Intramolecular Electron Transfer through Isomeric Forms of Dicyanobenzene

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Pentaamminecobalt(III)-µ-bis(nitrile)pentaammineruthenium(III) salts based on the three isomers of dicyanobenzene as the bridging groups have been prepared, and the rates of intramolecular electron transfer in the corresponding Co(III)-Ru(II) species have been measured as a function of temperature. The specific rates, s^{-1} at 25 °C, and the entropies of activation (cal mol⁻¹ K⁻¹) made from the three isomers of the bridging groups are para 4.2×10^{-3} , -3.5 ± 1.0 ; meta 1.8×10^{-4} , -10.5 \pm 2.0; ortho 1.9 \times 10⁻², -0.5 \pm 2.0. The enthalpies of activation are, within experimental error, the same for the three systems. The lower rate for the 1,3 isomer as compared to the 1,4 isomer can reasonably be ascribed to the reaction being less adiabatic for the former bridging group. The increased rate for the 1,2 isomer is more difficult to understand, and it is only partly accounted for by considering the effect of metal-to-metal separation.

Introduction

The properties of the intervalence band for mixed-valence molecules in many instances lead to estimates of the electronic coupling energy,^{1,2} and these quantities have a direct bearing on the issue of whether thermal electron transfer in such molecules is adiabatic or nonadiabatic. Unfortunately, in very few such molecules has it been possible to measure the rate of thermal electron transfer directly. There is some hope, however, of establishing a relation between observations made with mixed-valence molecules, on the one hand, and molecules having the same bridging groups but now attached to metal ions that, after intramolecular electron transfer, lead to an observable chemical change. Such rates of intramolecular electron transfer have been measured with Co(III) as the oxidant and either Ru(II) ammines³ or Fe(II) cyanides⁴ as the reducing agents.

Each of the two reducing agents offers some advantages, and the comparison of the results for the two types of systems has proven to be instructive.⁵ Most of the work done with Co(III) and Ru(II) as the reactants has involved as bridging groups either $A^{6,7}$ (the dotted line indicates that the connection between the



pyridine rings can be varied) or B the isomers.⁸ Only for the molecules based on A have both spectroscopic data and rates of intramolecular electron transfer been obtained. Considerable work has been done on the properties of mixed-valence molecules with bisnitriles as bridging groups,⁹ and in the interest of making the indicated comparisons it seems worthwhile to measure rates of intramolecular electron transfer in molecules with the same bridging group.

In earlier efforts¹⁰ to prepare molecules of the type $[CO^{III}N\equiv C\cdots C\equiv N Ru]^{5+}$ we encountered unexpected difficulties, which led to temporary abandonment of the efforts. In the course of the work described here, the cause of some of the difficulties was diagnosed and has been overcome. Measurements of the rates of intramolecular electron transfer for the three isomeric forms of [(NH₃)₅Co^{III}dcbRu^{II}(NH₃)₅] are herewith reported.

Experimental Section

Materials. Organic ligands were recrystallized according to standard procedures. Trifluoromethanesulfonic acid was purchased from 3M (product named Fluorad). Water was purified by a Barnstead Nanopure ultrafiltration system. Organic solvents were dried over 4-Å molecular sieves. Argon (99.995%, Liquid Carbonic) was deoxygenated by passing it through two ion scrubbing towers containing Cr(II).

Instruments. UV-vis spectra were recorded with a Beckman

CHART I

dcb TFMS triflic acid compounds I, II, and III	dicyanobenzene trifluoromethanesulfonate trifluoromethanesulfonic acid $[(NH_3)_5CoL-LRu(NH_3)_5]$ (TFMS) ₆ with 1,4-dcb, 1,3-dcb, and 1,2-dcb, respectively, as bridging groups. When symbols I, II, and III are modified by a superscript, they represent complex cations.
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Model 5270 spectrophotometer equipped with a thermostated cell holder. IR spectra were recorded with a Nicolet 7199 FT-IR. Cyclic voltammograms were recorded with an apparatus described previously.11 Microanalyses were performed by Chemical Analytical Services, Berkeley.

Preparations. Starting Materials. [Co(NH₃)₅(TFMS)]-(TFMS)₂¹² and [Ru(NH₃)₅(TFMS)](TFMS)₂¹³ were synthesized according to literature procedures.

Synthesis of $[(NH_3)_5Co(1,4-dcb)](TFMS)_3$. To 1,4-dcb (1.0 g) in propylene carbonate (20 mL) at 70 °C was added [Co-(NH₃)₅(TFMS)](TFMS)₂ (0.15 g), and the mixture was stirred at 60-70 °C for 2 h. Acetone (20 mL) and ether (200 mL) were added, and the resulting yellow solid was collected by filtration. This solid was dissolved in acetone (4 mL) and reprecipitated by adding ether (8 mL). Filtration yielded 0.12 g (66%) of [(NH₃)₅Co(1,4-dcb)](TFMS)₃. Anal. Calcd: C, 18.4; H, 2.7; N, 13.6. Found: C, 18.1; H, 2.8; N, 13.4.

Synthesis of $[(NH_3)_5Ru(1,4-dcb)Co(NH_3)_5](TFMS)_6(I)$. A mixture of [(NH₃)₅Co(1,4-dcb)](TFMS)₃ (114 mg), [Ru-(NH₃)₅(TFMS)](TFMS)₂ (100 mg), propylene carbonate (2 mL), and triflic acid (5 drops) was stirred at room temperature for 24 h. The resulting yellow precipitate was collected by filtration and washed successively with hot acetone, ether, and ether containing a trace of triflic acid. The yield was 85 mg (40%) of $[(NH_3)_5Ru(1,4-dcb)Co(NH_3)_5](TFMS)_6 (I)$. Anal. Calcd: C, 12.4; H, 2.5; N, 12.4. Found: C, 12.4; H, 2.5; N, 12.1.

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Synthesis of $[(NH_3)_5Co(1,3-dcb)](TFMS)_3$. To 1,3-dcb (2.0 g) in propylene carbonate (20 mL) at 70 °C was added [Co-(NH₃)₅(TFMS)](TFMS)₂ (0.30 g), and the mixture was stirred at 60-70 °C for 2 h. Acetone (20 mL) and ether (200 mL) were added, and the resulting yellow solid was collected by filtration. This solid was dissolved in acetone (4 mL) and reprecipitated by adding ether (8 mL). Filtration yielded 0.29 g (80%) of [(NH₃)₅Co(1,3-dcb)](TFMS)₃. Anal. Calcd: C, 18.4; H, 2.7; N, 13.6. Found: C, 18.6; H, 3.0; N, 13.4.

Synthesis of $[(NH_3)_5Ru(1,3-dcb)Co(NH_3)_5](TFMS)_6$ (I). A mixture of $[(NH_3)_5Co(1,3-dcb)](TFMS)_3$ (75 mg), [Ru-(NH₃)(TFMS)](TFMS)₂ (170 mg), propylene carbonate (1 mL), and triflic acid (2 drops) was stirred at room temperature for 3 days. Addition of acetone (2 mL) followed by ether (50 mL) gave a yellow precipitate, which was collected by filtration. The crude product was dissolved in acetone (3 mL) and reprecipitated by adding ether (5 mL). The purification step was repeated, and the product was then washed with ether containing a trace of triflic acid. The yield was 122 mg (87%) of $[(NH_3)_5Ru(1,3-dcb)Co-(NH_3)_5](TFMS)_6$ (II). Anal. Calcd: C, 12.4; H, 2.5; N, 12.4. Found: C, 11.3; H, 2.7; N, 11.1.

Synthesis of $[(NH_3)_5Co(1,2-dcb)](TFMS)_3$. To 1,2-dcb (1.6 g) in propylene carbonate (8 mL) at 70 °C was added [Co-(NH₃)₅(TFMS)](TFMS)₂ (0.30 g), and the mixture was stirred at 60-70 °C for 2 h. Acetone (8 mL) and ether (100 mL) were added, and the resulting yellow solid was collected by filtration. This solid was dissolved in acetone (4 mL) and reprecipitated by adding ether (8 mL). Filtration yielded 0.23 g (63%) of [(NH₃)₅Co(1,2-dcb)](TFMS)₃. Anal. Calcd: C, 18.4; H, 2.7; N, 13.6. Found: C, 17.7; H, 2.9; N, 13.1.

Synthesis of $[(NH_3)_5Ru(1,2-dcb)Co(NH_3)_5](TFMS)_6$ (III). A mixture of $[(NH_3)_5Co(1,2-dcb)](TFMS)_3$ (59 mg), [Ru- $(NH_3)_5(TFMS)](TFMS)_2$ (120 mg), propylene carbonate (1 mL), and triflic acid (2 drops) was stirred at room temperature for 2 days. Addition of acetone (2 mL) and ether (40 mL) gave a yellow precipitate, which was collected by filtration. The crude product was dissolved in acetone (3 mL) and reprecipitated by adding ether (3 mL). The product was washed with ether containing a trace of triflic acid. The yield was 67 mg (60%) of $[(NH_3)_5Ru(1,2-dcb)Co(NH_3)_5](TFMS)_6$ (III). Anal. Calcd: C, 12.4; H, 2.5; N, 12.4. Found: C, 12.3; H, 2.6; N, 11.1.

Synthesis of $[(NH_3)Ru(1,4-dcb)](TFMS)_3$, $[(NH_3)_5Ru(1,3-dcb)](TFMS)_3$ and $[(NH_3)_5Ru(1,2-dcb)](TFMS)_3$. These complexes were synthesized as described for the analogous cobalt complexes, the only difference being that the reaction time could be reduced to 1 h.

The yield of $[(NH_3)_5Ru(1,4-dcb)](TFMS)_3$ was 70%. Anal. Calcd: C, 17.4; H, 2.5; N, 12.9. Found: C, 17.3; H, 2.6; N, 12.7.

The yield of $[(NH_3)_5Ru(1,3-dcb)](TFMS)_3$ was 75%. Anal. Calcd: C, 17.4; H, 2.5; N, 12.9. Found: C, 17.3; H, 2.6; N, 12.7.

The yield of $[(NH_3)_5Ru(1,2-dcb)](TFMS)_3$ was 80%. Anal. Calcd: C, 17.4; H, 2.5; N, 12.9. Found: C, 17.6; H, 2.5; N, 12.6.

Kinetics Methods. We applied the strategy, developed earlier,³ of preparing the subject molecule in the [Co(III)L-LRu(III)] state and then adding an external reducing agent, which rapidly converts it to the reactive [Co(III)L-LRu(II)] state. There is an advantage to using a deficiency of the external reducing agent, because then the net change, after the initial reaction, is

$$[Co(III)L-LRu(II)] \rightarrow Co(II) + Ru(III)L-L \quad (1)$$

and the progress of the reaction can be followed by taking advantage of what, in the usual case, is an enormous decrease in $\pi^* \leftarrow \pi d$ absorption when Ru(II) is oxidized to Ru(III).¹⁴ This method, however, has these complications: When Ru(III)L-L accumulates, it puts a drain on the reactant [Co(III)L-LRu(II)] through the equilibrium [Co(III)L-LRu(II) + [Ru(III)L-L] = [Co(III)L-LRu(III)] + [Ru(III)L-L] and, faced as we were with the added fact that even in our acidic solutions the Ru(III) complexes undergo nitrile hydrolysis on the time scale of the

TABLE I: Nitrile Stretching Frequencies for the Dicyano Ligands and Their Co(III) and Ru(III) Complexes

compd ^{<i>a,b</i>}	ν , cm ⁻¹
$[(NH_3)_5Co(1,4-dcb)]^{3+}$	2298 (s), 2239 (m)
$[(NH_3)_5Co(1,3-dcb)]^{3+}$	2299 (s), 2240 (m)
$[(NH_3)_5Co(1,2-dcb)]^{3+}$	2301 (s), 2247 (m)
$[(NH_3)_5Ru(1,4-dcb)]^{3+}$	2276 (w), 2240 (m)
$[(NH_3)_5Ru(1,3-dcb)]^{3+}$	2280 (m), 2241 (m)
$[(NH_3)_5Ru(1,2-dcb)]^{3+}$	2278 (w), 2237 (m)
I ₆₊	2305 (s), 2286 (sh)
11 ₆₊	2306 (s), 2289 (sh)
III ⁶⁺	2293 (s), 2268 (sh)
1,4-dcb	2232 (m)
1,3-dcb	2234 (m)
1,2-dcb	2236 (m)

^a Metal complexes as TFMS salts. ^b In KBr pellets.

electron-transfer reaction, this approach was abandoned.

When the external reducing agent is in excess, the ruthenium species are retained in the II state. Under these conditions, reaction 1 is followed by

 $[Ru(III)L-L] + V(H_2O)_6^{2+} = [Ru(II)L-L] + V(H_2O)_6^{3+}$

and the net change is

$$[Co(III)L-LRu(II)] + V(H_2O)_6^{2+} \rightarrow Co^{2+} + [Ru(II)L-L] + V(H_2O)_6^{3+}$$

(Here V(H₂O)₆²⁺ is introduced as illustrative of other external reducing agents heretofore used.) By adopting this strategy we avoided the complications inherent in the first approach but with the particular choice of reducing agent made, we are left with a very small change in absorbance attending the net change. In our variation of this approach, we used [Ru(NH₃)₅isn]²⁺ as the external reducing agent, and the enormous decrease in $\epsilon_{,} \sim 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, attending the oxidation of this species to [Ru-(NH₃)₅isn]³⁺ provided a very sensitive way of following the progress of the reaction. The redox potential of the [Ru-(NH₃)₅isn]^{3+/2+} couple, 0.375 V,¹⁵ is sufficiently below those of the [Ru(NH₃)₅dcb]^{3+/2+} couples (>0.55 V) so that reduction of Ru(III) in [Co(III)dcbRu(III)] is virtually complete.

It should perhaps be mentioned that the direct reaction of the external reducing agent with [Co(III)L-LRu(II)] could be neglected. Even if it were significant, it could easily be measured and allowed for.

The electron-transfer rates for I and III were measured by adding a freshly made solution of the complex to a deoxygenated, thermostated solution of $[Ru(NH_3)_5(isn)]^{2+}$. Even if some hydrolysis occurs before the mixing, it is unlikely to interfere with the kinetic measurements since the hydrolysis product $[(NH_3)_5Ru(NH_2COC_6H_4CN)Co(NH_3)_5]^{6+}$ is not reduced by $[Ru(NH_3)_5(isn)]^{2+}$.

In the case of II the rate was so slow that the strict exclusion of oxygen became the most important consideration. We found that the best method was to add a deoxygenated solution of $[Ru(NH_3)_5(isn)]^{2+}$ to a solid sample of II in a spectrophotometric cell by means of a Zwickel flask. Measurements were begun when all of the solid had dissolved (ca. 5 min).

Results

Infrared Spectroscopy. The technique that proved most useful in characterizing the compounds synthesized in this work and in assessing their purity was infrared spectroscopy. The values of the C==N stretching frequencies for the various complexes are listed in Table I.

The free ligands show only one absorption in this region, but when one of the nitrile functions is coordinated to a 3+ metal ion, the complex exhibits two absorptions. One is found a few wavenumbers higher than the free ligand absorption and is assigned to the free nitrile group. The other is found at considerably

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TABLE II: Cyclic Voltammetry Data for Ruthenium-Dicyanobenzene Complexes^a

compd	$E_{1/2}$, V vs. NHE
$[(NH_3)_5Ru(1,4-dcb)]^{3+/2+}$	0.56
$[(NH_3)_5Ru(1,3-dcb)]^{3+/2+}$	0.54
$[(NH_3)_5Ru(1,2-dcb)]^{3+/2+}$	0.59
I ^{6+/5+}	0.57
II ^{6+/5+}	0.55
III ^{6+/5+}	0.63

^a Medium: 1.0 N HTFA; scan rate 0.2 V s⁻¹.

TABLE III: Hydrolysis Rates for Ru(III)-Bound Nitriles

compd	$k,^{a} s^{-1}$
[(NH ₃) ₅ Ru(1,4-dcb)] ³⁺ [(NH ₃) ₅ Ru(1,3-dcb)] ³⁺ [(NH ₃) ₅ Ru(1,2-dcb)] ³⁺ I ⁶⁺ II ⁶⁺ III ⁶⁺	$2 \times 10^{-4} 2 \times 10^{-4} 6 \times 10^{-4} 6 \times 10^{-4} 3 \times 10^{-4} 2 \times 10^{-3} $

^a In 1.0 N HTFA at 22 °C.

higher energy and is assigned to the metal-coordinated nitrile group. When the coordinated metal is cobalt, the $C \equiv N$ stretching frequency increases by ca. 65 cm⁻¹ and the peak is more intense than the peak due to the free nitrile group. In the analogous ruthenium complexes, which were synthesized for reference purposes, the frequency increase is only 40–45 cm⁻¹, and the peak due to the coordinated nitrile group is smaller than the one due to the free nitrile group.

The binuclear complexes show two peaks as expected. Due to the low intensity of the Ru-nitrile peak, this appears as a shoulder on the Co-nitrile peak. The peaks are shifted to higher energy (relative to the mononuclear complexes) for I and II, but to lower energy for III.

Electrochemistry. All electrochemical measurements were made on freshly prepared solutions. The couples are all reversible, with peak-to-peak separations of 60-70 mV. (See Table II).

Reactions. The compounds I, II, and III are all inherently unstable when pure and decompose to brown powders over a period of hours, even when kept under argon in the dark. It was found that a trace of triflic acid left on the solid prevented decomposition.

The complication that in our systems nitrile bound to Ru(III) undergoes hydrolysis even when in acidic solution has been mentioned. Some (rough) measurements of rate were made by cyclic voltammetry, and the results are summarized in Table III. The rates were, within the limits of error, observed to be the same at 1×10^{-2} M H⁺ as at 1.0 M H⁺. The hydrolysis rates (summarized in Table III) were estimated by analysis of the cyclic voltammograms as a function of time. The reversible $[(NH_3)_5Ru(NCR)]^{3+/2+}$ couple (Table II) disappears and in all cases but $[(NH_3)_5Ru(1,2-dcb)]^{3+}$ is replaced by a highly irreversible couple at lower potential. The cathodic wave at -0.14 V corresponds to reduction of $[(NH_3)_5Ru(NH_2COR)]^{3+,16}$ and the anodic wave at +0.10 V corresponds to oxidation of $[(NH_3)_5Ru(NH_2COR)]^{2+}$, which is formed by rapid aquation of $[(NH_3)_5Ru(NH_2COR)]^{2+}$.

 $[(NH_3)_5Ru(1,2-dcb)]^{3+}$ responds differently. At pH 0, the wave at +0.59 V, due to the $[(NH_3)_5Ru(1,2-dcb)]^{3+/2+}$ couple, is replaced by a reversible wave at +0.51 V, which in turn disappears and is replaced by a reversible wave at +0.29 V.

Kinetic Results. The rates of electron transfer are presented in Table IV. When the rate for I is measured in HTFA-NaTFA instead of in HCl-LiCl, it decreases by ca. 40%. This is a much smaller anion dependence than that found for systems where water is present in the first coordination sphere of ruthenium.^{6,8}

The rate data, and the quantities derived from them, are summarized in Table V.

TABLE IV: Rates of Electron Transfer in Binuclear Ru(II)-Co(III) Complexes

				temp,	
compd	medium	10 ⁵ [RuCo]	10 ⁴ [Ru(isn)]	°C	$k_{\rm et}, {\rm s}^{-1}$
I ^a	\mathbf{A}^{b}	4.9	1.5	17.0	1.67×10^{-3}
		5.1	2.0	18.8	2.03×10^{-3}
		4.5	1.7	22.0	2.98×10^{-3}
		6.1	1.8	22.4	3.08×10^{-3}
		4.1	1.8	23.0	3.33×10^{-3}
		5.9	1.6	23.9	3.82×10^{-3}
		5.1	1.7	25.9	4.63×10^{-3}
		7.3	2.0	26.8	5.28×10^{-3}
		3.5	2.1	28.2	6.10×10^{-3}
		4.6	1.9	28.8	6.52×10^{-3}
	Bc	6.5	2.1	20.5	$1.38 \times 10^{-3 d}$
Πe	Α	3.6	1.7	20.5	1.13×10^{-4}
		4.1	1.6	20.5	1.15×10^{-4}
		2.0	1.5	20.5	1.18×10^{-4}
		2.9	2.0	25.2	1.80×10^{-4}
		5.8	1.6	25.2	1.90 × 10 ⁻⁴
		2.2	1.3	25.2	1.92×10^{-4}
		5.2	1.6	29.8	3.10×10^{-4}
		4.6	1.8	29.8	3.17×10^{-4}
		3.6	1.7	29.8	3.22×10^{-4}
		2.4	1.7	34.7	5.45 × 10 ⁻⁴
		3.9	2.0	34.7	5.57 × 10 ⁻⁴
		3.8	2.1	34.7	5.68×10^{-4}
Пħ	Α	22	8.1	12.8	4.28×10^{-3}
		24	8.5	12.8	4.37×10^{-3}
		19	8.0	12.8	4.40×10^{-3}
		16	6.8	17.2	7.88×10^{-3}
		19	8.0	17.2	8.05×10^{-3}
		23	7.6	17.2	8.23×10^{-3}
		25	8.2	20.8	1.22×10^{-2}
		22	8.0	20.8	1.25×10^{-2}
		23	8.6	20.8	1.26×10^{-2}
		18	6.8	24.4	1.74×10^{-2}
		21	6.8	24.4	1.76×10^{-2}
		20	7.9	24.4	1.77×10^{-2}

 ${}^{a}\Delta H^{*} = 19.6 \pm 0.2 \text{ kcal/mol}^{-1}; \Delta S^{*} = -3.5 \pm 1.0 \text{ cal mol}^{-1} \text{ K}^{-1}.$ b Medium A: 0.01 N HCl, 0.99 N LiCl. ^c Medium B: 0.01 N HFTA, 0.99 N NaTFA. ^d Average of five measurements. ^c $\Delta H^{*} = 19.4 \pm 0.5 \text{ kcal mol}^{-1}; \Delta S^{*} = -10.5 \pm 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}.$ ${}^{f}\Delta H^{*} = 19.7 \pm 0.5 \text{ kcal mol}^{-1}; \Delta S^{*} = -0.5 \pm 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}.$

TABLE V: Summary of Rate Parameters^a

compd	ΔH^* , kcal mol ⁻¹	ΔS^* , cal mol ⁻¹ K ⁻¹	$k_{\rm et}^{,b} {\rm s}^{-1}$
I ⁵⁺ II ⁵⁺ III ⁵⁺	$19.6 \pm 0.2 \\ 19.4 \pm 0.5 \\ 19.7 \pm 0.5$	-3.5 ± 1.0 -10.5 ± 2.0 -0.5 ± 2.0	$4.2 \times 10^{-3} \\ 1.8 \times 10^{-4} \\ 1.9 \times 10^{-2}$

^a In 0.01 N HCl, 0.99 N LiCl. ^bAt 25 °C.

Discussion

In the adiabatic limit, the rate of intramolecular transfer responds to increased electron delocalization only to the extent that this lowers the activation energy. If we assume that this effect is small, there will be a regime in which the rate of electron transfer in the [Co(III)L-LRu(II)] series will increase only slightly as the oscillator strength of the intervalence bands for the corresponding mixed-valence molecule increases. When the reactions are nonadiabatic, the decrease of rates will parallel the decrease in electronic coupling. There are indications that these expectations are met in the earlier work with bridging groups of the 4,4-bipyridine type.^{6,7} The dinitrile bridging groups have important advantages over those based on pyridine in that they are easier to prepare. The present studies encompass only a small number of systems for which the corresponding mixed-valence studies have been completed.⁹ The major contributions we have made are to have overcome the preparative difficulties, to have introduced a useful modification of the method of measuring rates, and to have made a beginning in what may prove to be an instructive program.

Even though only three systems were studied, it is worth looking at the data more closely. A limitation of the kind of comparison

⁽¹⁶⁾ Diamond, S. E. Ph.D. Thesis, Stanford University, Stanford, CA, 1975, p 72.

we are in the process of making is that it is difficult to devise a series in which metal-to-metal electronic coupling is the only variable. The condition that the driving force be kept constant in a series is partially met by retaining the same lead-in groups. The electrochemical measurements have yielded only the changes in the reduction potential of the reducing agent, Ru(II). Because a major cause of the slight changes that are observed is likely the stabilization of Ru(II) by back bonding, the changes in the Co-(III)/Co(II) potentials are expected to be less than those observed for the ruthenium couple. If this is the case, then for compounds I and II virtually no correction for the change in driving force needs to be made, but on the basis of driving force alone, the rate for compound III is expected to be lower than for the others.¹⁷

Another variable is the distance separating the reacting sites. This affects charge trapping by the solvent, the energy of the intervalence band increasing with increasing distance;¹ correspondingly, the rate of intramolecular electron transfer is expected to decrease.

Neither the driving force nor the distance separating the sites is significantly different for compounds I and II, and the decrease in rate observed for the latter compared to the former, resulting as it does from a more negative entropy change for the former, can be ascribed to the electronic coupling being smaller for it. The conclusion then is that while thermal electron transfer for I may be adiabatic, that for II shows the effects of nonadiabaticity.

Three comparisons are now possible on the rate differences, measured in the intramolecular mode, between 1,4 and 1,3 isomers as the bridging groups. For bipyridine,^{6,7} nicotinates,⁸ and dicyanobenzenes (this work) the rate decreases are by factors of 10, 7, and 23, respectively, considerably less than the factor of 5.4×10^2 reported for the reaction of Cr²⁺ with nicotinamides bound to (NH₃)₅Co(III) through the pyridine nitrogen. Since the latter reactions were measured in the bimolecular mode, a difference in the concentrations of the precursor complex needs to be allowed for. This could partially explain the larger factor observed in the Cr(II)-Co(III) system than in the others. A more important cause of the difference likely is that the mechanism of electron transfer differs in the two classes of reactions. There is persuasive evidence^{18,19} that in the Cr(II)-Co(III) system electron transfer is stepwise, and thus the difference in the ease of $1-e^{-}$ reduction by Cr^{2+} of the bridging ligands, isonicotinamide and nicotinamide, is a factor in the rate ratio. When Ru(II) is the reducing agent, the reducing electron resides in an orbital of π d symmetry and is delocalized over the bridging ligand. There is no symmetry restriction barring reducing agent to bridging ligand transfer, and it is expected that now electron transfer is metal ion to metal ion. This expectation is in fact supported by experiment.²⁰ The energy gap between the reduced ligand state, [Co(III)(L-L-)Ru(III)], and the ground state will of course affect the delocalization between the metal centers, but the quantitative effect, here manifested as a change in tunneling frequency, will be different from that in the case of stepwise transfer. In any event, if the reactions are adiabatic, the effect of increased delocalization by mixing the excited state into the ground state will be small.

As mentioned earlier, on the basis of the difference in driving force for compounds I and III, a lower rate for the latter would be expected, amounting approximately to a factor of $3.^{17}$ If the reaction for I is adiabatic, then the rate for compound III cannot be much improved because of increased electronic coupling. (In fact, the observations⁹ made with the corresponding mixed-valence molecules suggests that the electronic coupling will be somewhat less in III than in I.)

We seem then to be left only with the difference in distance to account for the rate difference. The energy of the intervalence transition for 1,2-dcb as bridging group is 1×10^3 cm⁻¹ lower than it is for 1,4-dcb.9 The activation barrier for electron transfer for the two systems will, however, differ only by approximately

one-fourth of this energy difference,¹ and on this basis a lower rate for I compared to III by about a factor of 3 is expected. When a correction for the difference in driving force is made, the rates are expected to be equal. Considering that the effect of distance is being dealt with by using experimental results, the difference between expectation and observation (namely, a rate increase for III compared to I by a factor of almost 5) is disturbing.

It must be acknowledged, however, that there are weaknesses in the arguments presented. An obvious one is that proposed in considering the changes in driving force—the potentials for the Co(III)/Co(II) couples may in fact be quite sensitive to the ligand changes. Another factor that has been ignored is the difference in the electronic structure of the oxidizing agents used in the rate measurements—Co(III), a σ electron acceptor, and in the mixed-valence case, Ru(III), a π electron acceptor. It has tacitly been assumed that the symmetry restriction in the former case is overcome by a suitable distortion of the coordination sphere about Co(III) when it accepts an electron. This requirement should not affect the order of effectiveness of the different bridging groups, though it might affect their quantitative relation to each other.

We turn now to a consideration of other issues encountered in this work. An important one deals with the preparative method itself. We observed that unless the crystals containing the [Co-(III)L-LRu(III)] ion are left wetted by residual acid, they deteriorate very rapidly on storage, in an autocatalytic manner. The cause of the deterioration is likely this. It is known²¹ that the disproportionation of Ru(III) to Ru(II) and Ru(IV) takes place to a significant degree when the ruthenium bears a π acid ligand, and because of the high acidity of Ru(IV), the reaction is favored when the pH rises. When disproportionation occurs in the binuclear [Co(III)-Ru(III)] species, the resulting Ru(II) can reduce Co(III). This releases the base, ammonia, which in turn promotes the disproportionation. The role of the external acid then is to suppress the disproportionation. It is interesting in this connection that the preparation of complexes of the type $[(NH_3)_4(H_2O)-$ Co^{III}NC...CNRu^{III}(NH₃)₅] has been reported²² without mention of the preparative difficulty we have encountered. If there is in fact a difference between our case and that referred to above, it can be understood on the basis that H_2O in the first coordination sphere of Co(III) acts as an acid, which preserves the compound.

It is well-known that Ru(III) is more effective than Co(III) in promoting the transformation of coordinated nitriles to amides. The effect is so pronounced that often, as in our case, the reaction takes place rapidly, even with H_2O acting as the nucleophile. In the light of the earlier experience,²³ the observations made on the hydrolysis rates as reported in Table III are no cause for astonishment. The complex electrochemical behavior in acidic solution of compound $[(NH_3)_5Ru(1,2-dcb)]^{3+}$ compared to the isomeric forms can be explained by adapting the chemistry described²⁴ for $[(NH_3)_5Co(1,2-dcb)]^{3+}$ to the Ru(III) analogue:



^a Not observed in 1 M H^+ ; inferred on basis of observations made at lower acidity.

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The adaptations are minor. The first step of the sequence for Co(III) takes place with OH^- as the entering nucleophile; with Ru(III), H_2O suffices to hydrolyze the nitrile. Linkage isomerization, as in the second step, is expected to be more rapid for Ru(III) than for Co(III). It is so rapid that the intermediate $(NH_3)_5Ru(2-X]^{3+}$, where X is carboxamidocyanobenzene, is not observed at high acidity.

As the last point to be raised in the discussion we draw attention to the significantly lower intensity of the nitrile stretching frequency when the ligand is associated with Ru(III) than when associated with Co(III).²⁵ The conclusion as stated, which is based on observations with the mononuclear complexes, where the unencumbered nitriles serve as internal standards, as well as with the binuclear complexes, seems dependable. There are consistent differences also in the frequency shifts. We suggest that the differences are ascribable to the differences in electronic structure: πd^5 for Ru(III) and π^6 for Co(III). The vacancy in a low-lying orbital for the former, but not for the latter, leads to greater ligand-to-metal charge transfer for Ru(III). This effect has been invoked to account for the greater efficacy of Ru(III) compared to Co(III) in promoting nitrile hydrolysis and may be the cause of differences in the intensities of the IR frequencies. In the absence of a firm theoretical basis for the correlation offered, the suggestion is of course to be regarded as tentative.

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Registry No. I, 102575-67-7; I⁵⁺, 102575-77-9; II, 102575-69-9; II⁵⁺, 102575-78-0; III, 102575-71-3; III⁵⁺, 102575-79-1; $[(NH_3)_5Co(1,4-dcb)](TFMS)_3, 102575-72-4; [(NH_3)_5Co(TFMS)](TFMS)_2, 75522-50-8; [(NH_3)_5Ru(1FMS)](TFMS)_2, 84278-98-8; [(NH_3)_5Co(1,3-dcb)](TFMS)_3, 102575-73-5; [(NH_3)_5Co(1,2-dcb)](TFMS)_3, 102575-74-6; [(NH_3)_5Ru(1,4-dcb)](TFMS)_3, 90245-43-5; [(NH_3)_5Ru(1,3-dcb)]-(TFMS)_3, 90245-42-4; [(NH_3)_5Ru(1,2-dcb)](TFMS)_3, 90245-41-3; [(NH_3)_5Ru(1,4-dcb)]^{2+}, 46739-38-2; [(NH_3)_5Ru(1,3-dcb)]^{2+}, 46737-88-6; [(NH_3)_5Ru(1,2-dcb)]^{2+}, 102575-76-8.$

Distance, Stereoelectronic Effects, and the Marcus Inverted Region in Intramolecular Electron Transfer in Organic Radical Anions¹

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A series of molecules with the general structure A_1 -Sp- A_2 have been synthesized. Pulse radiolysis was used to convert them into negative ions, and the rates of intramolecular electron transfer were measured. In the first series studied Sp is the androstane skeleton with the acceptors attached to the 3- and 16-positions. The series consisted of eight molecules with $A_2 = 4$ -biphenyl and eight different A1 groups differing in electron affinity by 2.4 eV. The electron transfer rates differ by more than 3 orders of magnitude throughout the series and depend in a very nonlinear fashion on the free energy of the reaction. The rate-free energy profile reaches a maximum in methyltetrahydrofuran at approximately 1-eV exoergicity. At more negative free energies the rates fall off substantially, showing the existence of an "inverted region". In isooctane the rate maximum occurs at less exoergic reactions. The second series of molecules was designed to study the effect of the spacer which was varied from the steroid to decalins (eight compounds) and cyclohexanes (four compounds). No comprehensive distance dependence exists. Instead, the rates are strongly influenced by the donor-acceptor attachment geometry which influences the electronic coupling. This strong dependence on stereochemistry suggests that the major component of the coupling occurs through bonds. A semiquantitative relationship for the magnitude of this coupling with the number of bonds intervening between donor and acceptor was established. For the type of spacers studied it was found that the electron transfer rates are slowed down by 1 order of magnitude for each 2.0 bonds for a constant reorganization energy. This relationship is shown to hold only if the attachment stereochemistry throughout the series whose members are compared is held constant. The stereoelectronic effects are of substantial magnitude and are predicted to be very large in some special structures.

Introduction

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A number of years ago we initiated a collaborative research program between Argonne National Laboratory and The University of Chicago aimed at elucidating some of the intricacies of intramolecular long-distance electron transfer (LDET). Not too long ago "conventional wisdom" held the view that electron transfer (ET) between molecules required a proximity of electron donor (D) and acceptor (A) comparable to their van der Waals radii. Recent work by us and others has laid this myth to rest and has convincingly demonstrated that LDET not only exists but can be remarkably fast.²⁻⁵⁷ Long-distance electron transfer has

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been studied in several systems in which D and A have been kept apart by a rigid spacer group²⁻²² or by incorporating them in rigid

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