ering the activation energy required to form the increased coordination number activated complex of an associative mechanism. The greater reactivity of the more basic ligands would then be due to the stronger bonding of these more nucleophilic ligands. Finally, the inverse trend in the reactivity of unprotonated MoO_4^{2-} and WO_4^{2-} may be illusory, as the rate constants in column two of Tables XI and XII are mainly upper limits, and the real trend, if any, may not have been demonstrated. Nevertheless, when considering the kinetics data for mono complex formation with different ligands, higher order complex formation, and the kinetics of oxyanion protonation and polymerization, the most consistently applicable mechanism seems to be associative addition to tetrahedral XO_4^{2-} and associative substitution on octahedral HXO_4^-.

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References and Notes

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Intramolecular Electron Transfer Mediated by 4,4′-Bipyridine and Related Bridging Groups

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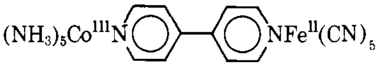
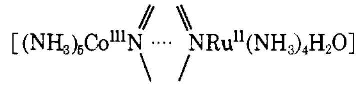
Abstract: At 25°, the first-order specific rates for the reduction of Co(III) by Ru(II) in the complexes of the type $[(NH_3)_5Co^{III}L\cdots LRu^{II}(NH_3)_4H_2O]$ with L···L as 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethylene, 3,3′-dimethyl-4,4′-bipyridine, bis(4-pyridyl) sulfide, and 1,2-bis(4-pyridyl)ethane are 44×10^{-3}, 18.7×10^{-3}, 5.5×10^{-3}, 4.9×10^{-3}, and $1.20 \times 10^{-3}\ s^{-1}$, respectively. The extinction coefficients for the mixed valence species, $[(NH_3(_5Ru^{III}L\cdots LRu^{II}(NH_3)_5]$, with the same bridging ligands decrease in the same order as do the specific rates recorded, and a relation of at least limited validity between these two kinds of measurements is thereby indicated. For the Co(III)–Ru(II) complexes with the first four bridging ligands the values of $\Delta H^{\ddagger}$ for intramolecular electron transfer are within experimental error constant ($\Delta H^{\ddagger}$ ranges from 20.0 to 20.3 kcal mol^{-1}) and the small differences in rate are reflected mainly in $\Delta S^{\ddagger}$ which ranges from 2.6 cal deg^{-1} mol^{-1} for the fastest reaction to −1.9 for the slowest. These results suggest that the Franck–Condon barrier for electron transfer is constant for the series, and that the slight rate differences result from the slower reactions being not quite adiabatic. In the four systems referred to, the bridging group apparently mediates in electron transfer, but in the reaction with the last-mentioned bridging ligand, electron transfer appears to take place directly between the metal centers.

Isied and Taube[1] have described a strategy for preparing complexes which contain within a single molecule Co(III) as an oxidizing agent and Ru(II) as a reducing agent, making it possible for these systems to measure the rates of net intramolecular electron transfer. Some of the advantages of such measurements over those of intermolecular rates for the purpose of understanding fundamental aspects of the charge transfer process itself have long been recognized.[1,2]

Our work is an extension of that of Isied et al.[1] We have selected for study a series in which the interaction between the metal centers can be altered while retaining about each a constant environment. The series we chose is based on 4,4′-bipyridine as the bridging group, with the changes in structure and composition being limited to the bridging group and, within it, to the connection between the pyridine rings. The study by Harriman and Maki[3] on intramolecular electron transfer in the radical anions derived from 4,4′-dinitrobiphenyl species with similar structural alterations in the 1,1′ positions was an added incentive for making the particular choice arrived at, as was that of Gaswick and Haim,[2e] who measured the rate of intramolecular electron transfer in



Our work has included not only measurements of the rate at which Co(III) is reduced by Ru(II) in a series of complexes of the type



but also of the rate as a function of temperature. A feature of the intermolecular electron transfer processes of the charge type (2+) + (2+) and (3+) + (2+) which have been so commonly studied is that $\Delta S^{\ddagger}$ tends to be very negative, values of -30 cal deg^{-1} mol^{-1} being not uncommon even at high ionic strength. The significance of the strongly negative values has remained obscure: are they simply the result of bringing together two positive ions of high charge, or do they in part reflect a property of the electron transfer process itself (negative values of $\Delta S^{\ddagger}$ are expected if the electron transfer act is nonadiabatic)?

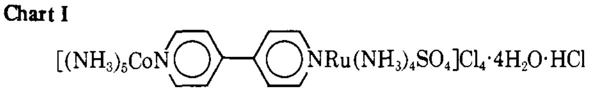
We have considered it worthwhile also to study the properties of the $Ru(NH_3)_5{}^{3+/2+}$ mixed valence species which are derived from the same bridging groups featured in the studies of net electron transfer. According to Hush,[4] unless the coupling between the metal ions in the mixed valence species is very strong, the energy of the intervalence band is related in a simple way to the Franck-Condon barrier for electron transfer. Moreover, the intensity of the intervalence band provides a measure of the valence delocalization in the mixed valence species. Both properties are important in reaching an understanding of basic aspects of the electron transfer process. Though Co(III) and Ru(III) have different electronic structures, it is reasonable to expect that some features of the measurements for the Ru(III)-Ru(II) system would carry over to the Co(III)-Ru(II) system.

Experimental Section

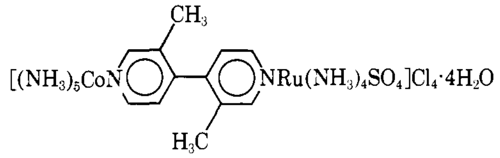
Preparations. The ligands 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethylene, and 1,2-bis(4-pyridyl)ethane were purchased from the Aldrich Chemical Co., Inc. Procedures described in the literature were followed for 3,3′-dimethyl-4,4′-bipyridine,[5] bis(4-pyridyl) sulfide,[6] and diazapyrene.[7] A sample of the latter compound was supplied by Professor Hunig, and we acknowledge this courtesy with thanks. Literature procedures were followed as well for aquopentaamminecobalt(III) perchlorate[8] and *trans*-chloro(sulfur dioxide)tetraammineruthenium(II) chloride.[9,10] In the preparation of the binuclear species, the mononuclear pentaamminecobalt(III) complexes of the bridging ligands were first synthesized, starting from the aquopentaammine complex, without substantial modification of literature procedures.[11,12] Even after several recrystallizations, the compounds prepared in this way were not pure enough, and they were further purified by ion exchange using Bio-Rad Ag-50W-X2, 200–400 mesh resin. A red zone containing $Co(NH_3)_5H_2O^{3+}$ was eluted with 2 M HCl and, following this, the orange-red heterocyclic complex was eluted with 4 M HCl. The solvent was removed at 50° by rotary evaporation, and the residue was dissolved in a minimum amount of water. The solution was filtered and the complex was precipitated as the perchlorate with 70% $HClO_4$. After cooling to −4° for 1 h, the solid was collected by filtration, and washed with methanol and ether. The yields of the desired cobalt(III) complex ranged from 8% in the case of 1,2-bis(4-pyridyl)ethane to 43% for bis(4-pyridyl) sulfide as the heteroligand.

The conversion of the mononuclear Co(III) complexes to the Co(III)-Ru(III) compounds was done as described by Isied and Taube.[1] Solids, analyzing as summarized in Chart I, resulted.

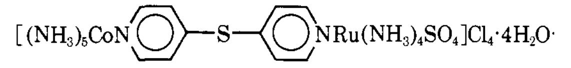
Chart I



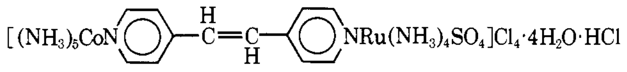
	C	H	N	Co	Ru	Cl	S
Calcd	14.72	5.44	18.88	7.22	12.39	21.73	3.93
Obsd	14.55	5.20	18.77	6.9	12.3	22.08	4.09



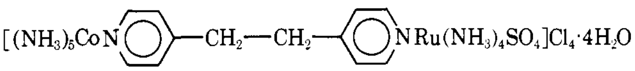
	C	H	N	Co	Ru	Cl	S
Calcd	17.85	5.87	19.08	7.30	12.52	17.56	3.97
Obsd	17.82	5.56	18.98	6.92	12.3	17.03	3.76



	C	H	N	Co	Ru	Cl	S
Calcd	14.80	5.34	18.99	7.26	12.46	17.48	7.90
Obsd	14.56	5.17	18.56	7.35	12.6	18.25	7.71

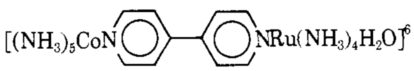


	C	H	N	Co	Ru	Cl	S
Calcd	17.12	5.51	18.30	7.00	12.00	21.06	3.81
Obsd	17.18	5.07	18.26	6.90	12.3	19.76	2.33



	C	H	N	Co	Ru	Cl	S
Calcd	17.85	5.87	19.08	7.30	12.52	17.56	3.97
Obsd	17.51	5.62	18.22	6.80	12.1	16.69	3.78

A kinetic anomaly was observed in the system with 4,4′-bipyridyl as the bridging group. Since, of the various complexes studied, this one reacts the most rapidly, it seemed a possibility, though, because of the time scale, a remote one, that the anomaly was connected with release of $SO_4{}^{2-}$ from Ru(II) being competitive with intramolecular electron transfer. It was important therefore to prepare a solid containing



rather than the corresponding sulfato form as the cation. This was done by reducing a solution of $[(NH_3)_5Co(PBP)Ru(NH_3)_4SO_4]Cl_4$[13] in 0.4 M CF_3COOH with a slight excess of $Ru(NH_3)_6{}^{2+}$. After 7–8 s, which is sufficiently long for release of $SO_4{}^{2-}$, the reaction was quenched using a slight excess of H_2O_2. Acetone was added to the mixture and after cooling the system to −4° for 30 min, the precipitate was collected by filtration. The material was purified by cation exchange, using 6 M HCl as the final eluent. After removing solvent by rotary evaporation at 40°, the solid was dissolved in a minimum amount of 1 M HCl and was precipitated by adding acetone and cooling to −4° for several hours.

μ-4,4′-Bipyridine-bis(pentaammineruthenium(II) hexafluorophosphate was prepared by mixing 0.5 g of $[Ru(NH_3)_5H_2O](PF_6)_2$ in 5 ml of degassed acetone with an equivalent amount of PBP. The reaction was allowed to continue for 4 h in the dark under argon. At the end of this time, 20 ml of ether was added to precipitate the binuclear complex. Characterization was for the most part done on the bis-[Ru(III)] complexes as the *p*-toluenesulfonate salts. The conversion was done by dissolving the crude [2,2] salt in 1 M HCl, and adding Br_2 until the purple color was discharged. The solution was filtered and 0.5 g of *p*-toluenesulfonic acid was added to the filtrate. The solid which formed on cooling was collected, washed with ethanol and ether, then redissolved at 40° in aqueous *p*-toluenesulfonic acid and filtered. Solid acid was added to the filtrate and the solution was cooled. The solid was collected, washed with ethanol and ether, and dried. Similar procedures were followed for the bis-[Ru(III)] complexes with DMPB, DPS, DPEy, DPEa, and DAP as the bridging groups. The analyses are summarized below: $[((NH_3)_5Ru)_2PBP](OTs)_6$. Calcd: C, 41.2; H, 5.2; N, 11.1; Ru, 13.3. Found: C, 37.9; H, 5.0; N, 10.4; Ru, 12.3. $[((NH_3)_5Ru)_2DMBP](OTs)_6$. Calcd: C, 41.0; H, 5.3; N, 10.0; Ru, 12.8. Found: C, 38.7; H, 5.3; N, 10.0; Ru, 12.2. $[((NH_3)_5Ru)_2DAP](OTs)_6$. Calcd: C, 41.9; H, 5.0; N, 10.5; Ru, 11.6.

Found: C, 39.9; H, 4.9, N, 9.8; Ru, 11.6. $[((NH_3)_5Ru)_2DPEy](OTs)_6$. Calcd: C, 41.0; H, 5.3; N, 10.6; Ru, 12.8. Found: C, 38.9; H, 5.0; N, 10.6; Ru, 11.2. $[((NH_3)_5Ru)_2DPS](OTs)_6$. Calcd: C, 39.3; H, 5.0; N, 10.6; Ru, 12.7. Found: C, 36.6; H, 4.9; N, 10.0; Ru, 12.0. $[((NH_3)_5Ru)_2DPEa](OTs)_6$. Calcd: C, 41.0; H, 5.3; N, 10.6; Ru, 12.8. Found: C, 36.5; H, 5.1; N, 10.3; Ru, 11.4. With the exception of H, the values are all ca. 7% low, perhaps owing to the inclusion of water of hydration. If 3 mol of water is assumed to be present in each case, the agreement of calculated and observed values is quite good.

The materials trifluoroacetic acid, HCl, NaCl, Eu_2O_3 (Alfa Inorganic), and Zn were all of high purity as supplied. Sodium trifluoroacetate (Eastman Organic) was purified by recrystallizing from ethanol. The reducing agents Eu^{2+} and $Ru(NH_3)_6{}^{2+}$ used in the kinetic experiments were produced from solutions of Eu_2O_3 in trifluoroacetic acid and $[Ru(NH_3)_6]Cl_3$ in trifluoroacetic acid, respectively, with zinc amalgam as the reducing agent.

In all preparations, deionized distilled water was redistilled from alkaline permanganate before use.

Methods. Following the procedure of Isied et al.,[1] the Co(III)–Ru(III) complex was converted to Co(III)–Ru(II) by adding Eu^{2+} or $Ru(NH_3)_6{}^{2+}$. As noted earlier, the rate of the conversion of a Co(III)–Ru(II) complex to Co^{2+} + Ru(III) is independent of which reducing agent is used. In some of the experiments, the $Co^{III}L\cdots L\,Ru^{III}$ complex was used in large excess over the reducing agent, method A, so as to minimize the complication arising from the reaction of the Ru(III) product with the binuclear complex:

$$Co^{III}L\cdots LRu^{II} + Ru^{III}L\cdots L \rightarrow Co^{III}L\cdots LRu^{III} + Ru^{II}L\cdots L \qquad (1)$$

Equilibration by reaction 1 is rapid compared to the reduction of Co(III), producing curvature in the first-order rate plots, and making it difficult to obtain accurate measurements of the rate of the net intramolecular electron transfer process. Initial rates need to be determined and thus any anomalies in the initial rates, which might be interesting in their own right, become particularly troublesome. Seidel,[14] working with related systems, noted that the $\pi^* \leftarrow \pi d$ absorption for the binuclear complex $Co^{III}L\cdots L\,Ru^{II}$ can differ sufficiently from that of $Ru^{II}L\cdots L$, so that this difference can be used to measure the rate of intramolecular electron transfer. In exploiting this observation a slight excess of the external reducing agent is used so that after the initial reduction, the net change being followed is:

$$Co^{III}L\cdots L\,Ru^{II} \rightarrow Co^{2+} + Ru^{II}L\cdots L \qquad (2)$$

In all cases, except that with PBP as the bridging group, where an initial anomaly to be described presently persists, this method (hereinafter referred to as B) gives excellent first order plots. Where applicable, method B is preferred, but it could not be used in all of the systems dealt with in our report. Comparisons of the two methods were made where both are applicable and results agreed within 10%. The difference tends to reflect a systematic rather than random error and apparently arises from bias in finding the initial rates using method A. Method B can be complicated by the reaction of the excess reducing agent or of the Ru(II) product with the $Co^{III}L\cdots L\,Ru^{II}$ complexes, but any such complications can readily be diagnosed and allowed for. Under our conditions, the complicating reactions were insignificant.

Measurements of absorption spectra in the uv–visible region were done on a Cary 15 and in the near-ir on a Cary 14 spectrophotometer, all at ambient temperature (22 ± 2°). For the latter measurements, matched Beckman near-ir silica cells (no. 75173) were used to remove solvent absorptions. To proudce the mixed valence complex, a solution of the bis-[Ru(III)] complex in acidic solution was prepared; a portion of the stock solution was reduced by amalgamated zinc to the [2,2] state, and equal volumes of the [3,3] and [2,2] solutions were then mixed.

The reduction potentials of the binuclear ruthenium complexes of the various ligands were measured in acidic solution by cyclic voltammetry.[15] The values of the formal reduction potentials are taken as the mean of the oxidation and reduction peaks and are referred to NHE. In none of the systems could a two-stage redox process be observed, but the apparent peak-to-peak separation exceeded that expected for a reversible 1 e^- reduction. This spreading is attributable to the existence of two stages [2,2]-[2,3]-[3,3] with slightly different values of E_f. For present purposes, only relative potentials are of consequence, and these can fairly be taken as the mean of the oxidation and reduction waves.

Table I. Absorption Characteristics of $Co^{III}L\cdots L\,Ru^{II}$ and $Ru^{II}L\cdots L$ Complexes

	$Co^{III}L\cdots L\,Ru^{II}$		$Ru^{II}L\cdots L$[a]	
L···L	λ max	Log ε	λ max	Log ε
PBP	555	4.2	561	4.2
DMBP	444	3.8	450	3.7
DPS	468	3.8	474	3.8
DPEy	564	4.1	570	4.1
DPEa	409	3.8	411	3.8

[a] For the protonated complexes.

Table II. Summary of the Optical Intervalence Transfer Transitions in the Bisruthenium Complexes

L···L	λ max,[a] nm	ε,[b] M^{-1} cm^{-1}	E_f, V	ΔE_p,[c] mV
PBP	1050	400	0.35	114
DAP	1090	450	0.42	130
DPEy	960	400	0.33	100
DMBP	860	90	0.34	95
DPS	855	70	0.36	130
DPEa		<10	0.31	80
DPM	d	<10	0.31	98

[a] In D_2O at ambient temperature. [b] Calculated assuming all Ru as [2,3]. [c] The separation of the cathodic and anodic peaks for a reversible 1 e^- change under our conditions $\Delta E_p \sim 70$ mV. [d] The complex in this case was not characterized as a solid salt.

Results

The characteristics of the low energy absorption bands of the cobalt(III) complexes of the various bridging ligands were observed to be as follows: (ligand, λ (nm), ε ($M^{-1}\,cm^{-1}$)) PBP, 475, 69; DMBP, 475, 69; DPS, 472, 69; DPEy, 475, 82; DPEa, 475, 68. Measurements were made on perchlorate salts in 0.1 M HCl.

The characteristics of the $\pi^* \leftarrow \pi d$ absorption bands of the $Co^{III}L\cdots LRu^{II}$ and $Ru^{II}L\cdots L$ complexes are summarized in Table I.

The results obtained in measuring the near-ir absorptions for equimolar mixtures of the [2,2] and [3,3] bisruthenium complexes are summarized in Table II. Included in the table are the results of the cyclic voltammetry measurements.

The results of the measurements on intramolecular electron transfer rates are summarized in Table III.

The fact that excellent first-order plots are obtained using method B tends to confirm the diagnosis which was made of the cause of curvature when method A is used to determine rates of reaction.[1] An anomaly has been mentioned as appearing in the experiments with PBP as the bridging ligand. The anomaly consists of a change in absorbance early in the reaction in a direction opposite to that caused by the intramolecular electron transfer process itself, but the time scale over which this absorption occurs is so great that it cannot be ascribed to the reduction of the Co(III)–Ru(III) complex by the external reducing agent. This possibility is moreover ruled out by the fact that the anomaly appears only in the one system which has been mentioned. It is not removed by replacing the sulfate on the ruthenium(III) by water, prior to reducing the Co(III)–Ru(III) complex.[16] (To be noted in this connection is the fact that the half-life measured for intramolecular electron transfer for the sulfato and the aquo complexes are identical, thus bearing out the conclusion[1] that the aquation of the Ru(II)–sulfato complex is rapid compared to the electron transfer reactions.) The cause of the anomaly is not un-

Table III. Intramolecular Electron Transfer Rates as Function of Temperature and of Ionic Strength

Bridging ligand	Reaction[a] medium	$[Co^{III}...Ru^{III}]$	Reducing[b] agent	Temp	$10^3\,k$, s^{-1}
PBP	A	7.9×10^{-4}	2.6×10^{-3}	10.6	7.37
		7.0×10^{-5}	1.5×10^{-3}	10.9	7.70
		8.6×10^{-5}	3.1×10^{-4}	11.1	7.97
		9.8×10^{-5}	4.9×10^{-4}	12.6	9.24[c]
		9.2×10^{-5}	5.0×10^{-4}	15.6	14.6
		8.6×10^{-5}	4.7×10^{-4}	17.9	18.5
		9.8×10^{-5}	8.0×10^{-4}	22.0	30.4
DMBP	A	3.2×10^{-4}	1.7×10^{-3}	13.6	1.34
		3.5×10^{-4}	1.2×10^{-3}	18.5	2.57
		3.1×10^{-4}	1.2×10^{-3}	24.9	5.46
		3.0×10^{-4}	1.2×10^{-3}	25.1	5.50
		2.5×10^{-4}	1.1×10^{-3}	29.3	8.94
		2.9×10^{-4}	1.1×10^{-3}	29.4	8.89
		3.1×10^{-4}	1.1×10^{-3}	33.0	13.6
	B	1.2×10^{-4}	1.2×10^{-3}	25.3	5.95
		1.3×10^{-4}	1.3×10^{-3}	25.5	6.26
DMBP	A	3.8×10^{-4}	2.3×10^{-5}	19.8	2.13
	C	4.1×10^{-4}	2.4×10^{-5}	11.6	0.97
		4.1×10^{-4}	2.1×10^{-5}	16.3	1.75
		4.4×10^{-4}	2.1×10^{-5}	20.5	2.81
		2.9×10^{-4}	2.1×10^{-5}	24.9	4.75
		4.7×10^{-4}	2.3×10^{-5}	29.2	8.56
	D	4.1×10^{-4}	2.1×10^{-5}	19.9	4.65
	E	4.1×10^{-4}	2.3×10^{-5}	19.2	4.81
		3.8×10^{-4}	2.3×10^{-5}	19.7	5.17
	F	3.5×10^{-4}	2.3×10^{-5}	19.4	4.99
		3.4×10^{-4}	2.3×10^{-5}	19.8	5.17
DPS	A	4.8×10^{-4}	1.7×10^{-3}	20.7	2.95
		4.8×10^{-4}	1.7×10^{-3}	21.5	3.47
		3.9×10^{-4}	2.3×10^{-3}	24.7	4.59
		5.1×10^{-4}	1.8×10^{-3}	24.9	4.92
		4.8×10^{-4}	1.8×10^{-3}	27.7	6.66
		4.8×10^{-4}	1.8×10^{-3}	28.8	7.58
		4.4×10^{-4}	1.7×10^{-3}	31.0	10.0
	D	3.1×10^{-4}	2.4×10^{-5}	11.5	1.65
		3.0×10^{-4}	2.2×10^{-5}	15.3	2.43
		3.1×10^{-4}	2.2×10^{-5}	21.7	5.78
DPEy	A	0.9×10^{-4}	3.1×10^{-4}	9.9	2.96
		1.3×10^{-4}	4.1×10^{-4}	14.5	5.33
		1.0×10^{-4}	3.4×10^{-4}	18.9	9.37
		1.0×10^{-4}	3.4×10^{-4}	19.0	9.63
		1.1×10^{-4}	3.5×10^{-4}	24.6	18.1
DPEa	G	4.0×10^{-4}	2.6×10^{-5}	24.8	1.00
	A	3.4×10^{-4}	2.6×10^{-5}	20.9	0.75
		3.4×10^{-4}	2.6×10^{-5}	21.0	0.78
		2.6×10^{-4}	2.3×10^{-5}	24.7	1.05
		3.1×10^{-4}	2.6×10^{-5}	24.9	1.18
		3.1×10^{-4}	2.6×10^{-5}	28.8	1.80
		3.1×10^{-4}	2.3×10^{-5}	30.0	2.16
		3.2×10^{-4}	2.6×10^{-5}	34.9	3.41
		3.7×10^{-4}	2.6×10^{-5}	35.3	3.73
		3.5×10^{-4}	2.6×10^{-5}	39.4	5.78
	B	3.6×10^{-4}	2.6×10^{-5}	24.8	1.32
	H	4.0×10^{-4}	2.6×10^{-5}	24.9	1.29

[a] Reaction media: A, 0.4 M CF_3COOH; B, 1.0 M CF_3COOH; C, 0.4 M CF_3COONa; D, 0.4 M HCl: E, 0.4 M NaCl; F, 0.4 M CsCl; G, 0.1 M CF_3COOH; H, 0.4 M CF_3COOH + 0.6 M CF_3COOLi. [b] When the external reducing agent is in excess (method B), $Ru(NH_3)_6^{2+}$; with oxidizing agent in excess (method A), Eu^{2+} was used. [c] $[(NH_3)_5Co(PBP)Ru(NH_3)_4OH_2]Cl_6$ rather than the $Ru-SO_4^{2-}$ complex was used as starting material.

derstood. It is in all likelihood a property of the PBP-ruthenium system alone. Subsequent work has shown[16] that the πd-π^* absorption for the Ru(II) complex has an anomalous variation with temperature. The two phenomena are probably related and the effects are being further investigated.

The plots of k/T vs. $1/T$ give good straight lines. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the various systems calculated from the plots are summarized in Table IV.

Discussion

An important result of these studies is the finding that $\Delta S^{\ddagger}$ is quite close to zero, the large negative values characteristic of the electron transfer reactions of the 3+, 2+ charge type having all but vanished when the rates are measured in the intramolecular mode. In view of the fact that $\Delta S^{\ddagger}$ for the reduction of pentaammineruthenium(III) is much the same as for pentaamminecobalt(III),[17] it seems rather certain that the small values of $\Delta S^{\ddagger}$ we have measured are not an idiosyncracy of the particular electronic structure of the reactants. This study therefore suggests the conclusion that the very negative values of $\Delta S^{\ddagger}$ registered for the 3+, 2+ reactions is largely the result of concentrating the charge in the dielectric medium,

Table IV. Activation Parameter in 0.4 M CF_3COOH

Bridging group	$10^3 k$ at 25°	$\Delta H^{\ddagger}$ [kcal/mol][a]	$\Delta S^{\ddagger}$ [eu][a]
PBP	44	20.1	+2.6
DPEy	18.7	20.2	+1.2
DMBP	5.5	20.2	−1.1
		20.3[b]	−1.1[b]
DPS	4.9	20.0	−1.9
DPEa	1.	19.5	−6.5

[a] Limits of error in $\Delta H^{\ddagger}$ are ±0.3 kcal mol^{-1} and 1.0 cal mol^{-1} deg^{-1}, respectively. [b] In 0.4 M CF_3COONa.

rather than being a property of the electron transfer act itself.

This conclusion needs to be examined in the context of the related observation that $\Delta S^{\ddagger}$ for reactions of the 2+, 2+ charge type with V^{2+} aq as reductant, when substitution is rate-determining for the redox process, is of the order of −15 cal mol^{-1} deg^{-1}.[18] The general mechanism which covers both the situation when precursor complex formation and when its decomposition is rate determining can be represented as

$$\mathrm{ox}^{2+} + \mathrm{red}^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [\text{precursor complex}]^{4+}$$

$$[\text{precursor complex}]^{4+} \xrightarrow{k_1} \text{products}$$

When the precursor complex is in equilibrium with the reactants $\Delta S^{\ddagger}$ (overall) = $\Delta S_f^{\ddagger} - \Delta S_r^{\ddagger} + \Delta S_1^{\ddagger}$. Letting $\Delta S^{\ddagger}$ (overall) and $\Delta S_f^{\ddagger}$ have typical values respectively of −30 cal mol^{-1} deg^{-1} and −15 cal mol^{-1} deg^{-1}, and letting $\Delta S_1^{\ddagger}$, as indicated by the present work, be about zero, $\Delta S_r^{\ddagger}$ = 15 cal mol^{-1} deg^{-1}. Since the precursor complex gains entropy when it undergoes charge separation to form $\mathrm{ox}^{2+} + \mathrm{red}^{2+}$, it seems reasonable that part of this appears in the stage precursor complex → activated complex of the net change.

Of note is the small range covered by the specific rates recorded in Table IV, in spite of what would appear to be large changes in the coupling between the two pyridine rings for the series of bridging groups studied. In DMBP, the planes of the two rings are obliged to be essentially perpendicular, while in DPEy there is no steric reason why they should not be coplanar. The small rate change (leaving out of consideration for the time being the DPEa case which will be dealt with presently), taken together with the fact that the local environments about the metal ions remain the same for the series, indicates that the principal barrier to electron transfer is the Franck-Condon activation barrier—that is, probability of electron tunneling is not a serious factor limiting reaction rates. The validity of this conclusion is borne out by the fact that $\Delta H^{\ddagger}$ for the four reactions under consideration is the same within ±0.2 kcal. The constancy of E_f for the Ru(III)-Ru(II) couples (cf. Table II) is in harmony with the experimental observation that $\Delta H^{\ddagger}$ is nearly identical for the four systems. Since the Co(III)-Co(II) couples are so irreversible, direct measurement of the values of E_f for them is impossible, but it seems likely that changes in driving force for them will be even less than for the Ru(III)-Ru(II) couples. For ruthenium(II) delocalization of πd electrons into the rings can affect E_f, but since Co^{2+} is derived from a first-row element, delocalization is expected to be less for it than it is for Ru(II). The observations cited here are at least qualitatively in agreement with the conclusions reached on theoretical grounds that a small amount of coupling between the orbitals of oxidant and reductant suffices to make the processes adiabatic.[19]

While the major conclusion to be reached is that the reaction rates are principally determined by the Franck-Condon activation barrier, the results in Table IV suggest that some effects ascribable to nonadiabaticity can be discerned. The rate differences parallel rather well[20] the intensities of the intervalence transitions in the corresponding Ru(II)-Ru(III) complexes, and these intensities are a measure[4] of the electron coupling between the charge exchanging centers. The equilibrium constants for the conproportionation reactions within the series are close to the statistical value of 4, but because they are probably not quite constant, the values of extinction coefficients measured may not reflect the relative values of extinction coefficients for the [2,3] species quantitatively. However, they do in all likelihood show them in the true order. That the rate differences appear in the values of $\Delta S^{\ddagger}$ rather than $\Delta H^{\ddagger}$ is in harmony with the effect of nonadiabatic transfer beginning to be felt in the series, but the rate differences are so small that the trend in $\Delta S^{\ddagger}$ cannot be taken as having been established experimentally.

Though a relation between the rates of net electron transfer as measured in the Co(III)-Ru(II) system, and the intensity of the intervalence transition, as measured in the Ru(II)-Ru(III) system, can reasonably be expected on the basis of current theories and is suggested by the data we have obtained, further work will be needed before the connection can be taken as established. In fact, it will be quite difficult to provide convincing evidence of such a connection even if it is real. This limitation exists because the two ways of measuring the electronic coupling through bridging groups overlap in scope only to a small extent. The method based on intensities of the intervalence band is useful only when the coupling is strong enough to give a measurable intensity. Values of ϵ as low as 1 M^{-1} cm^{-1} can probably be measured when a great deal of care is exercised, but it will be difficult to get quantitative measurements much below this value. On the other hand, when the coupling between the electronic systems is increased, the rate of net electron transfer for the series under consideration is expected to reach a saturation value,[21] and the scale based on these rates will be very useful only when the coupling is quite weak.

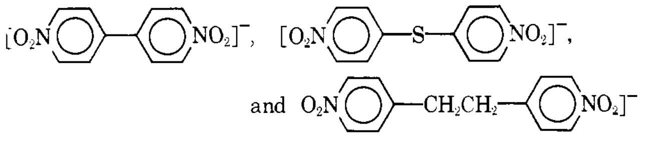
A point of some concern in connection with the foregoing discussion is that while $\Delta H^{\ddagger}$ for the net rate of electron transfer remains constant for the series (excluding that with DPEa as bridging ligand), the energy of the intervalence transition does change significantly. The 20% change recorded for the latter is far outside the limits of error allowable for $\Delta H^{\ddagger}$ measured for net electron transfer. This suggests that the reaction coordinate which provides the path for electron transfer in the Co(III)-Ru(II) system is in some respects different from that implied by the intervalence transition for the Ru(III)-Ru(II). Though for some purposes the systems we have chosen are well suited for the goals we had in mind in embarking on our study, the bridging groups have an inherent complication: activation to meet the Franck-Condon restriction may not be solely a matter of readjustment of the coordination spheres around the metal ions, but it may involve also changes in the relation of the pyridine rings to one another. That there is a contribution from this source, at least in relation to the energy of the intervalence transition is demonstrated by the comparison between the PBP and DMBP systems (λ_{max} at 1050 and 860 nm, respectively). Since the metal-metal distances are the same, any contribution to the Franck-Condon barrier from the energy required for charge separation developed in the solvent is the same, yet the energies of the intervalence transitions differ by 20%.

A possible difference between the reaction coordinate for net electron transfer from Ru(II) to Co(III) and the intervalence transition for Ru(II) to Ru(III) can be illustrated by a comparison of PBP and DMBP as bridging groups: Conceivably, even when the pyridine rings are far from coplanar, coupling between the metal ions centers may suffice for efficient transfer from Ru(II) to Co(III), but for the intervalence transition to have significant intensity, the rings may need to move toward a coplanar configuration.

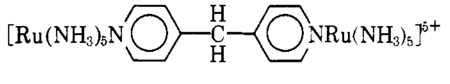
The fact that the intervalence transition for the sulfur bridged species can be observed is an item of particular interest. It suggests that the pyridine rings can interact making use of d orbitals on the sulfur, but before the suggestion is taken seriously, measurements with the -O- bridged species need to be made.[22]

In the four cases which have been considered to this point, the metal ions are so far apart that direct electron transfer can hardly be involved. That orbital coupling takes place through the bond systems rather than through space is borne out by the fact that an intervalence transition for a Ru(II)-Ru(III) mixed valence complex has until now not been observed even when the atoms are held in reasonably close proximity by a saturated bond system.[23] But even though the intervalence transition in Ru(II)···Ru(III) with DPEa as bridging ligand is so weak as to have escaped detection thus far, there is sufficient coupling for rather facile intramolecular electron transfer from Ru(II) to Co(III). It is quite likely that in this case, the bridging group does not provide the coupling mechanism, and that electron transfer takes place directly from Ru(II) to Co(III). The molecule can assume a configuration in which the aromatic rings are eclipsed, and in this configuration, the metal ions are quite close together. The data in Table III show that the rate of electron transfer is much more sensitive to ionic strength for the DPEa system than it is for a system of the other type. For the purposes of these comparisons, the data with Cl^- present must be left out of consideration. Earlier work has shown[1] that the rates are rather sensitive to $[Cl^-]$, an effect which is attributable to the fact that the trans-position on Ru(II) is labile, and Cl^- stabilizes Ru(III) relative to Ru(II) quite strongly. Thus with DMP as bridging ligand, increasing ionic strength from 0.4 to 1.0 (medium A vs. medium B) increases the rate by 6.3%, while the same change for DPEa as the bridging ligand produces an 18% increase. The sensitivity on the DPEa system arises because the configuration optimum for the direct electron transfer is only one out of many which the system can assume, and it requires the two positive centers to be brought close together. We have then a second example of intramolecular electron transfer, which, in terms of the electron transfer act itself, conforms to the outer sphere type, the bridging ligand serving only to keep oxidizing and reducing centers in proximity.[1]

Our results, with metal ions as the sites which trap the electrons, are in some respects qualitatively in agreement with those of Harriman and Maki[3] for the radical anions derived from 4,4′-dinitrobiphenyls. Using EPR line broadening, they observed for



values for k_{intra} of $\geq 10^8$ s, 9×10^6, and 2×10^6 s^{-1} at 25° Me_2SO. Unexpected on the basis of our observations is the high rate for k_{intra} when CH_2 spans the two p-nitrophenyl groups ($\geq 10^8$ s^{-1}). In contrast to the implications of this result, the low intensity of the intervalence transition for


$[Ru(NH_3)_5N\text{C}_5\text{H}_4\text{-CH}_2\text{-C}_5\text{H}_4NRu(NH_3)_5]^{5+}$

suggests very weak coupling between the aromatic groups in this system.

The work in progress[24] on net intramolecular electron transfer from $Fe(CN)_5{}^{3-}$ to Co(III) has not yet been carried far enough to provide useful comparisons with the present results. Of particular interest for establishing a relationship between intra- and intermolecular electron transfer rates would be data on the rates of reduction of pentaamminecobalt(III) complexes of the present ligands by Cr^{2+}, but such measurements have been done only with DPEy as bridging groups[25] among those featured in our study.

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(13) The following abbreviations will be used: 4,4′-bipyridine, PBP; 3,3′-dimethyl-4-4′-bipyridine, DMBP; bis-(4-pyridyl)sulfide, DPS; *trans*-1,2-bis(4-pyridyl)ethylene (DPEy); 1,2-bis(4-pyridyl)ethane, DPEa; 2,7-diazapyrene, DAP; bis(4-pyridyl)methane, DPM; *p*-toluenesulfonate, tosylate or OTs.

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(16) There is a possibility that Cl^- rather than H_2O occupies a position in the coordination sphere of Ru(III). Since the kinetic anomaly under discussion is not affected by the added step, we can nevertheless conclude that it is not ascribable to anion loss from the Ru(II) state.

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(21) Very strong coupling can of course lower the Franck–Condon barrier; this would produce a rate increase with increased interaction even for adiabatic processes, but such strong coupling in the present system, with the disparity in orbital symmetry, would require very special circumstances.

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