

# Solvent-Induced Electron Transfer and Delocalization in Mixed-Valence Complexes. Electrochemistry

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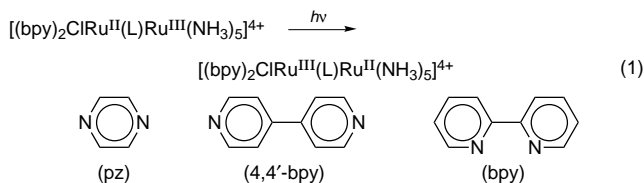
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**Abstract:** For the Ru<sup>III/II</sup> couple in [(bpy)<sub>2</sub>ClOs(4,4'-bpy)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>3+</sup> (bpy = 2,2'-bipyridine; 4,4'-bpy = 4,4'-bipyridine),  $E_{1/2}$  varies linearly with the donor number (DN) of the solvent with a slope of  $-26 \pm 3$  mV/DN unit ranging from nitromethane to dimethyl sulfoxide. For the Os<sup>III/II</sup> couple, the variation is  $-3 \pm 1$  mV/DN unit. Plots of  $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$  vs DN ( $E_{1/2}$  is the half wave potential for the first or second wave by cyclic voltammetry) undergo a change in slope at DN  $\sim 14$  where there is a change in oxidation states in the mixed-valence form from Os<sup>III</sup>–Ru<sup>II</sup> to Os<sup>II</sup>–Ru<sup>III</sup>. By extrapolation of these data,  $\Delta G^\circ$  for the mixed-valence equilibrium, [(bpy)<sub>2</sub>ClOs<sup>III</sup>(4,4'-bpy)Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>  $\rightleftharpoons$  [(bpy)<sub>2</sub>ClOs<sup>II</sup>(4,4'-bpy)Ru<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>, varies from +5.8 kcal/mol in nitromethane to  $-7.5$  kcal/mol in dimethyl sulfoxide. It differs from  $\Delta E_{1/2}$  by up to  $\sim 20\%$  even though it has sometimes been assumed in the literature that  $\Delta E_{1/2} = -\Delta G^\circ$ . For [(bpy)<sub>2</sub>ClOs(pz)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>3+</sup> (pz = pyrazine) both Os<sup>III/II</sup> and Ru<sup>III/II</sup> couples are significantly solvent dependent for solvents of DN < 24. In these solvents oxidation states in the mixed-valence form are Os<sup>III</sup>–Ru<sup>II</sup>. The slopes of  $E_{1/2}$  vs DN plots are  $-21 \pm 4$  mV/DN unit (Ru<sup>III/II</sup>) and  $-8 \pm 4$  mV/DN unit (Os<sup>III/II</sup>). At DN > 24 the oxidation states switch to Os<sup>II</sup>–Ru<sup>III</sup> and the solvent dependence reverts to being largely in Ru<sup>III/II</sup>. There is evidence in the electrochemical data, in comparisons between [(bpy)<sub>2</sub>ClOs(pz)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>3+</sup> and [(bpy)<sub>2</sub>ClOs(4,4'-bpy)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>3+</sup> for significant through-bridge electronic coupling in [(bpy)<sub>2</sub>ClOs<sup>III</sup>(pz)Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>, but not in [(bpy)<sub>2</sub>ClOs<sup>II</sup>(pz)Ru<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>. The difference in behavior is caused by extensive H-bonding to the solvent at  $-\text{Ru}^{\text{III}}(\text{NH}_3)_5^{3+}$  in [(bpy)<sub>2</sub>ClOs<sup>II</sup>(pz)Ru<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup>. This mixes solvent character into  $d\pi(\text{Ru}^{\text{III}})$  which decreases electronic coupling across the bridge.

## Introduction

The solvent helps determine the energies of charge transfer absorption bands<sup>1,2</sup> and the dynamics of electron transfer in solution.<sup>3,4</sup> The effect of solvent on intervalence transfer (IT) bands in mixed-valence complexes (e.g. eq 1, L = pyrazine (pz) or 4,4'-bipyridine (4,4'-bpy)) is especially well documented.<sup>2,5,6</sup>



Absorption bands acquire a solvent dependence from two sources.<sup>7</sup> Because of the Franck–Condon character of the

transitions, the final state is surrounded instantaneously by the solvent polarized as in the initial state, but in the electronic environment of the final state. This contributes a solvent reorganizational energy. For unsymmetrical complexes  $\Delta G^\circ \neq 0$ , and the free energy change is usually solvent dependent as well.<sup>1f,5d,8–10</sup>

For the couples  $[\text{Ru}(\text{NH}_3)_5(\text{L})]^{3+/2+}$ , specific interactions between individual solvent molecules and ammine ligands cause  $E_{1/2}$  to vary by  $\sim 400$  mV in solvents ranging from nitromethane

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to dimethyl sulfoxide.<sup>8b,10c</sup> Solvent variations have been used to “tune”  $\Delta G^\circ$ ,<sup>1f,5d,9,11</sup> explore specific solvation in mixed solvents,<sup>10a,12</sup> and probe electronic coupling in mixed-valence complexes.<sup>13</sup>

In this and the following manuscript we demonstrate that changes in solvent can be used to induce intramolecular electron transfer and interconvert oxidation states in [(bpy)<sub>2</sub>ClOs(L)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> (L = pz, 4,4'-bpy). For the L = pz complex this is accompanied by a significant change in the extent of through-bridge electronic coupling. These complexes were chosen for study since potentials for the couples [Os(bpy)<sub>2</sub>(py)Cl]<sup>2+/+</sup> and [Ru(NH<sub>3</sub>)<sub>5</sub>(py)]<sup>3+/2+</sup> are comparable in acetonitrile and yet only the latter is appreciably solvent dependent. This allows the energetics of intramolecular electron transfer in the bridged complexes to be tuned to an appreciable degree by varying the solvent. Part of this work has appeared in a preliminary communication and similar observations have been made for a related mixed-valence complex of Ru.<sup>11,12d,14</sup>

## Experimental Section

**Materials.** The solvents nitromethane (Gold Label spectrophotometric grade), nitrobenzene (Gold Label reagent grade), benzonitrile (HPLC grade), formamide (reagent grade), and dimethylacetamide (HPLC grade) were all obtained from Aldrich and used as received. Acetonitrile, propylene carbonate, acetone, methanol, dimethylformamide, and dimethyl sulfoxide were all obtained from Burdick and Jackson and used without further purification. House distilled water was purified by passing through a Millipore water purification system.

Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared from tetra-*n*-butylammonium bromide and HPF<sub>6</sub> by using the method of Calvert.<sup>15</sup> It was recrystallized three times from ethanol. The salt KPF<sub>6</sub> was purchased from Aldrich and recrystallized two times from water. A small sample of decamethylferrocene was kindly provided by Professor Michael Weaver.

**Preparation of Complexes.** The salts [(bpy)<sub>2</sub>ClOs(L)](PF<sub>6</sub>) (L = 4,4'-bpy, pz)<sup>16</sup> and [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)](PF<sub>6</sub>)<sub>2</sub><sup>9a</sup> were prepared by literature procedures and [(bpy)<sub>2</sub>ClOs(L)Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub> by a modification of a literature procedure.<sup>6c</sup> In a typical preparation for L = pz, 105 mg of [(bpy)<sub>2</sub>ClOs(pz)](PF<sub>6</sub>) (0.138 mmol) and 55 mg of [Ru(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)](PF<sub>6</sub>)<sub>2</sub> (0.112 mmol) were placed in a 25 mL Erlenmeyer flask. The flask was fitted with a rubber septum and purged with Argon (Baker, reagent grade) through syringe needles for 30 min. A volume of 4 mL of deaerated acetone was added by syringe and the mixture stirred at room temperature in the absence of light for 1 h. The volume of the solution was maintained by the occasional addition of 1-mL portions of deaerated acetone. The PF<sub>6</sub><sup>-</sup> salt was precipitated by adding the reaction mixture dropwise to 100 mL of stirring CH<sub>2</sub>Cl<sub>2</sub> and collected by filtration. The resulting solid was reprecipitated from acetone/CH<sub>2</sub>-Cl<sub>2</sub> and then from acetone/diethyl ether, stirred for 30 min in 75 mL of CH<sub>2</sub>Cl<sub>2</sub> to remove excess monomer, and collected by filtration. Typical yields were 65%.

**Electrochemical Measurements.** Both cyclic voltammograms and differential pulse polarograms were acquired by using a two compartment cell in which a platinum disk working electrode (2-mm diameter) and platinum wire auxiliary electrode occupied one compartment and the reference electrode occupied the second. The compartments were separated by a glass frit. For solvents of low donor number, where preferential solvation by water could occur, the electrochemical measurements were carried out in a Vacuum Atmospheres drybox, and a silver wire was used as a quasireference electrode. For solvents of high donor number, the experiments were carried out outside the drybox and a saturated calomel electrode (SCE) was used as the reference. Water from the atmosphere affected the potentials of the -Ru(NH<sub>3</sub>)<sub>5</sub><sup>3+/2+</sup> couple in solvents of low polarity. For example, in dry nitromethane exposed to the atmosphere, the potential drifted negatively within a period of minutes. The potential appropriate to the dry solvent was restored by adding molecular sieves as a drying agent.<sup>17</sup> All three electrodes were immersed in the same solvent/PF<sub>6</sub><sup>-</sup> electrolyte mixture. The sample and the internal reference compound Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> were added to the working/auxiliary compartment. The potential was controlled by using a PAR Model 173 potentiostat. For cyclic voltammetry, a PAR Model 175 universal programmer was used as a potential sweep generator. Current versus applied potential traces were recorded on a Hewlett-Packard 7015B X-Y recorder. Commercially available single (Cricket Graph) and multiparameter (Statworks) regression routines were used to plot the data and determine linear correlations.

## Results

Electrochemical data were obtained for [(bpy)<sub>2</sub>ClOs(L)Ru(NH<sub>3</sub>)<sub>5</sub>](PF<sub>6</sub>)<sub>3</sub> (L = pz, 4,4'-bpy) by cyclic voltammetry and differential pulse polarography in a series of solvents. The electrolyte was either KPF<sub>6</sub> or [N(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>](PF<sub>6</sub>) (TBAH) at 0.1 M except where a limited solubility dictated a lower concentration. Typically, two waves were observed except for L = 4,4'-bpy in benzonitrile, acetonitrile, or propylene carbonate where the waves were overlapping and could not be deconvoluted. Values of *E*<sub>1/2</sub> for the two waves and the differences between them are listed in Table 1. The Fe(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub><sup>+0</sup> couple was used as an internal reference in order to avoid junction potential effects.<sup>18</sup> The potentials for this couple vs the saturated calomel electrode (SCE) were, for example, -0.20, -0.09, and +0.01 V in acetonitrile, acetone, and dimethyl sulfoxide. Under our experimental conditions, *E*<sub>1/2</sub> values for the Fe(C<sub>5</sub>Me<sub>5</sub>)<sup>+0</sup> couple differed only slightly (but up to 55 mV in DMSO) from the data reported previously by Sahami and Weaver, who used a ClO<sub>4</sub><sup>-</sup> electrolyte.<sup>8a,19</sup>

For [(bpy)<sub>2</sub>ClOs(4,4'-bpy)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>3+</sup>, the variations in *E*<sub>1/2</sub> for the first, *E*<sub>1/2</sub>(1), and second, *E*<sub>1/2</sub>(2), waves with the donor number (DN) of the solvent<sup>20</sup> are illustrated in Figure 1. The solvents in which these measurements could be made were somewhat limited by a lack of solubility and/or the instability of the complexes toward decomposition. The assignments of the waves to redox couples were based on how the potentials of the couples varied with solvent and were verified by spectroscopic measurements.<sup>21</sup> In earlier work it was shown that variations in *E*<sub>1/2</sub> of 20–30 mV per donor number unit exist

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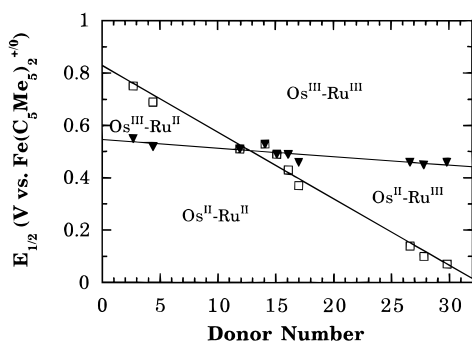
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**Table 1.**  $E_{1/2}$  and  $\Delta E_{1/2}$  ( $=E_{1/2}(2) - E_{1/2}(1)$ ) for  $[(bpy)_2ClOs(L)Ru(NH_3)_5]^{3+}$  ( $L = pz, 4,4'$ -bpy) in V vs  $[Fe(C_5Me_5)_2]^{+/0}$  at  $295 \pm 2$  K<sup>a</sup>

solvent (abbreviation, DN); <sup>b</sup> electrolyte	L = 4,4'-bpy			L = pz			$\Delta(\Delta E_{1/2})^c$
	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}$	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}$	
nitromethane (NM, 2.7); 0.05 M KPF <sub>6</sub>	0.55	0.75	0.20	0.60	1.10	0.50	0.30
nitrobenzene (NB, 4.4); 0.05 M TBAPF <sub>6</sub>	0.52	0.69	0.17	0.55	1.01	0.46	0.29
benzonitrile (BN, 11.9); 0.1 M TBAPF <sub>6</sub>	0.51		0	<i>d</i>	<i>d</i>	0.42 <sup>e</sup>	
acetonitrile (AN, 14.1); 0.1 M KPF <sub>6</sub>	0.53		0	0.48	0.88	0.40	0.40
propylene carbonate (PC, 15.1); 0.1 M KPF <sub>6</sub>	0.49		0	0.50	0.81	0.31	0.31 (0.32) <sup>f</sup>
propionitrile (PN, 16.1); 0.1 M KPF <sub>6</sub>	0.43	0.49	0.06				
acetone (AC, 17.0); ~0.07 KPF <sub>6</sub>	0.37	0.46	0.09	0.46	0.76	0.30	0.21 (0.34) <sup>f</sup>
methanol (MeOH, 19); ~0.07 M KPF <sub>6</sub>	<i>g</i>	<i>g</i>	0.09	<i>g</i>	<i>g</i>	0.30	0.21 (0.38) <sup>f</sup>
formamide (FA, 24); 0.1 M KPF <sub>6</sub>	<i>g</i>	<i>g</i>	0.25				
dimethylformamide (DMF, 26.6); 0.1 M KPF <sub>6</sub>	0.14	0.46	0.32	0.31	0.66	0.35	0.03
dimethylacetamide (DMA, 27.8); 0.1 M KPF <sub>6</sub>	0.10	0.45	0.35	0.28	0.67	0.39	0.04
dimethyl sulfoxide (DMSO, 29.8); 0.1 m KPF <sub>6</sub>	0.07	0.46	0.39	0.25	0.65	0.40	0.01

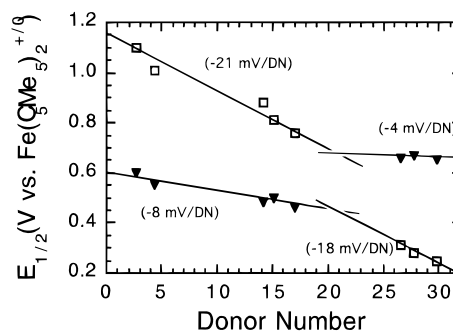
<sup>a</sup> For the  $Fe(C_5Me_5)_2^{+/0}$  couple,  $E_{1/2} = +0.307$  V vs SCE, in  $CH_3CN$ , 0.2 M in  $LiClO_4$  (Bard, A. J.; Faulkner, L. F. *Electrochemical Methods. Fundamentals and Applications*; John Wiley and Sons: New York, 1980). <sup>b</sup> Donor numbers were taken from ref 20c. <sup>c</sup>  $\Delta(\Delta E_{1/2}) = \Delta E_{1/2}(L=pz) - \Delta E_{1/2}(L=4,4'-bpy)$ . <sup>d</sup> The waves were irreversible in this solvent. <sup>e</sup> Estimated from the difference in oxidative peak potentials. <sup>f</sup>  $\Delta(\Delta E_{1/2}) = \Delta E_{1/2}(L=pz) - \Delta E_{1/2}(extr)$ , the  $\Delta E_{1/2}(extr)$  values were taken from Figure 3. <sup>g</sup>  $Fe(C_5Me_5)_2$  was insufficiently soluble in this solvent to utilize the  $[Fe(C_5Me_5)_2]^{+/0}$  couple as a reference.



**Figure 1.**  $E_{1/2}(1)$  and  $E_{1/2}(2)$  in V vs  $Fe(C_5Me_5)_2^{+/0}$  for  $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{3+}$  plotted against donor number (DN). The closed diamonds are points for the Os(III/II) couple and the open squares are for the Ru(III/II) couple. The slopes of the lines are  $-3 \pm 1$  unit and  $-26 \pm 3$  mV/DN unit, respectively. The potential–DN regions where the various oxidation state distributions are dominant are labeled on the figure.

for couples of the type  $[Ru(NH_3)_5(L)]^{3+/2+}$ .<sup>8b,9</sup> It is also known that  $E_{1/2}$  values for the polypyridyl couples are relatively insensitive to solvent.<sup>8</sup> Under our conditions,  $E_{1/2}$  for  $[Os(bpy)_2(py)Cl]^{2+/+}$  varied from 0.53 V in nitromethane to 0.44 V in dimethyl sulfoxide.<sup>19</sup> Near the “cross-over point” where the two lines in Figure 1 intersect, only a single wave appeared in the cyclic voltammograms. In these solvents the spectral properties of solutions containing the mixed-valence complex were used to establish the dominant oxidation state isomer and this provided the basis for assigning experimental potentials to the two couples.<sup>21</sup> The slope of the  $E_{1/2}$ –DN plot for the Ru(III/II) couple in Figure 1 is  $-26 \pm 3$  mV/DN unit. For the Os<sup>III/II</sup> couple, it is  $-3 \pm 1$  mV/DN unit. Four different oxidation state distributions, Os<sup>II</sup>–Ru<sup>II</sup>, Os<sup>II</sup>–Ru<sup>III</sup>, Os<sup>III</sup>–Ru<sup>II</sup>, and Os<sup>III</sup>–Ru<sup>III</sup>, coexist in the potential–donor number regions shown in the figure. The fractional composition of each depends on the applied potential and the donor number of the solvent. The potential–donor number region in which each is dominant is labeled in Figure 1.

The  $E_{1/2}(1)$  and  $E_{1/2}(2)$  values for  $[(bpy)_2ClOs^II(pz)Ru^II(NH_3)_5]^{3+}$  listed in Table 1 are shown plotted in Figure 2 as a function of donor number. In this case, both couples are solvent dependent at least for DN < 24. In this region the slopes are  $-21 \pm 4$  (Ru<sup>III/II</sup>) and  $-8 \pm 4$  mV/DN unit (Os<sup>III/II</sup>). The assignments of couples to waves were based on oxidation state markers that appear in near-UV–visible and near infrared (NIR) spectra.<sup>21</sup> From the data in Figure 2 there is a break in the  $E_{1/2}$ –DN plots which, by extrapolation, occurs at DN  $\sim$  22.



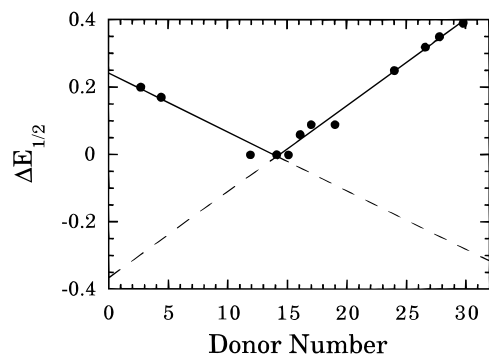
**Figure 2.**  $E_{1/2}(1)$  and  $E_{1/2}(2)$  in V vs  $Fe(C_5Me_5)_2^{+/0}$  for  $[(bpy)_2ClOs(pz)Ru(NH_3)_5]^{3+}$  plotted against donor number. The closed diamonds are the points for the Os(III/II) couple and the open squares are for the Ru(III/II) couple. The slopes of the linear correlations in the various donor number regions are shown on the figure.

As noted in the following paper, this coincides with a change in oxidation state in the mixed-valence ion from Os<sup>III</sup>–Ru<sup>II</sup> to Os<sup>II</sup>–Ru<sup>III</sup>. The two isomers coexist in trimethyl phosphate (DN = 23) and in formamide (DN = 24).<sup>21</sup>

## Discussion

The effect of solvent on  $E_{1/2}$  for the couples  $[Ru(NH_3)_5(L)]^{3+/2+}$  is thought to originate in specific hydrogen bonding interactions in which the N–H bonds of the ammine ligands act as electron pair acceptors and individual solvent molecules as donors.<sup>8–12</sup> In  $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{3+}$ , variations in  $E_{1/2}$  for the ammine couple correlate well with the donor number of the solvent, Figure 1. The donor number provides a measure of the relative ability of the solvent to donate an electron pair.<sup>20</sup>

The variations can be understood qualitatively. In a low donor number solvent such as nitromethane, the electron donor pairs on solvent molecules are weakly basic in the Lewis acid–base sense and H-bonding with the ammine ligands is weak. In dimethyl sulfoxide, which has a high donor number, electron pairs are more basic and H-bonding is stronger. Enhanced electron donation by H-bonding stabilizes Ru<sup>III</sup> relative to Ru<sup>II</sup> and decreases  $E_{1/2}$ . H-bonding provides a mechanism for electronic coupling between the solvent and the internal electronic structure of the complex. This effect is *in addition* to the usual electrostatic interactions that polarize the solvent. Specific H-bonding interactions with individual solvent molecules dominate the solvent dependence for ammine couples.<sup>8,12</sup> These are additive in the number of ammine ligands.<sup>8</sup> For  $[Ru(NH_3)_6]^{3+/2+}$  and  $[Ru(NH_3)_4(bpy)]^{3+/2+}$ , variations in  $E_{1/2}$  with solvent are  $-31$  and  $-17$  mV/DN unit, respectively. It is

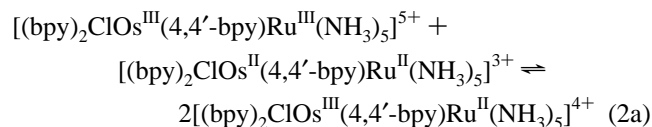


**Figure 3.** A plot of  $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$  versus donor number for  $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{3+}$ . The dashed lines are extensions of the best fit lines into regions where each of the mixed-valence isomers is thermodynamically unstable. The slopes of the lines are  $-17 \pm 4$  and  $26 \pm 4$  mV/DN.

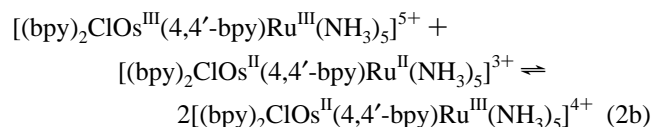
$-26 \pm 3$  mV/DN unit for the  $Ru^{III/II}$  couple in  $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{3+}$ . The  $[(bpy)_2ClOs^{III/II}(L)]^{2+/+}$  couple is only slightly solvent dependent because there are no ammine ligands and no molecular basis for strong, specific interactions with the solvent.  $E_{1/2}$  for the  $[Fe(bpy)_3]^{3+/2+}$  couple varies by only  $-(2-3)$  mV/DN unit.<sup>8a</sup>

**Solvent-Induced Intramolecular Electron Transfer in  $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{4+}$ .** The method of presenting the data in the  $E_{1/2}$ -DN plot in Figure 1 is deceiving in suggesting a phase diagram where variations in applied potential and donor number are both continuous. The donor number is not. The experiments were performed in pure solvents having discrete donor numbers. It remains to be seen if a continuous variation in potential, as suggested by the lines drawn in Figure 1, could be achieved by utilizing solvent mixtures.<sup>10a,12</sup>

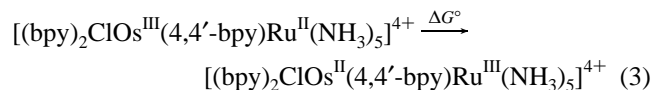
A plot of  $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$  as a function of donor number is shown in Figure 3. The quantity  $\Delta E_{1/2}$  is the driving force for comproportionation and related to the free energy of comproportionation by  $\Delta E_{1/2} = -\Delta G^\circ_{com}$ . There are two comproportionation equilibria. The one that dominates depends on the donor number of the solvent. At  $DN < 14.5$  it is,



and at  $DN > 14.5$ ,



For a hypothetical solvent with a donor number at the inflection point in Figure 3 ( $DN \sim 14.5$ ),  $\Delta G^\circ = 0$  for the intramolecular electron transfer in eq 3.



In this hypothetical solvent,  $\Delta G^\circ = 0$  for the equilibria in eqs 2a and 2b as well.

Figure 3 provides a graphical illustration of the fact that variations in solvent can be used to induce intramolecular electron transfer. There is a change in slope at  $DN \sim 14.5$  from  $-17 \pm 4$  to  $26 \pm 4$  mV/DN unit as the dominant form of the mixed-valence ion changes from  $[(bpy)_2ClOs^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$

to  $[(bpy)_2ClOs^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ . The change in sign of the slope can be explained qualitatively by examining the redox processes involved and the equilibria in eqs 2.

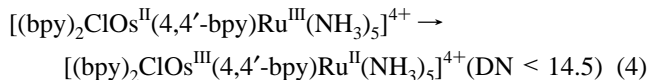
In low donor number solvents, oxidation of  $Os^{II}-Ru^{II}$  occurs to give  $Os^{III}-Ru^{II}$ . In high donor number solvents, oxidation gives  $Os^{II}-Ru^{III}$ .  $E_{1/2}$  for the two couples would be the same ( $\sim 0.53$  V) in a hypothetical solvent of donor number  $\sim 14.5$ . (Benzonitrile, acetonitrile, and propylene carbonate have donor numbers in this region and the  $Ru^{III/II}$  and  $Os^{III/II}$  waves overlap.)<sup>22</sup> If stabilization of  $-Ru^{III}(NH_3)_5^{3+}$  by electron pair donation from the solvent dominates, the left hand side of eq 2a is increasingly favored as the donor number is increased.  $\Delta E_{1/2}$ , the driving force for comproportionation, decreases.

In eq 2b the driving force for comproportionation increases with donor number because of enhanced stabilization of the two  $-Ru^{III}(NH_3)_5^{3+}$  groups on the right-hand side compared with only one on the left. The magnitudes of the slopes in the two regions are different, but the difference is nearly within experimental error. It may be caused by the different charge types of the ions in which  $-Ru^{III}(NH_3)_5^{3+}$  is found ( $+5$  or  $+4$ ).

By extrapolation, in a solvent of  $DN = 0$ , it would be easier to oxidize  $Os^{II}$  than  $Ru^{II}$  by  $\sim 0.29$  V. In DMSO, the solvent of highest donor number used, it is easier to oxidize  $Ru^{II}$  than  $Os^{II}$  by  $\sim 0.39$  V. Equilibrium at  $DN = 14-15$  results from a balance between ease of oxidation in the absence of donor number interactions, which favors oxidation at  $Os^{II}$ , and stabilization by solvent, which favors oxidation at  $Ru^{II}$ . The total variation with solvent for the  $Ru^{III/II}$  couple is  $\sim 0.78$  V. For the  $Os^{III/II}$  couple it is  $\sim 0.10$  V.

**Thermodynamics of Intramolecular Electron Transfer.** The  $E_{1/2}$  vs donor number data in Figure 3 are shown extended into donor number regions where the two mixed-valence isomers are thermodynamically unstable with regard to the disproportionation equilibrium in eq 2 (the dashed lines). In these regions the oxidation state distribution is the non-thermodynamic one,  $Os^{III}-Ru^{II}$  in solvents of high donor number, and  $Os^{II}-Ru^{III}$  in solvents of low donor number. The extrapolated values of  $\Delta E_{1/2}$  cannot be obtained by direct measurement. The mixed-valence isomers are unstable with regard to each other and with regard to disproportionation into  $Os^{III}-Ru^{III} + Os^{II}-Ru^{II}$ .

It is possible to calculate  $\Delta G^\circ$  for intramolecular electron transfer in reaction 3 in a particular solvent by taking the difference between the experimental and extrapolated values of  $\Delta E_{1/2}$  in Figure 3. For reaction 3, which is spontaneous at  $DN > 14.5$ ,  $\Delta G^\circ(eV) = 1/2[\Delta E_{1/2} - \Delta E_{1/2}(extr)]$ .<sup>23</sup> In this equation,  $\Delta E_{1/2}(extr)$  is the extrapolated value of  $\Delta E_{1/2}$  and can be read from the plot in Figure 3. A plot of  $\Delta G^\circ$  vs DN for reaction 3 is shown in Figure 4. In solvents of  $DN < 14.5$ , reaction 4 is spontaneous. In solvents of  $DN > 14.5$  reaction 3 is spontaneous.



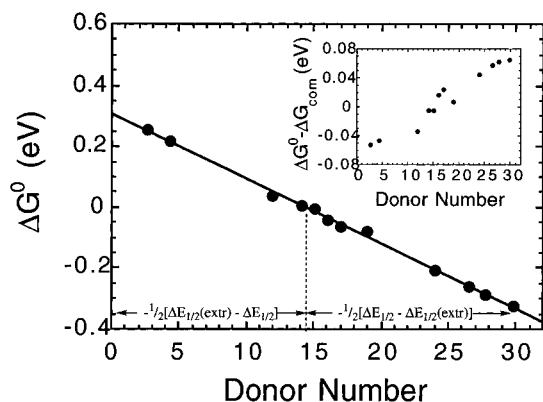
In the classical limit,  $\Delta G^\circ$  and the reorganizational energy ( $\chi$ ) determine the IT band energy.<sup>2,6d,7,24</sup>

$$E_{op} = \Delta G^\circ + \chi \quad (5)$$

In the older mixed-valence literature,  $\Delta E_{1/2}$  is sometimes equated to  $-\Delta G^\circ$ . In fact,  $\Delta E_{1/2}$  measures  $\Delta G^\circ_{com}$  for reaction 2 and

(22) (a) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278. (b) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

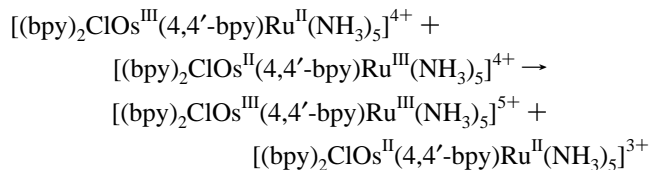
(23) This equation was derived by adding  $-\Delta G^\circ$  for eq 2a ( $=\Delta E_{1/2}$ ) and  $\Delta G^\circ$  for eq 2b in solvents of  $DN < 14.5$  ( $=\Delta E_{1/2}(extr)$ ). This gives  $\Delta G^\circ = \Delta E_{1/2} - \Delta E_{1/2}(extr)$ , for,  $2[(bpy)_2ClOs^{III}(4,4'-bpy)Ru^{II}(NH_3)_5]^{4+} \rightarrow 2[(bpy)_2ClOs^{II}(4,4'-bpy)Ru^{III}(NH_3)_5]^{4+}$ .  $\Delta G^\circ$  for eq 3 is  $1/2$  this value.



**Figure 4.** A plot of  $\Delta G^\circ$  versus donor number for the reaction,  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+} \rightarrow [(\text{bpy})_2\text{ClOs}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{4+}$ . A plot of  $(\Delta G^\circ - \Delta G^\circ_{\text{com}})$  versus donor number, where  $\Delta G^\circ_{\text{com}}$  refers to reaction 2b, is shown in the inset (see text).

not  $\Delta G^\circ$  for reaction 3. The difference is that in low donor number solvents the electrochemical experiment measures the  $\text{Os}^{\text{III/II}}$  couple in  $[(\text{bpy})_2\text{ClOs}^{\text{III/II}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+/3+}$  and the  $\text{Ru}^{\text{III/II}}$  couple in  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(4,4'\text{-bpy})\text{Ru}^{\text{III/II}}(\text{NH}_3)_5]^{5+/4+}$ . In high donor number solvents the  $\text{Os}^{\text{III/II}}$  couple is measured in  $[(\text{bpy})_2\text{ClOs}^{\text{III/II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+/4+}$  and the  $\text{Ru}^{\text{III/II}}$  couple in  $[(\text{bpy})_2\text{ClOs}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III/II}}(\text{NH}_3)_5]^{4+/3+}$ . As noted above, it is not possible to obtain  $\Delta G^\circ$  directly by electrochemical measurements.

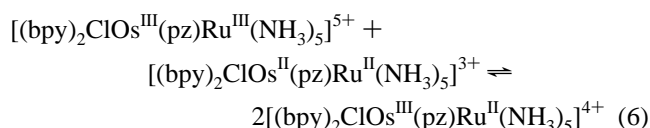
As shown in the inset in Figure 4, the difference between  $\Delta G^\circ$  and  $\Delta G^\circ_{\text{com}}$  increases as the donor number is increased or decreased from  $\text{DN} = 14.5$ . In the solvents studied, the difference is as large as 0.06 eV, at high or low donor number. The quantity  $\Delta G^\circ - \Delta G^\circ_{\text{com}}$  is the free energy change for the reaction,



The total variation in this range of solvents (0.12 eV) is  $\sim 20\%$  of the variation in  $\Delta G^\circ$ . From this, the relationship  $\Delta E_{1/2} = -\Delta G^\circ$  is not quantitatively valid.

There is a slight inconsistency between Figures 1 and 3 in the implied donor number at which the oxidation states interconvert. Based on spectroscopic measurements,  $\Delta G^\circ = 0$  for intramolecular electron transfer at the inflection point in Figure 3 ( $\text{DN} = 14\text{--}15$ ) as it should.<sup>21</sup> The crossing of the  $E_{1/2}$ -DN lines in Figure 1 occurs at a slightly lower donor number ( $\text{DN} = 12.8$ ) because four different couples are measured, e.g.,  $[(\text{bpy})_2\text{ClOs}^{\text{III/II}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+/3+}$ ,  $[(\text{bpy})_2\text{ClOs}^{\text{III/II}}(4,4'\text{-bpy})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+/4+}$ ,  $[(\text{bpy})_2\text{ClOs}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{III/II}}(\text{NH}_3)_5]^{4+/3+}$ ,  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(4,4'\text{-bpy})\text{Ru}^{\text{III/II}}(\text{NH}_3)_5]^{5+/4+}$ . The variations in the pairs of couples with solvent are slightly different.

**Solvent-Induced Electronic Delocalization in  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(\text{pz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{4+}$ .** Although  $\Delta E_{1/2} \sim 0$  V for  $[(\text{bpy})_2\text{ClOs}^{\text{II}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$  in acetonitrile, it is 0.36 V for  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(\text{pz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{4+}$ . From the latter value,  $\Delta G^\circ_{\text{com}} = -0.36$  V for the equilibrium,



A contributing factor to the enhanced stability of the pyrazine-bridged complex is greater electronic delocalization by through-bridge coupling. Enhanced coupling plays a role in comparing pyrazine and 4,4'-bipyridine as bridges in  $[(\text{NH}_3)_5\text{Ru}(\text{L})\text{Ru}(\text{NH}_3)_5]^{5+}$ <sup>13a,22b,25,26</sup> or  $[(\text{bpy})_2\text{ClOs}(\text{L})\text{OsCl}(\text{bpy})_2]^{3+}$ .<sup>28</sup> The stability of mixed-valence ions toward disproportionation depends on electrostatic effects and solvation energies, as well as electronic delocalization.<sup>13c,22b,24</sup> An estimate of the contribution from delocalization can be made by taking the difference,  $\Delta(\Delta E_{1/2}) (= [\Delta E_{1/2}(\text{pz}) - \Delta E_{1/2}(4,4'\text{-bpy})])$ , as an approximate means for cancelling solvation and electrostatic effects. (This is only an approximate comparison because of the difference in bridge lengths.) In propylene carbonate, acetone, and methanol, where the oxidation states are  $\text{Os}^{\text{III}}\text{--Ru}^{\text{II}}$  for  $\text{L} = \text{pz}$  and  $\text{Os}^{\text{II}}\text{--Ru}^{\text{III}}$  for  $\text{L} = 4,4'\text{-bpy}$ , a more appropriate comparison is between  $\Delta E_{1/2}(\text{pz})$  and  $\Delta E_{1/2}(\text{extr})$  for  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$ . The comproportionation equilibria in both cases then involve  $\text{Os}^{\text{III}}\text{--Ru}^{\text{II}}$ . The extrapolated values can be taken from Figure 3. This procedure gives  $\Delta(\Delta E_{1/2}) = 0.32$ , 0.34, and 0.38 V in propylene carbonate, acetone, and methanol respectively. When included with the data in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NO}_2$ , and  $\text{PhNO}_2$ , where  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(\text{L})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$  is the dominant isomer for both bridging ligands, the average value is  $\leq 0.34$  eV. This is the excess stabilization energy for pz as the bridge compared to 4,4'-bpy arising from electronic effects. It is an upper limit (by 50–100 meV) because of neglect of stabilization of the pyrazine-bridged complex by electrostatic effects.<sup>6b</sup>

The excess stabilization energy is for the equilibrium in eq 6. From magnetic measurements on related complexes, the contribution from  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(\text{pz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$  is expected to be negligible.<sup>27</sup> The value of  $\leq 0.34$  eV is determined by the extent of electronic delocalization in  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(\text{pz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$  and the degree of “ $\pi$ -crowding” in  $[(\text{bpy})_2\text{ClOs}^{\text{II}}(\text{pz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{3+}$ .<sup>13</sup> There is no way to separate the two by electrochemical measurements.

Delocalization is expected to play a role since there are well-defined orbital pathways for electronic coupling. They arise by mixing  $d\pi(\text{Os}^{\text{III}})$  and  $d\pi(\text{Os}^{\text{II}})$  with  $\pi$  and  $\pi^*(\text{pz})$  leading to  $d\pi(\text{Os}^{\text{III}})\text{--}\pi(\text{pz})\text{--}d\pi(\text{Ru}^{\text{II}})$  and  $d\pi(\text{Os}^{\text{III}})\text{--}\pi^*(\text{pz})\text{--}d\pi(\text{Ru}^{\text{II}})$  coupling.<sup>29–31</sup>

The effect of electronic delocalization in the  $\text{Os}^{\text{III}}\text{--Ru}^{\text{II}}$  mixed-valence ion is also seen in the increased sensitivity of the  $\text{Os}^{\text{III/II}}$  couple in  $[(\text{bpy})_2\text{ClOs}^{\text{II}}(\text{pz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{3+}$  to donor number ( $-8 \pm 4$  mV/DN) compared to  $[(\text{bpy})_2\text{ClOs}^{\text{III}}(4,4'\text{-bpy})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$  ( $-3 \pm 1$  mV/DN).<sup>13c</sup> This increase occurs at the expense of the  $\text{Ru}^{\text{III/II}}$  couple. If the loss in its sensitivity ( $21 \pm 4$  mV/DN compared to  $26 \pm 3$  mV/DN) mirrors the extent of delocalization,<sup>13a,c</sup>  $\sim 20\%$  of a unit electron is transferred across the bridge by orbital mixing.

**Solvent Coupling with Electronic Structure.** At  $\text{DN} > 24$  the oxidation states in  $[(\text{bpy})_2\text{ClOs}(\text{pz})\text{Ru}(\text{NH}_3)_5]^{4+}$  interconvert between  $\text{Os}^{\text{III}}\text{--Ru}^{\text{II}}$  and  $\text{Os}^{\text{II}}\text{--Ru}^{\text{III}}$  as shown by spectroscopic measurements.<sup>21</sup> The  $\text{Ru}^{\text{III/II}}$  couple reassumes most of the solvent dependence and the  $\text{Os}^{\text{III/II}}$  couple becomes nearly

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solvent independent (Figure 2). In these solvents  $\Delta(\Delta E_{1/2}) \sim 0$  for  $[(bpy)_2ClOs^II(pz)Ru^III(NH_3)_5]^{4+}$  compared to  $[(bpy)_2ClOs^II(4,4'-bpy)Ru^III(NH_3)_5]^{4+}$ , Table 1. There is no evidence for significant stabilization of  $Os^II-Ru^III$  by electronic delocalization.

Although the data are limited and the extrapolation long, the  $E_{1/2}$  vs DN lines in Figure 3 for the  $Os^III/II$  couple (top line) and  $Ru^III/II$  couple (bottom line) in the three solvents of high donor number (DMF, DMA, and DMSO) intersect at  $DN \sim 14-15$ . This is the same donor number region in which  $Os^III-Ru^II$  and  $Os^II-Ru^III$  are in equilibrium in  $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{4+}$ . By extrapolation, it is the donor number region where  $[(bpy)_2ClOs^II(pz)Ru^III(NH_3)_5]^{4+}$  would be in equilibrium with a hypothetical form of  $[(bpy)_2ClOs^III(pz)Ru^II(NH_3)_5]^{4+}$  having the delocalization energy of  $[(bpy)_2ClOs^II(pz)Ru^III(NH_3)_5]^{4+}$ .

The increase in donor number at which  $Os^III-Ru^II$  and  $Os^II-Ru^III$  are in equilibrium, from  $DN \sim 14.5$  for  $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{4+}$  to  $DN \sim 23$  for  $[(bpy)_2ClOs(pz)Ru(NH_3)_5]^{4+}$ ,<sup>21</sup> is also a consequence of enhanced delocalization for  $L = pz$ . A higher donor number (and enhanced solvation) is required to stabilize  $-Ru^III(NH_3)_5^{3+}$  and overcome enhanced delocalization in  $Os^III-Ru^II$ .

The implied difference in electronic structure between  $[(bpy)_2ClOs^II(pz)Ru^III(NH_3)_5]^{4+}$  and  $[(bpy)_2ClOs^III(pz)Ru^II(NH_3)_5]^{4+}$  is striking and of fundamental importance in accounting for the properties of the mixed-valence ion.<sup>21</sup> The difference between isomers lies in specific solvent effects and differences between  $-Ru^III(NH_3)_5^{3+}$  and  $-Ru^II(NH_3)_5^{2+}$  in the extent of their H-bonding with the solvent. In  $Os^II-Ru^III$ , electron pair donation to  $-Ru^III(NH_3)_5^{3+}$  from the solvent by H-bonding mixes solvent character into  $d\pi(Ru^III)$  by electron donation. This mixing is enhanced in higher donor number solvents which decreases  $d\pi(Ru^III)-\pi(pz)$  mixing and  $d\pi(Os^II)-\pi(pz)-d\pi(Ru^III)$  coupling across the bridge. H-bonding is less important at  $-Ru^II(NH_3)_5^{2+}$  and promotes through-bridge coupling. Electron donation to  $d\pi(Ru^II)$  by H-bonding increases electron content at  $d\pi(Ru^II)$  increasing  $\pi^*(pz)-d\pi(Ru^II)$  mixing and  $d\pi(Os^III)-\pi^*(pz)-d\pi(Ru^II)$  coupling across the bridge.

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