prepared according to a published procedure, decarboxylating pyrazine-2,3,5-tricarboxylic acid.[15] 1,4,7-Triazacyclononane was prepared by following published methods.[16] Pyrimidine-4-carboxylic acid was obtained by oxidation of 4-methylpyrimidine with $KMnO_4$.[17] All other N-heterocyclic carboxylic acids were commercially available and were used without further purification.

Preparation of Monomeric Ruthenium Pentaammine Complexes. Preparation of $[Ru^{II}(NH_3)_5(pyraz\text{-}2,6\text{-}H_2)](ClO_4)_2\cdot 1,5H_2O$ and of $[Ru^{III}(NH_3)_5(pyraz\text{-}2,6\text{-}H_2)](ClO_4)_3\cdot H_2O$ have been described previously[18] as have been the syntheses of $[Ru(NH_3)_5(pyr\text{-}4\text{-}H)]^{2+/3+}(ClO_4)_{2/3}$ and of $[Ru(NH_3)_5(pyr\text{-}3\text{-}H)]^{2+/3+}(ClO_4)_{2/3}$.[19]

$[Ru^{III}(NH_3)_5(pyr\text{-}3,5\text{-}H_2)](ClO_4)_3\cdot 3H_2O$ and $[Ru^{III}(NH_3)_5(pym\text{-}4\text{-}H)](ClO_4)_3\cdot 4H_2O$. These two complexes were prepared by a modified method described by Gaunder and Taube.[19b] $[Ru(NH_3)_5Cl]Cl_2$ (0.2 g) was added to 4 mL of an aqueous solution of silver trifluoroacetate, which was prepared by dissolving 0.15 g of Ag_2O in 4 mL of hot water by dropwise addition of trifluoroacetic acid until a clear solution was obtained. After stirring of the above solution at 50 °C for 5 min, the precipitated AgCl was filtered off. The cooled, argon-scrubbed solution was reduced with zinc amalgam (20 min) at 20 °C. The solution of $[Ru^{II}(NH_3)_5OH_2](F_3CCO_2)_2$ was then transferred with a syringe into a reaction vessel containing an aqueous suspension (15 mL) of the respective N-heterocyclic ligand (15-fold excess over Ru^{II}) under an argon atmosphere. The solution was stirred 30 min at room temperature after which time the deep red solution was filtered and the excess ligand was discarded. Addition of $NaClO_4$ leads to the precipitation of $[Ru^{II}(NH_3)_5L](ClO_4)_2$ salts. If the ruthenium(III) species are the desired products, oxidation of the solution containing the ruthenium(II) complexes was achieved by dropwise addition of a solution of $Ag(I)(CF_3CO_2)$ until a clear yellow solution was obtained. After removal of metallic silver by filtration and addition of solid $NaClO_4$ yellow crystals precipitated at 5 °C (5 h). The products were recrystallized from a minimum amount of methanol/0.1 M $HClO_4$ mixture. Yield, 60%.

Preparation of Binuclear Cobalt(III) Complexes. $[Co_2(NH_3)_6(\mu\text{-}OH)_3](ClO_4)_3$,[20] $[Co_2([9]aneN_3)_2(\mu\text{-}OH)_3](ClO_4)_3$,[16b] and $[Co_2(dien)_2(\mu\text{-}OH)_2(H_2O)_2](ClO_4)_4$[21] were prepared by published procedures.

Preparation of Tri- and Pentanuclear Ru^{III}–L–Co^{III} Complexes. Acidic solutions containing the monomeric $[Ru(NH_3)_5L](ClO_4)_3$ complex were treated with $[Co_2(NH_3)_6(\mu\text{-}OH)_3](ClO_4)_3$, $[Co_2([9]aneN_3)_2(\mu\text{-}OH)_3](ClO_4)_3$, or $[Co_2(dien)_2(\mu\text{-}OH)_2(H_2O)_2](ClO_4)_4$. A typical preparation is as follows: To 0.33 mmol of $[Ru(NH_3)_5(pyr\text{-}4\text{-}H)](ClO_4)_3$ dissolved in 5 mL of 0.2 M $HClO_4$ at 50 °C 0.5 mmol (or 1.2 mmol for pentanuclear species) of the binuclear $[Co_2(NH_3)_6(\mu\text{-}OH)_3](ClO_4)_3$ was added. The deep red solution was stirred for 20 min at 50 °C. Upon cooling (5 °C) and adding 0.5 g of $NaClO_4$ red crystals precipitated (24 h), which were filtered off and recrystallized from a 1:1 mixture of methanol/0.2 M $HClO_4$. Elemental analyses of all new complexes are given in Table I. Complexes with pyrimidine-4-carboxylate and pyrazine-2,6-dicarboxylate bridging ligands are sensitive to light and decompose even when kept in the dark within 1 week.

Cyclic Voltammetry. The apparatus used for these measurements has been described previously.[18] The formal redox potentials measured by cyclic voltammetry of the Ru(III)/Ru(II) couples in the trinuclear and pentanuclear Ru–Co(III) cations exhibit reversible behavior (Table II). The observed peak-to-peak separation was in all cases 55–70 mV. At scan rates >500 mV s^{-1} no interference of intramolecular electron-transfer processes from Ru(II) to Co(III) were observed.

Kinetic Measurements. The procedure for measuring intramolecular electron-transfer rate constants was adopted from Isied, Zawacky, and Taube.[1,4] Solutions of the tri- or pentanuclear Ru^{III}–Co^{III} complexes (~10^{-5} M) were treated with an excess of reducing agent ($[V(OH_2)_6]^{2+}$, $[Cr(OH)_2)_6]^{2+}$, $[Eu(OH_2)_6]^{2+}$, ascorbate; [red] ~ 10^{-3} M). Outer-sphere reduction of the (μ-carboxylato)bis(μ-hydroxo)bis[triamminecobalt(III) moiety by the aquo complexes of Cr^{2+}, V^{2+}, and Eu^{2+} are generally very slow as compared to the outer-sphere reduction of Ru(III) ammine complexes; e.g., for the V_{aq}^{2+} reduction of (μ-acetato)bis(μ-hydroxo)bis[triamminecobalt(III)] cation a second-order rate constant of 6.2×10^{-2} M^{-1} s^{-1} at 25 °C is observed[22] whereas for the reduction of $[Ru(NH_3)_5(pyr)]^{3+}$ by V_{aq}^{2+} k equals 3.0×10^5 M^{-1} s^{-1}.[23]

After the rate-determining reduction of the first Co(III) center of a binuclear bis(μ-hydroxo)bis[(amine)cobalt(III)] unit via an intramolecular electron transfer from Ru(II) to Co(III), the second Co(III) is reduced much faster presumably via then possible inner-sphere paths by excess reductant. The generated intermediate Ru(III) center is also rapidly reduced by excess reductant. Therefore, the actual reaction products of the original trinuclear or pentanuclear precursor complex are $[Co(OH_2)_6]^{2+}$, $[Ru^{II}(NH_3)_5L]^{2+}$ (L is the former bridging ligand), and NH_4^+. The net change observed is given by eq 3. The reactions were

$$Ru^{III}LCo^{III}{}_n + \text{reductant} \rightarrow Ru^{II}L + nCo^{2+} + \text{oxidized product} + mNH_4^+ \quad (3)$$

initiated by adding the respective reductant solution to 20 mL of oxygen-free and thermostated solution of $Ru^{III}LCo^{III}{}_n$ complex and were

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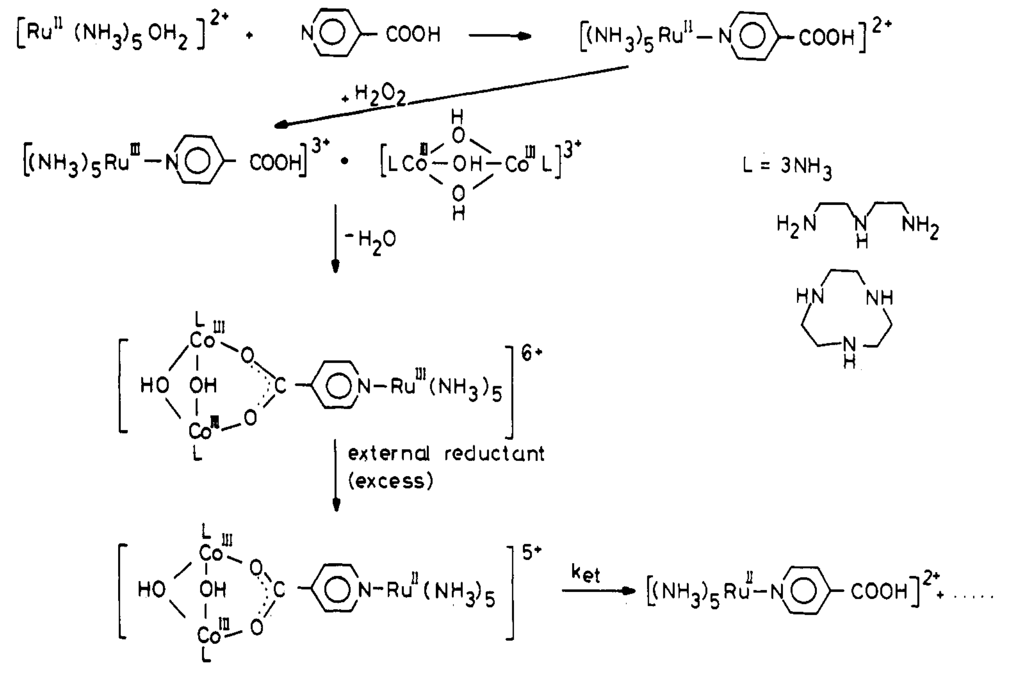

Table II. Formal Redox Potentials of the Ru(III)/Ru(II) Couple of Monomeric Ruthenium Complexes and of Polynuclear Ru–Co^{III} Complexes and Maximum of Absorption in the Visible Region

complex	medium[d]	$E_{1/2}$, V[a]	λ_{max},[b] nm (log ϵ)
Ia	A	0.35	498 (4.04)
Ib	A	0.39	504 (4.02)
Ic	A	0.40	502 (4.04)
IIa	A	0.34	416 (3.73)
IIb	A		420 (3.66)
IIc	A	0.39	418 (3.60)
III	A	0.49	536 (4.00)
IV	A	0.39	450 (3.72)
V	C	0.52	542 (4.04)
Va	A	0.60	546 (4.04)
$(NH_3)_5Ru(pyraz\text{-}2,6\text{-}H_2)^{3+/2+}$	A	0.58	538 (4.02)
$(NH_3)_5Ru(pyraz\text{-}2,6)^{1+/0}$	D	0.45	506 (4.00)
$(NH_3)_5Ru(pyr\text{-}4)^{2+/1+}$	C	0.31	462
$(NH_3)_5Ru(pyr\text{-}4\text{-}H)^{3+/2+}$	A	0.39[c]	497
$(NH_3)_5Ru(pyr\text{-}3\text{-}H)^{3+/2+}$	A	0.34	420
$(NH_3)_5Ru(pyr\text{-}3)^{2+/1+}$	C	0.27	
$(NH_3)_5Ru(pym\text{-}4\text{-}H)^{3+/2+}$	A	0.46	506
$(NH_3)_5Ru(pym\text{-}4)^{2+/1+}$	B	0.41	
$(NH_3)_5Ru(pyr\text{-}2,4\text{-}H_2)^{3+/2+}$	A	0.26	
$(NH_3)_5Ru(pyr\text{-}2,4)^{1+/0}$	B	0.19	

[a] Vs. NHE. [b] Absorption maximum of Ru(II) species. [c] $E_{1/2}$ = 0.382 in 0.1 M *p*-toluenesulfonic acid.[32] [d] A, 0.1 M $HClO_4$; B, citrate/HCl buffer, pH 3.0; C, $HClO_4$ + $LiClO_4$ (0.1 M), pH 4.0; D, acetate buffer, pH 5.0.

followed spectrophotometrically for 6–8 half-lives. Plots of ln $(A_t - A_\infty)$ vs. time were linear for at least 5 half-lives in all cases, and first-order rate constants, k_{obsd}, were obtained from nonlinear least-squares fitting with k_{obsd} and A_∞ (absorption at the end of the reaction) being adjustable parameters.[24] The observed value of A_∞ and the calculated one agreed within experimental error of the last digit of the reading of the instrument.

The observed first-order rate constants were found to be independent of the concentration and nature of the reductants used and independent of the concentration of the respective $Ru^{III}LCo^{III}{}_n$ complex.

Results

Synthesis of Complexes. Scheme I shows a general synthetic route to polynuclear complexes containing $Ru^{II}(NH_3)_5$ and (μ-carboxylato)bis(μ-hydroxo)bis[(amine)cobalt(III)] units which are connected via a bridging ligand which is an aromatic N-heterocyclic carboxylic acid. The synthesis involves the reaction of a $[(NH_3)_5Ru^{III}L]^{3+}$ species containing one or two uncomplexed carboxylic groups at the N-heterocycle (pyridine, pyrimidine, or pyrazine) with tris(μ-hydroxo)bis[(amine)cobalt(III)] cations in acidic solution under mild conditions (~60 °C). The Ru^{III}–L–$Co^{III}{}_n$ complexes were isolated as perchlorate salts in small amounts only (~100 mg) because of their potential hazard (they are potentially explosive).

Electronic Spectra and Electrochemistry. In Table II electronic spectra of tri- and pentanuclear precursor complexes of the Ru^{II}–Co^{III} type are summarized. The formal redox potentials of Ru(III)/Ru(II) within these complexes are also given. The electronic spectra of complexes I–Va exhibit an intense absorption maximum in the visible at 420–540 nm (log ϵ ~ 4), which is characteristic for a $\pi d \rightarrow \pi^*$ charge-transfer band of the respective Ru(II) center. The oxidized forms of I–Va show the typical d–d absorption band in the visible of the (μ-carboxylato)bis(μ-hydroxo)bis[(amine)cobalt(III)] structural unit (e.g., amine = $3NH_3$, λ_{max} = 524 nm and ϵ = 110 L mol^{-1} cm^{-1}[25]) which is independent of the nature of the $(NH_3)_5Ru^{III}L$ moiety. It is noted that the coordination of $Ru^{II}(NH_3)_5L$ (L = N-coordinated carboxylato ligand) to dinuclear Co(III) moieties causes a significant bathochromic shift of the $\pi d \rightarrow \pi^*$ transition of the Ru(II) center as does simple protonation of the uncoordinated carboxylic group: e.g., $[(NH_3)_5Ru^{II}(pyr\text{-}4\text{-}H)]^{2+}$, λ_{max} = 497 nm; $[(NH_3)_5Ru^{II}(pyr\text{-}4)]^{+}$, λ_{max} = 465 nm, Ia = 498 nm. This indicates an enhanced electron delocalization of the Ru(II) centers. Interestingly, the formal redox potentials (Table II) of Ru^{III}/Ru^{II} couples indicate a stabilization of the +II oxidation state on protonation of the carboxylate group and—to a lesser extent—on coordination to Co(III) ($[Ru(NH_3)_5(pyr\text{-}4)]^{2+/1+}$, 0.31 V; $[Ru(NH_3)_5(pyr\text{-}4\text{-}H)]^{3+/2+}$, 0.39 V; Ia, 0.35 V). In strongly acidic solutions V is protonated at the uncoordinated heterocyclic nitrogen of the pyrazine ring. The formal redox potentials of the Ru(III)/Ru(II) couples of protonated and of unprotonated forms, Va and V, differ by 0.08 V (Table II). Protonation stabilizes again the +II oxidation state; i.e., the Ru(II) center in Va is the weaker reductant.

Electron Transfer in Complexes Ia–c, IIa–c, and III–V. Detailed results of rate measurements are summarized in tables that are available as supplementary material. A compilation of intramolecular rate constants at 25 °C and respective activation parameters is given in Table III for complexes Ia–c, IIa–c, II, IV, V, and Va. Figure 1 shows a typical scan spectrum of the elec-

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Table III. Summary of Kinetic Data on the Intramolecular Electron Transfer of Ru^{II}–Co^{III} Complexes

complex	k_{et}, s^{-1} [a]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta\Delta G_0$,[c] kcal mol^{-1}
Ia	0.065	15.5 ± 0.1	−12.0 ± 0.2	19.1	8
Ib	0.0016	16.3 ± 0.3	−16.5 ± 1.0	21.2	
Ic	5.2×10^{-5}	18.2 ± 0.2	−16.9 ± 0.6	23.2	
IIa	0.029	15.4 ± 0.3	−13.8 ± 1.0	19.5	7.84
IIb	0.0012	17.3 ± 0.2	−13.6 ± 0.6	21.3	
IIc	9.0 ± 10^{-6}	18.8 ± 0.2	−18.2 ± 0.7	24.2	
III	0.013	19.0 ± 0.5	−2.9 ± 1.0	19.9	11.1
IV	0.015	16.7 ± 0.3	−10.7 ± 1.0	19.9	9.0
V	0.001	18.9 ± 0.2	−8.5 ± 0.7	21.4	12.0
Va	3.4 ± 10^{-4}	18.9 ± 0.3	−10.9 ± 0.9	22.1	13.8
$[(H_2O)Ru^{II}(NH_3)_4(pyr\text{-}4)Co(NH_3)_5]^{4+}$	0.012[b]	19.7 ± 0.2	−1.0 ± 0.5		
$[(H_2O)Ru^{II}(NH_3)_4(pyr\text{-}3)Co(NH_3)_5]^{4+}$	0.0018[b]	20.2 ± 0.2	−3.0 ± 0.6		

[a] At 25 °C, [I] = 0.1 M. [b] Reference. [c] See text.

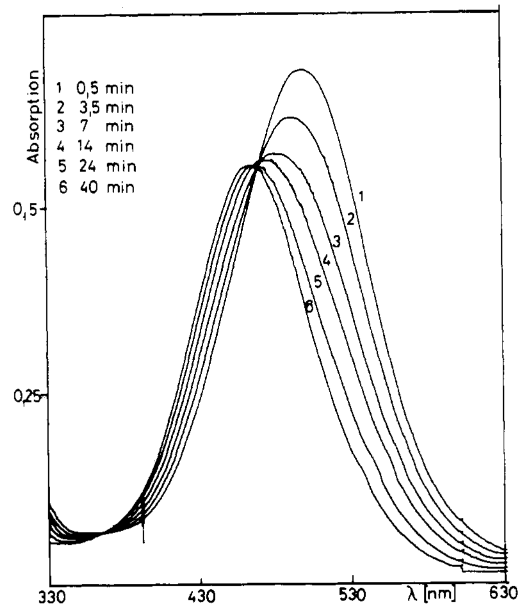

Figure 1. Scan spectrum of the reaction of complex Ib at 25 °C (pH 4.0; acetate buffer; [I] = 0.1 M; [Ib] = 1.7×10^{-5} M; [ascorbate] = 1×10^{-3} M).

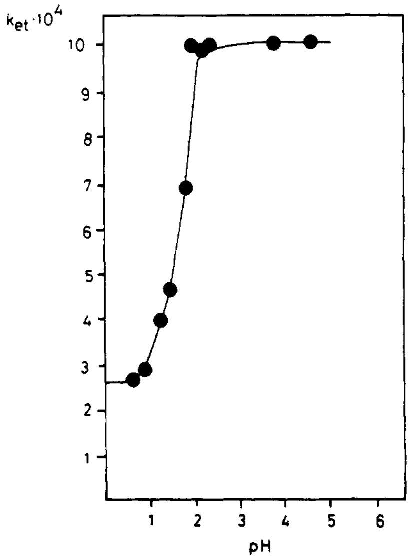

Figure 2. Plot of the observed first-order rate constants of intramolecular electron transfer in complex V vs. pH of the reaction medium at 25 °C ([I] = 0.1 M; [ascorbate] = 3×10^{-3} M; [V] = 2×10^{-5} M).

tron-transfer process in Ib, run under conditions with excess reductant (ascorbate) at pH 4 (acetate buffer) and 25 °C. The observed shift of the absorption maximum corresponds to a shift of the πd → π* charge-transfer band of the Ru^{II}–pyr-4 unit in the starting binuclear species Ib (504 nm) and the final product $[(NH_3)_5Ru^{II}(pyr\text{-}4)]^{1+}$ (462 nm). This difference in spectra has been used to follow the intramolecular electron transfer—a first-order process. The final product $[(NH_3)_5Ru^{II}L]^{2+}$ (where L is the former bridging ligand) has in all cases been spectrophotometrically identified. The observed spectra at the end of a reaction were identical with genuine samples of the monomeric Ru(II) species. Since complexes Ia–c, IIa–c, and IV in the oxidized forms (Ru^{III}–L–$Co^{III}{}_n$) do not have suitable lead—in functions available for inner-sphere-type reactions, a variety of aquo–metal ion reductants were used in large excess over the oxidants to reduce rapidly the Ru(III) center to Ru(II) via an outer-sphere electron transfer. The rates of the following intramolecular electron-transfer processes were found to be independent of the nature of the reductant used (e.g., $Eu^{2+}{}_{aq}$, $V^{2+}{}_{aq}$, $Cr^{2+}{}_{aq}$). Nevertheless, ascorbate was used as external reductant in most cases.

In III the bridging ligand pyrimidine-4-carboxylate has one uncoordinated nitrogen, which may serve as lead-in function, although steric hindrance makes this unlikely. Therefore, ascorbate was used as external reductant in order to avoid complications by inner-sphere-type reactions. The intramolecular electron-transfer rate constant was found to be independent of hydrogen ion concentration (0.10–1.0 × 10^{-5} M). This is taken as an indication that even at $[H^+]$ = 0.1 M no appreciable protonation of the uncoordinated heterocylic nitrogen takes place in contrast to complex V.

Figure 2 demonstrates the dependence of the intramolecular electron-transfer rate constant in V on the pH of solution. V contains a pyrazine-2,6-carboxylate bridge between the N-coordinated $Ru^{II}(NH_3)_5$ unit and the four Co(III) centers. The second nitrogen of the pyrazine ring is uncoordinated and may therefore be protonated in acidic solution. Thus the unprotonated and N-protonated forms of V react at different rates. A pK_a value of 1.6 ± 0.2 for the dissociation of Va is determined from the kinetic data in Figure 2.

Discussion

When discussing reactivity differences of intramolecular electron-transfer processes within structurally similar, bridged binuclear transition-metal complexes (e.g., Ru^{II}–L–Co^{III} or Fe(II)-L-Co(III)), it has become customary to assume that for these inner-sphere-type reactions a relation holds that is analogous to the Marcus formalism derived for outer-sphere electron-transfer reactions.[4,11–13] In particular, the assumption of a half-power dependence of the observed rate constant, k_{et}, with respect to K_1, has been used to suggest that the actual electron transfer (k_1) is the rate-determining step, eq 1 and 2, and not k_2, in which case k_{et} would be expected to vary linearly with K_1 (k_1/k_{-1}). A free energy relation is proposed for these intramolecular electron-transfer reactions, $\Delta G^{\ddagger} \approx 0.5\Delta G_0$, but the experimental evidence must be considered to be circumstantial to date.

In the series of complexes IIa, IV, V, and Va the oxidant is always a (μ-carboxylate)bis(μ-hydroxo)bis[triamminecobalt(III)] structural unit, whereas the reductant is a $Ru^{II}(NH_3)_5L$ moiety and L represents the bridging ligands nicotinate, pyridine-3,5-

Table IV. Summary of Rate Parameters

complex	$E_{1/2}$,[a] V	k,[b] s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	ref
$[(H_2O)Ru^{II}(NH_3)_4(pyr\text{-}3)Co^{III}(NH_3)_5]^{4+}$	0.35	1.8 ± 10^{-3}	20.2	−3.0	4
$[(H_2O)Ru^{II}(NH_3)_4(pyr\text{-}4)Co^{III}(NH_3)_5]^{4+}$	0.39	12.4×10^{-3}	19.7	−1.0	1, 4
$[(SO_3)Ru^{II}(pyraz)Co^{III}(NH_3)_5]^{3+}$	0.64	12.8×10^{-3}	22	+10.4	4, 5
$[(NH_3)_4(H_2O)Ru^{II}(pyraz\text{-}H)Co^{III}(NH_3)_5]^{4+}$	0.51	1.3×10^{-4}			4
$[(NH_3)_5Ru^{II}(pyraz\text{-}2,6)Co^{III}(dien)]^{3+}$	0.72	0.059	18.4	−2.0	18

[a] Redox potential for the Ru(III)/Ru(II) couple in the Ru–Co species. [b] At 25 °C.

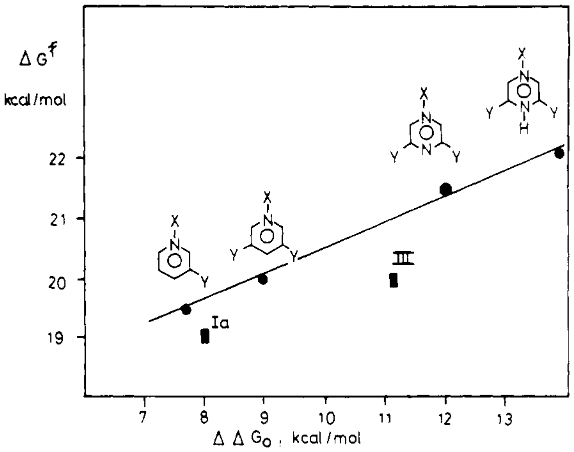

Figure 3. Correlation of the free enthalpy of activation of intramolecular electron transfer vs. the relative driving force, $\Delta\Delta G_0$ ($X = Ru^{II}(NH_3)_5$; $Y = (NH_3)_3Co^{III}(\mu\text{-}OH)_2(\mu\text{-}carboxylate)Co^{III}(NH_3)_3$).

dicarboxylate and pyrazine-2,6-dicarboxylate. The distance between the metal centers Ru(II) and Co(III) is identical in all cases, because the carboxylato groups are always in the meta position with respect to N-coordinated $Ru^{II}(NH_3)_5$. The formal redox potentials of the respective Ru(III)/Ru(II) couples vary within the series from 0.34 V for IIa to 0.60 V for Va. It has not been possible to measure the redox potentials of the Co(III)/Co(II) couples, but it is plasubile to assume that they do not vary extensively on changing the substituents of the μ-carboxylato groups. It is noted that the position of the first d–d absorption band of the cobalt(III) centers and the molar absorption coefficients are constant for the $Ru^{III}\text{-}L\text{-}Co^{III}{}_n$ species; even the ^{59}Co NMR spectra exhibit identical chemical shift values for a series of different (μ-carboxylato)bis(μ-hydroxo)bis[triammine)cobalt(III)] cations.[26] Therefore, the difference of driving force of intramolecular electron transfer in IIa, IV, V, and Va is considered to be due to differences of the reducing capacity of the Ru(II) centers and values for $\Delta\Delta G_0$ may be calculated (Table III). Figure 3 shows a nice linear correlation between the enthalpy of activation and the relative differences of driving force for complexes IIa, IV, V, and VA. The slope is found to be 0.47, which is in excellent agreement with the expected value of 0.5 from the Marcus relation.[14] This system of structurally very similar complexes represents an experimental verification that, indeed, a Marcus analogous formalism for inner-sphere intramolecular electron-transfer reactions is valid.

Interestingly, the reactivity difference of the protonated and unprotonated forms, V, and Va, stems from differing driving forces of the Ru(II), the protonated species being the weaker reductant, which concurs with the observation that the deprotonated form of the monomeric $[Ru^{II}(NH_3)_5(pyraz\text{-}2,6)]^0$ complex is a stronger reductant than the protonated $[Ru^{II}(NH_3)_5(pyraz\text{-}2,6\text{-}H_2]^{2+}$, although in this instance uncoordinated carboxylate groups are protonated and probably not the pyrazine nitrogen. The ratio of observed intramolecular electron-transfer rate constants of V and Va, $k_{et}{}^{V}/k_{et}{}^{Va}$, is measured to be 3, which agrees reasonably well with a calculated value of 4.7 assuming a half-power dependence of k_{et} with respect to $K_1{}^{V}$ and $K_1{}^{Va}$. In Figure 3 the data points for complexes Ia and III are also included. The bridging ligands isonicotinate and pyrimidine-4-carboxylate have the coordinating carboxylato group in the para position with respect to the N-coordinated $Ru^{II}(NH_3)_5$ group. The rate of intramolecular electron transfer in Ia is faster than is observed for the corresponding meta analogue IIa by a factor of 2. For Ic and IIc a factor 6 in favor of the para-substituted complex is observed; whereas for Ib and IIb only a factor of 1.3 has been determined. For the two complexes $[(H_2O)(NH_3)_4Ru^{II}LCo(NH_3)_5]^{4+}$ with L = isonicotinate and nicotinate, the isonicotinate species reacts faster by a factor of 6.7.[1,4] Since the redox potentials of Ru(III)/Ru(II) couples in the pairs Ia/IIa and Ic/IIc differ only by 10 mV (the meta-substituted species, Ic and IIc, having a slightly *larger* driving force than Ia and IIa), the observed reactivity difference *cannot* be an effect of driving force. These small effects are believed to reflect the influence of changes in electronic coupling. As will be discussed below, from the activation parameters (Table III) we conclude that our reactions exhibit a substantial degree of adiabaticity. Taube has argued[5] that the observed insensitivity of rate on the nature of the bridging ligand is evidence for the adiabaticity of electron transfer in his complexes. This was bolstered by near zero values of entropies of activation.

Throughout the series of complexes discussed in the preceding paragraph, the oxidizing capacity of the cobalt(III) centers was assumed to be constant and the reactivity differences were discussed in terms of differing reducing capacities of the Ru^{II} centers. Now we shall focus on effects on electron-transfer rates due to changing nonmediating ligands coordinated to cobalt(III), i.e., substitution of ammonia ligands for diethylenetriamine or 1,4,7-triazacyclononane. Within the series Ia–c and IIa–c the bridging ligand is always the same, and therefore, the distances between Ru^{II} and Co^{II} centers are identical, and the redox potentials of Ru(III)/Ru(II) couples are very similar. Between Ia and Ic a reactivity difference of 2.7 may be calculated, if the differing reducing power of Ru^{II} were the only source. This is to be compared with an experimental factor, $k_{et}{}^{Ia}/k_{et}{}^{Ic}$, of 1250. Thus, in order to simplify the discussion, the reducing power of Ru^{II} centers in the series Ia–c and IIa–c is taken to be constant. An exact quantitative evaluation of the effect of the nonbridging ligands is hampered, because the redox potentials of Co(III)/Co(II) couples are not known. A somewhat arbitrary correlation may nevertheless be constructed to demonstrate that differing driving forces (due to varying Co(III)/Co(II) redox potentials) may account for the observed reactivity differences. The redox potentials of the couples $[Co([9]aneN_3)_2]^{3+/2+}$,[27] $[Co(dien)_2]^{3+/2+}$,[28] and $[Co(NH_3)_6]^{3+/2+}$ [29] are known to be −0.41, −0.21, and +0.10 V, respectively. It is clear that substitution of six ammonia for two diethylenetriamine and two 1,4,7-triazacyclononane ligands lowers the oxidizing capability of the cobalt(III) centers successively. Assuming the effect on the Co(III)/Co(II) redox potentials on substitution of NH_3 ligands in complexes Ia and in IIa by dien and $[9]aneN_3$ to be of the same order and magnitude, relative driving force differences, $\Delta\Delta G_0$, may be calculated. A plot of these, admittedly, arbitrary $\Delta\Delta G_0$ values vs. the measured free enthalpy of activation, $\Delta G^{\ddagger}$, is shown in Figure 4. A fairly linear dependence of $\Delta G^{\ddagger}$ on $\Delta\Delta G_0$ is observed;

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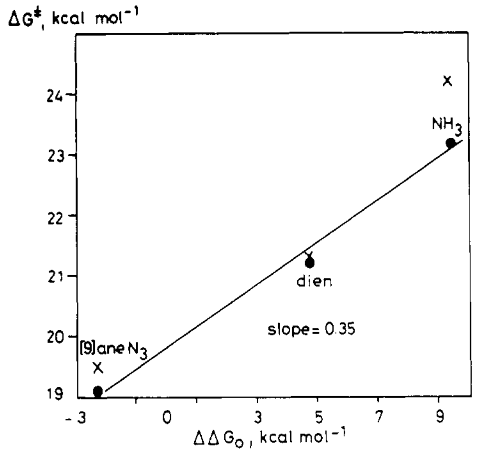


Figure 4. Correlation of the free enthalpy of activation of intramolecular electron transfer vs. relative driving force (for derivation of $\Delta\Delta G_0$ see text). (●) complexes Ia–c; (X) complexes IIa–c.

the slope is 0.35, which is to be compared with a theoretical value of 0.5 predicted by the Marcus relation. Despite the uncertainty of the validity of the above quantitative assessment of ΔG_0 for the binuclear Ru^{II}–L–Co^{III}_n species, it appears that —at least— qualitatively the reactivity differences are satisfactorily accounted for by driving force differences of the Co(III)/Co(II) couples in complex Ia–c and IIa–c.[33]

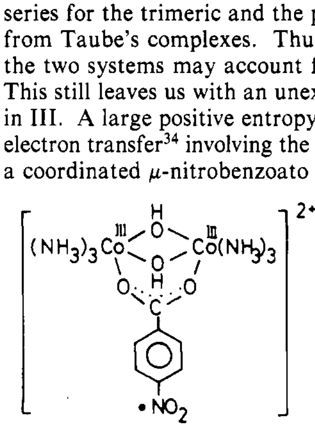
Inspection of the rate constants and activation parameters in Table III reveals that these data are rather insensitive to the nature of the bridging ligand when the oxidant is the bis(μ-hydroxo)-bis[triamminecobalt(III)] unit and the reductant a $Ru(NH_3)_5$ moiety (Ia, IIa, IV, V, and Va). Striking is this insensitivity when comparing couples Ia, IIa and IV, V (or V, Va). In the latter case pyridine-3,5-dicarboxylate and pyrazine-2,6-dicarboxylate are the bridging ligands with rather different aromatic rings. The same behavior is detected for couples Ib, IIb and Ic, IIc where pyridine-4-carboxylate and pyridine-3-carboxylate are the bridging ligands and the nonbridging ligands coordinated to Co(III) are dien or [9]aneN$_3$. The variation of nonbridging ligands $3NH_3$ → dien → [9]aneN$_3$ (Ia–c, IIa–c) is reflected in an increasing enthalpy of activation.

The rates of reaction prove to be insensitive to changes in coupling. This has been observed for complexes $[(H_2O)Ru^{II}(NH_3)_4LCo^{III}(NH_3)_5]^{4+}$, where L is nicotinate or isonicotinate by Taube and co-workers.[1,4] It is reasonable to ascribe this behavior to a transmission coefficient κ of electron transfer, eq 4

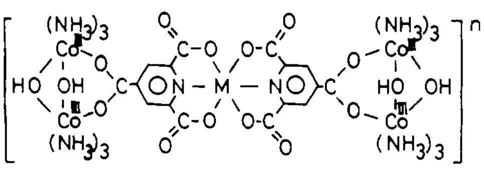
$$\text{rate constant} = \nu\kappa(kT/h)e^{\Delta S^{*}/R}e^{-\Delta H^{*}/(RT)} \qquad (4)$$

of unity for all complexes and that the reactions approach the adiabatic regime. Small reactivity differences may be taken as indication that none of the reactions is cleanly in the adiabatic regime.

The most puzzling results of the present study are the observed large negative entropies of activation ($\Delta S^{*} = -15 \pm 3$ cal K^{-1} mol^{-1}) with the exception of III ($\Delta S^{*} = -3$ cal K^{-1} mol^{-1}). These are in marked contrast to Taube's series,[1-5] where values near zero have been reported (Table IV), which have been discussed previously as an indication for adiabatic electron transfer. It is difficult to see why our reactions become more nonadiabatic, which may be inferred from the negative values of ΔS^{*}, merely by substituting the $(H_2O)(NH_3)_4Ru^{II}$ unit by $(NH_3)_5Ru^{II}$ and $Co(NH_3)_5$ by the dimeric unit $(NH_3)_6Co_2(OH)_2$, but this certainly is a possibility.[34] A different rationalization can be invoked. The overall charge of our complex cations is higher by one unit for the trimeric species Ia–c, IIa–c, and III, by four units for IV and V, and by five units for Va, as compared to Taube's binuclear complexes, but it should be pointed out that the charge per volume (charge distribution) is very likely the same within the present series for the trimeric and the pentameric species, but different from Taube's complexes. Thus different solvation barriers for the two systems may account for the entropy effects observed. This still leaves us with an unexplained near zero value for ΔS^{*} in III. A large positive entropy of activation for intramolecular electron transfer[34] involving the dinuclear cobalt(III) oxidant and a coordinated μ-nitrobenzoato radical[30] has been observed, VI,



VI: $\Delta H^{\ddagger} = 18.4$ kcal mol^{-1}
$\Delta S^{\ddagger} = +19.4$ cal K^{-1}mol^{-1}



VIIa: M = Ti^{III} $\Delta H^{\ddagger} = 14$ kcal mol^{-1}; $\Delta S^{\ddagger} = -6$ cal K^{-1}mol^{-1}
n = 5+

VIIb: M = Fe^{II} $\Delta H^{\ddagger} = 24$ kcal mol^{-1}; $\Delta S^{\ddagger} = +11$ cal K^{-1}mol^{-1}
n = 4+

whereas in system VII a near zero value and for the structurally similar complex VIIb again a positive entropy of activation has been observed.[31]

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Supplementary Material Available: Tables of intramolecular electron-transfer rate constants for complexes Ia–c, IIa–c, III, IV, V, and Va (7 pages). Ordering information is given on any current masthead page.

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(33) This interpretation implies that the self-exchange electron-transfer rates of the $LCo^{III}(OH)_2/LCo^{II}(OH)_2$ moieties do not vary extensively with L. This may be an over-simplification. Furthermore, the solvent (outer-shell) reorganization term drops along the series $3NH_3$ → dien → [9]aneN$_3$ by virtue of the increasing ligand size. This drop opposes the effect of diminishing driving force; the Ru^{III}–Ru^{II} self-exchange rate increases.

(34) Hupp and Weaver have recently analyzed the origin of positive entropies of activation of intramolecular electron-transfer processes in more detail within the Marcus frame. They also conclude that negative values of ΔS^{*} infer "the presence of decidedly nonadibatic pathways". Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 256.