

# Intervallence Transfer and Electron Transfer in the Mixed-Valence Ion $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$ <sup>1</sup>

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**Abstract:** The properties of the mixed-valence ion  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$ , including the appearance of a symmetric  $\nu(\text{pyz})$  stretch in the solution IR, are consistent with localized Ru(II) and Ru(III) valences and only slight delocalization between the ions. An intervalence transfer (IT) band appears in the near-infrared (near-IR), whose properties are predicted by the Hush theory. The rate of intramolecular thermal electron transfer calculated for the mixed-valence ion using the Hush theory compares favorably with the estimated rate of thermal electron transfer within the ion-pair for the outer-sphere reaction:  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^+ + [(\text{phen})_2\text{Ru}(\text{py})\text{Cl}]^{2+} \rightarrow [(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^{2+} + [(\text{phen})_2\text{Ru}(\text{py})\text{Cl}]^+$ . From the solvent dependence of the IT band,  $\lambda_i$  and  $\lambda_o$  have been estimated for the intramolecular electron transfer. A prediction made by the Marcus and Hush theories of outer-sphere electron transfer has been verified for  $\lambda_i$  values for intramolecular electron transfer using the ions  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$ ,  $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{4+}$ , and  $[(\text{NH}_3)_5\text{Ru}(4,4'\text{-bpy})\text{Ru}(\text{NH}_3)_5]^{5+}$ . By comparing the properties of  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$  with the properties of the Creutz and Taube ion,  $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{NH}_3)_5]^{5+}$ , it is concluded that there is a large resonance energy for the latter ion, and that it is clearly outside the weak interaction limit to which the Hush theory applies.

Hush has developed a treatment which describes the properties of intervalence transfer (IT) bands in mixed-valence compounds for cases where valences are localized and interactions between metal sites are weak.<sup>2</sup> An important element of the Hush theory is that the properties of IT bands can be used to obtain detailed information about intramolecular thermal electron transfer processes; information which is very seldom available using other experimental techniques.

For certain mixed-valence ions, e.g.,  $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{4+}$  and  $[(\text{NH}_3)_5\text{Ru}(4,4'\text{-bpy})\text{Ru}(\text{NH}_3)_5]^{5+}$ , the predictions made by Hush have been verified.<sup>3-5</sup> However, for the closely related Creutz and Taube ion,  $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{NH}_3)_5]^{5+}$ , the properties of its near-infrared (near-IR) band are far different from the predictions made by Hush.<sup>6,7</sup> There is an element of confusion introduced by the latter ion which must be clarified if the Hush theory is to be used with confidence to estimate rate data for thermal electron transfer processes. It is also essential that the predictions made by the Hush theory be verified by independent experiments, and one approach is to make comparisons with closely related outer-sphere electron transfer reactions.

## Experimental Section

**Measurements.** Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer. Ultraviolet-visible spectra were obtained using Cary Model 14, Cary Model 17, Unicam Model SP800B, or Bausch and Lomb Spectronic 210 spectrophotometers at room temperature. Near-infrared spectra were recorded on a Cary 14 spectrophotometer.

**Materials.** Nitrobenzene and propylene carbonate (Reagent Grade) were passed through a column of alumina and stored over Davison 4 Å molecular sieves. Dimethyl sulfoxide (Reagent Grade), D<sub>2</sub>O (MSD Isotopic Products), and acetonitrile (MCB, Spectrograde) were used without further purification or dried over Davison 4 Å molecular sieves. Water (H<sub>2</sub>O) was purified by distillation from alkaline permanganate. Ceric ammonium nitrate was obtained commercially (G. F. Smith). A solution of Ce(IV) perchlorate in 6 M HClO<sub>4</sub> was obtained from G. F. Smith and Co. and analyzed spectrophotometrically for Ce(IV).<sup>8</sup> All other chemicals and solvents were reagent grade and were used without further purification.

**Preparations.** The complexes  $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ru}(\text{phen})_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$ ,  $[\text{Ru}(\text{bpy})_2(\text{NO})\text{Cl}](\text{PF}_6)_2$ , and  $[\text{Ru}(\text{phen})_2(\text{NO})\text{Cl}](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$  were prepared and purified as described earlier.<sup>9</sup>

$[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2$ . The complex,  $[(\text{bpy})_2\text{Ru}(\text{NO})\text{Cl}](\text{PF}_6)_2$  (404.6 mg, 0.526 mmol), was initially dissolved in acetone (10–15 ml) and the resulting solution was protected from light. An equimolar amount of KN<sub>3</sub> (42.7 mg) dissolved in methanol

(10–15 ml) was added dropwise to the solution producing the desired, purple-red solvento complex. In a separate 125-ml round-bottom flask, an equimolar amount of  $[(\text{bpy})_2\text{Ru}(\text{pyz})\text{Cl}](\text{PF}_6)$  (354.6 mg) was dissolved in acetone (10–15 ml) and protected from light. The solution of  $[(\text{bpy})_2\text{Ru}(\text{S})\text{Cl}]^+$  (S = acetone) was then added to the solution of  $[(\text{bpy})_2\text{Ru}(\text{pyz})\text{Cl}]^+$ , and the final volume was diluted with acetone to ~70 ml. The flask was flushed with argon (10–15 min), and the solution was allowed to reflux with a continual stream of argon flowing over the mixture. After ~24 h, the solution was added dropwise to stirring anhydrous ether (~300 ml). The resulting brown-purple precipitate was collected on a glass frit and washed with CH<sub>2</sub>Cl<sub>2</sub> (~60 ml) with some loss of product. The remaining product was suspended in water (10–15 ml), protected from light, and stirred for ~1 h in order to remove the potassium hexafluorophosphate by-product. The suspension was then filtered through a glass frit, and the undissolved product was dried in a vacuum desiccator over Drierite. Yield = 467 mg (70%). Anal. Calcd for  $[\text{Ru}_2(\text{C}_{10}\text{H}_5\text{N}_2)_4(\text{C}_4\text{H}_4\text{N}_2)\text{Cl}_2](\text{PF}_6)_2$ : C, 41.7; H, 2.86; N, 11.0. Found: C, 41.4; H, 2.80; N, 11.0.

$[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_4$ . The salt,  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2$  (100.2 mg, 0.079 mmol), was dissolved in acetone (15–20 ml) and protected from light. The salt does not readily dissolve in acetone, but the addition of a small amount of acetonitrile (2–3 ml) speeds up dissolution considerably. Tetra-*n*-butylammonium chloride (~0.5 g) was added to the solution resulting in an immediate precipitation of  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]\text{Cl}_2$ . The salt was collected on a glass frit and washed with several portions (~30 ml) of acetone. The complex was then dissolved in ~1 M hydrochloric acid (10–15 ml) and protected from light. Acetonitrile (1–2 ml) was used to complete dissolution. Ceric ammonium nitrate (86.7 mg, 1.58 mmol) was added to the stirred solution which gave an immediate dark yellow color. A saturated solution of ammonium hexafluorophosphate in ~1 M hydrochloric acid (~10 ml) was quickly added giving a brown precipitate. The precipitate was collected on a glass frit and washed with several portions (~10 ml) of ~0.5 M hydrochloric acid and placed in a vacuum desiccator over Drierite overnight. Yield = 70 mg (57%). The purity of the compound was checked in the following manner. An ~10<sup>-4</sup> M solution (acetonitrile) of the complex was prepared and protected from light. One drop of 60% N<sub>2</sub>H<sub>4</sub> in H<sub>2</sub>O was added to ~10 ml of the solution. The spectrum of the resulting solution was then recorded and was essentially identical with that of the  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{2+}$  ion ([2,2]). The characteristic absorbance maximum of the [2,2] ion appeared with ~90% of the expected intensity.

$[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_3$ . The salt was prepared by the addition of the appropriate stoichiometric amounts of the fully oxidized and fully reduced complexes. The complexes  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2$  (48.8 mg, 0.039 mmol) and  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_4$  (60.0 mg, 0.039 mmol), were placed in a 50-ml erlenmeyer flask and protected from light. Acetonitrile (10–15 ml) was added and the solution stirred for ~5 min. The solution was

added dropwise to stirred anhydrous ether (~250 ml) to produce a purple-red precipitate. The salt was collected on a glass frit and air dried. Yield = 99 mg (90%). The purity of the mixed-valence complex was checked using the hydrazine reduction method used above for the fully oxidized complex.

**[Ru(bpy)<sub>2</sub>(py)Cl]PF<sub>6</sub>·H<sub>2</sub>O.** A solution of KN<sub>3</sub> (52.9 mg, 0.652 mmol) in methanol (5 ml) was added dropwise with stirring to a solution of [Ru(bpy)<sub>2</sub>(NO)Cl](PF<sub>6</sub>)<sub>2</sub> (502 mg, 0.652 mmol) in acetone (30 ml). The solution was stirred for 15 min, and pyridine (6 ml) added and the solution stirred for a further 90 min; all of the steps were carried out in subdued light. The product was precipitated by filtering the solution into a large excess (ca. 250 ml) of ether, and was filtered and dried in vacuo. The brown solid was recrystallized from methylene chloride/pentane, and then acetone/ether. Yield 300 mg, 70%. Anal. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)Cl]PF<sub>6</sub>·H<sub>2</sub>O: C, 43.5; H, 3.35; N, 10.1. Found: C, 43.6; H, 3.26; N, 10.1.

**Preparation of [Ru(phen)<sub>2</sub>(py)Cl]PF<sub>6</sub>·H<sub>2</sub>O.** This complex was prepared using essentially the same method as given above for the bipyridine complex, but using [Ru(phen)<sub>2</sub>(NO)Cl](PF<sub>6</sub>)<sub>2</sub> as the starting material. Yield, 90%. Anal. Calcd for [Ru(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)Cl]PF<sub>6</sub>·H<sub>2</sub>O: C, 47.1; H, 3.14; N, 9.5. Found: C, 46.6; H, 2.81; N, 9.7.

**Preparation of [Ru(phen)<sub>2</sub>(py)Cl](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O.** The Ru(III) complex was prepared using a method developed by Johnson.<sup>10</sup> The salt [Ru(phen)<sub>2</sub>(py)Cl]PF<sub>6</sub>·H<sub>2</sub>O (300 mg, 0.406 mmol) was ground with HCl (5 ml of 0.5 M) in a mortar and pestle in the dark for 1 min. A solution of Ce(IV) in 6 M HClO<sub>4</sub> (0.32 M; 1.4 ml, 0.448 mol) was added slowly with grinding, and the total volume of the solution was brought to 10 ml by the addition of 0.50 M HCl. The mixture was ground for 10 min, NaClO<sub>4</sub> (2.8 g, 23 mmol) was added, and the mixture ground for a further minute. The green solid was filtered, washed with ice-cold 0.5 M HClO<sub>4</sub> and ether, and dried in vacuo. Yield 270 mg, 84%. Anal. Calcd for [Ru(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)Cl](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O: C, 43.0; H, 3.06; N, 8.6. Found: C, 43.0; H, 2.62; N, 8.7.

**Preparation of [Ru(bpy)<sub>2</sub>(py)Cl](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.** The Ru(III) complex was prepared using an analogous method to that given for the phen complex. Yield, 90%. Anal. Calcd for [Ru(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)Cl](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O: C, 41.3; H, 2.92; N, 9.6. Found: C, 41.1; H, 3.00; N, 9.6.

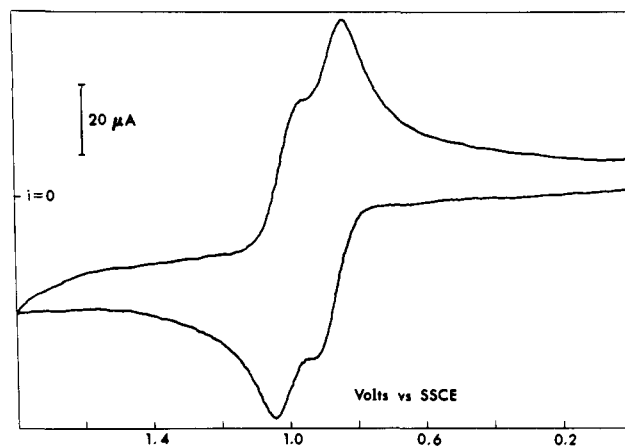
**Solutions.** Solutions in dry acetonitrile were stable in the absence of light for several days. However, even in normal laboratory lighting, considerable decomposition (presumably substitution) occurred rapidly. Consequently, all solutions used for spectral, electrochemical or kinetic measurements were protected from the light.

**Kinetic Measurements.** Kinetic measurements were made using an Aminco stopped-flow apparatus with a Beckman-DU unit as a monochromator. The drive syringes and mixing chamber were thermostated using a Forma Scientific Model 2220 circulator-water bath. Condensation of atmospheric moisture at lower temperatures was prevented by passing a stream of dry nitrogen through the cell compartment.

The photomultiplier voltage output from the spectrometer was amplified, and either displayed on a Tektronix Model 564B storage oscilloscope or passed through an analog/digital converter and analyzed by a Raytheon 706 computer using the program WIGWAM 04.<sup>11</sup> In the second case, the data were displayed (using the computer program) on a Hewlett-Packard Model 7004B X-Y recorder.

The solutions were made up immediately prior to use, and protected from the light. All kinetic runs were obtained by mixing solutions of Ru(bpy)<sub>2</sub>(py)Cl<sup>+</sup> and Ru(phen)<sub>2</sub>(py)Cl<sup>2+</sup>, and following the optical density changes at either 290 (absorbance decrease) or 266 nm (absorbance increase). The concentrations of the complexes were varied over the range 1.4–4.4 × 10<sup>-6</sup> M. In all cases the reaction was found to be first order to two half-lives or more. No supporting electrolyte was added since the reaction rate increases with increasing ionic strength, and the rate at the complex concentrations used was close to the limit allowed by the instrumentation.

**Electrochemical Measurements.** All electrochemical measurements were made at platinum electrodes vs. the saturated sodium chloride calomel electrode (ssce), and are uncorrected for junction potentials. In all experiments, standard three-electrode operational amplifier circuitry was used as described previously<sup>12</sup> with a PAR Model 173 potentiostat for potential control and a PAR Model 175 Universal programmer as a sweep generator for voltammetric experiments. All measurements were carried out in acetonitrile solution containing 0.1 M [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]PF<sub>6</sub> (TBAH) as the supporting electrolyte, in a



**Figure 1.** A 200 mV/s cyclic voltammogram of [(bpy)<sub>2</sub>ClRu(py)RuCl(bpy)<sub>2</sub>]<sup>2+</sup> (3.0 × 10<sup>-3</sup> M) in 0.1 M TBAH-CH<sub>3</sub>CN.

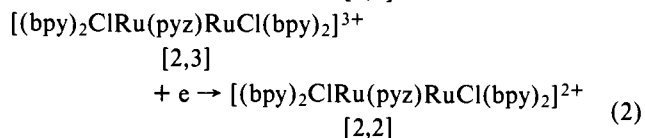
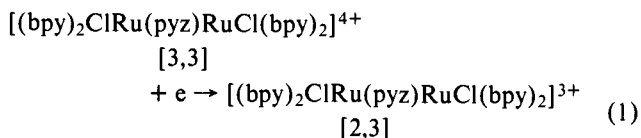
thermostated cell with a Forma Scientific Model 2095 circulator-water bath for temperature control.

Half-wave potentials ( $E_{1/2}$ ) for the Ru(III)/Ru(II) couples and electrochemical reversibility were determined by cyclic voltammetry and stirred solution voltammetry. In cyclic voltammetry, reversibility was based on the ratio of cathodic to anodic currents ( $i_c/i_a$ ) and the separation in potential of the peaks ( $\Delta E_p$ ). A more precise criterion is obtained from a plot of potential ( $E$ ) vs.  $\log(i_L - i)/i$  (where  $i_L$  is the limiting current) using stirred-solution voltammetry where a slope of 59 mV indicates kinetic reversibility. The complex concentrations were 3–4 × 10<sup>-3</sup> M in all measurements.

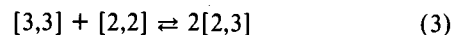
## Results

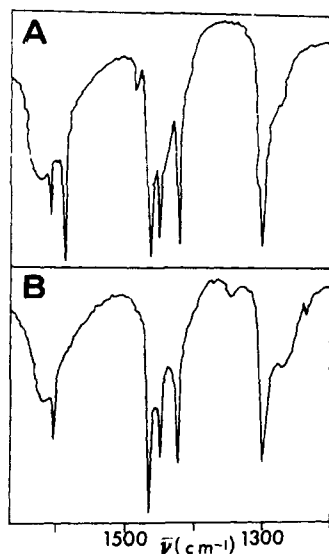
**Electrochemistry.** A cyclic voltammogram of [(bpy)<sub>2</sub>ClRu(py)RuCl(bpy)<sub>2</sub>]<sup>2+</sup> in 0.1 M [N(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]PF<sub>6</sub>-acetonitrile vs. the ssce at 25 ± 2 °C is shown in Figure 1. There are two anodic waves in the potential region 0–2.0 V.  $E_{1/2}$  values for the two waves are at 0.89 and 1.01 V. The  $E_{1/2}$  values were calculated from the cyclic voltammograms ( $E_{p,a} - E_{p,c}/2$ ). The peak separation for each wave is somewhat larger ( $\Delta E_p = 75$ –80 mV) than theoretically predicted ( $\Delta E_p = 58$  mV) for an electrochemically reversible process. Brown has suggested that under our experimental conditions uncompensated solution resistance can cause an increase in the observed  $\Delta E_p$  values.<sup>13</sup> It has also been suggested that the large  $\Delta E_p$  values could result from the close proximity of the two waves.<sup>13</sup> Since the current is additive for each process, the result could be a slight apparent increase in  $\Delta E_p$ . Variation of the scan rate (50–500 mV/s) showed no appreciable change in peak positions. Also, the ratio of anodic to cathodic peak currents ( $i_{p,a}/i_{p,c}$ ) was ~1 for each of the processes.

Coulometry experiments showed that each of the two waves is a one-electron transfer process (eq 1 and 2).

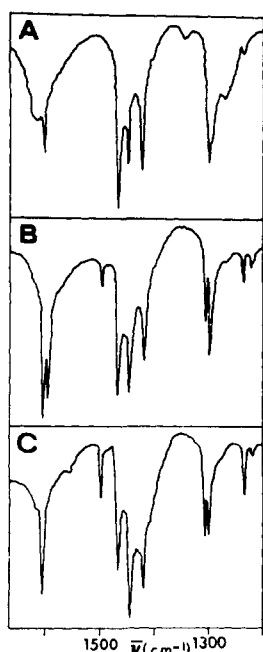


Using the abbreviations [3,3] for the 4+ ion, [2,3] for the 3+ ion, and [2,2] for the 2+ ion,  $K$  for the conproportionation equilibrium in eq 3 is 10<sup>2</sup> as calculated from the  $E_{1/2}$  values at 25 ± 2 °C.





**Figure 2.** Solution infrared spectra ( $\text{CD}_3\text{CN}$ ) of  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^+$  (A) and  $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{2+}$  (B) (some absorbance by  $\text{H}_2\text{O}$  occurs in the  $\sim 1600\text{-cm}^{-1}$  region).



**Figure 3.** Solution infrared spectra ( $\text{CD}_3\text{CN}$ ) of  $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{2+}$  (A),  $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{3+}$  (B), and  $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{4+}$  (C) (some absorbance by  $\text{H}_2\text{O}$  appears in the  $1600\text{-cm}^{-1}$  region).

The equilibrium constants in 0.1 M  $[\text{N}(\text{n-C}_4\text{H}_9)_4] \text{PF}_6^-$  acetonitrile and in pure acetonitrile appear to be essentially the same, which is expected from the charge types involved in the equilibrium. Solutions of [2,3] have the same  $\nu_{\text{max}}$  and  $\epsilon$  values in both media ( $\pm 5\%$ ).

From the value of  $K$ , solutions containing [2,3] also contain  $\sim 10\%$  of the [2,2] and [3,3] ions. Quantitative calculations based on [2,3], which appear later in the paper, have been corrected for the equilibrium.

**Ultraviolet-Visible Spectra.** Table I lists  $\lambda_{\text{max}}$  values and extinction coefficients for the ions  $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{n+}$  ( $n = 2$ , [2,2];  $n = 3$ , [2,3];  $n = 4$ , [3,3]). Spectral data are also given for the parent ions  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^{n+}$  ( $n = 1, 2$ ). The [2,3] and [3,3] ions are stable in acetonitrile with only slight decomposition ( $\sim 10\%$ ) after 1–2

**Table I.** Electronic Spectra of the Ions  $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{n+}$  ( $n = 2, 3, 4$ ) and  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^{n+}$  ( $n = 1, 2$ ) in Acetonitrile

Complex	$\lambda_{\text{max}}^a$	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ ) <sup>b</sup>
$[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^+$	478	$9.9 \times 10^3$
	384	$8.4 \times 10^3$
	350 (sh)	
	292	$5.0 \times 10^4$
$[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^{2+ c}$	243	$2.0 \times 10^4$
	423	$2.0 \times 10^3$
	312	$2.8 \times 10^4$
	300	$2.8 \times 10^4$
	246	$2.7 \times 10^4$
$[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{2+}$	513	$2.6 \times 10^4$
	497 (sh)	
	339	$1.2 \times 10^4$
	292	$9.2 \times 10^4$
	243	$3.8 \times 10^4$
$[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{3+}$	508	$1.4 \times 10^4$
	475 (sh)	
	310 (sh)	
	292	$6.0 \times 10^4$
	244	$4.1 \times 10^4$
$[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{4+}$	430	$4.0 \times 10^3$
	310	$5.0 \times 10^4$
	300	$5.0 \times 10^4$
	246	$4.9 \times 10^4$

<sup>a</sup>  $\pm 2$  nm in acetonitrile. <sup>b</sup> Estimated error in  $\epsilon$  values is  $\pm 5\%$ .

<sup>c</sup> Species generated in solution by suspending  $\text{PbO}_2$  in a solution of the complex and then filtering.

h if protected from light. Trace water in the solvent causes some reduction of Ru(III), but the addition of one drop of  $\sim 1$  M  $\text{HClO}_4$  per 50 ml of acetonitrile prevents the reaction. Solid samples of the +4 ion were stable for weeks when protected from moisture.

**Infrared Spectra.** Figures 2 and 3 show the infrared spectra ( $\text{CD}_3\text{CN}$ ) for  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^+$  and [2,2], and the [2,2], [2,3], and [3,3] ions in the region  $1200\text{--}1600 \text{ cm}^{-1}$ . For the [2,3] ion, a band is observed at  $1599 \text{ cm}^{-1}$  which is not present for the [2,2] or [3,3] ions, but which appears for  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^+$ . The other bands in this region are characteristic of bis(2,2'-bipyridine) complexes of Ru(II) or Ru(III). Except for the band at  $1599 \text{ cm}^{-1}$ , the spectrum of the [2,3] ion is the sum of the spectra of the [3,3] and [2,2] ions. The estimated error in the infrared values is  $\pm 2 \text{ cm}^{-1}$ .

**Near-Infrared Spectra.** The near-infrared (near-IR) spectra of the [2,2], [2,3], and [3,3] ions ( $\sim 10^{-3}$  M) were recorded in acetonitrile using 1.0-cm matched Infrasil cells from 2200 to 800 nm. No bands were found in this region for the [2,2] or [3,3] ions, but a band was observed at 1300 nm ( $0.769 \mu\text{m}^{-1}$ ) for the [2,3] ion ( $\epsilon 455 \text{ M}^{-1} \text{cm}^{-1}$ , Figure 4). In addition, the band displayed a solvent dependence as shown by the data in Table II. The near-infrared spectrum of the [2,3] ion was recorded in  $\text{CD}_3\text{CN}$  out to 2600 nm, and no new bands were found in the 2200–2600-nm region.

In a preliminary communication<sup>14</sup> it was reported that a near-IR band could not be observed for [2,3]. The earlier work failed to appreciate the relatively low intensity of the IT band, and the photolability of the [2,3] ion.

**Data for the Self-Exchange Experiment.** The half-wave potentials for the  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^{3+/2+}$  and  $[\text{Ru}(\text{phen})_2(\text{py})\text{Cl}]^{3+/2+}$  couples were measured in acetonitrile in the range  $5\text{--}35^\circ \text{C}$ . Both couples were electrochemically reversible ( $\Delta E_p = 59\text{--}61 \text{ mV}$ ), and the measured values are given in Table III.

For a reversible reaction,  $E_{1/2}$  differs from a formal re-

**Table II.** Solvent Dependence of the Near-Infrared Band Maximum for  $[(bpy)_2ClRu(py)RuCl(bpy)_2]^{3+}$ 

Solvent	$\lambda_{max}$ ( $\pm 10$ nm)	$(1/n^2 - 1/D_s)^a$
Water (D <sub>2</sub> O)	1270	0.546
Acetonitrile	1300	0.526
Propylene carbonate	1335	0.481
Dimethyl sulfoxide	1365	0.438
Nitrobenzene	1400	0.384

<sup>a</sup> Values calculated using indices of refraction and bulk dielectric constants found in: A. J. Gordon and R. A. Ford, "The Chemist's Companion", Interscience, New York, N.Y., 1972, pp 4-11.

**Table III.**  $E_{1/2}$  Values for the  $[Ru(bpy)_2(py)Cl]^{2+/+}$  and  $[Ru(phen)_2(py)Cl]^{2+/+}$  Couples in Acetonitrile

$T^a$	$E_{1/2}$ (V vs. ssce)	
	$[Ru(bpy)_2(py)Cl]^{3+/2+ b}$	$[Ru(phen)_2(py)Cl]^{3+/2+ b}$
5.0	0.776	0.785
15.0	0.777	0.784
20.0	0.777	0.782
25.0	0.785	0.778
35.0	0.784	0.788

<sup>a</sup> °C,  $\pm 0.1^\circ$ . <sup>b</sup>  $\pm 0.005$  V.

**Table IV.** Temperature Dependence of the Self-Exchange Reaction

$T, ^\circ C$	$k_{ex}$
5.7	$3.1 (\pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1} a$
15.0	$4.1 (\pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1} b$
25.0	$4.9 (\pm 0.3) \times 10^7 \text{ M}^{-1} \text{ s}^{-1} c$

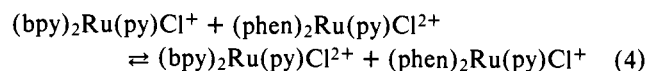
<sup>a</sup> Mean of 42 runs; error is standard deviation. <sup>b</sup> Mean of 41 runs; error is standard deviation. <sup>c</sup> Mean of 25 runs; error is standard deviation.

duction potential by a term involving diffusion coefficients which is usually small:

$$E_{1/2} = E' - \frac{0.059}{n} \log \frac{D_{red}}{D_{ox}}$$

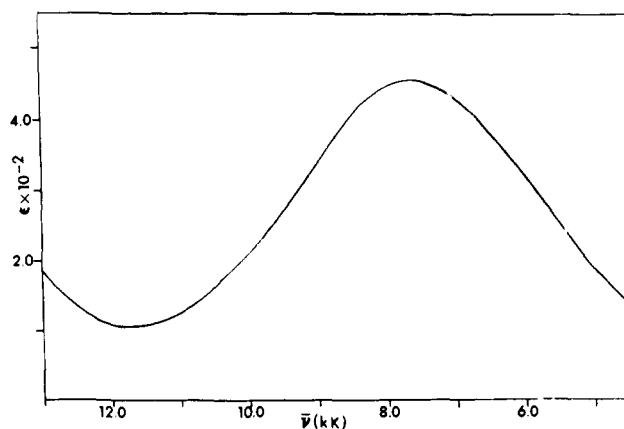
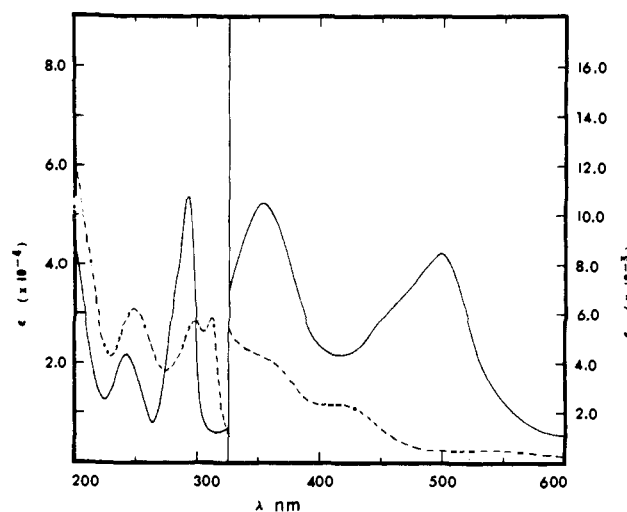
where  $E'$  is the formal potential, uncorrected for junction effects. Since the ratios of the diffusion coefficients, and the junction potentials at the reference electrode should be essentially identical for the two couples, the identity of the half-wave potentials (within experimental error) for the two couples is interpreted to indicate that their formal reduction potentials are also identical.

For the net reaction studied kinetically:

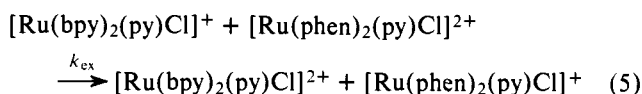


$\Delta E^{0'}$  =  $0.00 \pm 0.01$  V and  $K$  =  $1.0 \pm 0.5$ . The visible-UV spectra of the Ru(II) and Ru(III) forms of the complexes  $Ru(bpy)_2(py)Cl^{2+/+}$  and  $Ru(phen)_2(py)Cl^{2+/+}$  in acetonitrile solution are given in Figures 5 and 6, respectively.

In one experiment, stoichiometric quantities of  $Ru(bpy)_2(py)Cl^+$  and  $Ru(phen)_2(py)Cl^{2+}$  were mixed and the spectrum of the resultant solution is given in Figure 7. Also shown in Figure 7 is a computed spectrum assuming equimolar concentrations for all four Ru species. The close matching between the two curves reinforces a value  $K$  = 1.0 for the equilibrium in eq 4.

**Figure 4.** Near-infrared spectrum of  $[(bpy)_2ClRu(py)RuCl(bpy)_2]^{3+}$  in acetonitrile.**Figure 5.** Visible-UV spectra of  $[Ru(bpy)_2pyCl]^+$  (—), and  $[Ru(bpy)_2pyCl]^{2+}$  (---) in acetonitrile solution.

**Kinetics.** The rate of the net reaction in eq 5 was studied at three temperatures, and the results are given in Table IV.



The observed rate constants,  $k'$ , were first order, regardless of the relative concentrations of the two solutions, and second-order rate constants,  $k_{ex}$ , were computed using the relationship developed in ref 15. The reaction rates were close to the physical limits of the instrumentation and, consequently, rate data were obtained at very low reactant concentration ( $1.4$ – $4.4 \times 10^{-6}$  M), resulting in high signal-to-noise ratios. Several runs were carried out at each concentration and temperature to allow a statistically meaningful treatment of the data. From a plot of  $\ln k$  vs.  $1/T$  the activation parameters for the self-exchange reactions are:  $E_a$  =  $3.9 \pm 0.6$  kcal/mol whence  $\Delta H^\ddagger$  =  $E_a - RT$  =  $3.3 \pm 0.6$  kcal/mol,  $\Delta G^\ddagger$  ( $25^\circ$ ) =  $7.0 \pm 0.1$  kcal/mol,  $\Delta S^\ddagger$  ( $25^\circ$ ) =  $-12 \pm 2$  eu.

## Discussion

**Oxidation State Description of the Mixed-Valence Ion.** Room temperature ESCA<sup>16</sup> and low temperature Mossbauer<sup>17</sup> experiments indicate that equal amounts of Ru(II) and Ru(III) exist in solid samples of the [2,3] ion. Because of the relatively long lifetime of the Mossbauer experiment the rate of electron transfer between the two metal centers must be slower than

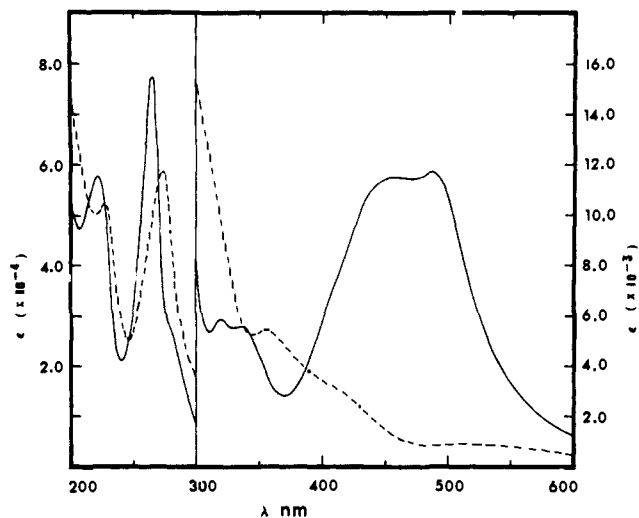


Figure 6. Visible-UV spectra of  $[\text{Ru}(\text{phen})_2\text{pyCl}]^+$  (—), and  $[\text{Ru}(\text{phen})_2\text{pyCl}]^{2+}$  (---) in acetonitrile solution.

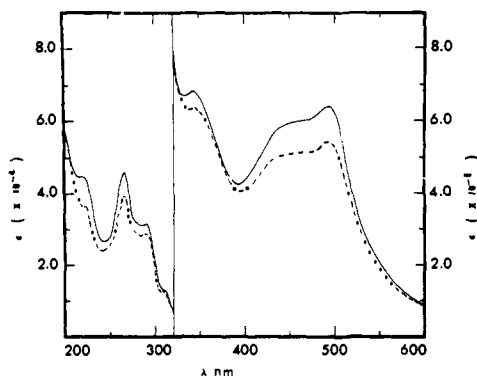


Figure 7. Visible-UV spectrum of reaction mixture after mixing equimolar quantities of  $[\text{Ru}(\text{bpy})_2\text{pyCl}]^+$  and  $[\text{Ru}(\text{phen})_2\text{pyCl}]^{2+}$  in acetonitrile solution (—), and a calculated spectrum assuming equimolar amounts of the Ru(II) and Ru(III) forms of both cations (---).

$10^7$ – $10^9$   $\text{s}^{-1}$  at the temperature of the experiment ( $\sim 4$  K).

The Mossbauer and ESCA results are not entirely conclusive. The [2,3] ion is favored only slightly in solution (eq 3), and the solid state could consist of equal amounts of [2,2] and [3,3] salts. In the solid state the Creutz and Taube system exists as the mixed-valence ion,  $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{NH}_3)_5]^{5+}$ . ESCA<sup>16</sup> and low temperature ( $\sim 40$  K) Mossbauer results<sup>18</sup> indicate distinct Ru(II) and Ru(III) sites, but the important observation is that solid state electronic spectra, including the appearance of the intervalence transfer band of the mixed-valence ion, are essentially the same in the solid state and in dilute aqueous solutions of the ion at 25 °C.<sup>19</sup> Given the pentaammine results, there is no precedence for significant disproportionation in solid samples of  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$ .

It is also conceivable that a change in electronic structure could occur upon cooling solid samples of the [2,3] ion. However, the consistency of the results at 4 K (Mossbauer experiment) and room temperature (ESCA experiment) appear to rule out this possibility. Finally, it should be noted that assignment of localized valences based on the appearance of different peaks in an ESCA spectrum has been questioned by Hush.<sup>20</sup> Hush has shown that for a symmetrical, delocalized ground state there are two accessible unsymmetrical photoionized states, and that the peak separation arising from the two photoionized states can be close to that for isolated M(II) and M(III) ions.

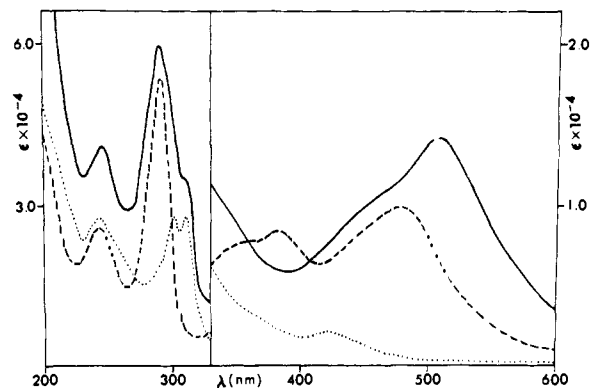


Figure 8. Electronic spectra of  $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{3+}$  (—),  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^+$  (---), and  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^{2+}$  (···) in acetonitrile.

The electronic spectra of the [2,3] ion and of the parent Ru(II),  $[(\text{bpy})_2\text{Ru}(\text{pyz})\text{Cl}]^+$ , and Ru(III),  $[(\text{bpy})_2\text{Ru}(\text{pyz})\text{Cl}]^{2+}$ , complexes in acetonitrile are shown in Figure 8. The spectrum of the [2,3] ion is essentially the sum of the spectra of the monomeric Ru(II) and Ru(III) complexes both in the UV and visible. The only exception is the shift in the  $t_2[\text{Ru}(\text{II})] \rightarrow \pi^*(\text{pyz})$  CT band from 384 nm in  $[(\text{bpy})_2\text{Ru}(\text{pyz})\text{Cl}]^+$  to 508 nm in [2,3]. Similar shifts in related complexes have been attributed to stabilization of the MLCT excited state by the positive charge of the remote ion.<sup>4,21</sup>

The remaining absorption bands for [2,3] are also found in either the monomeric Ru(II) or Ru(III) complexes. The spectral similarities indicate that discrete Ru(II) and Ru(III) sites are present in the dimers and that the electronic environments at the two sites are little changed from the monomeric complexes. The pattern of  $\pi \rightarrow \pi^*(\text{bpy})$  bands at  $\sim 300$  nm in bis(2,2'-bipyridine)ruthenium complexes is dependent in a systematic way upon whether the ruthenium ion is Ru(II) or Ru(III).<sup>22–24</sup> Evidence for both Ru(II) and Ru(III) sites in the dimer comes from the appearance of the intense band at 292 nm and the shoulder at 310 nm. Shoulders also appear in the dimer in the same spectral regions as the  $t_2[\text{Ru}(\text{II})] \rightarrow \pi^*(\text{bpy})$  (478 nm) and  $\pi(\text{Cl}) \rightarrow t_2[\text{Ru}(\text{III})]$  (423 nm) transitions for  $[(\text{bpy})_2\text{Ru}^{\text{II}}(\text{pyz})\text{Cl}]^+$  and  $[(\text{bpy})_2\text{Ru}^{\text{III}}(\text{pyz})\text{Cl}]^{2+}$ , respectively. The  $t_2[\text{Ru}(\text{II})] \rightarrow \pi^*(\text{bpy})$  transition in  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{Cl}]$  type complexes is known to be sensitive to fairly slight changes in the remaining ligand.<sup>25</sup> The similarity in energies for the transition for the monomer and mixed-valence dimer argues that the influence of the remote Ru(III) site on the  $t_2(d\pi)$  levels of Ru(II) is small, and therefore, that the metal–metal interaction cannot be appreciable. The same conclusion is reached from the electrochemical data. The potentials for the [2,3]  $\rightarrow$  [2,2] and [3,3]  $\rightarrow$  [2,3] couples are close to the value for the  $[(\text{bpy})_2\text{Ru}(\text{pyz})\text{Cl}]^{2+/+}$  couple in the same medium even though the charge types involved are different.

The conclusions reached for [2,3] can be contrasted to the conclusions reached for the ion  $[(\text{bpy})_2\text{ClRuORuCl}(\text{bpy})_2]^{2+}$ .<sup>26</sup> For the oxo-bridged dimer the electronic spectrum and redox properties bear no resemblance to related complexes of Ru(II) or Ru(III), and the ion is apparently delocalized.

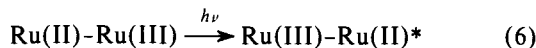
The most important aspect of the solution ( $\text{CD}_3\text{CN}$ ) infrared spectrum for the [2,3] ion is the appearance of the moderately intense band at  $1599$   $\text{cm}^{-1}$  since the band is not present for either the [2,2] or [3,3] ions (Figure 3). The band occurs at nearly the same energy ( $1589$   $\text{cm}^{-1}$ ) as the band assigned as  $\nu(\text{pyz})$  in the monomeric complex  $[(\text{bpy})_2\text{Ru}(\text{pyz})\text{Cl}]^+$ .<sup>27a</sup> The  $\nu(\text{pyz})$  ( $\nu_{8g}$ ) band is a symmetrical stretch and infrared inactive in the  $D_{2h}$  symmetry of the free ligand.<sup>27b</sup> When bound as a monodentate ligand, the  $D_{2h}$  symmetry is

lost, the transition becomes dipole allowed, and the band appears in the infrared.<sup>27c</sup> In the [2,2] and [3,3] ions, effective local  $D_{2h}$  symmetry is apparently reestablished at the pyrazine and the band is absent in the IR.

In  $[(bpy)_2ClRu(py)RuCl(bpy)_2]^{3+}$ , local  $D_{2h}$  symmetry will be lost if there are discrete Ru(II) and Ru(III) sites on the lifetime of the infrared experiment.  $\nu(py)$  appears in the IR for [2,3]. Electron transfer between the Ru(II) and Ru(III) sites must be slow on the infrared time scale and, therefore, there are localized Ru(II) and Ru(III) sites in the mixed-valence ion.

Two other explanations could account for the appearance of the  $\nu(py)$  band. The local  $D_{2h}$  symmetry at pyrazine would be lost if there were preferred rotamers in the dimer because of the low symmetry at the ruthenium sites. This explanation seems unlikely because  $\nu(py)$  is not observed for the [2,2] and [3,3] dimers. Also, a moderately intense 2,2'-bipyridine vibration  $\nu(bpy)$ , occurs in the same region as  $\nu(py)$  (at 1604 and 1606  $cm^{-1}$  for the [2,2] and [3,3] ions, respectively, Figure 3). The band at 1599  $cm^{-1}$  is nearly within experimental error ( $\pm 2 cm^{-1}$ ) of the bpy bands. The band at 1599  $cm^{-1}$  could be  $\nu(bpy)$  for Ru(II) and the 1604- $cm^{-1}$  band  $\nu(bpy)$  for Ru(III), an interpretation which is also consistent with localized valences. However, this explanation seems unlikely since in the unsymmetrical +3 and mixed-valence +4 ions,  $[(NH_3)_5Ru(py)RuCl(bpy)_2]^{n+}$  ( $n = 3, 4$ ), both  $\nu(py)$  (1595  $cm^{-1}$ ) and  $\nu(bpy)$  (1605  $cm^{-1}$ ) are present in  $CD_3CN$ .<sup>27a</sup>

**Intervallence Transfer.** An absorption band is observed in the near-IR spectrum of the [2,3] ion (Figure 4) which can be assigned to an IT transition (eq 6). Bands are not observed in this region for the [2,2] and [3,3] ions.



In the [2,3] ion there appear to be localized valences and weak metal-metal interactions, and the treatment given by Hush<sup>2</sup> should apply to the properties of the IT band.

Assuming a Gaussian band shape, a lower limit for the bandwidth at room temperature can be calculated from eq 7 where  $\bar{\nu}_{max}$  is the IT band maximum and  $\bar{\nu}_{1/2}$  the bandwidth at half-height (both in  $\mu m^{-1}$ ).

$$\bar{\nu}_{max} = (\bar{\nu}_{1/2})^2 / 2.31 \quad (7)$$

Since  $\bar{\nu}_{max} = 0.77 \mu m^{-1}$  in acetonitrile, the calculated value for  $\bar{\nu}_{1/2}$  is 0.42  $\mu m^{-1}$  which is in good agreement with the experimental value of 0.49  $\mu m^{-1}$ .

The IT band for  $[(bpy)_2ClRu(py)RuCl(bpy)_2]^{3+}$  is essentially Gaussian with perhaps a shoulder appearing at lower energies. This distortion may affect somewhat the comparison made using eq 7. The appearance of a shoulder could conceivably mean that more than one IT band exists. Multiple IT bands could occur because of the nondegeneracies in the Ru(II)  $t_2$  donor and Ru(III)  $t_2$  acceptor orbitals arising from the low symmetry at the ruthenium ion sites.

The energy of the IT band,  $E_{op}$ , is shown plotted against  $1/n^2 - 1/D_s$  in Figure 9 where  $n^2$  and  $D_s$  are the optical and static dielectric constants of the solvent, respectively. The predicted linear relationship is found. The deviation of the  $D_2O$  value from the line drawn in Figure 9 may reflect the ability of the relatively small water molecule to penetrate somewhat between the planar bipyridine ligands. In that case the dielectric continuum approximation used to predict the linear relation is not fully appropriate. Strong association of water molecules with 2,2'-bipyridine complexes has been noted previously.<sup>28-30</sup> The sensitivity of  $E_{op}$  to changes in solvent is less for  $[(bpy)_2ClRu(py)RuCl(bpy)_2]^{3+}$  than for  $[(NH_3)_5Ru(4,4'-bpy)Ru(NH_3)_5]^{5+4}$  which is expected given the larger size of the 2,2'-bipyridineruthenium sites (see eq 23 in the next section).

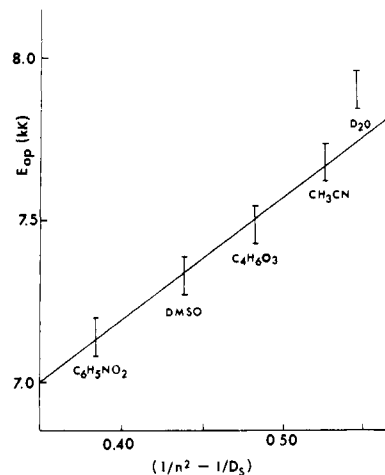


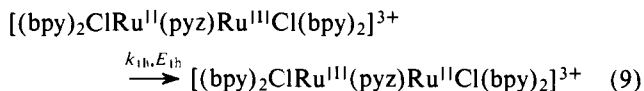
Figure 9. Plot of  $(1/n^2 - 1/D_s)$  vs.  $E_{op}$  for the IT transition in  $[(bpy)_2ClRu(py)RuCl(bpy)_2]^{3+}$ .

The extent of delocalization of the exchanging electron in mixed-valence ions can be estimated from the properties of their IT bands.<sup>2,31</sup> A measure of delocalization in both the ground and excited states is  $\alpha^2$  which can be calculated from eq 8, where  $d$  is the internuclear separation between ruthenium ions (in Å) and  $\epsilon_{max}$  the molar extinction coefficient at  $\bar{\nu}_{max}$ . The experimental  $\alpha^2$  value is the average of  $\alpha^2$  values for the ground and mixed-valence (vertical) excited states. If delocalization is small, the electronic wave functions used for overlap are relatively unperturbed, and  $\alpha^2$  is a direct measure of delocalization in the ground state. Using the values  $d = 6.9 \text{ \AA}$ ,<sup>32a</sup>

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\epsilon_{max}\bar{\nu}_{1/2}}{\bar{\nu}_{max}d^2} \quad (8)$$

and in acetonitrile,  $\bar{\nu}_{max} = 0.77 \mu m^{-1}$ ,  $\bar{\nu}_{1/2} = 0.49 \mu m^{-1}$ , and  $\epsilon = 455 M^{-1} cm^{-1}$  gives  $\alpha^2 = 2.6 \times 10^{-3}$ . The value for  $\alpha^2$  is in the same range as values calculated for the unsymmetrical dimer  $[(NH_3)_5Ru^{III}(py)Ru^{II}Cl(bpy)_2]^{4+}$  ( $\alpha^2 = 2.6 \times 10^{-3}$ )<sup>3</sup> and for the trimer  $[(NH_3)_5Ru^{III}(py)Ru^{II}(bpy)_2(py)-Ru^{III}(NH_3)_5]^{8+}$  ( $\alpha^2 = 1.3 \times 10^{-3}$  per Ru(III)-Ru(II) unit)<sup>33</sup> in the same medium. In all three cases there is good evidence for localized valences, delocalization from Ru(II) to Ru(III) is less than 1%,<sup>2,27a,31</sup> and the properties of the IT bands are accounted for satisfactorily by the Hush theory.

**Thermal Electron Transfer.** Hush has shown that for a symmetrical complex the relationship between  $E_{op}$  for the light-induced electron transfer process (eq 6) and the energy of activation ( $E_{th}$ ) for the related thermal electron transfer process (eq 9) is given by eq 10.<sup>2</sup>



$$E_{op} \geq 4E_{th} \quad (10)$$

If delocalization from Ru(II) to Ru(III) is slight,

$$E_{op} \sim 4E_{th} \quad (10a)$$

or including the effect of the resonance or delocalization energy  $\beta$ ,

$$E_{th} \sim \frac{E_{op}}{4} - \beta \quad (10b)^{32}$$

For reaction 9,  $T\Delta S^* \sim 0$ ,<sup>34</sup> and the thermal rate constant can be written as,

$$k_{th} = \nu_{et} \exp[-(\Delta G^*/RT)] \sim \nu_{et} \exp[-(E_{th}/RT)] \quad (11)$$

Estimates for the frequency factor,  $\nu_{\text{et}}$ , of  $\sim 10^{11} \text{ s}^{-1}$  are available from the results of excited state quenching experiments.<sup>35-37</sup> A value of  $10^{11} \text{ s}^{-1}$  may be too low for reaction 9 for two reasons. Experiments using time-resolved psec. spectroscopy give a direct estimate for  $\nu_{\text{et}}$ , but if  $\Delta G^\circ$  is large and favorable the measured rate constant gives only a lower limit for  $\nu_{\text{et}}$  since this corresponds to electron transfer in the "abnormal free energy region".<sup>38-40</sup> The frequency factor for electron transfer is given very crudely by eq 12 where  $\beta$  is the delocalization or resonance energy and  $h$ , Planck's constant.<sup>41</sup>

$$\nu_{\text{et}} \sim 4\beta/h \quad (12)^{42}$$

In the quenching experiments, electron transfer occurs by an outer-sphere mechanism and the resonance energy between quencher and excited state is probably small,<sup>35</sup> and certainly smaller than the resonance energy across the bridging pyrazine in  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$ .

If delocalization is small the resonance energy should be about the same in the activated complex as in the ground state. The resonance energy in [2,3] can be estimated crudely as  $\beta \leq 0.049 \text{ eV}$  from eq 13 which gives  $\nu_{\text{et}} \leq 5 \times 10^{13} \text{ s}^{-1}$ .

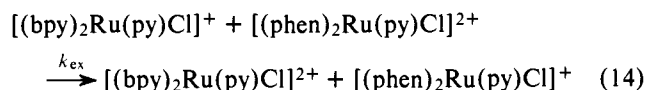
$$\beta \leq \alpha \bar{\nu}_{\text{max}} \quad (13)^{2b,32a}$$

Choosing the value above for  $\beta$  and using eq 10b gives  $E_{\text{th}} \geq 4.4 \text{ kcal/mol}$ . Taking this value for  $E_{\text{th}}$ , the estimate of  $\nu_{\text{et}}$  given above, and using eq 11 gives that  $k_{\text{th}} < 3 \times 10^{10} \text{ s}^{-1}$  for the [2,3] ion in acetonitrile solution at 25 °C.

The value calculated for  $k_{\text{th}}$  using the Hush approximation and eq 11 is only an estimate, but it is important to establish whether or not the value is correct even to within an order of magnitude. The direct measurement of electron transfer rates through bridging ligands has been achieved in certain unsymmetrical complexes where the rate of electron transfer is slow,<sup>43-45</sup> but experimental methods for measuring rates for reactions like 9 have remained elusive. For a weak interaction case where the properties of the IT band are accounted for satisfactorily by the Hush theory, the observation of an IT band demonstrates the existence of the related thermal process, and so evidence for thermal electron transfer can be obtained even through long bridging ligands.<sup>3-5,33</sup> If in addition,  $k_{\text{th}}$  can be estimated as described above, rate comparisons between systems can be made conveniently since measurements of  $E_{\text{op}}$  are relatively straightforward.

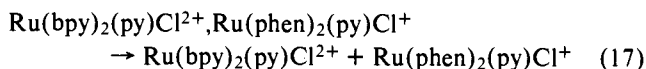
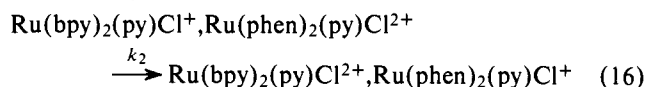
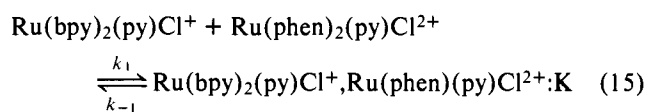
An upper limit for  $k_{\text{th}}$  in  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$  can be obtained from the  $\nu(\text{pyz})$  infrared band (Figure 3). The lifetime of the IR excited state can be estimated from the uncertainty principle and the band width at half height. Using an estimated band width of  $15 \text{ cm}^{-1}$  gives  $\Delta t \geq 2 \times 10^{-13} \text{ s}$  and since the rate of thermal electron transfer must be slow on this time scale,  $k_{\text{th}} < 5 \times 10^{12} \text{ s}^{-1}$ . The estimate of  $\Delta t$  is only approximate since other effects may broaden the IR band,<sup>46</sup> but it certainly gives a reasonable estimate of an upper limit for  $k_{\text{th}}$  which is higher than the value calculated above.

An estimate for  $k_{\text{th}}$  can also be obtained from the results of the electron transfer experiment described in an earlier section. For the reaction,



$\Delta G^\circ$  is 0, and so  $k_{\text{ex}}$  provides a reasonable estimate for the  $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}]^{2+/+}$  self-exchange rate. Mechanistically, the overall reaction occurs through two steps which determine the magnitude of  $k_{\text{ex}}$ . The first step involves ion-pair formation between reactants, and the second, electron transfer within the ion-pair:

#### Scheme I



The numerical value for electron transfer within the ion pair,  $k_2$ , should give a rough estimate for  $k_{\text{th}}$ . The inner- and outer-sphere reorganizational energies which largely determine the magnitudes of  $k_{\text{th}}$  and  $k_2$ <sup>47-49</sup> should be similar for the two reactions. The dimeric ion and the pyridine complexes have very similar chemical properties as shown by their electronic spectra and redox potentials. In both processes the electron donor and acceptor sites are held in relatively close proximity. However,  $k_2$  is expected to be smaller than  $k_{\text{th}}$  because the resonance energy should be less in the outer-sphere case making  $E_{\text{th}}$  slightly larger (eq 10b) and  $\nu_{\text{et}}$  smaller (eq 12).

The relationship between  $k_{\text{ex}}$  and the constants in Scheme I is,

$$k_{\text{ex}} = \frac{k_1 k_2}{k_{-1} + k_2} \quad (18)$$

The experimental value for  $k_{\text{ex}}$  at 25 °C is  $\sim 10^2$  below the diffusion-controlled limit calculated using the Debye-Smoluchowski equation.<sup>50,51</sup> The correction for diffusion effects should be negligible and assuming that  $k_{-1} > k_2$  gives,

$$k_{\text{ex}} = k_2 K \quad (19)$$

The ion-pair equilibrium constant  $K = 0.41$  can be estimated from the Fuoss equation,<sup>52-55</sup> and using that value and eq 19 gives  $k_2 = 1.2 \times 10^8 \text{ s}^{-1}$ .

$k_2$  and  $k_{\text{th}}$  are not directly comparable because the distances between the metal sites are different in the two cases (6.9 Å for [2,3] and 12.1 Å in the self-exchange reaction), and the outer-sphere reorganizational energy depends on the internuclear separation,  $d$  (see below). The correction in the outer-sphere reorganizational energy  $\Delta(G_0^*)$ , which would make the two cases comparable can be calculated from eq 20 where  $n^2$  and  $D_S$  were defined previously and  $d_1$  and  $d_2$  are the two internuclear separations.<sup>57</sup>

$$\Delta(\Delta G_0^*) = \frac{e^2}{4} \left( \frac{1}{d_1} - \frac{1}{d_2} \right) \left( \frac{1}{n^2} - \frac{1}{D_S} \right) \quad (20)$$

The corrected value for  $k_{\text{th}}$  using the larger internuclear separation is  $k'_{\text{th}} \leq 3 \times 10^8 \text{ s}^{-1}$ .

It should be noted that the comparison between  $k'_{\text{th}}$  and  $k_2$  should be valid since both the self-exchange and IT experiments were carried out in dilute solution under nearly ideal conditions. The energy of the IT band appears to be relatively insensitive to added electrolyte which is predicted theoretically.<sup>47,48</sup> The overall rate of outer-sphere electron transfer will of course be dependent on ionic strength because of the pre-equilibrium in eq 15.

The calculated values for  $k_{\text{th}}$  and  $k_2$  are only approximate. However, the agreement found in the two values reinforces the validity of the Hush treatment for obtaining at least approximate values for thermal electron transfer rates in mixed-valence systems and demonstrates the expected close relationship between outer-sphere electron transfer processes and inner-sphere processes where delocalization between sites is small.<sup>2,48</sup>

The intervalence transfer experiment allows access to in-

formation about the activation process for electron transfer which is usually not available from other experiments. The IT band energy is related to the Marcus-Hush reorganizational energy term for thermal electron transfer by,

$$E_{op} = \lambda_i + \lambda_o \quad (21)$$

where  $\lambda_i$  and  $\lambda_o$  are the outer and inner sphere reorganizational contributions to  $\lambda$ .<sup>47-49</sup> In eq 21,  $\lambda$  is given by  $\lambda = 4\Delta G^*$ , where  $\Delta G^*$  is the free energy of activation for thermal electron transfer, and  $\lambda_i = 4\Delta G_i^*$  and  $\lambda_o = 4\Delta G_o^*$  where the contribution from the resonance energy is neglected.<sup>47-49</sup> Since  $T\Delta S^* \sim 0$  for the electron transfer step,

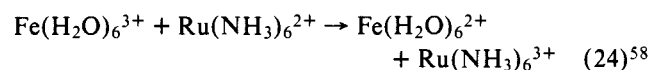
$$4E_{th} = \lambda \quad (22)$$

Using a dielectric continuum model, Marcus and Hush have derived eq 23 for  $\lambda_o$ , where  $r_1$  and  $r_2$  are the molecular radii of the two metal sites in the activated complex for thermal electron transfer and the remaining terms were defined previously.<sup>47,48</sup>

$$\lambda_o = e^2 \left( \frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d} \right) \left( \frac{1}{n^2} - \frac{1}{D_S} \right) \quad (23)$$

$\lambda_i$  is expected to be relatively independent of changes in solvent so that from eq 21 and 23 and the plot of  $E_{op}$  vs.  $(1/n^2 - 1/D_S)$  in Figure 9, the intercept is equal to  $\lambda_i$  and  $\lambda_o$  in a given solvent can be calculated using eq 21. For  $[(bpy)_2ClRu(pyZ)RuCl(bpy)_2]^{3+}$  in acetonitrile,  $\lambda_i = 16.1$  kcal/mol and  $\lambda_o = 6.0$  kcal/mol, which gives  $\Delta G_i^* = 4.0$  kcal/mol and  $\Delta G_o^* = 1.5$  kcal/mol. The intervalence transfer experiment thus allows the activation barrier to electron transfer to be partitioned between inner- and outer-sphere reorganizational contributions.

The variation of IT band energies with solvent has also been measured for  $[(NH_3)_5Ru(4,4'-bpy)Ru(NH_3)_5]^{5+4}$  and for  $[(NH_3)_5Ru(pyZ)RuCl(BPY)_2]^{4+,5}$ . The properties of all three ions are consistent with localized valences and small delocalization. Marcus and Hush have derived expressions for outer-sphere electron transfer between unlike ions, e.g., eq 24,<sup>47-49</sup> and the equations should apply to inner-sphere reactions where delocalization is small.



For an inner-sphere reaction where the donor and acceptor sites are held fixed to the bridging ligand,  $\Delta G^*$  is given by eq 25,

$$\Delta G^* = \frac{\lambda}{4} \left( 1 + \frac{\Delta G^{o'}}{\lambda} \right)^2 \quad (25)$$

where  $\Delta G^{o'}$  is the overall free energy change in the appropriate medium.

$\lambda$  can be expressed in terms of  $\lambda$  values for the individual self-exchange reactions ( $Ru(NH_3)_6^{3+/2+}$ ,  $Fe(H_2O)_6^{3+/2+}$ ) as,

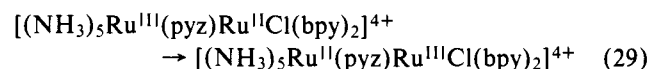
$$\lambda = \frac{\lambda_1 + \lambda_2}{2} \quad (26)$$

and for the inner- and outer-sphere terms,

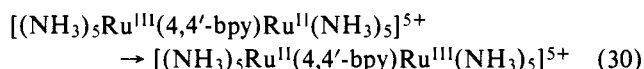
$$\lambda_i = \frac{\lambda_{i,1} + \lambda_{i,2}}{2} \quad (27)$$

$$\lambda_o = \frac{\lambda_{o,1} + \lambda_{o,2}}{2} \quad (28)$$

$\lambda_i$  for reaction 29,

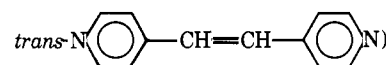
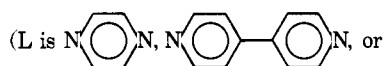


should be related to  $\lambda_i$  for reactions 9 ( $\lambda_{i,1}$ ) and 30 ( $\lambda_{i,2}$ ),



by eq 27. The experimental value of  $\lambda_i$  for eq. 29 is 12.9 kcal/mol.<sup>5</sup> The value calculated using  $\lambda_{i,1} = 16.1$  kcal/mol and  $\lambda_{i,2} = 10.0$  kcal/mol<sup>4</sup> is 13.0 kcal/mol which is in excellent agreement with the experimental value.  $\lambda_o$  values for the three reactions should also be related but because of the difference in bridging ligands, the internuclear separations are different and the comparison cannot be made directly.

**Comparisons with Other Systems.** The mixed-valence ions  $[(NH_3)_5Ru(4,4'-bpy)Ru(NH_3)_5]^{5+,4}$ ,  $[(bpy)_2ClRu(pyZ)RuCl(bpy)_2]^{3+,5}$ ,  $[(NH_3)_5Ru(L)RuCl(bpy)_2]^{4+,3,5}$  and  $[(NH_3)_5Ru(L)Ru(bpy)_2(L)Ru(NH_3)_5]^{6+/5+33}$

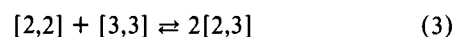


have localized valences, have only slight Ru(II) to Ru(III) delocalization, and exhibit class II behavior in the Robin and Day sense.<sup>31</sup> The extent of delocalization in the unsymmetrical ions is somewhat limited by the redox inequivalency of the different ruthenium ion sites.<sup>33</sup>

The oxo-bridged ion  $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$  has multiple redox properties and is delocalized.<sup>26</sup> In contrast to pyrazine as a bridge, there is strong coupling between ruthenium ions across the bridging oxide ion and the redox properties are carried by orbitals which are delocalized over both ruthenium ions. Taube and his co-workers have shown that in related systems the resonance energy is sufficiently high across bridging dinitrogen (e.g., in *cis*- $[(NH_3)_4ClOs(N_2)Os(NH_3)_4Cl]^{4+,59}$  and even across cyanogen ( $[(NH_3)_5Ru(NCCN)Ru(NH_3)_5]^{5+,60}$  to give delocalized, mixed-valence ions.

The most interesting comparison with  $[(bpy)_2ClRu(PYZ)RuCl(bpy)_2]^{3+}$  is the comparison with the Creutz and Taube ion  $[(NH_3)_5Ru(pyZ)Ru(NH_3)_5]^{5+}$ . The results of many experiments have been reported for the Creutz and Taube ion,<sup>6,7</sup> but a truly satisfactory description of the oxidation state properties of the ion has not been given. An absorption band has been observed for the ion in the near-IR, but the bandwidth is far narrower than predicted by eq 7, and the band energy is invariant to changes in solvent. In the IR only one  $\delta(NH_3)(sym)$  frequency is observed at an energy intermediate between band positions expected for Ru(II) and Ru(III) pentaammines.<sup>6,7,21</sup> However, both the results of Mossbauer<sup>18</sup> and ESCA<sup>16</sup> experiments have been interpreted in terms of different, chemically discrete Ru(II) and Ru(III) sites although the interpretation of the results of the latter experiment has been questioned by Hush.<sup>20</sup>

Some insight can be gained into the difference between  $[(bpy)_2ClRu(pyZ)RuCl(bpy)_2]^{3+}$  and the Creutz and Taube ion from redox potential values for the two, one-electron processes  $[3,3] + e \rightarrow [2,3]$  and  $[2,3] + e \rightarrow [2,2]$ . The redox potentials can be used to calculate  $\Delta G^{o'}$  for the conproportionation equilibrium for both ions (eq 3).



In 0.10 M TBAH-acetonitrile,  $\Delta G^{o'} = 0.12$  V for the bpy system and 0.43 V for the pentaammine system. In both systems the mixed-valence ion is favored by a statistical factor of 4 or  $RT/nF \ln 4 = 0.036$  V. Both mixed-valence ions are favored slightly by an electrostatic factor which can be estimated to be  $\sim 0.028$  V using a simple Coulombic model.<sup>61</sup> Neglecting differences arising from changes in solvation energies, the remaining value for  $\Delta G^{o'}$  (0.056 V for the bpy mixed-valence



ion) must reflect the partial delocalization of the exchanging electron from Ru(II) to Ru(III). The value calculated for this effect is in the same range as the resonance energy estimated by eq 13 ( $\beta \leq 0.049$  eV).

The Creutz and Taube ion is favored by an additional factor of 0.31 V (7.1 kcal/mol) over  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$  which must come largely from the effects of greater electron donation from Ru(II) to Ru(III). An enhanced stability for the mixed-valence ion of 7.1 kcal/mol is large when it is realized that  $\Delta G^*$  for intramolecular electron transfer in  $[(\text{NH}_3)_5\text{Ru}(4,4'\text{-bpy})\text{Ru}(\text{NH}_3)_5]^{5+}$  is  $\sim 6\text{--}7$  kcal/mol in acetonitrile from IT measurements.<sup>4</sup> The Creutz and Taube ion may or may not be delocalized, but it is clearly outside the weak interaction limit to which the Hush theory applies.

It has been suggested that the Creutz and Taube ion may represent an intermediate case lying between the limiting localized and delocalized descriptions,<sup>60,62</sup> where there is extensive delocalization but inequivalent metal sites. The same considerations may also apply in part to the mixed-valence biferrocene ion  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{-C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)]^+$  where  $\Delta G^{\circ'}$  for eq 3 is also large and favorable and reorganizational energies are expected to be low.<sup>63,64</sup>

Strong Ru(II)  $\rightarrow \pi^*(\text{bpy})$  back-bonding is an important feature in the chemistry of ruthenium complexes of 2,2'-bipyridine as evidenced by their spectral and redox properties.<sup>23-25,65,66</sup> Less electron donation from Ru(II) to Ru(III) is anticipated for  $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{3+}$  because competitive back-bonding to the bpy ligands must decrease the available electron density for delocalization through the  $\pi^*$  system of the bridging pyrazine ligand. By appropriate synthetic modifications in which the nonbridging ligands are varied systematically, it will be possible to explore the region of delocalization between the bpy and pentaammine ions.

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## References and Notes

- (1) A preliminary account of this work has appeared: R. W. Callahan and T. J. Meyer, *Chem. Phys. Lett.*, **39**, 82 (1976).
- (2) (a) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967); (b) N. S. Hush, *Electrochim. Acta*, **13**, 1005 (1968).
- (3) (a) R. W. Callahan, T. J. Meyer, and G. M. Brown, *J. Am. Chem. Soc.*, **96**, 7829 (1974); (b) *Inorg. Chem.*, **14**, 1443 (1975).
- (4) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7827 (1974).
- (5) M. J. Powers, R. W. Callahan, T. J. Meyer, and D. J. Salmon, *Inorg. Chem.*, **15**, 1457 (1976).
- (6) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **91**, 3988 (1969).
- (7) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
- (8) J. N. Braddock, Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1973.
- (9) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).
- (10) E. C. Johnson, Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1975.
- (11) T. H. Ridgway, Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1971; R. M. Wightman, Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1974.
- (12) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).
- (13) G. M. Brown, Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1974, and private communication.
- (14) S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Ferguson, and T. J. Meyer, *J. Am. Chem. Soc.*, **94**, 300 (1972).
- (15) For a reaction  $a + b \rightleftharpoons c + d$  where  $K = k_1/k_{-1} = 1$ , such as in the present instance, if  $c_0 = d_0 = 0$  and  $x$  is the extent of reaction, the rate law is given by

$$\ln \left[ 1 - \frac{(a_0 + b_0)x}{a_0 b_0} \right] = -(a_0 + b_0)k_1 t + \ln a_0 b_0$$

If at equilibrium  $x = x_e$ , then the rate law becomes

$$\ln(x_e - x) - \ln x_e = -(a_0 + b_0)k_1 t$$

If  $A_e$  and  $A_t$  are absorbances at equilibrium and at time  $t$ , respectively,

$$\ln(A_e - A_t) = -(a_0 + b_0)k_1 t + \text{constant}$$

Consequently, a first order rate plot yields an observed rate constant  $k' = (a_0 + b_0)k_1$ , so that  $k_1 = k'/(a_0 + b_0)$ .

- (16) P. Citrin, *J. Am. Chem. Soc.*, **95**, 6472 (1973).
- (17) M. L. Good, private communication.
- (18) M. L. Good, C. Creutz, and S. Chandra, *Inorg. Nucl. Chem. Lett.*, **9**, 171 (1973).
- (19) I. M. Treitel, Ph.D. Dissertation, California Institute of Technology, 1971.
- (20) N. S. Hush, *Chem. Phys.*, **10**, 361 (1975).
- (21) C. Creutz, Ph.D. Dissertation, Stanford University, 1971.
- (22) G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, **24**, 275 (1971).
- (23) J. N. Braddock and T. J. Meyer, *J. Am. Chem. Soc.*, **95**, 3158 (1973).
- (24) G. M. Bryant, J. E. Fergusson, and H. K. Powell, *Aust. J. Chem.*, **24**, 257 (1971).
- (25) W. L. Bowden, W. F. Little, T. J. Meyer, and D. J. Salmon, *J. Am. Chem. Soc.*, **97**, 6897 (1975).
- (26) T. R. Weaver, T. J. Meyer, S. A. Adeyemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray, and D. Untereker, *J. Am. Chem. Soc.*, **97**, 3039 (1975).
- (27) (a) R. W. Callahan, Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1975; (b) R. C. Lord, A. L. Martin, and F. A. Miller, *Spectrochim. Acta*, **9**, 113 (1959); (c) M. Goldstein and W. D. Unsworth, *Spectrochim. Acta, Part A*, **27**, 1055 (1971).
- (28) D. R. Gere and C. E. Meloan, *J. Inorg. Nucl. Chem.*, **25**, 1507 (1963).
- (29) S. Burchett and C. E. Meloan, *J. Inorg. Nucl. Chem.*, **34**, 1207 (1972).
- (30) G. N. LaMar and G. R. Van Hecke, *Inorg. Chem.*, **12**, 1767 (1973).
- (31) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10**, 247 (1967).
- (32) (a) B. Mayoh and P. Day, *Inorg. Chem.*, **13**, 2273 (1974); (b) B. Mayoh and P. Day, *J. Am. Chem. Soc.*, **94**, 2885 (1972).
- (33) M. J. Powers, R. W. Callahan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, **15**, 894 (1976).
- (34) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", Ronald Press, New York, N.Y., 1966, pp 128-129.
- (35) D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).
- (36) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968).
- (37) K. B. Eisenthal, *Acc. Chem. Res.*, **8**, 118 (1975).
- (38) R. A. Marcus, *J. Chem. Phys.*, **43**, 2654 (1965); **52**, 2803 (1970).
- (39) S. Efrima and M. Bixon, *Chem. Phys. Lett.*, **25**, 34 (1974).
- (40) R. P. VanDuyn and S. F. Fischer, *Chem. Phys.*, **5**, 183 (1974).
- (41) W. Kauzmann, "Quantum Chemistry", Academic Press, New York, N.Y., 1957, pp 534-536.
- (42) In Eq. 12  $\nu_{el}$  is the frequency of electron oscillation between Ru(II) and Ru(III) in the activated complex for thermal electron transfer where the coordination environments around the two sites are identical;  $1/\nu_{el}$  is the lifetime of the exchanging electron initially located on Ru(II).
- (43) S. S. Isied and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).
- (44) D. Gaswick and A. Haim, *J. Am. Chem. Soc.*, **96**, 7845 (1974).
- (45) A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).
- (46) S. F. A. Kettle and I. Paul, *Adv. Organomet. Chem.*, **10**, 199 (1972).
- (47) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); *J. Phys. Chem.*, **67**, 853 (1963).
- (48) N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1961).
- (49) Reference 34, Chapter 6.
- (50) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).
- (51)  $k_D$  was calculated from

$$k_D = \frac{2RT}{3000\eta} \left( 2 + \frac{r_A}{r_B} + \frac{r_B}{r_A} \right) \frac{\delta}{e^{\delta} - 1}$$

where  $r_A$  and  $r_B$  are the "average" molecular radii of the diffusing ions taken to be 5.8 and 6.3 Å for  $[\text{Ru}(\text{bpy})_2(\text{py})\text{Cl}]^+$  and  $[\text{Ru}(\text{phen})_2(\text{py})\text{Cl}]^{2+}$ , respectively, and  $\eta = 3.45 \times 10^{-3}$  poise at 25 °C. The term  $\delta$  is given by

$$\delta = Z_A Z_B e^2 / d D_S k T$$

where the various terms have been defined previously or are defined below. Ionic strength corrections are negligible for the dilute solutions used.

- (52) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
- (53) P. Hemmes, *J. Am. Chem. Soc.*, **94**, 75 (1972).
- (54) C. T. Lin and D. B. Rorabacher, *Inorg. Chem.*, **12**, 2402 (1973).
- (55) In acetonitrile at 25 °C

$$K = (2.524 \times 10^{-3}) d^3 \exp \left[ \frac{-9.03 Z_1 Z_2}{dRT} \right]$$

with  $d$  the internuclear separation between ions in Å and  $Z_1 Z_2$  the product of ionic charges. An ionic strength correction is unnecessary because the self-exchange rate was measured in dilute solution with no added electrolyte. Using a value for  $d$  of 12.1 Å gives  $K = 0.41$  at 25 °C. Further, in the dilute solutions used, solution conductivity measurements on related complexes indicate that complications arising from ion-pairing with the negative counterions are probably unimportant.<sup>26</sup> If there are additional interactions between the complexes not included in the continuum treatment used by Fuoss in deriving eq 20, such as stacking interactions between the aromatic ring systems,<sup>56</sup>  $K$  will be larger than calculated and  $k_2$  smaller.

- (56) G. R. Cayley and D. W. Margerum, *J. Chem. Soc., Chem. Commun.*, 1002 (1974).
- (57) Equation 21 was derived from eq 23.  $k_{in}$  for a given internuclear separation  $d$  is given by  $k_{in} = \nu_{el} \exp(-\lambda/4RT)$  where  $\lambda/4$  is the sum of the inner- and outer-sphere reorganizational energies for thermal electron transfer. For a different value of  $d$  and  $\lambda, \lambda'$ , the corrected rate constant  $k_2'$  can be calculated from:  $k_{in}' = k_{in} \exp(\lambda - \lambda')/4RT$ , if the resonance energy and thus  $\nu_{el}$  remain the same, which is appropriate for the case considered here. If, as is also appropriate here, the inner-sphere reorganizational energy is taken to be the same for the two distances,  $k_{in}' = k_{in} \exp[-(\Delta\lambda_0)/4RT]$  where  $\Delta\lambda_0 = \lambda_0 - \lambda_0' = 4\Delta(\Delta G_0^*)$ .
- (58) H. Taube and T. J. Meyer, *Inorg. Chem.*, **7**, 2369 (1968).
- (59) R. H. Magnuson and H. Taube, *J. Am. Chem. Soc.*, **94**, 7213 (1972).

- (60) G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, **97**, 5310 (1975).  
 (61) The electrostatic energy was estimated by a thermochemical cycle in which the [2,2] and [3,3] ions are separated as monomeric spheres of radius 6.9/2 Å ( $\frac{1}{2}$  the Ru(py<sub>2</sub>)Ru distance) to infinity and recombined to give [2,3]. For the individual steps in 0.1 M TBAH-CH<sub>3</sub>CN,<sup>55</sup>

$$\Delta G^{\circ'} = \frac{9.10 Z_1 Z_2}{r} \left( \frac{1}{1 + 0.482 r l^{1/2}} \right)$$

in which  $r = 6.9$  Å,  $Z_1$  and  $Z_2$  are the ionic charges, and  $l$  is the ionic strength.

- (62) T. J. Meyer, *Adv. Chem. Ser.*, **No. 150**, Chapter 7 (1976).  
 (63) D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, **6**, 1 (1973).  
 (64) J. P. Pladziewicz and J. H. Espenson, *J. Am. Chem. Soc.*, **95**, 56 (1973); E. S. Yang, M.-S. Chan, and A. C. Wahl, *J. Phys. Chem.*, **79**, 2049 (1975).  
 (65) J. Cramer, Ph.D. Dissertation, University of North Carolina, Chapel Hill, 1975.  
 (66) D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N.Y., 1964, Chapter 6.

## Electron Transfer. 24. Catalysis of Outer-Sphere Reactions by Noncoordinated Pyridine Derivatives<sup>1</sup>

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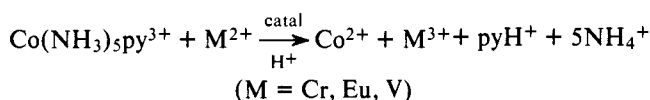
**Abstract:** The reductions, by Eu<sup>2+</sup>, of a number of Co(III) complexes having no bridging groups are catalyzed by noncoordinated pyridine derivatives having unsaturated substituents  $\gamma$  to the ring nitrogen. Powerful catalysis is observed with 4-pyridinecarboxylic acid (III), its *N*-methyl derivative (I), isonicotinamide (IV), and 4-pyridineacrylic acid (V). Kinetic evidence supports a mechanism in which the catalyst is reduced ( $k_1$ ) by Eu<sup>2+</sup> to a radical intermediate, after which this intermediate may react either with Eu<sup>3+</sup> present ( $k_{-1}$ ) or with the Co(III) oxidant ( $k_2$ ). Catalytic effectiveness in these systems is proportional to  $k_1 k_2 / k_{-1}$ . Measurements under steady-state conditions have given values of  $k_1$  and the ratio  $k_2 / k_{-1}$  for ten cobalt(III) oxidants with each of the four catalysts. In addition, earlier pulse radiolytic data<sup>9</sup> allow estimates of  $k_{-1}$  for several of the isonicotinamide catalyzed reactions. The pattern of  $k_2 / k_{-1}$  values for the various oxidants is the same for each of the four catalysts and is also similar to the patterns set by the specific rates for reductions by Eu<sup>2+</sup>, V<sup>2+</sup>, Cr<sup>2+</sup>, and Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> in the absence of catalysis. Log-log plots of  $k_2 / k_{-1}$  vs.  $k_{\text{uncatalyzed}}$  are linear for the more slowly reacting oxidants, and slopes of the regression lines are near unity with all four catalysts. In this reactivity region, our catalytic systems conform closely to Marcus' model.<sup>23</sup> With the more reactive oxidants,  $k_2 / k_{-1}$  ratios approach a maximum value near 15, corresponding to specific rates in the range 10<sup>6</sup>-10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup> for reaction of the radical intermediate with the Co(III) center. For these Co(III)-radical reactions, as for the even more rapid reactions of Co(III) with the nicotinamide radical (XIV) and with the hydrated electron, the multiplicity barrier presumed to be associated with the conversion of low-spin Co(III) to high-spin Co(II) is minimal.

Electron transport processes in living systems commonly involve a plurality of redox species, each of which may exist in either an oxidized or reduced form. The most strongly oxidizing and most strongly reducing members of such groupings rarely react directly, although such action is strongly favored thermodynamically. Instead, an electron is passed successively from one "chain-member" to another which is somewhat more strongly oxidizing and ultimately arrives at the most powerfully oxidizing member of the series.<sup>2</sup> This mode of action arises, in large part, from the appropriate positioning of such electron transport sites in cell membranes. In effect, the intermediate members of a chain are catalyzing electron transfer between members at either extreme.

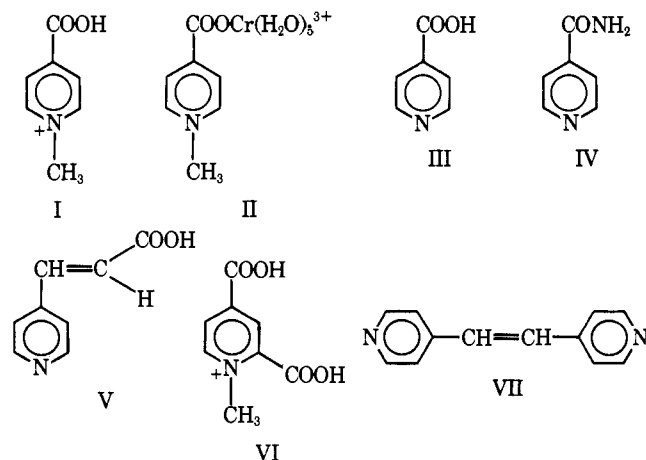
Few situations analogous to this have been described for simple *in vitro* systems involving metal centers. Although there are numerous instances in which added species have been found to accelerate electron transfer between such centers,<sup>3</sup> these catalysts generally function either by coordinating with the oxidizing center and acting as a bridge in an inner-sphere process<sup>4</sup> or by alteration of the character of the reducing agent by prior attachment to it.<sup>3,5</sup>

In 1971 it was reported<sup>6</sup> that several pyridinecarboxylate derivatives strongly catalyze the Cr<sup>2+</sup> and Eu<sup>2+</sup> reductions of such slowly reacting outer-sphere oxidants as (NH<sub>3</sub>)<sub>6</sub>Co<sup>3+</sup> and (NH<sub>3</sub>)<sub>5</sub>pyCo<sup>3+</sup>. When such catalysts as *N*-methylpyridine-4-carboxylic acid (I) and its (H<sub>2</sub>O)<sub>5</sub>Cr<sup>III</sup> complex (II) were employed at the 10<sup>-4</sup> M level at pH 4-5, Cr(II) reductions which, in the absence of catalysis, exhibited half-life periods exceeding 1 h were accelerated into the stop-flow region.<sup>6a</sup>

Related examples of catalysis of V<sup>2+</sup> reductions by dicarboxylic acid VI<sup>7</sup> and of Eu<sup>2+</sup> and Cr<sup>2+</sup> reductions by olefin VII<sup>8</sup> were noted shortly afterwards.



Catalysts:



The structural features common to the catalysts, the chemical nature of the reactants, the kinetic behavior of these catalyzed reactions,<sup>6</sup> and their inhibition<sup>6b,7</sup> by Eu<sup>3+</sup> and V<sup>3+</sup>