Inorg. Chem. **1989**, *28*, 3791–3795

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Redox Thermodynamics of Dinuclear Transition-Metal Complexes. Unusual Entropy and Electronic Coupling Effects in Mixed Solvents

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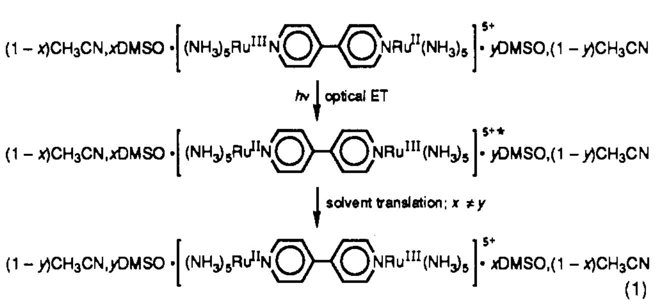
Received March 30, 1989

As a guide to the thermodynamics of intramolecular electron-transfer processes, the redox thermodynamics of three dinuclear transition-metal systems have been investigated in mixtures of acetonitrile and dimethyl sulfoxide (DMSO) as solvent. The specific systems are (2,2′-bipyridine)$_2$ClRu–L–Ru(NH$_3$)$_4$(pyridine)$^{5+/4+/3+}$, where L is pyrazine, 4,4′-bipyridine, or bis(pyridyl)ethane. A special feature is that the tetraammineruthenium redox site in each interacts specifically with hydrogen-bond-accepting (electron-pair-donating) solvents (as demonstrated by various optical and electrochemical measurements (Curtis et al. *Inorg. Chem.* **1986**, *25*, 4233; **1987**, *26*, 2660)) whereas the (polypyridyl)ruthenium site does not. Thus, the formal potential (E_f) for the ammine fragment is shifted to progressively less positive values as the solvent is enriched in DMSO. Measurements of E_f for the Ru$^{III/II}$–polypyridyl fragment demonstrate that the solvational effects are readily transmitted electronically from the ammine fragment when pyrazine is the bridge. Variable-temperature E_f measurements reveal a sharp positive "spike" in plots of the half-reaction entropy for each of the tetraammine couples versus mixed-solvent composition. A statistical calculation shows that the entropy spike is a direct consequence of the unsymmetrical preferential solvation of (2,2′-bipyridine)$_2$Ru^{II}–L–Ru^{III}(NH$_3$)$_4$(pyridine)$^{4+}$ versus (2,2′-bipyridine)$_2$Ru^{II}–L–Ru^{II}(NH$_3$)$_4$(pyridine)$^{3+}$, as found elsewhere for monomeric redox couples and as earlier predicted from optical intervalence studies. Further examination shows that the entropy effects also are transmitted electronically from the tetraammine site to the polypyridyl site and are detectable in both the pyrazine- and 4,4′-bipyridine-bridged cases. An evaluation of the overall intervalence thermodynamics reveals that $\Delta S°$ "leads" $\Delta G°$ on a solvent molar composition coordinate. This suggests that unusual mixed-solvent-induced variations in activation parameters might also be observed in related kinetic experiments.

Introduction

Both our laboratories have been working recently on problems relating to the preferential solvation of metal complexes in binary mixed solvents.[1,2] The motivation stems from a desire to understand the molecular details of solvent reorganization in various charge-transfer reactions and from a more general interest in redox reactivity in mixed-solvent environments. In our previous work the main experimental probe has been optical charge-transfer absorbance measurements for the metal-to-metal (or intervalence) transition occurring within dinuclear mixed-valence complexes. From those measurements it has become clear that the most interesting mixed-solvent phenomena are likely to be found in those cases where there is *unsymmetrical* preferential solvation—in other words, where a redox site in one oxidation state is preferentially solvated to an extent different from that in another. As an example, in selected mixed-valence experiments unsymmetrical selective solvation can lead to a substantial increase in the Franck–Condon barrier to optical electron transfer.[1,2] One way of understanding the effect is to note that in mixed solvents, instantaneous optical electron transfer is coupled energetically to the subsequent need for net solvent translation as shown, for example, by eq 1.

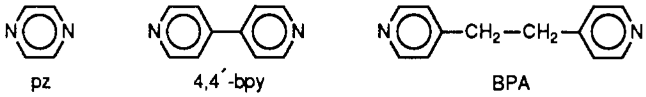


(1)

Besides the optical phenomena, there are likely to be additional manifestations of unsymmetrical preferential solvation. For example, because of the barrier effects, rates for related thermal electron exchange reactions should go through a pronounced minimum in the compositional region where unsymmetrical effects are greatest.[1,2] This prediction has not yet been tested directly, but there is extensive circumstantial evidence from various other heterogeneous (electrochemical)[3] and bimolecular homogeneous kinetic investigations in mixed solvents.[4]

Another prediction is that significant entropy effects ought to exist—both in a kinetic and thermodynamic sense—whenever unsymmetrical selective solvation accompanies a redox process.[2] In a related paper[5] we have investigated the second issue (thermodynamics) for a series of monomeric redox couples by using an electrochemical nonisothermal cell method.[6] Substantial entropic redox (half-reaction) effects were indeed found, and these could be reasonably well described by a simple two-phase statistical model of unsymmetrical selective solvation.[5]

In this paper we expand on that problem by extending the thermodynamic study to unsymmetrical dinuclear complexes of the type (bpy)ClRu–L–Ru(NH$_3$)$_4$(py)$^{5+/4+/3+}$, where bpy is 2,2′-bipyridine, py is pyridine, and the bridging ligand can be pyrazine (pz), 4,4′-bipyridine (4,4′-bpy), or bis(pyridyl)ethane (BPA). The motivations for the study were the following: (1) The initial suggestion that unusual entropy effects might accompany redox transformations in mixed-solvent environments came specifically from studies involving the pyrazine-bridged dinuclear



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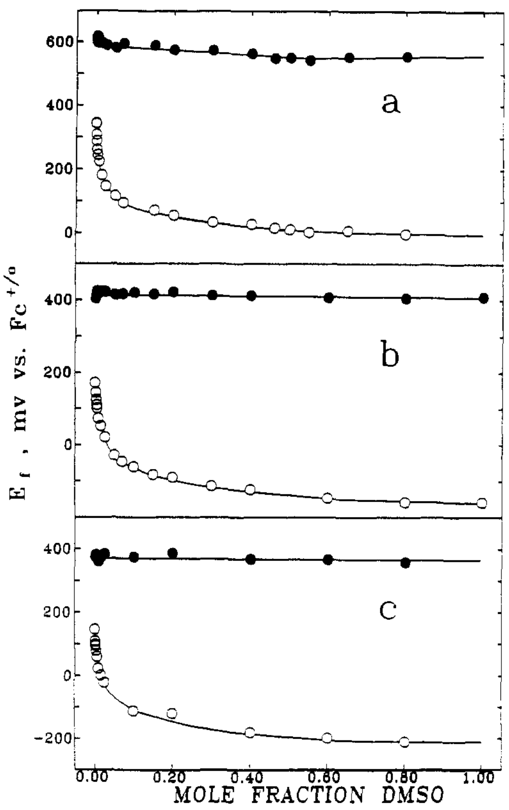

Figure 1. E_f vs solvent composition (CH_3CN + DMSO mixtures) for various $(bpy)_2ClRu\text{-}L\text{-}Ru(NH_3)_4(py)^{5+/4+/3+}$. Ferrocenium/ferrocene was employed as an internal reference. Note that in each panel the 5+/4+ couple is designated by filled circles, and the 4+/3+ couple, by open circles. Key to redox couples: (a) L = pyrazine; (b) L = 4,4'-bipyridine; (c) L = bis(pyridyl)ethane.

system.[2] Furthermore, optical data exist that permit the prediction to be quantified.[2] (2) The available evidence indicates that in such systems, preferential solvation in dimethyl sulfoxide (DMSO) + acetonitrile mixtures is confined to the ammine end of the complex.[2] There is an opportunity, therefore, to discover how (or, even, if) special solvational effects can be communicated through various bridges to the "noninteracting" end of the complex. (3) Sequential electrochemical thermodynamic measurements involving the local redox sites, i.e. the 5+/4+ and 4+/3+ couples, ought to provide a reasonable basis for describing the overall thermodynamics for the intramolecular electron-transfer process, which interrelates the two possible forms of the mixed-valence (4+) ion:

$$(bpy)_2ClRu^{II}\text{-}L\text{-}Ru^{III}(NH_3)_4(py)^{4+} \rightleftarrows (bpy)_2ClRu^{III}\text{-}L\text{-}Ru^{II}(NH_3)_4(py)^{4+} \quad (2)$$

Information of this kind would then provide a basis for predicting and understanding activation parameters for mixed-solvent redox events in related systems.

What has emerged from the present investigation is further evidence that unsymmetrical preferential solvation can lead to unusual thermodynamic properties for individual (half-reaction), as well as overall (two-center), redox processes. We have also obtained evidence from the thermodynamic measurements for some surprising site-to-site coupling phenomena. Entropy measurements, in particular, are found to be sensitive probes of coupling.

Experimental Section

Materials. Prepurified solvents were obtained from Fischer and Aldrich. Tetraethylammonium hexafluorophosphate (TEAH) was prepared from tetraethylammonium bromide and hexafluorophosphoric acid. The crude salt was recrystallized three times from water. $[(bpy)_2ClRu\text{-}pz\text{-}Ru(NH_3)_4(py)](PF_6)_3$,[7] and $[(bpy)_2ClRu(4,4'\text{-}bpy)](PF_6)$[7,8] were prepared and purified by literature methods. $[(bpy)_2ClRu\text{-}BPA\text{-}Ru(NH_3)_4(py)](PF_6)_3$ was obtained in an analogous fashion, except that the $(bpy)_2ClRu\text{-}BPA^+$ fragment was synthesized from a nitrosyl intermediate.[9] Anal. Calcd: C, 33.8; H, 3.4; N, 11.7; F, 26.0. Found (two determinations): C, 30.88 (32.94); H, 3.57 (4.00); N, 11.33 (9.46); F, 25.69. $[(bpy)_2ClRu\text{-}4,4'\text{-}bpy\text{-}Ru(NH_3)_4(py)](PF_6)_3$ was prepared and purified in the same way as the BPA-bridged complex. Anal. Calcd: C, 32.6; H, 3.2; N, 12.0. Found: C, 31.0; H, 3.75; N, 9.86.

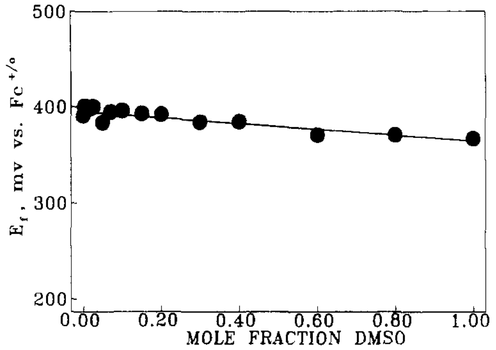

Figure 2. E_f vs solvent composition for reduction of $(bpy)_2ClRu^{III}(4,4'\text{-}bpy)^{2+}$. Ferrocenium/ferrocene was employed as an internal reference.

Measurements. Electrochemical measurements were made in a three-compartment nonisothermal cell (working compartment, nonisothermal bridge, and reference compartment) with the same solvent composition in all three parts. Either a gold wire or platinum disk served as the working electrode, with a gold or platinum wire as the counter electrode and a saturated (NaCl) calomel electrode as the reference. Formal potentials (E_f) were obtained from reversible differential-pulse voltammograms (typically at 2 mV/s) or cyclic voltammograms by using either a PAR 174A polarographic analyzer or IBM EC225 potentiostat and a Houston Omnigraphic recorder. Differential-pulse voltammetry proved to be particularly useful for discriminating against solvent oxidation (especially for high mole fractions of DMSO). The supporting electrolyte in all of the experiments was 0.1 M TEAH.

Half-reaction entropies, ΔS°_{rc} ($=\bar{S}^\circ_{red} - \bar{S}^\circ_{ox}$), were determined from variable-temperature E_f measurements obtained in a nonisothermal cell configuration:[6]

$$\Delta S^\circ_{rc} \approx F(dE_f/dT)_{ni} \quad (3)$$

Typically for each entropy determination, 7-10 potentials were obtained in increments of ca. 5 °C. The measurement precision was ca. 1.5 eu within a single lab and 2-3 eu between labs.

Results

Half-Reactions. Formal potentials for the three dinuclear complexes (eq 4) are plotted in Figure 1 as a function of mixed-solvent composition. Figure 2 shows a related plot for the

$$(bpy)_2ClRu^{III}\text{-}L\text{-}Ru^{III}(NH_3)_4(py)^{5+} + e^- \xrightarrow{E_f(1),\ \Delta S^\circ_{rc}(1)} (bpy)_2ClRu^{II}\text{-}L\text{-}Ru^{III}(NH_3)_4(py)^{4+} + e^- \xrightarrow{E_f(2),\ \Delta S^\circ_{rc}(2)} (bpy)_2ClRu^{II}\text{-}L\text{-}Ru^{II}(NH_3)_4(py)^{3+} \quad (4)$$

control reaction involving $(bpy)_2ClRu(4,4'\text{-}bpy)^{2+/+}$. In both figures the potentials have been converted to the ferrocenium/ferrocene scale, since this couple has been proposed as a solvent-independent reference.[10] Important observations are that the tetraammineruthenium(III) reduction potentials are strongly dependent on solvent composition, whereas the $(bpy)_2ClRu^{III}(L)$ potentials are not.

Half-reaction entropies, $\Delta S^\circ_{rc}(1)$ and $\Delta S^\circ_{rc}(2)$, for the metal-based couples in the three dinuclear complexes are plotted in Figures 3-5 as a function of mixed-solvent composition. For $(bpy)_2ClRu(4,4'\text{-}bpy)^{2+/+}$ they are shown in Figure 6. From the figures the most striking results are the following: (1) The reaction entropies for all three $(L)Ru(NH_3)_4(py)$ fragments exhibit an asymmetric "spike" in the solvent composition plot at a point that corresponds to about 0.5-1 mol % DMSO + 99.5-99 mol %

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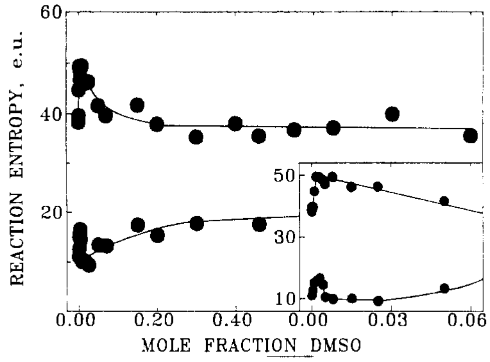

Figure 3. ΔS°_{rc} vs solvent composition (CH_3CN + DMSO mixtures) for the reduction of $(bpy)_2ClRu^{III}$–pz–$Ru^{III}(NH_3)_4(py)^{5+}$ (bottom) and $(bpy)_2ClRu^{II}$–pz–$Ru^{III}(NH_3)_4(py)^{4+}$ (top).

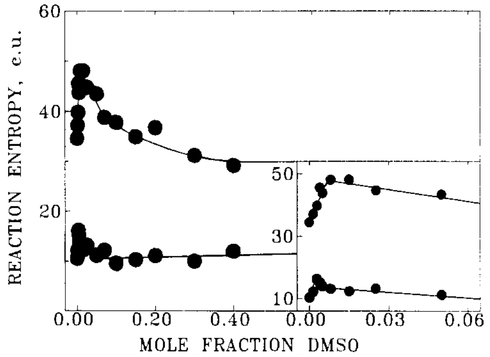

Figure 4. ΔS°_{rc} vs solvent composition (CH_2CN + DMSO mixtures) for the reduction of $(bpy)_2ClRu^{III}$–4,4′-bpy–$Ru^{III}(NH_3)_4(py)^{5+}$ (bottom) and $(bpy)_2ClRu^{II}$–4,4′-bpy–$Ru^{III}(NH_3)_4(py)^{4+}$ (top).

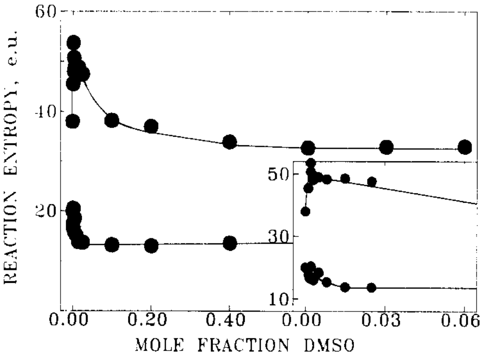

Figure 5. ΔS°_{rc} vs solvent composition (CH_3CN + DMSO mixtures) for the reduction of $(bpy)_2ClRu^{III}$–BPA–$Ru^{III}(NH_3)_4(py)_5{}^+$ (top) and $(bpy)_2ClRu^{II}$–BPA–$Ru^{III}(NH_3)_4(py)^{4+}$ (bottom).

CH_3CN. (2) For all four $(bpy)_2ClRu(L)$ couples the spike at ca. 1 mol % DMSO is absent. (3) For the pyrazine- and 4,4′-bipyridine-bridged dinuclear complexes, however, there exists an even sharper spike in the entropy plot at 0.3 mol % DMSO. (Neither rigorous solvent drying nor intentional contamination with water modified this result.) Its absence for the mononuclear complex and for the BPA-bridged dinuclear complex clearly indicates that it is a genuine chemical effect (i.e. it is not due to unusual thermal liquid-junction phenomena or to other artifacts that might be unique to particular mixed-solvent compositions). (4) Values for ΔS°_{rc} are uniformly higher for the ruthenium–ammine versus ruthenium–polypyridine fragments.

Intervalence Reactions. Half-reaction data for the two ends of each asymmetric dimer can be combined to yield an apparent redox thermodynamic parameter for the net intervalence process (eq 2; forward direction) as shown:

$$\Delta G_{app} = F[E_f(1) - E_f(2)] \tag{5}$$

$$\Delta S_{app} = \Delta S^\circ_{rc}(2) - \Delta S^\circ_{rc}(1) \tag{6}$$

$$\Delta H_{app} = \Delta G_{app} - T\Delta S_{app} \tag{7}$$

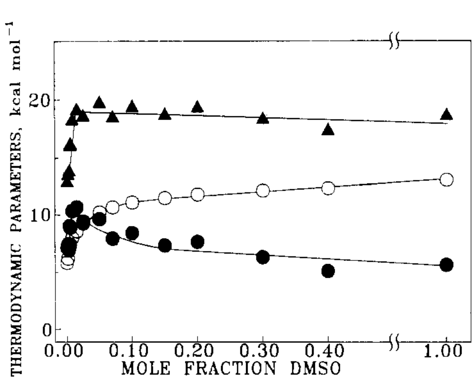

Figure 6. Apparent overall free energy, entropy, and enthalpy changes for eq 1 (electrochemically determined; see text) as a function of solvent composition (CH_3CN + DMSO mixtures): (○) ΔG_{app}; (▲) ΔH_{app}; (●) $T\Delta S_{app}$.

It is important to note that the reliability of parameters obtained in this way does not rest upon the validity of either the "ferrocene" assumption or the "nonisothermal cell assumption". (Any shortcomings in either will be negated once the difference between two half-reactions is taken.) Nevertheless, the parameters are still only an approximation to the true intramolecular thermodynamics quantities, since other factors are known to contribute to the redox potentials.[11] For example, the difference between $E_f(1)$ and $E_f(2)$ can also reflect electrostatic, statistical, and electronic mixing contributions, and it is possible that one or more of these might also display a significant temperature dependence. In the present cases, because $E_f(1)$ and $E_f(2)$ are so dissimilar, statistical contributions can safely be neglected. The other two effects are likely to be important for the pyrazine-bridged case. On the other hand, for the BPA-bridged complex, all three effects are likely to be small on account of the larger separation distance, saturation in the bridge, etc. It would seem for the BPA and 4,4′-bpy-bridged complexes, at least, that the apparent intervalence parameters from eq 5–7 would be very good representations of the true thermodynamic quantities. Representative data for the 4,4′-bipyridine-bridged system are shown in Figure 6.

Discussion

Formal Potentials. Consistent with previous studies, E_f values for the ammine-containing couples show a strong dependence on solvent composition, while the bipyridyl couples do not. For the former, the effects have been interpreted in terms of oxidation-state-dependent hydrogen-bonding interactions between basic (in a Lewis sense) solvent functionalities and acidic ammine hydrogens.[1,2,12] Preferential stabilization of the Ru^{III} form by hydrogen bonding accounts for the negative shifts in formal potential in the presence of a strongly electron-donating solvent like DMSO. The fact that the shifts occur with relatively small amounts of DMSO (Figure 1) is indicative of substantial preferential solvation. In contrast, the absence of large potential shifts for the (polypyridyl)ruthenium couples suggests that here specific ligand–solvent interactions are weak or absent. Again, these findings are consistent with previous reports.[13]

A more interesting issue for the ligand-bridged complexes is whether solvational effects at the amminemetal center can be transmitted to the noninteracting polypyridyl end. In principle, an electronic basis for such transmission exists in the mixed-valence form of the complex through partial delocalization of the odd valence electron. On the other hand, delocalization is not possible in the filled d^6–d^6 configuration. Furthermore, it is energetically unlikely in the d^5–d^5 configuration because of the inaccessibility

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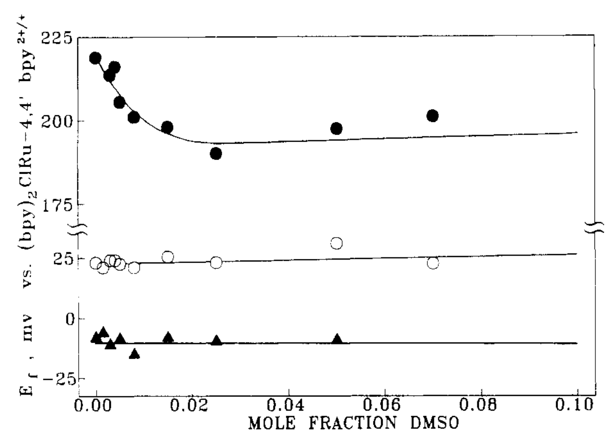

Figure 7. Expanded plots of E_f vs solvent composition for various $(bpy)_2ClRu\text{-}L\text{-}Ru(NH_3)_4(py)^{5+/4+}$ couples (cf. Figure 1). $(bpy)_2ClRu(4,4'\text{-}bpy)^{2+/+}$ was used as an internal reference. Key to redox couples: (●) L = pyrazine; (○) L = 4,4'-bpy; (▲) L = BPA.

of d^4 ruthenium,[14] at least for these ligand environments.

We have examined the issue of bridge-transmitted solvational effects by evaluating in a more detailed way the available electrochemical data. Figure 7 shows a greatly expanded plot of the mixed-solvent formal potentials for $(bpy)_2ClRu\text{-}L\text{-}Ru(NH_3)_4(py)^{5+/4+}$. In order to correct for any possible deficiencies in the ferrocene assumption and also to account for possible residual interactions between the solvent and the $(bpy)_2ClRu^{III/II}$ fragment, we have employed the $(bpy)_2ClRu(4,4'\text{-}bpy)^{2+/+}$ monomeric redox couple in place of ferrocenium/ferrocene as the reference. From the plot, with pyrazine as the bridge, there is a clear indication of a remote-site electrochemical effect. The 5+/4+ potential shifts with added DMSO in a way that is reminiscent of the 4+/3+ couple. For 4,4'-bpy as the bridge there are also slight potential shifts. These, however, are in the positive rather than negative direction. Furthermore the shifts occur uniformly over the entire solvent range, rather than selectively as in the pyrazine case. We therefore attribute the shifts to effects other than remote-site mixing.

Returning to the pyrazine case, the relative magnitude of the induced potential shift at the (polypyridyl)ruthenium site can provide a semiquantitative measure of ligand-mediated mixing effects. We have shown elsewhere that Mulliken charge-transfer theory can be used to derive the relationships[15]

$$\frac{\delta E_f(Ru_b)}{\delta E_f(Ru_a)} = m' \qquad (8)$$

and

$$(m')^{1/2} \approx a/b \qquad (9)$$

where $\delta E_f(Ru_b)$ is the shift in potential at site b in response to a shift ($\delta E_f(Ru_a)$) at site a. In eq 9, a and b are coefficients for the zero-order wave functions (ψ_a and ψ_b) describing complete localization of the excess electron on either Ru_a or Ru_b. A first approximation to the wave function is then

$$\psi = a\psi_a + b\psi_b \qquad (10)$$

From the mixed-solvent experiments, $\delta E_f(Ru_b)$ is 35 ± 6 mV and $\delta E_f(Ru_a)$ is 330 ± 5 mV, yielding 0.33 for a/b. If we impose the additional condition that $a^2 + b^2$ equal unity, then the solutions are $a^2 = 0.10 \pm 0.02$ and $b^2 = 0.90 \pm 0.02$; i.e., valence localization is about 90% complete. These results are in good agreement with those from a related electrochemical experiment ($b^2 = 0.9$, $a^2 = 0.1$) where perturbations were introduced at the tetraammineruthenium site by systematically changing the ligand *trans* to the bridge.[15] The absence of significant shifts in the (polypyridyl)ruthenium potential when the bridge is either 4,4'-bpy or BPA indicates that in those cases valence localization is virtually complete.

One other subtlety in the 5+/4+ data needs to be noted: The 5+/4+ potentials actually show a *sharper* (albeit smaller) dependence on solvent composition in the dilute DMSO region than do the potentials for the 4+/3+ (ruthenium ammine) couple (cf. Figures 1 and 7). A simple explanation becomes available when one considers carefully the nature of the chemical entity that induces the potential shifts. In the 5+/4+ case, $(py)(NH_3)_4Ru^{III}$ can be regarded as a solvent-tunable "substituent" that indirectly influences E_f. On the other hand, in the 4+/3+ case the properties of the *reduced* form of tetraammineruthenium pyridine are involved as well. Our previous optical studies show that $(py)(NH_3)_4Ru^{III}$ is much more readily selectively solvated by DMSO than is $(py)(NH_3)_4Ru^{II}$.[2] Furthermore, the redox potential interrelating the two shows a functional dependence on solvent that is intermediate between the available optical data for the individual oxidation states. It follows then, that with Ru^{III} as the oxidation state at the remote redox site, the 5+/4+ potential will shift more readily (but less extensively) than will the potential measured directly at the $(py)(NH_3)_4Ru^{III/II}$ site.

Reaction Entropies. The pattern of reaction entropies at the $(py)(NH_3)_4Ru\text{-}L$ end of each of the three dinuclear complexes is strongly reminiscent of the pattern described for mononuclear ammine complexes in an accompanying report.[5] In that report, the most striking feature—the initial sharp rise in ΔS°_{rc} and the more gradual decline with increasing amounts of DMSO—was shown to be due to unsymmetrical selective solvation effects (cf. eq 1). As noted above, binding of DMSO in the secondary coordination sphere is more strongly favored with $(py)(NH_3)_4Ru^{III}$ than $(py)(NH_3)_4Ru^{II}$. If the mole fraction of DMSO (m_{DMSO}) is sufficiently small that binding is incomplete, then reduction of Ru^{III} leads to release of DMSO into the bulk. Intuitively, such a process would seem to involve a net entropy increase and, indeed, this is the case. In the preceding article,[5] quantitative predictions were offered in the form of eq 11 and 12. In eq 11, con =

$$\Delta S_{con} = R(n_{CH_3CN} \ln m_{CH_3CN} + n_{DMSO} \ln m_{DMSO} - n_{CH_3CN} \ln m'_{CH_3CN} - n_{DMSO} \ln m'_{DMSO}) + S_4 \qquad (11)$$

$$\Delta S^\circ_{rc}(con) = \Delta S^{red}_{con} - \Delta S^{ox}_{con} \qquad (12)$$

configuration, n_i is the number of moles of solvent i in the secondary coordination sphere (per mole of solute), m'_i is the mole fraction of solvent i in the secondary coordination sphere, and S_4 is a hypothetical entropy for mixing 1 mol of (initially isolated) selectively solvated solute back into $N - n_{CH_3CN} - n_{DMSO}$ moles of bulk solvent, where N is the total number of moles of solvent initially present. The physical basis for eq 11 is described in the accompanying article[5] and in greater detail in an early report by Frankel, Langford, and Stengle.[16] Briefly, however, the equation views selective solvation as a phase-transfer problem (bulk → secondary coordination sphere). Within that context, it then describes the entropic cost of *preferentially* solvating 1 mol of a very dilute solute in a binary mixed solvent. Equation 12 relates the solvent configuration entropies for the individual oxidation states to the experimental observable in the electrochemical measurement. Specifically, $\Delta S^\circ_{rc}(con)$ is the "extra" component of the reaction entropy that is found only in mixed solvents.

To evaluate eq 11 and 12 and obtain a "theoretical" prediction of the mixed-solvent dependence of ΔS°_{rc}, estimates for the various solvation numbers (n) and mole fractions (m_i and m'_i) are required. (S_4 is expected to be nearly independent of bulk solvent composition and independent of the solute oxidation state as well, so its contribution should cancel in eq 12.) Estimates for m'_i can be obtained if it is assumed that solvatochromic shifts for appropriate charge-transfer transitions are scaled linearly with the composition of the secondary coordination layer in the vicinity of the ammine binding sites. For $(py)(NH_3)_4Ru^{II}\text{-}L$, the metal-to-bridging-ligand

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(14) The "resonance configuration" for one-electron exchange would be d^4–d^6 (or d^6–d^4).

(15) de la Rosa, R.; Chang, P. J.; Salaymeh, F.; Curtis, J. C. *Inorg. Chem.* **1985**, *24*, 4231.

(16) Frankel, L. S.; Langford, C. H.; Stengle, T. R. *J. Phys. Chem.* **1970**, *70*, 1376.

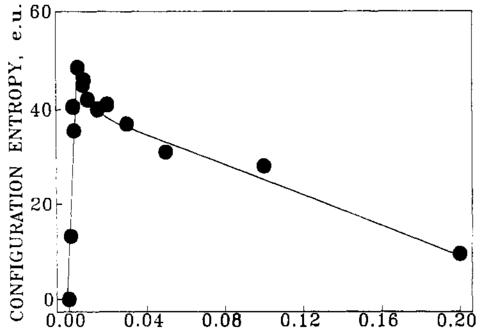

Figure 8. Calculated configuration reaction entropies (eq 11 and 12) for the reduction of $(bpy)_2ClRu^{II}$–pz–$Ru^{III}(NH_3)_4(py)^{4+}$ in mixtures of CH_3CN + DMSO as solvent. (Note that the required E^{MLCT} data for several of the points were interpolated; see text and ref 2 and 5 for details.)

transition can be employed.[2] For $(py)(NH_3)_4Ru^{III}$–L, it has been argued that the intervalence transition is a suitable choice.[2] The various n_i can then be obtained if the total solvation number ($n_{DMSO} + n_{CH_3CN}$) for the tetraammine fragment is known. Unfortunately, it is not. A value of 8 will be assumed, however, in view of the choice of 10 for the related pentaammine(pyridine)ruthenium(III/II) couple.[5] Finally, values for m_i are obtained by direct measurement.

For the case where L is pyrazine, the necessary optical data are available from earlier work.[2] After use of these to calculate n_i and m_i and insertion of the values into eq 11, followed by eq 12, the configuration reaction entropies in Figure 8 are obtained. Comparison to Figure 4 shows that there is very good agreement with experiment, at least with regard to the position of the peak and overall functional dependence of $\Delta S°_{rc}$(con) on the bulk solvent composition. With respect to the magnitude, however, the agreement is poor. The "theoretical" values for $\Delta S°_{rc}$(con) are considerably larger than those portions of $\Delta S°_{rc}$(experiment), which can most obviously be attributed to configuration effects. The origin of the discrepancy is not obvious. It exists, however, in experiments involving monomeric complexes as well; possible explanations are explored in the preceding report. Despite the numerical discrepancy, the overall agreement between experiment and calculation is good. This suggests that the underlying physical model for the entropy effects is largely correct.

The one remaining issue is the nature of the entropy "spike" for the 5+/4+ couple (Figures 3 and 4). The key points are (1) that it appears only with the pyrazine- and 4,4′-bpy-bridged dinuclear complexes and (2) that it appears at even smaller values of m_{DMSO} than for the 4+/3+ couple. The first point strongly suggests that the entropy effect has its origins in selective solvation effects that are transmitted by the bridge from the $(py)(NH_3)_4Ru$ site. The significance of the second point is more difficult to assess. It is worth noting, however, that if the entropy effect is transmitted electronically, then the tetraammine site will exert an influence only in the $(bpy)_2ClRu^{II}$–pz–$Ru^{III}(NH_3)_4(py)^{4+}$ (mixed-valence) state; oxidation to the 5+ state effectively shuts off the electronic influence of the tetraammine site. Returning to the 4+ state, it needs to be appreciated that the remote solvational/electronic influence comes only from the oxidized form of the tetraammine couple. The relevant entropic quantity, then, would appear to be ΔS^{ox}_{con} not $\Delta S°_{rc}$(con)(4+/3+). Our calculations show that the former quantity peaks at an earlier point than the does the latter in an m_{DMSO} plot. This could account, at least qualitatively, for the shift of the entropy spike for the 5+/4+ couple in comparison to the 4+/3+ system.

If our interpretation is correct, then mixed-solvent reaction entropy measurements represent a surprisingly sensitive probe of ligand-mediated electronic coupling. The entropy measurements are less sensitive, perhaps, than optical intervalence absorbance measurements, but certainly more sensitive than single-temperature potential measurements. Unfortunately, the entropy experiments do not provide a quantitative indication of coupling effects. Certainly pyrazine provides much stronger coupling than 4,4′-bipyridine in the dinuclear complexes, yet the entropic effects are similar. The $\Delta S°_{rc}$ experiments might still be of unique value, however, in those particular instances where (1) interferences to the optical intervalence spectrum exist and (2) only threshold measures of site-to-site coupling are desired.

Intervalence Thermodynamics. The chief value of the electrochemical estimates of the mixed-solvent thermodynamics for intervalence transfer may lie in the approximate predictions they provide about activation parameters for the corresponding kinetically controlled events. For low-driving-force reactions, these are conventionally given by[17,18]

$$\Delta G^* \approx \tfrac{1}{2}\Delta G° + \Delta G^*_{int} \qquad (13)$$

$$\Delta H^* \approx \tfrac{1}{2}\Delta H° + \Delta H^*_{int} \qquad (14)$$

$$\Delta S^* \approx \tfrac{1}{2}\Delta S° + \Delta S^*_{int} \qquad (15)$$

where "int" denotes the so-called intrinsic parameters found in the absence of a thermodynamic driving force. If eq 13–15 are taken to be approximately correct, then from Figure 6 preferential solvation effects on the activation free energy for intramolecular electron transfer (and, therefore, upon the rate itself) are predicted to lag behind the effects of both ΔS^* and ΔH^*.[19] The same should hold true for bimolecular cross-reactions. We are unaware, however, of any kinetic data that bear directly on the issue.

Acknowledgment. J.C.C. gratefully acknowledges the Research Corp. for financial support. J.T.H. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Matching support (J.T.H.) was provided by the National Science Foundation through the Presidental Young Investigator Program under Grant No. CHE-8552627. Industrial matching funds were generously provided by the Atlantic Richfield Foundation, the James S. Kemper Foundation, Rohm and Haas, Mead Imaging, and the Newport Corp. R.L.B. acknowledges support as a Shell Graduate Fellow. We also thank James Thiel for help with the figures.

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(17) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(18) Admittedly, reactions like eq 2 do not fully satisfy the low-driving-force condition. On the other hand, their rates are probably next-to-impossible to measure anyway, at least by conventional methods. The discussion surrounding eq 13–15 likely would be fully appropriate, however, for the (presumably much slower) intramolecular redox reactions of mixed-metal analogues such as $(bpy)_2ClOs$–L–$Ru(NH_3)_5^{4+}$ (Doorn, S. K.; Hupp, J. T., work in progress).

(19) This assertion perhaps is overly simplistic in that potentially significant solvent variations in the intrinsic parameters[2,7] have been neglected.