Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Metal to Metal Interactions in Weakly Coupled Mixed-Valence Complexes Based on Ruthenium Ammines

JAMES E. SUTTON and H. TAUBE*

A series of binuclear pentaammineruthenium complexes bridged by 4,4'-dipyridyl-type ligands were prepared. The bridging ligands used were 4,4'-dipyridyl, 3,3'-dimethyl-4,4'-dipyridylmethane, 4,4'-dipyridylamine, 4,4'-dipyridylethylene, and 4,4'-dipyridylacetylene. Absorption spectra have been determined as well as electrochemical properties. Of special interest to us was the determination of the stability of the mixed valence relative to the isovalent state. The comproportionation constants, in most instances determined by spectrophotometric titration, at 25 °C were found to be 20, 9.8, 6.7, ~26, ~14, and 13.8, respectively, for the systems based on the bridging ligands mentioned above. The stabilization of the mixed-valence state arising from electron delocalization was estimated from the oscillator strength of the intervalence band with the use of Hush's theory, and the Kirkwood–Westheimer ellipsoid model was used to calculate the electrostatic interaction. According to our analysis, in all cases the resonance coupling in the mixed-valence state makes a minor contribution to its stability, the major factors being the electrostatic interaction, a destabilization of the [2,2] state by delocalization and stabilization of the [3,2] state by the inductive effect of the 3+ charge. The properties of the mononuclear pentaammineruthenium complexes containing 4,4'-dipyridylmethane and 4,4'-dipyridylamine are also reported in this study.

Introduction

The development of a new technique to measure the equilibrium between the three oxidation states of weakly coupled mixed-valence complexes based on a redox titration of the binuclear molecule has made possible a systematic investigation of the various factors which influence this equilibrium.[1] In the case of ruthenium complexes, the three oxidation states of interest correspond to the two isovalent ions with both metal centers in either the 2+ or 3+ oxidation state and the intermediate mixed-valence state containing one metal center nominally in each oxidation state (these states will be represented by [2,2], [3,3] and [2,3], respectively). The equilibrium constant (K_c) for the comproportionation reaction in these binuclear systems is defined in eq 1. The determi-

$$K_c = [2,3]^2/([2,2][3,3]) \qquad (1)$$

nation of K_c relies on monitoring the near-infrared absorption characteristic of the mixed-valence oxidation state during the course of the redox titration. This absorption is commonly known as the intervalence-transfer transition (IT); in a weakly coupled mixed-valence ion, it corresponds to an optically excited electron transfer between the metal centers. In addition to providing a means of following the redox titration, the extent of coupling between the metal centers as well as the stabilization of the mixed-valence ion resulting from resonance delocalization of the exchanging electron can be determined from the characteristics of the IT transitions.[1]

The properties of the μ-(4,4'-dipyridyl)-bis(pentaammineruthenium)(5+) ion previously studied indicated that the resonance stabilization due to coupling of the metal centers may not be a major factor in determining the compropor-

tionation constant.[1] It was also pointed out that the electrostatic repulsion between the metal centers of these binuclear complexes will favor the mixed-valence state relative to the isovalent forms. So that more insight into the importance of these contributions to the comproportionation equilibrium could be gained, a series of binuclear bis(pentaammineruthenium) ions bridged by various 4,4'-dipyridyl-type ligands has been prepared and studied. The complexes considered here are based on the following bridging ligands:
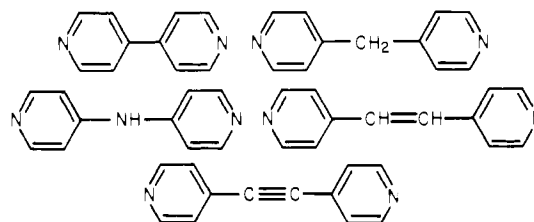
Although many of these complexes have previously been described,[2] new synthetic routes were developed to provide products of higher purity than obtained in earlier studies. The preparation of the 4,4'-dipyridylacetylene molecule is reported in this paper for the first time, (independent of our work it has also been prepared by A. Ludi and co-workers of the University of Bern).

The approximation to the electrostatic repulsion between the metal centers made in the earlier paper was based on point charges in a continuous dielectric medium.[1] This approach has been refined here by modeling the binuclear complex as an ellipsoid containing point charges, following the treatment developed by Kirkwood and Westheimer for symmetric, dibasic

---

(1) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(2) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512. Rieder, K.; Taube, H. *Ibid.* **1977**, *99*, 7891.

acids.[3] In addition to the resonance and electrostatic contributions to K_c, the electronic destabilization of the [2,2] state and the stabilization of the [2,3] state by the inductive effect of the 3+ charge are discussed qualitatively as further contributions to K_c.

Experimental Section

Materials. House-line distilled water was purified by redistillation from alkaline permanganate. Traces of oxygen were removed from argon (99.995%) by passing it through a scrubbing tower charged with 0.5 M chromium(II) (from $Cr(ClO_4)_3$) in 0.5 M $HClO_4$ over zinc/mercury amalgam. Europium oxide (Research Chemicals) was used as supplied. D_2O–DCl (0.1 M) was prepared by diluting 12.1 M D_2O–DCl (International Chemical and Nuclear) with D_2O (MSD Isotopes, Merck). Europium(III) was prepared by dissolving a weighed amount of Eu_2O_3 in 0.1 M D_2O–DCl.

Sephadex-SP-C25-120 strongly acidic cation-exchange resin was purchased from Sigma and allowed to swell in water before packing the column as a slurry. The column was then cleaned by elution with 2 M HCl followed by distilled water before use.

Buffer solutions were prepared following established procedures and checked with a pH meter before use.

4,4'-Dipyridyl and 4,4'-dipyridylethylene (trans) were purchased from Aldrich and used without further purification.

4,4'-Dipyridyl Ketone. The procedure outlined in the literature for the preparation of this compound was followed with minor modification.[4] A solution of 4-bromopyridine was prepared by neutralizing the corresponding hydrochloride salt (Aldrich) in water and extracting the free base into ether, maintaining the solutions at 0 °C. After the ether extract was decolorized with activated charcoal and dried over magnesium sulfate, the concentration of the bromopyridine was determined spectrophotometrically.

The crude 4,4'-dipyridyl ketone obtained by evaporating the chloroform extract (see literature procedure) was initially recrystallized from hot methanol followed by hot water.

4,4'-Dipyridylmethane was prepared by a procedure developed by Gaus and Haim.[5] The product obtained after separation on an alumina column was used without further purification.

4,4'-Dipyridylamine. The literature procedure for the preparation of this ligand was followed with the product being purified by recrystallization from hot water.[6]

3,3'-Dimethyl-4,4'-dipyridyl. This compound was generously provided by Prof. H. Fischer who prepared it according to established procedures.[7]

4,4'-Dipyridylacetylene. The literature procedure for the preparation of the 2,2' isomer was used as a guide in preparing the 4,4' analogue.[8]

Fifty milliliters of diethylamine (Aldrich) was placed in a 100-mL, three-neck, round-bottom flask and degassed with argon. Ten grams of 4-bromopyridine hydrochloride was added and enough water introduced dropwise to fully dissolve the bromopyridine salt. A 70-mg sample of bis(triphenylphosphine) palladium dichloride (Strem) and 35 mg of copper(I) iodide (Ventron) were added before a slow stream of acetylene gas was bubbled through the solution continuously for 24 h. The resulting solution was rotary evaporated to dryness and the residue dissolved in 10 mL of 1 M hydrochloric acid. The hydrochloride salt was precipitated by addition to 150 mL of rapidly stirred acetone. The crude product was dissolved in a minimum amount of 1 M hydrochloric acid and crystallized by slow addition of ethanol. The collected solid was washed with ethanol and ether before being dried in a vacuum desiccator; yield 0.6 g (10%). Anal. Calcd for $C_{12}H_8N_2\cdot2HCl$: C, 56.94; H, 3.98; N, 11.07. Found: C, 56.39; H, 4.08; N, 10.99.

The hydrochloride salt could be neutralized in water to yield colorless crystals of the free ligand. Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.55. Found: C, 79.97; H, 4.61; N, 15.38.

Ruthenium Complexes. Hexaammineruthenium chloride was purchased from Matthey Bishop and converted into the corresponding

chloropentaammineruthenium(III) chloride following established procedures.[9]

Caution! Many of the complexes reported were prepared as perchlorate salts and were handled cautiously in small quantities. Although no shock-induced explosions were encountered, heating resulted in detonation.

Aquopentaammineruthenium(II) Hexafluorophosphate. A 100-mg sample of finely ground $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 5 mL of water containing a few drops of 0.1 M trifluoromethylsulfonic acid and degassed with argon before reducing over zinc/mercury amalgam for 1 h. Two milliliters of degassed, saturated aqueous ammonium hexafluorophosphate (Ozark-Mahoning) was added dropwise, producing a yellow crystalline product which was collected by filtration under an argon atmosphere. The product was washed with 10 mL of degassed ethanol and dried in a vacuum desiccator; yield 150 mg (90%). This material was used immediately to avoid decomposition.

Monoprotonated (4,4'-Dipyridylamine)pentaammineruthenium(II) Hexafluorophosphate. A 100-mg sample of finely powdered $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 9 mL of water and degassed with argon before reducing over zinc/mercury amalgam for 1 h. Then, 70 mg of 4,4'-dipyridylamine was suspended in 2 mL of water and the mixture degassed for 1 h. The ruthenium solution was transferred into the ligand suspension with the use of a stainless-steel needle. This produced a red-orange solution which was allowed to react overnight in the absence of light. The solution was filtered into solid ammonium hexafluorophosphate, producing a solid which was filtered and washed with 1:1 ethanol–ether and ether before drying in a vacuum desiccator. The crude solid was recrystallized twice from 5 mL of hot water; yield 60 mg (22%). Anal. Calcd for $[Ru(NH_3)_5(dipyridylamine\cdot H^+)](PF_6)_3$: C, 15.14; H, 3.18; N, 14.13. Found: C, 15.04; H, 3.34; N, 14.00.

Monoprotonated (4,4'-Dipyridylamine)pentaammineruthenium(III) Perchlorate Dihydrate. The procedure as outlined above for the ruthenium(II) analogue was repeated with the exception that after 18 h the reaction mixture was acidified by adding 1 mL of 6 M hydrochloric acid and oxidized by passing chlorine gas through until no further color change was observed. The crude product was precipitated by addition to 150 mL of rapidly stirred acetone, collected, washed with acetone and ether, and air dried. The binuclear complex is a major contaminant and was separated from the mononuclear complex on a Sephadex-SP column (0.5 × 3 in.) by eluting with hydrochloric acid. After uncomplexed ruthenium was eluted with 0.35 M hydrochloric acid, the desired product was eluted with 0.45 M and the remaining binuclear complex with 0.6 M HCl. The eluant containing the mononuclear complex was rotory evaporated to dryness and the residue dissolved in 5 mL of water. An equal volume of saturated, aqueous sodium perchlorate was added, producing crystals which were collected, washed with cold 0.1 M perchloric acid, ethanol, and ether, and dried in a vacuum desiccator; yield 30 mg (11%). Anal. Calcd for $[Ru(NH_3)_5(4,4'-dipyridylamine\cdot H^+)](ClO_4)_4\cdot2H_2O$: C, 15.16; H, 3.69; N, 14.15. Found: C, 14.94; H, 3.69; N, 13.94.

Monoprotonated (4,4'-dipyridylmethane)ruthenium(II) hexafluorophosphate was prepared by a procedure analogous to the corresponding 4,4'-dipyridylamine complex. A single recrystallization from hot water yielded 20 mg (8%). Anal. Calcd for $[Ru(NH_3)_5(4,4'-dipyridylmethane\cdot H^+)](PF_6)_3$: C, 16.67; H, 3.31; N, 12.38. Found: C, 16.58; H, 3.29; N, 12.25.

μ-(4,4'-Dipyridyl)-bis(pentaammineruthenium(III)) perchlorate dihydrate was prepared according to the procedure outlined in the literature.[1]

μ-(4,4'-Dipyridylamine)-bis(pentaammineruthenium(III)) Chloride Dihydrate. A 155-mg sample of $[Ru(NH_3)_5H_2O](PF_6)_2$ was dissolved in 5 mL of thoroughly degassed acetone to which 20 mg of 4,4'-dipyridylamine was added and allowed to react for 6 h under argon. A crude product was precipitated by adding the solution to 200 mL of rapidly stirred ether, collected, and dissolved in 25 mL of 1 M hydrochloric acid. A 10% excess of aqueous potassium peroxydisulfate was used to oxidize the complex which was again precipitated by adding it to 200 mL of rapidly stirred acetone. The collected product was dissolved in water and purified in a Sephadex-SP column, the product eluting with 0.8 M hydrochloric acid. The rotory evaporated residue was dissolved in water and precipitated by adding the solution to 150 mL of rapidly stirred acetone. The product was collected,

(3) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506; **1938**, *6*, 513.

(4) Minn, F. L.; Trichilo, C. L.; Hurt, C. R.; Filipescu, N. *J. Am. Chem. Soc.* **1970**, *92*, 3600.

(5) Gaus, P. L.; Haim, A.; Johnson, F. *J. Org. Chem.* **1977**, *42*, 564.

(6) Koenigs, E.; Jung, G. *J. Prakt. Chem.* **1933**, *137*, 145.

(7) Stoehr, C.; Wagner, M. *J. Prakt. Chem.* **1893**, *48*, 1.

(8) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tet. Lett.* **1975**, *50*, 4467.

(9) Vogt, L.; Katz, J.; Wiberly, S. *Inorg. Chem.* **1965**, *4*, 1157.

washed with acetone and ether, and dried in a vacuum desiccator; yield 35 mg (38%). Anal. Calcd for [(Ru(NH₃)₅)₂(4,4'-dipyridyl-amine)]Cl₆·2H₂O: C, 15.16; H, 5.47; N, 22.98. Found: C, 15.46; H, 5.33; N, 22.85.

μ-(4,4'-Dipyridylmethane)-bis(pentaammineruthenium(III)) chloride was prepared following a procedure analogous to the one used to produce the corresponding 4,4'-dipyridylamine bridged system, taking care not to expose the oxidized product to acidities below 0.10 M (disproportionation being accelerated by base). The solid obtained was found to be unstable, requiring determination of its properties on freshly prepared samples; yield 50 mg (54%). Anal. Calcd for [(Ru(NH₃)₅)₂(4,4'-dipyridylmethane)]Cl₆: C, 17.49; H, 5.34; N, 22.26. Found: C, 17.58; H, 5.57; N, 20.58.

μ-(4,4'-Dipyridylacetylene)-bis(pentaammineruthenium(III)) chloride trihydrate was synthesized following the method outlined for the 4,4'-dipyridylamine complex, purifying the oxidized product on a Sephadex-SP column (0.5 × 3.0 in.). After impurities were eluted with 0.4 M hydrochloric acid, the eluant produced with 0.8 M HCl was concentrated on a rotary evaporator whereby crystals of the orange solid were produced. The filtered product was washed with ethanol and ether before drying it in a vacuum desiccator; yield 60 mg (60%). Anal. Calcd for [(Ru(NH₃)₅)₂(4,4'-dipyridylacetylene)]Cl₆·3H₂O: C, 17.59; H, 5.41; N, 20.52. Found: C, 17.43; H, 5.30; N, 20.16. This material was observed to decompose spontaneously in a vacuum desiccator when protected from light. Thus, measurements on this material were made with freshly prepared samples.

μ-(4,4'-Dipyridylethylene)-bis(pentaammineruthenium(III)) perchlorate dihydrate was prepared by using the procedure outlined for the 4,4'-dipyridylamine complex with the exception of the purification procedure. The anion of the crude chloride salt was exchanged by precipitating the dissolved complex from solution by adding solid sodium perchlorate. The perchlorate salt was recrystallized from 3 mL of hot water. The solid was filtered, washed with ethanol and ether, and dried in a vacuum desiccator; yield 40 mg (31%). Anal. Calcd for [(Ru(NH₃)₅)₂(4,4'-dipyridylethylene)](ClO₄)₆·2H₂O: C, 12.14; H, 3.74; N, 14.16. Found: C, 12.47; H, 3.64; N, 13.92.

μ-(3,3'-Dimethyl-4,4'-dipyridyl)-bis(pentaammineruthenium(III)) perchlorate hydrate was prepared by the procedure outlined for the 4,4'-dipyridylamine system and purified as follows. The crude oxidized product was purified on a Sephadex-SP column (0.5 × 3 in.) by eluting the bridged complex with 0.8 M hydrochloric acid. The solid obtained by rotory evaporation was dissolved in 2 mL of water, and solid sodium perchlorate was added until precipitation began. The solution was then filtered and the filtrate cooled slowly, producing a yellow solid which was collected, washed with 1 M perchloric acid, ethanol, and ether, and dried in a vacuum desiccator; yield 45 mg (35%). Anal. Calcd for [(Ru(NH₃)₅)₂(3,3'-dimethyl-4,4'-dipyridyl)](ClO₄)₆·H₂O: C, 12.30; H, 3.79; N, 14.35. Found: C, 12.53; H, 4.05; N, 14.20.

Determination of K_c. The method outlined in the literature for the redox titration of binuclear complexes[1] was followed except that the solutions were protected from light. The spectrophotometer beam was allowed to pass through the sample cell only during measurement of the absorbance. Some of the titrations were conducted with a 1-cm flow-through cell.

Spectroscopic Determination of pK_a. The apparatus used for the comproportionation titration was also used for the spectrophotometric determination of pK_a, except that the reservoir was fitted with a glass microelectrode for monitoring pH.

Aliquots of titrant were added to the buffered sample solution and the spectra recorded at each pH. Absorbance measurements were corrected for dilution. The ratios, R_{abs}, of the absorbance at an absorption maximum for the protonated species (λ_1) compared to the absorbance at an absorption maximum for the unprotonated species (λ_2) were determined for each pH and plotted against pH, producing a standard S-shaped titration curve. At the half-equivalence point the protonated and unprotonated complexes are in equal concentration resulting in a value of the ratio determined above equal to

$$(\epsilon_{\lambda_1}{}^{H+} + \epsilon_{\lambda_1})/(\epsilon_{\lambda_2}{}^{H+} + \epsilon_{\lambda_2})$$

where $\epsilon_{\lambda_1}{}^{H+}$, $\epsilon_{\lambda_2}{}^{H+}$, ϵ_{λ_1}, and ϵ_{λ_2} represent the extinction coefficients for the protonated and unprotonated species at λ_1 and λ_2, respectively. This ratio was evaluated from the spectra of the pure compounds, and the pH at which R_{abs} equaled this ratio on the titration curve was taken as the pK_a of the complex being studied.

Instrumentation. All electronic spectra were recorded on a Beckman Model 5270 spectrophotometer using matched quartz cells.
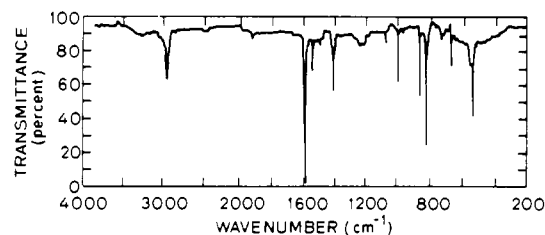

Figure 1. Infrared spectrum of 4,4'-dipyridylacetylene obtained in CHCl₃.

Table I. Infrared Spectrum (ν, cm⁻¹) of 4,4'-Dipyridylacetylene[a]

3080 (w),[b] 3050 (w), 2990 (s, br), 1596 (vs), 1543 (s), 1520 (w), 1495 (w), 1410 (s), 1225 (w, br), 1065 (w), 990 (s), 860 (s), 819 (vs), 656 (s), 528 (vs)

[a] In CHCl₃. [b] Key: vs, very strong; s, strong; w, weak; br, broad.

Electrochemical measurements were made with the use of a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer system. Formal potentials were measured by cyclic voltammetry using a carbon paste electrode. Carbon paste was purchased from Bio-Rad, Inc. Potentials were measured against a saturated calomel electrode (SCE) at 25 °C and are uncorrected for junction potentials. Potentials were corrected to the normal hydrogen electrode scale by adding 0.244 V to the observed value. The volt-ammetric measurements were made at a sweep rate of 100 mV/s in a standard H cell with the test solution compartment separated from the reference electrode compartment by a fine-porosity glass frit.

pH values were determined with a Brinkman Model 101 pH meter equipped with a glass combination microelectrode purchased from Metrohm (Model EA 125). The meter was calibrated at two pH values in the range of interest with use of standard buffer solutions.

Proton NMR. ¹H NMR spectra were obtained in a Varian T-60 spectrometer. Resonances were measured relative to DOH or Me₄Si.

Results

4,4'-Dipyridylacetylene. The standard dehydrobromination route to synthesizing the title ligand could not be used because of the failure of our attempts to brominate 4,4'-dipyridyl-ethylene. As a result, the desired ligand was prepared with the aid of a palladium catalyst. The considerably lower yield compared to the preparation of the 2,2' isomer under similar conditions[8] (10% vs. 60%) is believed to be related to the instability of the 4-bromopyridine reactant.

The infrared spectrum of this ligand obtained in chloroform solution is shown in Figure 1 with the major absorptions listed in Table I. The absence of an absorption in the 2000–2500-cm⁻¹ region shows that there is no change in dipole during the symmetric stretching of the central triple bond. The mode should, however, be Raman active, and in fact an intense absorption is observed in the Raman spectrum at 2230 cm⁻¹. In addition, a weak absorption is observed at 2170 cm⁻¹ which is attributed to a Fermi resonance between the acetylene stretch and the combination band formed by summing the absorptions at 656 and 1543 cm⁻¹ found in the infrared spectrum.

The ¹H NMR of the of the dihydrochloride obtained in 0.1 M DCl–D₂O showed two doublets centered at 3.5 and 4.1 ppm vs. DOH corresponding to the 3,3'- and 4,4'-protons. The integrated intensities of the two resonances are equal as expected.

The UV–visible spectrum of the free ligand in chloroform consists of the following absorptions (λ (10⁻⁴ϵ)): 294.5 (1.79), 286 (1.83, sh), 277.5 (2.46), 272 (2.11, sh), 263.5 (1.83, sh).

Binuclear Complexes. Considerable difficulty was encountered in obtaining acceptable elemental analyses for the series of complexes considered in this study. The nitrogen analyses, even when performed on a single preparation, were observed to vary outside the expected range for replications. Special mention is made of this because it caused a great deal
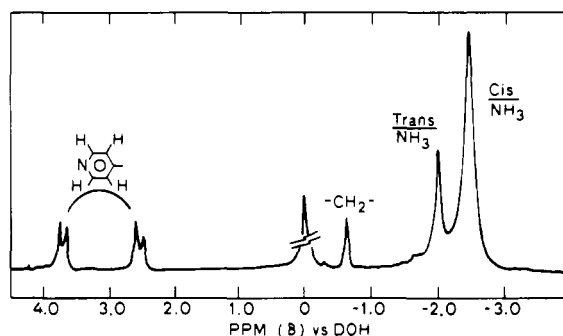
Figure 2. ^{1}H NMR spectrum of μ-(4,4'-dipyridylmethane)-bis-(pentaammineruthenium)(4+) in 0.1 M DC–D$_2$O. [Dimer] = 0.13 M. Sample prepared by reducing the [3,3] complex with Zn/Hg amalgam.
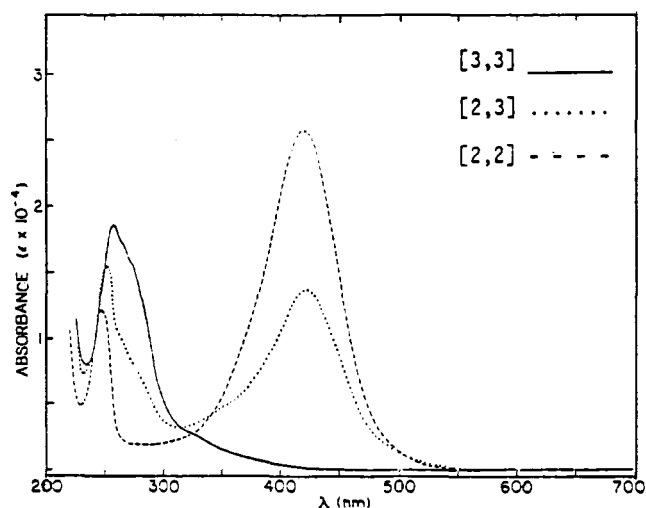

Figure 3. UV–visible spectra of μ-(4,4'-dipyridylmethane)-bis(pentaammineruthenium)(4+, 5+, 6+) in 0.1 M HCl. [2,3] spectrum corrected for comproportionation.

Table II. UV-Visible Spectra of Dipyridyl-Bridged Bis(pentaammineruthenium) Binuclear Complexes[a]

bridging ligand	[2,2][b] λ, nm	[2,2][b] log ε	[2,3][c] λ, nm	[2,3][c] log ε	[3,3] λ, nm	[3,3] log ε
(4,4'-dipyridyl)	249	4.18	238	4.02	235	4.05
	365	sh	260	4.14	290	4.13
	521	4.42	300	sh		
			525	4.10		
(dimethyl)	258	4.01	260	4.11	268	sh
	439	4.31	280	sh	280	4.14
			338	sh		
			439	4.01		
—CH$_2$—	246	4.08	251	4.19	256	4.27
	421	4.41	275	sh	265	sh
			350	sh	275	sh
			421	4.14	324	sh
—NH—	218	4.12	219	4.15	222	4.17
	276	4.20	296	4.31	318	4.41
	442	4.32	335	3.81	355	4.12
			445	4.14	505	3.74
			500	sh		
—CH≡CH—	294	4.28	306	4.32	227	sh
	376	sh	376	sh	324	4.44
	545	4.45	547	4.18	340	sh
					386	sh
—C≡C—	272	sh	287	4.17	229	sh
	286	4.16	300	sh	284	sh
	300	sh	333	sh	316	4.33
	539	4.37	385	sh	350	sh
			531	4.16		

[a] In 0.1 M HCl. [b] Obtained by reducing [3,3] with Zn/Hg amalgam or Eu^{2+}. [c] Obtained by mixing equal concentrations of [2,2] and [3,3]. Extinction coefficients are corrected for the comproportionation equilibrium.
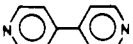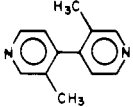
of difficulty. In all cases, excluding the dipyridylmethane-bridged complex, acceptable analyses were obtained by modifying conditions such as carrier-gas flow rate and the nature of the combustion catalyst added in the micro procedure. These variations did not alter the observed carbon and hydrogen results, and the value for nitrogen never exceeded that calculated from the ideal composition.

Although the analysis of the 4,4'-dipyridylmethane analogue yielded the expected values for carbon and hydrogen, that for nitrogen fell below the expected levels by an amount equivalent to one nitrogen atom per binuclear complex, and it seemed a possibility that one of the coordinated ammonias had been replaced by water in the course of the preparation. As an independent check on the composition, the ^{1}H NMR spectrum of the fully reduced binuclear complex was measured, with the result as depicted in Figure 2. Integration of the signals reveals the presence of eight equivalent ammonias in the cis positions relative to the bridging ligand and two in the trans positions, and we conclude, despite the microanalytical result, that no ammonia has been lost.

The salient features of the UV–visible spectra recorded in 0.1 M HCl for the three oxidation states of the dipyridyl-bridged binuclear complexes are summarized in Table II. The spectrum of the 4,4'-dipyridyl complex has appeared previously;[1] that of the 4,4'-dipyridylmethane complex is shown in Figure 3. It should be noted that the entries made in Table II for the mixed-valence species are based on calculations using the values of K_c to obtain the concentration of the [3,2] form in equilibrium with the isovalent forms.
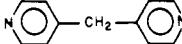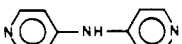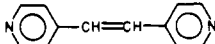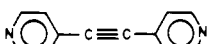
The prominent features in the spectra for the fully reduced complexes are the bands in the visible and near-ultraviolet region arising from $\pi^* \leftarrow d\pi$ and $\pi^* \leftarrow \pi$ transitions, respectively, while the weak band at $\sim$380 nm is probably a ligand field transition. The fully oxidized species shows the $\pi^* \leftarrow \pi$ transition at higher energy than is the case for the reduced form, and the weak band observed in the latter is absent. The strong and rather broad band in the near-ultraviolet region probably arises from a $d\pi \leftarrow \pi$ transition (perhaps transitions). The spectra for the intermediate mixed oxidation states show features of both isovalent forms.

Aside from the minor variations in position and intensity of the above mentioned transitions, the only complexes exhibiting different behavior are the [3,3] and [3,2] species with 4,4'-dipyridylamine as bridging ligand where, in addition to the absorptions found for the oxidized forms of the analogous systems, a new absorption was observed in the visible region. By taking into account the spectrum of the (4-amino-pyridine)pentaammineruthenium(III) complex, we assigned this band as a $d\pi \leftarrow \pi$ transition originating in the highest occupied molecular orbital of the bridging ligand which contains the nitrogen lone-pair electrons of the amine linkage.[10] The spectrum of the reduced species showed no new features.

The properties of the intervalence absorptions for the molecules based on this series of bridging ligands are summarized in Table III. For all except the 4,4'-dipyridylamine analogue, the intervalence transitions overlap on their high-energy side with intense charge-transfer absorptions in the visible region. In these cases the bandwidths at half-heights were taken as twice the half-width at half-height on the low-energy side. As is the case for the majority of complexes belonging to the weakly coupled classification, the bandwidths are broader than predicted by Hush's theory.[11] The absorption
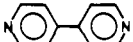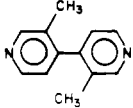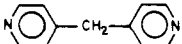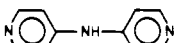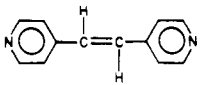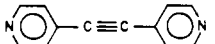
(10) Sutton, J. E.; Taube, H., to be submitted for publication.

Table III. Near-Infrared Spectra of Mixed-Valence Dipyridyl-Bridged Bis(pentaammineruthenium) Binuclear Complexes[a]

bridge	λ_{max}, nm	ϵ, M^{-1} cm^{-1} [b]	$10^{-3}\Delta\nu_{1/2}$, cm^{-1} obsd[d]	calcd	$10^2 f^d$
(bridge structure)	1030	920	5.2	4.7	2.20
(bridge structure)	890	165	6.2[e]	5.1	0.43
(bridge structure)	810	30	7.1	5.3	0.10
(bridge structure)	920	1010	6.4[e]	5.0	2.97
(bridge structure)	960	~760	5.3	4.9	~1.85
(bridge structure)	920	640	5.4	5.0	1.59

[a] In 0.1 M DCl-D$_2$O. [b] Corrected for the comproportionation equilibrium. [c] Determined as twice the half-width at half-height on the low-energy side of the transition except where noted. [d] f is the oscillator strength. [e] Measured directly.

Table IV. Reduction Potentials for Dipyridyl-Bridged Bis(pentaammineruthenium) Binuclear Complexes[a]

bridge	E_{av}, V vs. NHE[b]	ptp, mV[c]	$E_{1/2}$, V vs. NHE[d] +6/5+	+5/4+	K_c
(bridge structure)	0.369	111	0.407	0.331	20[g]
(bridge structure)	0.337	81	0.366	0.308	9.8[h]
(bridge structure)	0.334	78	0.358	0.310	6.7[i]
(bridge structure)	0.246	127	0.288	0.204	~26[f,g]
(bridge structure)	0.336	84	0.370	0.302	~14[f,g]
(bridge structure)	0.379	80	0.413	0.345	14[g]

[a] In 0.1 M HCl; scan rate 0.1 V/s. [b] Average potential of the oxidation and reduction wave maxima. [c] Peak-to-peak separation between the resolved reduction and oxidation wave maxima. [d] Calculated from E_{av} and the comproportionation constant. [e] Titrated in 0.1 M DCl-D$_2$O. [f] Approximate due to decomposition during titration. [g] [Dimer] = 6 × 10^{-4} M. [h] [Dimer] = 3 × 10^{-3} M. [i] [Dimer] = 2 × 10^{-2} M.

profiles are found to be Gaussian on their low-energy side.

The cyclic voltammograms of the dipyridyl-bridged systems were measured in 0.1 M HCl. The 4,4'-dipyridylamine complex clearly exhibited two overlapping waves with only a single maximum resolved for the oxidation and reduction processes, the other maxima expected appearing as shoulders. For each of the other complexes, a single wave was observed with an anomalously large peak-to-peak separation. The midpoint between the resolved maxima and the corresponding peak-to-peak separations are summarized in Table IV for the series
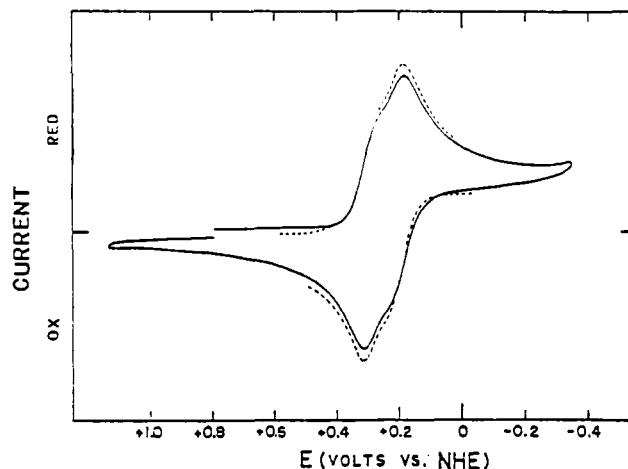

Figure 4. Cyclic voltammogram of μ-(4,4'-dipyridylamine)-bis-(pentaammineruthenium)(6+) in 1 M HCl, scan rate = 0.10 V/s. Dashed line represents simulated voltammogram assuming $K_c = 26$ (amplitude increased for clarity).

of dipyridyl-bridged dimers. All voltammograms were found to be reversible in the sense that the oxidation and reduction wave currents were equal.

Because the redox waves were not clearly resolved for the dipyridyl-bridged molecules, determination of the comproportionation constants by electrochemical means was given up in favor of a titration method. Titrations were performed by starting with the fully oxidized complex and adding aliquots of europous ion. 0.1 M DCl-D$_2$O was used as the solvent except for the 4,4'-dipyridylmethane binuclear titration where a higher concentration of the reducing agent was required and a higher concentration of acid was needed to dissolve the europium oxide. Because many of the complexes had intense charge-transfer bands in the visible region tailing into the spectral range of the intervalence absorption, absorbance measurements were made at two wavelengths: the band maximum and the low-energy shoulder of the absorption. No difference between the comproportionation constants calculated for the two sets of data was observed except for the 4,4'-dipyridylmethane-bridged dimer, and the difficulty in this case is attributed to the low intensity of the intervalence absorption. The concentration of the binuclear complex calculated from the weight of the sample titrated with that calculated from the amount of europous ion required to reach the equivalence point was found to agree within the weighing error. The comproportionation constants for the entire series are summarized in Table IV.

As shown by spectrophotometric analyses, it was found that the oxidized dimers bridged by 4,4'-dipyridylmethane and 4,4'-dipyridylacetylene were unstable in the solid phase, thereby producing Ru(II). This decomposition occurred even when the samples were stored in a vacuum desiccator protected from light. Thus, measurements on these systems were performed immediately after isolation. The disproportionation reaction was not observed in acidic solution but was accelerated in base as has been observed for other ruthenium(III) complexes.[12]

Titration of the 4,4'-dipyridylamine system was complicated by interference from decomposition of the reduced complex. A value of 26 for K_c was determined in a rapid titration. Comparison of the cyclic voltammogram with that of the 4,4'-dipyridine system indicates a larger comproportionation constant for the amine linked complex. The simulated voltammograms produced by summing two reversible one-electron waves separated by the value of ΔE corresponding to $K_c = 26$

(11) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(12) Rudd, De F. P.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1543.

Table V. Variation of the Comproportionation Constant with Ionic Strength

I^b	K_c
4,4'-Dipyridyl-Bridged Bis(pentaammineruthenium)^a	
0.1	20
0.3	22
0.5	23
1.0	24
Solvent Dependence^c	
acetone	~34
ethylene glycol	23

^{a} Titrated in 0.1 M DCl–D$_2$O. [Dimer] = 6 × 10^{-4} M.　^{b} Ionic strength adjusted with NaCl.　^{c} Titrated with Ru(NH$_3$)$_6$$^{2+}$. [Dimer] = 6 × 10^{-4} M.

agree well with the experimental trace, as shown in Figure 4.† This agreement fixes K_c as 24 ± 2. The 4,4'-dipyridyl-ethylene-bridged molecule was observed also to decompose during the titration procedure, but the rate of decomposition was considerably less than that of the corresponding 4,4'-dipyridylamine.

Because the extinction coefficients of the intervalence transitions covered a wide range for the complexes studied, the concentrations of the binuclear systems used for titration were of necessity different. This required consideration of the effect of ionic strength on the comproportionation constant. The comproportionation constant of the 4,4'-dipyridyl-bridged binuclear complex was studied as a function of ionic strength in the range 0.1–1.0 M (sodium chloride). The results as reported in Table V indicate a slight increase with increasing ionic strength. The dependence of K_c on solvent was also investigated. Titrations were performed in ethylene glycol and acetone, yielding values of K_c = 24 and 34, respectively. With acetone as solvent, a silicone tube was used in the peristaltic pump because of its resistance to the acetone, and the tube was quite permeable to oxygen. The error introduced by oxygen leakage is expected to depress the apparent K_c, and thus 34 is a lower limit on the true value in acetone.

Mononuclear Pyridyl Complexes. The spectra for the corresponding pentaammineruthenium(II) mononuclear complexes containing monoprotonated dipyridyls have been reported in the literature for most of the bridging ligands investigated here.^{2} The 4,4'-dipyridylamine and 4,4'-dipyridylmethane complexes were studied in this work to extend the series. Table VI summarizes the spectra for the two oxidation states of these complexes in the protonated and deprotonated form. The assignment of the transitions is unchanged from those made for the corresponding binuclear systems. The cyclic voltammograms were observed to be reversible; they yielded the redox potentials summarized in Table VII.

The pK_a for the uncomplexed pyridine moiety of the 4,4'-dipyridylamine complex was determined spectrophotometrically by following the procedure outlined in the Experimental Section for both oxidation states. The ligand-to-metal charge-transfer band of the oxidized complex was titrated while the $\pi^* \leftarrow d\pi$ transition was monitored for the reduced form. The shifts observed for these absorptions were consistent with their previous assignment. pK_a values of 5.8 and 7.3 were found for the 3+ and 2+ oxidation states, respectively. These observations can be compared to those found for the two pK_a's reported for the free ligand of 7.1 and 4.4 determined in 20% ethanol–80% water.^{13} The approximate equality of the pK_a of the ruthenium(II) complex and the monoprotonated free ligand has also been observed for the 4,4'-dipyridyl system.^{14}
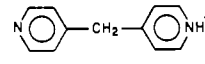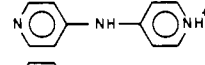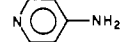
Table VI. UV–Visible Spectra of Pentaammineruthenium Dipyridyl Mononuclear Complexes

ligand	Ru(II)^a		Ru(III)	
	λ, nm	log ε	λ, nm	log ε
[structure: N⟨⟩–CH$_2$–⟨⟩NH$^+$]	219	3.92	215	sh
	250	3.83	254	3.95
	260	sh	260	sh
	423	3.84	275	sh
			320	sh
[structure: N⟨⟩–NH–⟨⟩NH$^+$]	218	4.10	221	4.10
	253	3.51	320	4.39
	295	4.34	346	3.93
	456	4.05	468	3.42
[structure: N⟨⟩–HN–⟨⟩N]^c	217	4.18	217	4.23
	287	4.36	303	4.46
	369	sh	347	4.00
	424	4.08	511	3.56
[structure: N⟨⟩–NH$_2$]^d	239	3.95	253	4.05
	359	3.78	321	3.68
	388	sh	505	3.51

^{a} Obtained by reducing the Ru(III) complex with Zn/Hg amalgam or Eu^{2+}.　^{b} In 0.1 M HCl.　^{c} pH 8.　^{d} Coordinated through the pyridine nitrogen.

Table VII. Reduction Potentials for Mononuclear Pentaammineruthenium Dipyridyl Complexes^a

ligand	$E_{1/2}$, V vs. NHE	ptp, mV^b
[structure: N⟨⟩–CH$_2$–⟨⟩NH$^+$]	0.335	70
[structure: N⟨⟩–NH–⟨⟩NH$^+$]	0.309	60
[structure: N⟨⟩–NH$_2$]	0.149	66^c

^{a} In 0.1 M HCl; scan rate 0.1 V/s.　^{b} Peak-to-peak separation between reduction and oxidation waves.　^{c} Reference 10.

At pH values higher than ~9, a second reaction occurred for the oxidized complex. Disproportionation to Ru(II) and Ru(IV) of ruthenium(III) ammine complexes at high pH values has already been reported.^{12} The observations made for the 4,4'-dipyridylamine complex are consistent with the earlier work. Monitoring the spectrum at pH 10.6 revealed an isosbestic point as the absorption at 522 nm decreased and was replaced by a new band at 410 nm, the latter absorption corresponding to the ruthenium(II) complex produced. No protonation of the amine nitrogen was observed in acid concentrations up to 2 M. Assignment of the observed pK_a to protonation of the heterocyclic nitrogen rather than the central amine is based on its similarity to the value reported for the free ligand. It has been found that the central nitrogen of the free ligand is not significantly protonated even in concentrated sulfuric acid.^{13}

Attempts to determine the pK_a values for the mononuclear complex containing 4,4'-dipyridylmethane using a similar approach were not successful. For the reduced complex the $\pi^* \leftarrow d\pi$ charge-transfer transition did not change significantly on raising the pH to 10. The ruthenium(III) complex was observed to disproportionate rapidly before the desired data were obtained. The pK_a values for this system are not expected to differ greatly from those found for free dipyridyls. Further study of the disproportionation reaction with this ligand indicated that the ruthenium(II) complex produced depended on the conditions under which the reaction occurred. In the absence of oxygen, the expected (4,4'-dipyridylmethane)-pentaammineruthenium(II) complex was produced, but if the

†**Note Added in Proof.** The logic applied here is in error (see: Richardson, D. E.; Taube, H. *Inorg. Chem.* **1980**, *20*, 1283), but no major conclusions are thereby affected. From our measured value of ptp (cf. Table IV) as 127 mV and Table II of the reference above, K_c is calculated as 32.

(13) Sobczyk, L.; Koll, A. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1964**, *12*, 831.
(14) Creutz, C. Ph.D. Thesis, Stanford University, 1970, p 91.

reaction mixture was not purged with argon, the 4,4'-dipyridyl ketone complex formed. The product assignments were made by comparing the absorption spectra of the products with authentic samples. The 4,4'-dipyridyl ketone complex was prepared (λ_{max} = 558 nm, pH 8), exhibiting the same pH dependence of the $\pi^* \leftarrow d\pi$ transition as observed for the product of the disproportionation reaction. Light did not alter the reaction. In the course of this work it was found that the 4,4'-dipyridyl ketone complex could be reduced to the corresponding 4,4'-dipyridylcarbinol species with zinc/mercury amalgam; the identification was made by the similarity of spectra reported for related compounds[2] (λ = 440 nm, pH 1).

Discussion

The binuclear complexes studied in this work provide a good opportunity to assess the various factors which influence the extent of coupling between the metal centers and the stability of the mixed-valence compared to the isovalent state. Because each molecule contains a bridge of the dipyridyl type, the ruthenium centers for all are in similar environments and the differences in the bridging ligands affect mainly the extent of electronic coupling and the distance between the two metal centers.

The derivation of the equations necessary to calculate the resonance coupling between the metal centers has been presented previously. The expressions for the energies of the ground and first excited states were simplified by assuming the overlap between these states (S_{12}) to be zero. Although this condition can be satisfied by the correct selection of the basis orbitals, it is more meaningful to retain a basis set which is easily interpreted such as the d orbitals of the metals and the π orbitals of the ligand. This approach is identical with that of Mulliken for weak charge-transfer complexes[15] and results in approximate expressions for the ground- and excited-state energies (E_g and E_e, respectively) at the equilibrium geometry given by eq 2 where E_1° and E_2° are the zero-order

$$E_g \simeq E_1^\circ - \beta_1^2/h\nu_{IT}$$

$$E_e \simeq E_2^\circ + \beta_2^2/h\nu_{IT} \tag{2}$$

energies for the ground and excited states, respectively. The energy of the intervalence transition is $h\nu_{IT}$ and the form of β is given by eq 3 where H_{12} is the resonance integral. In this

$$\beta_i = H_{12} - E_i^\circ S_{12} \tag{3}$$

form, the resonance energy corrections for the ground and excited states due to electron delocalization are equal to $\beta_1^2/h\nu_{IT}$ and $\beta_2^2/h\nu_{IT}$, respectively, for the molecular geometry corresponding to the intervalence transition. The mixing coefficients for the ground (a) and excited (b) states are given by eq 4. Where the two potential energy surfaces for the
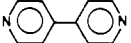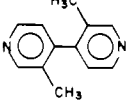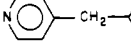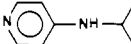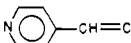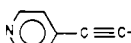
$$a = \beta_1/h\nu_{IT} \qquad b = \beta_2/h\nu_{IT} \tag{4}$$

ground and excited states cross, the resonance interaction breaks the degeneracy of the states symmetrically by an amount equal to 2β where $\beta = \beta_1 = \beta_2$ as a consequence of the zero-order degeneracy.

The equations given above indicate that the ground-state stabilization due to electron delocalization as well as the splitting (2β) of the surfaces at the geometry when the Franck–Condon restriction is satisfied can be calculated from the mixing coefficient and the energy of the intervalence transition. The necessary relationships between the mixing coefficient and the oscillator strength of the intervalence transition are provided by Hush.[11]

It should be mentioned that the validity of Hush's approach to calculate transition dipole strengths from spectroscopic data,

Table VIII. Coupling Parameters for Dipyridyl-Bridged Bis(pentaammineruthenium) Binuclear Complexes[a]
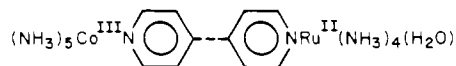
bridge	$10^2 a$ [b]	$\beta^2/h\nu_{IT}$, cal/mol [c]	2β, kcal/mol [d]
	4.04	45	2.2
	1.66	8.9	1.1
	0.82	2.4	0.6
	4.61	66	2.9
	2.93	26	1.8
	2.62	21	1.6

[a] Determined from the properties of the intervalence transfer transition. [b] See eq 4. [c] Stabilization of ground state at equilibrium geometry. [d] Splitting of degenerate potential surfaces at crossover point.

which is then used to calculate the oscillator strength, has been questioned.[16] This challenge is based on a comparison of observed and predicted dipole strengths of far-infrared transitions observed for the pyrazine-bridged bis(pentaammineruthenium) complex in which the experimentally determined values were much smaller than predicted. However, the transitions used for the comparison are believed to correspond to electron delocalization between metal centers rather than the transitions of interest in this work which are vertical transitions of the electron into vibrationally excited states. The pyrazine-bridged dimer exhibits properties characteristic of substantial valence delocalization while the dipyridyl-bridged ions are clearly valence trapped. Regardless of the accuracy of individual values, it is likely that their ordering for different systems is still reliable.

With use of the methods outlined, the mixing coefficients and resonance stabilization energies for the series of dipyridyl-bridged dimers were calculated from the intervalence transfer transitions and are summarized in Table VIII. Even for the most strongly coupled system, that bridged by 4,4'-dipyridylamine, the mixing coefficient indicates that the transferring electron spends considerably less than 1% of its time associated with the ruthenium(III) center. This limited extent of delocalization is consistent with the classification of these systems as valence trapped. The corresponding delocalization energies are seen to contribute only a very minor part of the stabilization of the mixed-valence oxidation state relative to the isovalent forms.

The validity of the resonance energies determined in this way is supported by observations made on rates of intramolecular electron transfer. Although such rates have not been measured for the symmetrical ruthenium binuclear species, the corresponding rates for the cobalt–ruthenium complexes of the type

have been investigated for this series of bridging ligands.[2] It has been pointed out that when 2β is greater than about 1 kcal/mol, thermal electron transfer will be adiabatic.[17] A

(15) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley: New York, 1969; Chapter 2.

(16) Schatz, P. N.; Piepho, S. B.; Krausz, E. R. *Chem. Phys. Lett.* **1978**, *55*, 539.

comparison of ΔH^* and ΔS^* values for reactions in which Co(III) is reduced in an intramolecular mode by Ru(II) indicates that ΔH^* remains essentially constant while the values of ΔS^* span a considerable range. The constancy of the values of ΔH^* is understood on the basis that the environments about the two metal ions in the series remains the same; the large value ($\sim$20 kcal mol^{-1}) is understood to result from the large distortion of the coordination sphere around the cobalt(III) center required to match the acceptor orbital of σ symmetry with the electron carrier orbitals of the bridging system which have π symmetry. The value of ΔS^* remains almost constant for a number of the dipyridyl ligands studied here except for 4,4'-dipyridylmethane where a value 9.6 cal/(deg mol) more negative than that determined for the 4,4'-dipyridyl complex is observed. This behavior is taken to indicate that all but the methylene coupled systems are in, or at least close to, the adiabatic regime while the 4,4'-dipyridylmethane is showing the effects of nonadiabaticity.[2] These conclusions are consistent with the 2β values calculated here (Table VIII) which indicate all should be adiabatic except the 3,3'-dimethyl-4,4'-dipyridyl bridge which is borderline and 4,4'-dipyridylmethane which is clearly too weakly coupled to belong to the adiabatic regime.
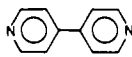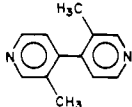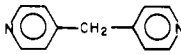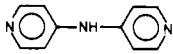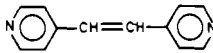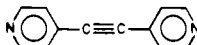
As a further check, the rate constant for intramolecular electron transfer (k_{et}) can be calculated from the properties of the intervalence band and compared with that calculated from the bimolecular rate constant for electron transfer between Ru(NH$_3$)$_5$L^{3+} and Ru(NH$_3$)$_5$L'$^{2+}$, where L and L' are pyridine derivatives. With use of the value of $k_{bimol} = 1.1 \times 10^5$ M^{-1} s^{-1} at $\mu = 0.10$, k_{et} was estimated[18] as 1.6×10^8 s^{-1}. In calculating k_{et} from the intervalence band, ΔH^* is set equal to $E_{op}/4$ less half the splitting at the crossover point, and ΔS^* is taken as 0.[2] The value of k_{et} so obtained, 3.2×10^8 s^{-1}, is in reasonably good agreement with that estimated from k_{bimol}.

Regardless of the absolute magnitudes of the resonance energies calculated, the relative values appear to be significant. Comparisons are simplified when the same number of atoms bridge the two pyridine rings, insuring similar metal–metal distances. When the two pyridine rings are directly joined, the coupling is considerably decreased when methyl groups are substituted at the 3,3'-positions, forcing the rings to be essentially perpendicular. This limits the overlap of the π systems for the two rings, thus weakening the communication across the bridging ligand. This effect is also reflected in the considerably lower energy of the $\pi^* \leftarrow d\pi$ transition observed for the 4,4'-dipyridyl complex. When the π systems of the two rings become coupled, they split apart in energy, the extent of splitting being directly related to the extent of coupling. The splitting decreases the energy gap between the lowest π^* ligand level and the metal $d\pi$ orbitals. Because the coupling is inhibited for the dimethyl derivative, the π^* level remains higher in energy as indicated by the blue shift in the $\pi^* \leftarrow \pi d$ transition compared to those for 4,4'-dipyridyl.

Comparing the two systems in which the pyridyls are bridged by a single atom between the rings, we note, as evidenced by the intensity of the intervalence transition, that the lone-pair electrons of the central nitrogen are quite effective at coupling the two ring systems, whereas very little coupling occurs across a methylene bridge. The coupling which is responsible for the weak intervalence absorption observed for the latter system is presumed to occur by the direct but weak overlap of the π^* systems of the two pyridine rings.

Owing to decomposition encountered during the measurement of the physical properties of the 4,4'-dipyridylethylene-bridged complex, the resonance energies determined for it are

Table IX. Model Ellipsoid^a Parameters for Dipyridyl Bridged Bis(pentaammineruthenium) Binuclear Complexes

bridge	r, $\mathring{A}$ ^{b}	V, $\mathring{A}^3$ ^{c}	a, $\mathring{A}$ ^{d}	b, $\mathring{A}$ ^{e}	λ_0 ^{f}	R, $\mathring{A}$ ^{g}	μ ^{h}
N—(ring)—(ring)—N	11.3	6.14	9.15	4.00	1.11	16.5	0.685
N—(ring)—(ring)—N (3,3'-dimethyl)	11.3	6.14	9.15	4.00	1.11	16.5	0.685
N—(ring)—CH$_2$—(ring)—N	10.5	5.84	8.75	3.99	1.12	15.6	0.674
N—(ring)—NH—(ring)—N	10.9	5.99	8.95	4.00	1.12	16.0	0.681
N—(ring)—CH=CH—(ring)—N	13.8	7.11	10.4	4.04	1.09	19.1	0.723
N—(ring)—C≡C—(ring)—N	14.0	7.18	10.5	4.04	1.08	19.4	0.722

^{a} Confocal elliptical coordinates (λ, μ) defined as $\lambda = (d_1 + d_2)/R$ and $\mu = (d_1 - d_2)/R$, where d_1 and d_2 are the distances from the point (λ, μ) to the foci 1 and 2, respectively. ^{b} Determined from crystallographic data and CPK space-filling models. ^{c} $V = 4/3\pi x^3 + \pi r x^2$; $x = 3.5$ Å. ^{d} $a = (r/2) + x$; semi-major axis, r = distance between metal center. ^{e} $b = (3V/4\pi a)^{1/2}$; semi-minor axis. ^{f} $\lambda_0 = (a^2/a^2 - b^2)^{1/2}$; the equation of the ellipsoid. ^{g} $R = 2a/\lambda_0$; the distance between the foci. ^{h} $\mu = r/R$; the placement of the metal centers as the major axis.

not accurate, but they can be taken to show that the coupling is greater for 4,4'-dipyridylethylene than for 4,4'-dipyridyl-acetylene as bridging group. The decreased electronic coupling in the latter case suggests that the two pyridine rings tend not to remain coplanar in the mixed-valence oxidation state, thus reducing interactions between the two halves of the binuclear complex. It was expected at the outset that the further desaturation of the two carbon fragments of the ethylene bridge would keep the two rings coplanar and improve the interaction. After considering the magnitude of the resonance stabilization which results from such interactions ($\sim$40 cal/mol), it is clear that the rotational barrier from these interactions is far too small to overcome thermal disordering effects at room temperature ($\sim$600 cal/mol).

The stabilization of the mixed-valence molecule resulting from electron delocalization is just one factor determining the overall stability of the mixed-oxidation state relative to the isovalent forms, which per mole becomes $^1/_2RT \ln (K_c/4)$ (the factor 4 is the purely statistical contribution to K_c). It has been pointed out that a second contribution may arise from the mutual repulsion of the two positively charged metal centers joined by the bridging ligand.[1] This contribution was originally approximated by calculating the energy of bringing two point charges in a continuous dielectric medium to a distance equivalent to the metal–metal separation of the complex. A more realistic model for linear binuclear complexes consists of two point charges embedded in an ellipsoidal cavity of dielectric constant D_i surrounded by a medium of dielectric constant D_s. This type of model has been treated by Kirkwood and Westheimer to account for the differences between successive acid dissociation constants of symmetric dibasic acids (ΔpK_a) which result from electrostatic interactions.[3] This case is equivalent to the electrostatic interaction between the metal centers of the complexes studied here. Ehrenson[19] has generalized the original derivation to allow the charges to move away from the foci symmetrically along the major axis, thus improving the model.

(17) Sutin, N. *Inorg. Biochem.* New York, 1973, 2, Chapter 19.
(18) Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* 1979, 18, 3374.

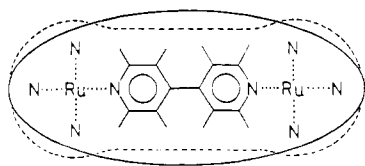(19) Ehrenson, S. *J. Am. Chem. Soc.* 1976, 98, 7510.

Figure 5. Comparison between molecular geometry and model ellipsoid for μ-(4,4'-dipyridyl)-bis(pentaammineruthenium)(5+).

Application of these equations requires the ellipsoid parameters to be specified. This was done[20] with the aid of molecular models and crystallographic data. These parameters are summarized in Table IX, and a scale model of the ellipsoid is shown in Figure 5.

For the dielectric constant inside the cavity, D_i, a value of 2 was chosen, it being recognized that the pyridine units are not free to realign with an applied electric field. The energy is in any event not very sensitive to D_i because of the rodlike shape of the cavity. The value of the dielectric for the surrounding medium, D_s, was approximated from the 4,4'-dipyridylmethane complex on the assumption that the various electronic factors for it are minimal. There is a complication because the molecule is bent; a value of $D_s = 125$ was chosen as the average of the values required by the ellipsoidal model on the one hand and a point-charge model on the other to account for the observed value of K_c. The weak dependence of K_c on ionic strength shown for the dipyridyl complex justifies the use of a single value. This value, it should be noted, incorporates the effect produced by the ions in the medium.

The results for the calculations are summarized in Table X where ΔG_E represents the energy difference due to electrostatics and ΔG_R is the resonance contribution to the observed stabilization. The results indicate that the electrostatic contribution stabilizes the mixed-valence oxidation state by roughly 125 cal relative to the isovalent forms. The small size of this value is not surprising considering that most of the electric field lines are conducted through the solvent which in the case of water is quite efficient at shielding the two charged centers from each other. This conclusion is verified by the titrations conducted in nonaqueous solvent (Table V) where the value of D_s has been decreased considerably with a corresponding increase in the comproportionation constant. The observed increases are not as large as expected on the basis of the change in D_s, but this is probably a result of increased ion pairing as the dielectric constant of the solvent decreases.

If the centers of charge for the complexes are seen as independent units by the solvent, there will be no significant activity coefficient effects because reactants and products have the same number of ions of each charge type. That the centers act independently is supported by the good agreement between observed and calculated solvent reorganization energies for the 4,4'-dipyridyl-bridged bis(pentaammineruthenium) complex where it was assumed that the ruthenium centers were independent.[21]

If the contributions to the stability of the mixed oxidation state so far considered are added together, they still fall short of explaining the measured comproportionation constants for this series of complexes. So that the major factors responsible for the stability of the isovalent state could be exposed, the energies of the isovalent and mixed-valence states will be referred to the completely dissociated state, consisting of two Ru(II), two Ru(III), and two bridging ligands. These are first partially assembled to produce Ru^{II}L$\cdots$L and Ru^{III}L$\cdots$L. Now in producing the isovalent state, Ru(II) is added to the former

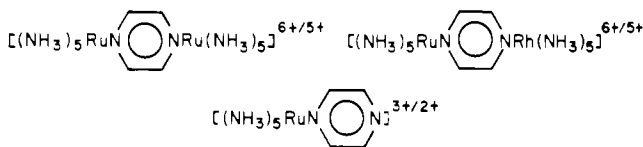**Table X.** Contributions to the Comproportionation Constant for Dipyridyl-Bridged Bis(pentaammineruthenium) Binuclear Complexes

bridge	K_c	ΔG, cal/mol[a]	ΔG_E, cal/mol[b]	$\Delta G_R{}^c$
	20	470	140	45
	9.8	260	140	9
	6.7	150	150[d]	2
	~26	550	140	66
	~14	370	93	26
	13.8	360	88	21

^{a} $\Delta G = \frac{1}{2}RT \ln (K_c/4)$ in cal/(mol of mixed-valence ion). ^{b} Calculated for point charges in an ellipsoid except as noted ($D_i = 2$; $D_s = 125$). ^{c} Calculated from the intervalence transfer transition. ^{d} ΔG is assumed to be equal to ΔG_E (electronic coupling by delocalization very weak).

and Ru(III) to the latter. In assembling Ru^{III}L$\cdots$LRu^{III} it is virtually certain that if electrostatic effects are allowed for, nothing further is at issue. But in assembling Ru^{II}L$\cdots$LRu^{II} it must be borne in mind that adding the second Ru(II) does not produce quite the same stabilization by πd - π* delocalization as the first, and thus there is an inherent electronic instability in the [2,2] state. Consider now the mixed-valence state: when Ru(II) is added to Ru^{III}L$\cdots$L, there is an extra stabilization because Ru(III) lowers the π* orbital on the ligand and thus increases the affinity of Ru(II) for the bridging ligand. This effect is strikingly revealed in the Ru^{II}–pyrazine (pz) system where the affinity of pzH$^+$ for Ru(NH$_3$)$_5$H$_2$O^{2+} has been found to be almost 2 orders of magnitude greater than that of pz.[22] To be noted as well is the fact that the affinity of Ni^{2+}(aq) for (NH$_3$)$_5$Ru(pz)$^{2+}$ is approximately a factor of 2 greater than it is for free pyrazine.[23] The importance of the inductive effect of the positive charge is clearly brought out in comparing E_f for the three couples:

$$[(NH_3)_5RuN\bigcirc NRu(NH_3)_5]^{6+/5+} \quad [(NH_3)_5RuN\bigcirc NRh(NH_3)_5]^{6+/5+}$$

$$[(NH_3)_5RuN\bigcirc N]^{3+/2+}$$

These values are 0.76, 0.71, and 0.49 V, respectively.[24] Rh(III), which having a πd^6 configuration, cannot participate in delocalization to the same extent as Ru(III) (πd^5); nevertheless, it exerts almost the same effect on E_f as the latter ion.

The difference in energy between the destabilizing interaction of the reduced complex and the stabilizing influence of the mixed-oxidation state resulting from coupling might be expected to alter the average geometry around the group joining the two rings when the oxidation state is changed. If such a rearrangement does take place upon oxidation, it should be reflected in the physical properties of the system. Although the spectra for the mixed-valence oxidation state are to a first

(20) Sutton, J. E. Ph.D. Thesis, Stanford University, 1979. This contains details on all aspects of the calculation of the electrostatic contribution to K_c.
(21) Creutz, C. *Inorg. Chem.* **1978**, *17*, 3723.

(22) Ford, P.; Gaunder, R.; Rudd, DeF. P.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.
(23) Pereira, M. S.; Malin, J. M. *Inorg. Chem.* **1974**, *13*, 386.
(24) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086; **1969**, *91*, 3988.

approximation made up of equal contributions from the two isovalent states, as expected for weakly coupled systems, definite perturbations in the spectra are observed. In the 4,4'-dipyridyl complex, the $\pi^* \leftarrow \pi d$ and $\pi^* \leftarrow \pi$ transitions are shifted to lower energy in the mixed-valence spectrum, compared to the same transitions in the isovalent states.[1] In addition, the former absorption is observed to be considerably broadened on the low-energy side, an effect which cannot be attributed to the intervalence transition; the broadening could be indicative of a significant rearrangement of the bridging ligand geometry upon oxidation. That this is not a result of asymmetry introduced in the mixed-valence state is apparent from the absence of such changes in the 4,4'-dipyridylmethane complex where the asymmetry is present but the electronic communication is not. As predicted, those complexes which stand to gain from such a rearrangement (4,4'-dipyridyl, 4,4'-dipyridylethylene, 4,4'-dipyridylacetylene) show considerable broadening of the $\pi^* \leftarrow \pi d$ transition upon oxidation to form the mixed-valence ion. Consistent with the idea that free rotation around the triple bond in the acetylene derivative breaks up coupling in the fully reduced state, the broadening of the more strongly coupled ethylene derivative is greater. For the dimethyldipyridyl-bridged dimer, rearrangement is sterically hindered while the 4,4'-dipyridylmethane is too weakly coupled to improve stability by rearranging upon oxidation to form the mixed-valence species. As a result, these latter two complexes do not show significant broadening of the $\pi^* \leftarrow \pi d$ transition when the spectra for the reduced and mixed-valence oxidation states are compared.

The properties of the mononuclear complexes containing 4,4'-dipyridylmethane and 4,4'-dipyridylamine also reflect the extent of coupling between the two pyridine rings. For the methylene-bridged ligand coordinated to ruthenium(II), the presence or absence of a proton on the free pyridine function results in a shift of the $\pi^* \leftarrow \pi d$ transition of less than 1.2×10^3 cm^{-1}. In contrast, coupling of the rings in the 4,4'-dipyridylamine manifests itself as shifts of 2.2×10^3 and 2.4×10^3 cm^{-1} in the charge-transfer transitions for the ruthenium(III) and -(II) complexes upon protonation, respectively.

Cyclic voltammetry of the (4,4'-dipyridylmethane)ruthenium(II) mononuclear complex as a function of pH indicates the difference in pK_a values for the oxidized and reduced complexes does not exceed $\sim 0.3 pK_a$ units. A difference of this size is expected to result from electrostatic interactions alone, supporting the conclusion that significant coupling between the pyridine rings does not occur.

For the ruthenium(II) 4,4'-dipyridylamine mononuclear complex, the metal center has little effect on the pK_a of the ligand. This implies that back-bonding from the ruthenium center has canceled the effect of the positive charge of the metal. Oxidation to the ruthenium(III) complex would then be expected to lower pK_a by increasing the electrostatic interaction and reducing the back-bonding. A decrease of 1.5 pK_a units is observed, but this decrease is less than that which results when the metal center is replaced by a proton (2.9 units). The shifts in pK_a observed when either a proton or a ruthenium(III) are present at one end of the ligand are considerably larger than expected from electrostatic interactions of point charges at the two pyridine nitrogens, indicating electronic coupling between the two rings is responsible for the observed shifts.

Studies on dipyridyl-bridged binuclear complexes of the ruthenium–cobalt type support the conclusions on the extent of coupling reached in this work as a function of the linkage joining the two pyridine rings.[2]

In conclusion, these studies on weakly interacting systems indicate that the major factors (apart from the obvious one of electrostatic origin) contributing to the stability of the mixed-valence relative to the isovalent state are an inherent instability of the [2,2], and the inductive effect of the 3+ charge in the mixed-valence state, with stabilization by electron delocalization making only a minor contribution. In fact, even for the Creutz–Taube ion, in which delocalization is much greater than in the systems we have studied, this stabilization is rather small. This conclusion follows on comparing the value E_f for

$$[(NH_3)_5RuN \bigcirc NRu(NH_3)_5]^{6+/5+}$$

with that of

$$[(NH_3)_5RuN \bigcirc NRh(NH_3)_5]^{6+/5+}$$
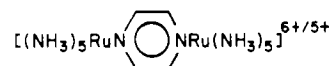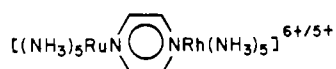
0.76 and 0.71, respectively. The inductive effects of Rh^{3+} and Ru^{3+} are expected to be the same, and the main difference between the two is that metal to metal delocalization in the Ru(II)–Rh(III) case is minor (Rh(III), it should be noted, has a πd^6 electron configuration, so that Rh(II) in the same environment will be a state at very high energy). When the 0.5-V difference is corrected for the statistical factor of 2, favoring reduction of Ru(III)–Ru(III) compared to Ru(III)–Rh(III), the stabilization of the Ru(III)–Ru(II) state attributable to delocalization in only 0.036 V or ca. 1 kcal.