Specific and Nonspecific Solvation Contributions to Intervalence Electron Transfer Transitions and Redox Potentials in Ruthenium Ammine Complexes

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A series of binuclear complexes of general formula $L_mRu-BL-RuL'_m{}^{n+}$ where L and L′ are monodentate or bidentate ligands bound to one metal center and BL is a bridging ligand are analyzed with the recently reported unified solvation model (USM). The solvent dependence of $\Delta E_{1/2}$ and E_{IT} data are analyzed for cases where L is the same as L′ and where L and L′ differ. Data for the change in $E_{1/2}$ and E_{IT} as the Lewis base, B, is varied in $(bpy)_2ClRupyz\ Ru(NH_3)_4B$ (where bpy is 2,2′-bipyridine and pyz is pyrazine) are also correlated. The USM provides the relative contributions of specific and nonspecific solvation to the solvent dependence of the physicochemical property. The factoring of the solvent dependence permits the construction of potential energy surfaces providing unprecedented detail concerning the influence of solvent donor−acceptor and solvation contributions to these measurements. The ability of USM to correlate Franck−Condon energies and the failure of donor numbers (DN) to do so emphasizes the need for a dual parameter treatment of the specific interaction. In contrast to nonsymmetrical binuclear complexes, the solvent dependence of the E_{IT} bands for symmetrical complexes is not correlated by solvent donor and polarity parameters but is fit to the dielectric constants and refractive indices of the Marcus−Hush dielectric continuum model. A rationale for this disparate behavior of symmetrical and unsymmetrical binuclear complexes is given.

Introduction

In the area of solvent effects, it has been widely accepted that the solvent dielectric constant, dipole moment, refractive index, or various functions thereof fail to explain the influence of solvent on physicochemical properties.[1] This conclusion has led to various empirical scales of solvent polarity (*Z*, ET(30), π^*, etc.)[1] which, in most instances, combine specific donor−acceptor interactions and nonspecific interactions of solute with solvent into a single parameter. A unified solvation model (USM) was offered[2] to provide a set of solvent parameters, *S*′, that could be used to estimate *nonspecific solvation* with the equation

$$\Delta\chi = PS' + W \tag{1}$$

$\Delta\chi$ is the measured physicochemical property in a solvent, *S*′ is the solvent parameter that gauges the magnitude of the nonspecific solvation, *P* is the susceptibility of the probe to solvent effects, and *W* is the value of the physicochemical property when *S*′ equals zero. Specific solvent−solute interactions are treated with the physicochemical version of the *E* and *C* equation[3]

$$\Delta\chi = E^*_A E_B + C^*_A C_B + W \tag{2}$$

where $E^*_A E_B$ and $C^*_A C_B$ are the electrostatic and covalent contributions to the measured property with the subscripts A and B referring to acceptor and donor parameters. The combined equation

$$\Delta\chi = E^*_A E_B + C^*_A C_B + PS' + W \tag{3}$$

treats systems in which both specific and nonspecific interactions contribute.[2c,d]

From this perspective it is not surprising that attempts[4] to understand the solvent dependence of the kinetics of electron-transfer reactions and the energetics of intervalence transitions (IT) in mixed-valence compounds with a dielectric continuum model that employs the solvent refractive index and dielectric constant could be incomplete. Such improper estimates of nonspecific solvation and specific donor−acceptor interactions can lead to incorrect conclusions about the important factors influencing the chemistry.[2f]

A modification of Marcus−Hush theory[4] which uses S′ to gauge nonspecific solvation and eq 2 to treat specific interactions was reported.[2f] The model successfully correlated bimolecular electron-transfer rates for the metallocenes ($\Delta G \approx 0$) and concludes[2f] that there is no basis for a reported[5] solvent friction correction in the interpretation of this data when proper estimates of solvation are made. This conclusion illustrates the point that the goal of data fits with USM is not simply data fitting, but more importantly, to provide an understanding of the fundamental factors influencing the solvent dependence of the physicochemical properties of the solute.

In the area of mixed-valence chemistry, intervalence-transfer band energies, E_{IT}, for many of the complexes considered here have been fit successfully[6−9] with donor number (DN) or the Marcus and Hush function $(1/\eta^2 - 1/D_S)$. Donor numbers have

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Table 1. Fit of Spectral and Electrochemical Data for $(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4B$

	$E_{1/2}(Ru^{\alpha}B)(CH_3CN)$		$\Delta E_{1/2}(CH_3CN)$		$E_{IT}(CH_3CN)$		$E_{1/2}(Ru^{\alpha}B)(DMF)$		$\Delta E_{1/2}(DMF)$		$E_{IT}(DMF)$	
B[a]	exptl	calcd[b]	exptl	calcd[c]	exptl	calcd[d]	exptl	calcd[e]	exptl	calcd[f]	exptl	calcd[g]
C_5H_5N	0.722	0.702	0.283	0.274	1.046	1.033	0.455	0.453	0.538	0.533	1.378	1.351
4-$CH_3C_5H_4N$	0.684	0.684	0.296	0.295	1.051	1.060	0.424	0.441	0.548	0.539	1.360	1.360
3-ClC_5H_4N	0.769	0.745	0.223	0.225	0.950	0.969	0.485	0.483	0.515	0.518	1.319	1.329
3,5-$(CH_3)_2C_5H_3N$	0.667	0.677	0.296	0.303	1.070	1.071	0.450	0.436	0.531	0.542	1.348	1.364
3-FC_5H_4N	0.709	0.742	0.228	0.229	0.990	0.974						
4-AcC_5H_4N	0.762	(0.764)[a]	0.228	(0.208)[a]	1.04	(0.95)[a]	0.437	(0.511)[a]	0.527	(0.490)[a]	1.37	(1.31)[a]
NH_3	0.553	0.552	0.418	0.420	1.198	1.198	0.255	0.255	0.720	0.720	1.512	1.512

[a] The experimental data are reported in ref 6. The E_B and C_B values employed are given in ref 3. The 4-CH_3CO, 3-F, and 3,5 dimethylpyridine employed E_B values of 1.59, 1.67, and 1.85 with C_B values of 3.37, 3.11, and 3.80, respectively, see ref 3c. Because of uncertainty[3] in the E_B and C_B values, 4-AcC_5H_4N is given 0.1 the weight of the other donors in the data fit and is not included in the calculations of the fit deviations. [b] The first half-wave potential of the complex in volts, V, attributed to the $Ru(NH_3)_4B$ fragment in CH_3CN solvent. Calculated with $E_{1/2}\alpha = -0.315(\pm0.043)E_B - 0.011(\pm0.016)C_B + 1.303(\pm0.042)$; $\bar{x} = 0.015$, % fit = 6.8; $C_A^*/E_A^* = 0.034$. [c] Difference in the first and second half-wave potentials of the complex in volts, V, in CH_3CN solvent. Calculated with $\Delta E_{1/2} = 0.332(\pm0.011)E_B + 0.020(\pm0.004)C_B - 0.388(\pm0.019)$; $\bar{x} = 0.003$, % fit = 1.5; $C_A^*/E_A^* = 0.06$. [d] Energy of the intervalence transition E_{IT} in electron volts in acetonitrile solvent. Calculated with $E_{IT} = 0.406(\pm0.03)E_B + 0.0337(\pm0.01)C_B + 0.191(\pm0.03)$; $\bar{x} = 0.010$, % fit = 1.3; $C_A^*/E_A^* = 0.08$. [e] Same as footnote *b* in DMF solvent. Calculated with $E_{1/2}^{\alpha} = -0.321(\pm0.03)E_B + 0.019(\pm0.009)C_B + 0.959(\pm0.00)$; $\bar{x} = 0.007$, % fit = 3.0; $C_A^*/E_A^* = 0.06$. [f] Same as footnote *c* in DMF solvent. Calculated with $\Delta E_{1/2} = 0.257(\pm0.02)E_B - 0.034(\pm0.006)C_B + 0.198(\pm0.00)$; $\bar{x} = 0.006$, % fit = 2.9; $C_A^*/E_A^* = -0.13$. [g] Same as footnote *d* in DMF solvent. Calculated with $E_{IT} = 0.252(\pm0.04)E_B - 0.018(\pm0.013)C_B + 0.967(\pm0.00)$; $\bar{x} = 0.011$, % fit = 5.5; $C_A^*/E_A^* = -0.07$.

been used successfully to fit $E_{1/2}$ and E_{IT} values for binuclear complexes where the bridge capping groups (*i.e.*, the two metal environments) are different and one metal center has hydrogen-bonding acceptor ligands (NH_3). For these cases, the usual observation is that E_{IT} values do not correlate well with $(1/\eta^2 - 1/D_S)$ but do correlate with DN. On the other hand, E_{IT} values for the symmetrical ($\Delta E = 0$) binuclear complex $[Ru(NH_3)_5(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$ (bpy is bipyridine) correlate well with $(1/\eta^2 - 1/D_S)$ despite the presence of NH_3 ligands which undergo specific hydrogen bonding interaction with donor solvents. While donor numbers do not correlate E_{IT} data for the symmetrical $[Ru(NH_3)_5(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$ complex, data for other complexes with identical capping groups are better fit with donor numbers.[10]

In this article, the unified solvation model will be extended to interpret solvent influence on the redox chemistry and spectroscopy of mixed-valence binuclear ruthenium complexes and their monomeric analogs. It will first be shown that variations in redox energies and E_{IT} due to contributions of inner-sphere donor ligands can be correlated well by the model of eq 3. The model will then be used to estimate the contributions of specific and nonspecific solute−solvent interactions to the redox energetics and intervalence band energies of binuclear mixed-valence complexes. Explanations will be offered for the requirement of different properties to understand the solvent influence on symmetrical and unsymmetrical binuclear complexes. Finally, the solvatochromism of related mononuclear complexes will be examined.

Results and Discussion

Donor Variation in $[(bpy)_2(Cl)Ru^{II}(pyz)Ru^{III}(NH_3)_4B]^{4+}$. The first data set analyzed involves donor, B, variation in the series of complexes $[(bpy)_2(Cl)Ru^{II}(pyz)Ru^{III}(NH_3)_4B]^{4+}$ (where bpy is 2,2′-bipyridine, pyz is pyrazine, and B is a monodentate donor ligand trans to the bridge). Table 1 summarizes the reported[6] electronic transitions, E_{IT}, and half-wave potentials of base adducts in the solvents CH_3CN and *N*,*N*-dimethylformamide (DMF). The label ($Ru^{\alpha}B$) refers to the $Ru(NH_3)_4B$ fragment, and the label Ru^{β} refers to the $Ru(bpy)_2Cl$ fragment; Ru is assumed to be Ru(III) unless otherwise noted. The quantity $\Delta E_{1/2}$ is the difference in the second and first half-wave potentials.

$$\Delta E_{1/2} = E_{1/2}(Ru^{\beta}) - E_{1/2}(Ru^{\alpha}B) \quad (4)$$

With the solvent held constant, the experimental data are fit to eq 2 using reported[3] E_B and C_B values for B. As can be seen, there is excellent agreement between the $E_{1/2}(Ru^{\alpha}B)$ experimental values and those obtained (calculated) by substituting the reported[3] donor E_B and C_B values into the equations given in the footnotes to Table 1. The equations are the best fit parameters for eq 2 from the individual data fits. The $\Delta E_{1/2}$ and E_{IT} values are fit even better than $E_{1/2}(Ru^{\alpha}B)$ as indicated by $\bar{x}$ and the percent fit ($100 \times \bar{x}$/range of values). The same electrostatic and covalent donor parameters (E_B and C_B) that are used to predict the enthalpy of interaction of these donors with a wide range of Lewis acids correlate variations in the $E_{1/2}$, $\Delta E_{1/2}$, and E_{IT} values for these unsymmetrical binuclear complexes. The *W* values from these fits provide an estimate of the physicochemical property of a hypothetical complex with a ligand B° attached that has dispersion but no donor or acceptor tendencies with respect to the metal center.

The relationship between E_{IT} and $\Delta E_{1/2}$ for these complexes has been discussed thoroughly by Curtis and co-workers[6]. They show that in the context of Marcus−Hush theory, eq 5 applies

$$\begin{aligned} E_{IT} &= E_{FC} + \Delta E \\ &= E_{FC} + \Delta E_{1/2} + T\Delta S + [E_{1/2}(Ru^{\beta'}) - E_{1/2}(Ru^{\beta})] \\ &= E_{FC} + \Delta E_{1/2} + X \end{aligned} \quad (5)$$

for a given mixed-valent binuclear complex, where $E_{1/2}(Ru^{\beta'})$ is the hypothetical $E_{1/2}$ of the Ru^{β} site if the effects of electrostatic interaction and electronic delocalization between the sites are removed. $\Delta E_{1/2}$ represents the free energy change for the comproportionation reaction of eq 6. ΔE is the zero-

$$Ru^{\beta}(II)-Ru^{\alpha}(II) + Ru^{\beta}(III)-Ru^{\alpha}(III) \rightleftharpoons 2Ru^{\beta}(II)-Ru^{\alpha}(III) \quad (6)$$

order energy difference between the $Ru^{\alpha}(III)-Ru^{\beta}(II)$ and $Ru^{\alpha}(II)-Ru^{\beta}(III)$ states, and E_{FC} is the Franck−Condon energy arising from the vertical nature of an intervalence transition.

A consequence of the analysis expressed in eq 5 is that E_{IT} and $\Delta E_{1/2}$ are strongly correlated quantities. Indeed, if the

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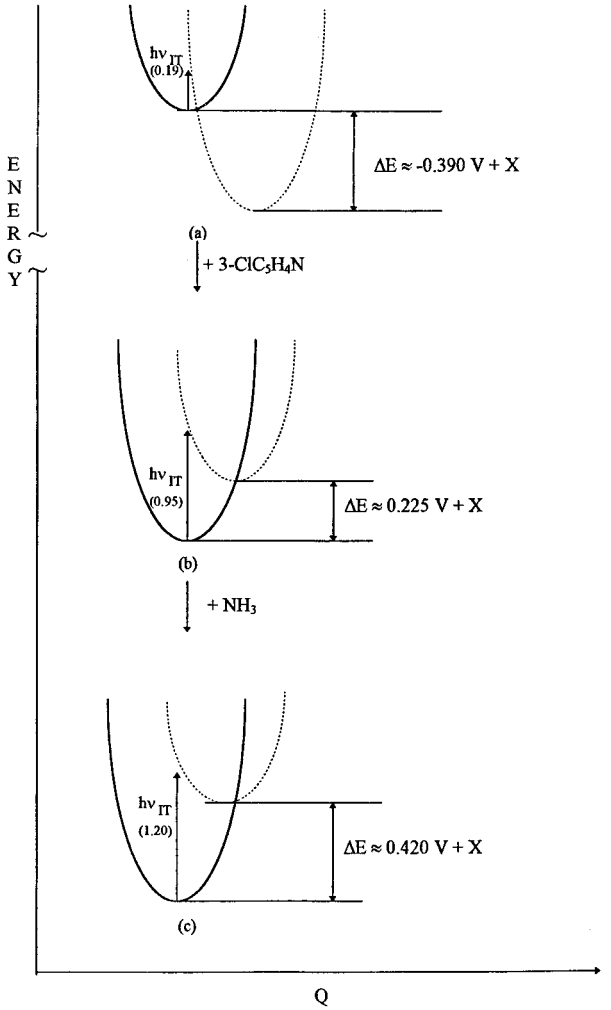


Figure 1. Influence of ligand coordination on potential energy curves in CH_3CN solvent: (a) $[Ru(bpy)_2Cl(pyz)Ru(NH_3)_4B^o]^{4+}$ in CH_3CN; (b) $Ru(bpy)_2Cl(pyz)Ru(NH_3)_4{\cdot}3\text{-}ClC_5H_4N^{4+}$; (c) $Ru(bpy)_2Cl(pyz)Ru(NH_3)_4{\cdot}NH_3^{4+}$. The dashed line is $Ru^{\beta}(III)-Ru^{\alpha}(II)$ and the solid line is $Ru^{\beta}(II)-Ru^{\alpha}(III)$. Q is a plot of the $Ru^{\beta}-N$ distance as the sum $Ru^{\beta}-N$ and $Ru^{\alpha}-N$ is held constant.

variation of the E_{FC}, ΔS, and $E_{1/2}(Ru^{\beta\prime})$ terms with changing ligand B is negligible, then $\delta(E_{IT}) = \delta(\Delta E_{1/2})$ for two different B ligands. This correlation has been experimentally verified for the compounds in Table 1, as shown by Curtis and co-workers,[6] and $\delta(E_{IT})/\delta(\Delta E_{1/2}) \simeq 1$ (acetonitrile solvent). Therefore, for the systems in Table 1, the comparable quality of the fits eq 3 for $\Delta E_{1/2}$ and E_{IT} are not surprising.

The parameters E_A*, C_A*, and W from fits of the redox potentials and E_{IT} enable us to construct the potential energy surfaces shown in Figure 1. Note that the quantity X must be used to relate $\Delta E_{1/2}$ to ΔE (see eq 5), and X and E_{FC} are dependent on the nature of B. When any one of the bases in Table 1 (or even CH_3CN) is attached to Ru^{α}, the ground state in acetonitrile solvent becomes $Ru^{\beta}(II)-Ru^{\alpha}(III)$. Compared to $3\text{-}ClC_5H_4N$, the donor NH_3 lowers the energy of $Ru^{\beta}(II)-Ru^{\alpha}(III)$ even more than it lowers $Ru^{\beta}(III)-Ru^{\alpha}(II)$, giving rise to a larger ΔE for NH_3 than $3\text{-}ClC_5H_4N$. The E_A*E_B and C_A*C_B values indicate that the dominant property of the base that causes $\Delta E_{1/2}$ to increase is its tendency to undergo electrostatic bonding. The larger the E_B value of B, the stronger the electrostatic interaction of the base with Ru^{α}.

It is relevant that the dominance of the electrostatic interaction with Ru(III) compared to Ru(II) leads to a larger $\Delta E_{1/2}$ for NH_3 ($E_B = 2.31$; $C_B = 2.04$) than pyridine ($E_B = 1.78$; $C_B = 3.54$). The opposite donor order would exist if $\Delta E_{1/2}$ were dominated by the covalent interaction. Since $\Delta E_{1/2}$ represents the difference in the minima of the two potential energy curves, the dominance of $\Delta E_{1/2}$ by the electrostatic term implies that the difference in the bond strength of the metal−ligand interaction for $Ru^{\beta}(III)-Ru^{\alpha}(II)-B$ compared to $Ru^{\beta}(II)-Ru^{\alpha}(III)-B$ is mainly electrostatic.

The positive E_A* and C_A* for the E_{IT} fit indicates that stronger donors, *i.e.* larger E_B and C_B, increase E_{IT} as seen for a change in B from $3\text{-}ClC_5H_4N$ (Figure 1b) to NH_3 (Figure 1c). The energy of the intervalence transition is also dominated by the electrostatic bond-forming properties of the donor. In this case, increased electrostatic interaction of B with Ru^{α} increases the transition energy because the excited state of the

$$(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4B \rightarrow \{(bpy)_2Cl\,Ru^{III}(pyz)Ru^{II}(NH_3)_4B\}^* \quad (7)$$

transition is stabilized less by a strong electrostatic donor than is the ground state. Thus, in Figure 1, E_{IT} is seen to increase as $\Delta E_{1/2}$ increases. Again, NH_3 has a greater influence than pyridine on this transition because of its larger E_B value. The W value refers to the same transition, $Ru^{\beta}(II)-Ru^{\alpha}(III) \rightarrow Ru^{\beta}(III)-Ru^{\alpha}(II)$, in all systems.

Figure 1a illustrates the ground and excited intervalence state potential surfaces for the hypothetical compound $[(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4B^o]^{4+}$, where the ligand B^o has no donor character ($E_B = C_B = 0$). The large negative value of W (−0.388 eV) from the $\Delta E_{1/2}$ fit suggests that in acetonitrile the ground state of this hypothetical complex is $Ru^{\beta}(III)-Ru^{\alpha}(II)$ assuming that the correction term X is small. When true donors are substituted for B^o, the ground state becomes $Ru^{\beta}(II)-Ru^{\alpha}(III)$ as observed for all the ligands in Table 1. Coordination of a donor to Ru^{α} lowers the energy of the $Ru^{\beta}(II)-Ru^{\alpha}(III)$ state more than that of the $Ru^{\beta}(III)-Ru^{\alpha}(II)$ state as a consequence of the higher Lewis acidity of $Ru^{\alpha}(III)$ compared to $Ru^{\alpha}(II)$.

Compared to CH_3CN, the more basic but less polar solvent DMF decreases $E_{1/2}$ ($Ru^{\alpha}B$) and increases $\Delta E_{1/2}$ by 0.12−0.30 V. This is attributed to an increase in electron density on the nitrogen of the ammonia ligand from hydrogen bonding to the stronger donor solvent, DMF, and will be discussed in detail below. The trend in DMF solvent with varying B is the same as that in CH_3CN with the electrostatic component of the donor dominating the trend. However, it is interesting to note that the main difference in the $\Delta E_{1/2}$ values in the two solvents is attributed to the W value. The positive W value for $\Delta E_{1/2}$ in DMF leads to $[ClRu^{II}(pyz)Ru^{III}(NH_3)_4B^o]^{4+}$ being the hypothetical ground state even with B^o attached (again assuming that X is small). This is attributed to the stabilization of $Ru^{\alpha}(III)$ by the increased Lewis basicity of the NH_3 ligands resulting from the 3-center hydrogen bond of DMF to N−H. Consistent with increased stabilization of $Ru^{\beta}(II)-Ru^{\alpha}(III)$ in DMF, the sensitivity of ΔE to the base change is decreased compared to CH_3CN solvent as shown by a decrease in E_A*.

The above discussion and predictions do not consider that π-back-bonding occurs from Ru(II) into pyridine. The net effect of back-bonding is to lower the $Ru^{\beta}(III)-Ru^{\alpha}(II)$ excited state energy. If the extent of π-back-bonding was roughly the same for all substituted pyridines or if it increased in proportion to a decrease in the donor C_B value, the C_A* value could accommodate these trends in the data fit. This would lead to incorrect predictions if the E_A*, C_A*, and W values were used to estimate results for a σ-donor whose C_B/E_B ratio differed from NH_3. The influence of solvent hydrogen bonding to NH_3 on the E_B and C_B values of NH_3 could also influence the B = NH_3 system

Table 2. Solvent Effects on Spectral and Electrochemical Data for bpy_2Cl Ru(II)pyz Ru(III)$(NH_3)_4L^{4+}$

	$(bpy)_2$Ru(II)Clpyz Ru(III)$(NH_3)_5$4+				$(bpy)_2$Ru(II)Clpyz Ru(III)$(NH_3)_4C_5H_5N^{4+}$			
	$\Delta E_{1/2}$		E_{IT}		$\Delta E_{1/2}$		E_{IT}	
solvent (S')	exptl	calcd[b]	exptl	calcd[c]	exptl	calcd[d]	exptl	calcd[e]
C_6H_5CN (2.63)	0.400	0.427	1.144	1.153	0.240	0.271	0.957	0.969
CH_3CN (3.00)	0.418	0.422	1.205	1.215	0.288	0.293	1.027	0.999
$(CH_3)_2CO$ (2.58)	0.547	0.569	1.205	1.255	0.352	0.385	1.099	1.105
$HC(O)N(CH_3)_2$(DMF, 2.80)	0.720	0.679	1.516	1.458	0.541	0.511	1.349	1.308
$CH_3C(O)N(CH_3)_2$ (2.70)	0.714	0.710	1.505	1.493	0.548	0.538	1.373	1.357
$(CH_3)_2SO$ (3.00)	0.745	0.766	1.589	1.594	0.619	0.605	1.409	1.443
$C_6H_5NO_2$[a] (2.61)	0.316	0.304	1.025	0.991	0.196	0.152	0.771	0.787
$(CH_3O)_3PO$[a] (2.79)	0.633	0.646	1.422	1.482	0.461	0.497	1.278	1.323
P−C (3.10)	0.535	0.547	1.290	1.287	0.340	0.391	1.074	1.092
CH_3NO_2 (3.07)	0.315	0.307	0.994	1.040	0.170	0.152	0.769	0.800
n-C_3H_7CN (2.70)	0.400	0.410	1.44	1.187	0.203	0.271	1.016	0.992
$(CH_2)_4SO_2$ (2.88)	0.538	0.507	1.265	1.242	0.342	0.350	1.086	1.055

[a] Experimental data from ref 6. Refined E_B and C_B values were used in this data fit. Key: $NO_2C_6H_5$, $E_B = 1.27$ and $C_B = 0.57$; $(CH_3O)_3PO$, $E_B = 2.42$ and $C_B = 0.98$; CH_3NO_2, $E_B = 1.09$ $C_B = 0.70$; n-C_3H_7CN, $E_B = 1.81$, $C_B = 0.54$; $(CH_2)_4SO_2$, $E_B = 1.61$, $C_B = 1.09$ and P. C., $E_B = 1.51$, $C_B = 1.32$. Known parameters were assigned weights of 1.0, C_6H_5CN, and $(CH_3O)PO$ values of 0.5 and CH_3NO_2, P−C, n-C_3H_7CN, and $(CH_2)_4SO_2$ values of 0.2 in the data fit. [b] Difference in first and second half wave potentials. Calculated with $\Delta E_{1/2} = 0.207\ (\pm 0.03)E_B + 0.245\ (\pm 0.04)C_B + 0.019\ (\pm 0.05)S' - 0.150\ (\pm 0.13)$; $\bar{x} = 0.018$; $R^2 = 0.979$. [c] Intervalence electronic transition in eV. Calculated with $E_{IT} = 0.340\ (\pm 0.05)E_B + 0.159\ (\pm 0.06)C_B + 0.193\ (\pm 0.07)S' - 0.035\ (\pm 0.2)$; $\bar{x} = 0.021$; $R^2 = 0.969$. [d] Calculated with $\Delta E_{1/2} = 0.218\ (\pm 0.04)E_B + 0.194\ (\pm 0.05)C_B + 0.087\ (\pm 0.06)S' - 0.461\ (\pm 0.17)$; $\bar{x} = 0.028$; $R^2 = 0.962$. [e] Calculated with $E_{IT} = 0.373\ (\pm 0.04)E_B + 0.212\ (\pm 0.05)C_B + 0.114\ (\pm 0.06)S' - 0.105\ (\pm 0.16)$; $\bar{x} = 0.025$; $R^2 = 0.985$.

Table 3. Solvatochromism of Ruthenium(II) and (III) Ammine Complexes[a]

	$Ru^{II}(NH_3)_5$py		$Ru^{II}(NH_3)_5$-4CNpy$^+$		$Ru^{II}(NH_3)_5$-($bpCH_3^+$)		$Ru^{II}(NH_3)_4$(py)-($bpCH_3^+$)		$Ru^{II}(NH_3)_4$-bpy		$Ru^{III}(NH_3)_5$-dmapy		$\Delta E_{1/2}$(Ru-$(NH_3)_4$L)	
solvent	exptl	calcd[b]	exptl	calcd[c]	exptl	calcd[d]	exptl	calcd[e]	exptl	calcd[f]	exptl	calcd[g]	exptl	calcd[h]
CH_3CN	24.57	24.51	18.42	18.40	17.12	17.08	17.95	17.91	19.12	19.01	16.98	16.97	−1.51	−1.50
C_6H_5CN	24.27	24.50	17.92	(18.34)	16.67	(17.05)	17.04	(17.88)	18.98	18.93	17.15	17.10		
$(CH_3)_2CO$	23.92	23.85	18.18	18.10	16.53	16.43	17.48	17.36	18.73	18.61	17.33	17.40	−1.46	−1.44
$HC(O)N(CH_3)_2$	22.94	23.03	17.21	17.36	15.20	15.36	16.18	16.35	18.05	18.13	18.62	18.48	−1.24	−1.28
$CH_3CON(CH_3)_2$	22.78	22.78	17.06	17.09	14.93	15.00	15.87	16.02	17.92	17.95	18.98	18.91		
$(CH_3)_2SO$	22.52	22.49	17.12	17.00	14.88	14.74	15.95	15.79	17.83	17.86	18.80	18.97	−1.22	−1.18
$[(CH_3)_2N]_3PO$	21.79	21.74	16.16	16.17	13.72	13.66	14.99	14.79	17.36	17.27	20.28	20.30		
P−C	23.98	24.09	18.32	18.51	16.67	16.88	17.57	17.77	18.80	18.90	16.89	16.66	−1.45	−1.48
$C_6H_5NO_2$			18.35	(19.00)	16.89	(18.06)	17.76	(18.81)	18.98	19.42	15.94	16.13		

[a] The experimental data are from ref 9. [b] Metal to ligand charge transfer transition in Ru(II)$(NH_3)_5$ $C_5H_4N^{2+}$ in 10^3 cm^{-1}. Calculated with $\nu = -1.64\ (\pm 0.3)E_B - 1.01\ (\pm 0.5)C_B - 0.14\ (\pm 0.8)S' + 28.34\ (\pm 0.1)$; $\bar{x} = 0.08$. [c] MLCT $[Ru^{II}(NH_3)_5(4CN\text{-}C_5H_4NCH_3+)]^{3+}$ (4-cyano-*N*-methylpyridinium in 10^3 cm^{-1}). Calculated with $\nu = -1.65\ (\pm 0.2)E_B - 0.19\ (\pm 0.3)C_B + 0.08\ (\pm 0.5)S' + 21.00\ (\pm 0.1)$; $\bar{x} = 0.09$. [d] MLCT in $[Ru^{II}(NH_3)_5(NCH_3\text{-}4,4\text{-}bpy^+)]^{3+}$ (*N*-methyl-4,4′-bipyridine) in 10^3 cm^{-1}. Calculated with $\nu = -2.27\ (\pm 0.3)E_B - 0.82\ (\pm 0.5)C_B - 0.05\ (\pm 0.8)S' + 21.53\ (\pm 0.1)$; $\bar{x} = 0.010$. Systems in parentheses were omitted from the fit and calculated with the above equation. [e] MLCT in $[Ru^{II}(NH_3)_4(C_5H_5N)(NCH_3\text{-}4,4'\text{-}bpy^+)]^{3+}$ in 10^3 cm^{-1}. Calculated with $\nu = -2.12(\pm 0.4)E_B - 0.66\ (\pm 0.5)C_B - 0.06\ (\pm 0.9)S' + 22.0\ 5(\pm 0.1)$; $\bar{x} = 0.015$. [f] MLCT in Ru(II)$(NH_3)_4bpy^{2+}$ in 10^3 cm^{-1}. Calculated with $\nu = -1.08\ (\pm 0.1)E_B - 0.43\ (\pm 0.2)C_B + 0.12\ (\pm 0.3)S' + 20.73\ (\pm 0.1)$; $\bar{x} = 0.011$. [g] LMCT in $Ru^{III}(NH_3)_5(NC_5H_4N(CH_3)_2)^{2+}$ (4-dimethylamino)pyridine) in 10^3 cm^{-1}. Calculated with $\nu = 2.53\ (\pm 0.1)E_B + 0.102\ (\pm 0.1)C_B - 0.28\ (\pm 0.2)S' + 13.59\ (\pm 0.1)$; $\bar{x} = 0.10$. [h] $\Delta E_{1/2}$ given by $E_{1/2}$ ($pyd^{+/0}$) − $E_{1/2}(Ru^{III/II})$ for $[Ru^{II}(NH_3)_5(4\text{-}CN\text{-}NCH_3C_5H_4N^+)]^{3+}$ in V. Calculated with $\Delta E_{1/2} = 0.324\ (\pm 0.04)E_B + 0.098\ (\pm 0.1)C_B + 0.059\ (\pm 0.06)S' - 2.28(\pm 0.03)$; $\bar{x} = 0.03$.

and be a source of error in E_A*, C_A*, and W values from the fit. Resolution of these problems requires study of ligands that are non-protonic and are only capable of σ-bonding. Such a study has the potential of detecting a π- and σ-donor component to the interactions discussed above and of providing a more reliable set of E_A*, C_A*, and W values for prediction of the influence of σ-donors.

***S′* Correlations with Other Relevant Parameters.** Before analyzing solvent influence on these complexes, it is useful to assess the relationships of S', E_B, and C_B to various parameters used in the literature to fit data for mononuclear and binuclear ruthenium complex ions. The analysis will be limited to a set of solvents that are commonly used in these studies. Generally, these are solvents with S' values > 2.5.

We first note that S' itself is not correlated with either E_B or C_B ($r^2 = 0.0$ for 12 polar solvents in Tables 2 and 3 with well-established S', E_B, and C_B values). Thus, fits with eq 3 will be unique since P, E_A, and C_A will be uncorrelated variables in the optimization.

For 10 solvents used extensively in this work (acetone, nitrobenzene, DMA, DMF, acetonitrile, DMSO, nitromethane, benzonitrile, propylene carbonate, and HMPA), we examined correlations of S' with $1/D_S$, $1/n^2 - 1/D_S$, dipole moment, and DN. The best of the resulting poor correlations was with $1/D_S$ ($r^2 = 0.53$). This is not surprising since S' is derived to a large extent from data for spectroscopic transitions that involve a large dipole change from the ground to the excited state, and energies of such transitions are expected to depend strongly on the static dielectric response of the solvent to the dipole moment of the ground state. The correlation with $1/\eta^2 - 1/D_S$ was very bad ($r^2 = 0.3$).

Correlations of S' with either dipole moments or DN are virtually nonexistent ($r^2 \leq 0.1$) for these ten solvents. It should be noted that some correlation of S' with dipole moment is present when a larger range of solvents (S' values from 1 to 3) is considered. Clearly S′ does not correlate to any of the properties of polar solvents commonly used for the solvent dependence analyses of these complexes.

Effects of Solvent Variation on Spectroscopic and Electrochemical Data. The influence of solvent variation on the

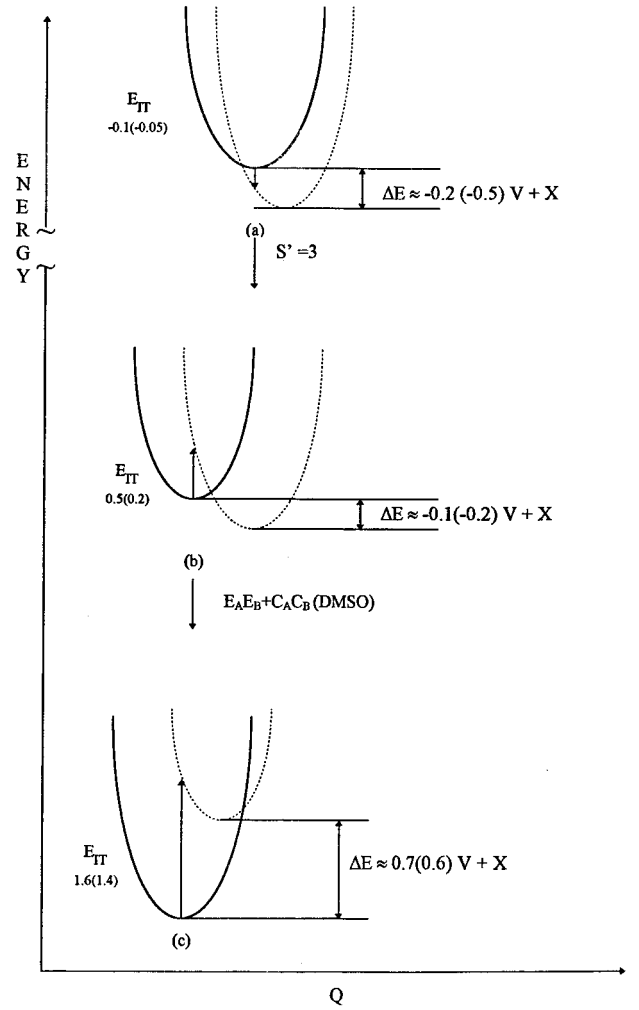


Figure 2. 2. Potential energy surfaces for the mixed valence binuclear complex $(bpy)_2Ru^{II}Cl(pyz)\ Ru^{III}(NH_3)_5^{4+}$ (solid lines) and $(bpy)_2ClRu^{III}(pyz)Ru^{II}(NH_3)_5^{4+}$ (dashed lines). Part a indicates the ΔE in a nonbasic, nonsolvating solvent ($E_B = C_B = S' = 0$) with the resulting E_{IT}. The values given are for $Ru(NH_3)_5$ and those in parentheses are for $Ru(NH_3)_4C_5H_4N$. Part b indicates the influence of $E_B = C_B = 0$ and $S' >$ O on ΔE and on the corresponding E_{IT}. Part c represents the situation for $E_B = C_B \neq$ and $S' \geq 0$. The numbers given are for $(CH_3)_2SO$ solvent.

$\Delta E_{1/2}$ and E_{IT} values of the B = NH_3 and B = pyridine complexes in Table 2 have been correlated previously with donor numbers (DN).[6,7] Fits comparable to the ones obtained using eq 3 result when the solvents in Table 2 are fit to the donor number scale. However, the literature[2c,10,11] indicates that the one-parameter donor number scale is a complex combination of a one parameter description of donor strength plus a nonspecific solvation component. Good correlations with DN do not lead to understanding of the separate specific and nonspecific components of the interaction. This will be shown to cause problems when $E_{IT} - \Delta E_{1/2}$, the Franck−Condon Energy, is fit to donor numbers. Accordingly, the experimental data in Table 2 were analyzed with eq 3, and the results are given in Table 2. The errors given in the footnotes to Table 2 should be consulted to obtain the error limits on the parameters. In several instances the parameters are comparable in magnitude to the error in them indicating that if they were zero there would be no difference in the fit. The resulting parameters are used to construct the potential energy curves in Figure 2. The *W* values lead to the potential energy curve in Figure 2a where the values for $[bpy_2ClRu(pyz)Ru(NH_3)_4B]^{3+/4+/5+}$ (B = NH_3) are indicated and those for B = C_5H_4N are given in parentheses. As above, the values of $\Delta E_{1/2}$ and E_{IT} will be strongly correlated (eq 5). In this analysis, the values of *X* for different solvents are expected to be approximately equal. The value of ΔE is clearly more negative for the pyridine analog than for the ammonia complex as anticipated from our discussion of Figure 1.

The nonspecific solvation contribution to the measured quantities is given by PS'. For $\Delta E_{1/2}$, the *P* values are zero within experimental error or small (0.02 ± 0.05 and 0.09 ± 0.06 respectively for B = NH_3 and pyridine with errors reported as one σ) indicating that the nonspecific solvation of $Ru^{\beta}(II)-Ru^{\alpha}(III)$ and $Ru^{\beta}(III)-Ru^{\alpha}(II)$ is comparable. It should be emphasized that nonspecific solvation in this case involves solvating a very large complex ion that has solvent in the first solvation layer specifically coordinated to NH_3.

The bulk solvent is therefore far removed from both Ru centers. Thus, in a solvent that is a poor donor (i.e. in a hypothetical solvent, S, with $E_B = C_B = 0$ and $S' = 3$) the *P* value from this fit indicates that nonspecific solvation of $(bpy)_2ClRu^{III}(pyz)Ru^{II}(NH_3)_5S_n^{4+}$ would not be able to reverse the ground states. This is illustrated in Figure 2b where the states have the same relative energy differences for the minima as in a solvent with $S' = 0$. In contrast, the contribution of PS' to the variation in E_{IT} is substantial ($P = 0.21 \pm 0.07$ eV for B = NH_3). As shown below, this indicates that the nonspecific solvation contribution has a significant effect on the Franck−Condon energy for the transition, E_{FC}.

In all solvents studied, the dominant contribution to the change in $\Delta E_{1/2}$ from that of the *W* value comes from the specific hydrogen bonding interaction. The $E_A{}^*E_B + C_A{}^*C_B$ contribution is large enough that even in the weakest donor solvent studied, the magnitude of this term overcomes the negative *W* term making $\Delta E_{1/2}$ positive and the ground state $Ru^{\beta II}(pyz)Ru^{\alpha III}NH_3$. This leads to the potential energy curve shown in Figure 2c for the solvent DMSO.

The *W* values for E_{IT} are -0.03 ± 0.2 and -0.1 ± 0.2 for B = NH_3 and pyridine. These are zero within experimental error but are shown for E_{IT} in Figure 2a for purposes of illustration. The influence of nonspecific solvation on E_{IT} is slightly larger than that on $\Delta E_{1/2}$. In $(CH_3)_2SO$, B = NH_3 has a 0.6 ± 0.2 and B = C_5H_4N a 0.3 ± 0.2 eV contribution from PS'. The above discussion of the parameters from the fits of the data in Table 2 are summarized by the potential energy curves in Figure 2.

The dominant influence of the solvent on $\Delta E_{1/2}$ involves the specific interaction which consists of an electrostatic and covalent component. For $(CH_3)_2SO$, the specific interaction makes a 0.8 eV contribution to the solvent effect when B = NH_3 or C_5H_4N. The electrostatic and covalent terms for $\Delta E_{1/2}$ and for E_{IT} have the same sign. The negative end of the solvent dipole hydrogen bonds more strongly to the ammonia of $Ru^{\beta}(II)-Ru^{\alpha}(III)$ than to $Ru^{\beta}(III)-Ru^{\alpha}(II)$. Thus, the specific donor−acceptor interaction stabilizes the $Ru^{\beta}(II)-Ru^{\alpha}(III)$ state more than the $Ru^{\beta}(III)-Ru^{\alpha}(II)$ state and influences both $\Delta E_{1/2}$ and E_{IT} as shown in Figure 2. The stabilization of the $Ru^{\beta}(II)-Ru^{\alpha}(III)$ state by this specific interaction leads to a positive $E_A{}^*$ term and $C_A{}^*$ term for both $\Delta E_{1/2}$ and E_{IT}. The covalent contribution to the bonding is best understood in terms of a three-center molecular orbital description. The electron density in the nonbonding orbital is mainly on the ammine nitrogen and the donor solvent atom. This density on nitrogen stabilizes the $Ru^{\beta}(II)-Ru^{\alpha}(III)$ state increasing $\Delta E_{1/2}$ and E_{IT} as reflected by a positive $C_A{}^*$ for both $\Delta E_{1/2}$ and E_{IT}.

(11) (a) Riddle, F. L., Jr.; Fowkes, F. M. *J. Am. Chem. Soc.* **1990**, *112*, 3259. (b) Lim, Y. Y.; Drago, R. S. *Inorg. Chem.* **1972**, *11*, 202.

A larger change in E_{IT} than in $\Delta E_{1/2}$ with specific and nonspecific solvation is accounted for by a change in the minima of the potential energy curves on the Q axis as shown in parts b and c of Figure 2.

The quantity $E_{IT} - \Delta E_{1/2}$ is related to the Franck−Condon energy.[6] Specifically, if X is constant in eq 5, then $\delta(E_{IT} - \Delta E_{1/2}) = \delta(E_{FC})$ as the solvent is varied. A poor plot of $E_{IT} - \Delta E_{1/2}$ vs the solvent donor number[6] resulted in a correlation coefficient of 0.74 for the pentammine system. The fit of the pentammine system to eq 3 produces an $\bar{x} = 0.02$ and a correlation coefficient of 0.92 with $W = 0.11 \pm 0.2$, $E_A^* = 0.13 \pm 0.03$, $C_A^* = -0.09 \pm 0.04$, and $P = 0.17 \pm 0.1$. The E_A, C_A, P, and W parameters are in good agreement with the values obtained by subtracting the E_A^*, C_A^*, and W values for E_{IT} from the corresponding values for $\Delta E_{1/2}$ (e.g. $E_A^*(E_{IT}) - E_A^*(\Delta E_{1/2}) = E_A^*(E_{IT} - \Delta E_{1/2})$) as expected. For the solvents employed, the one-parameter donor number (DN) scale has a major contribution from a specific donor−acceptor interaction with a C/E ratio of 0.6 and a small contribution from nonspecific solvation. The Franck−Condon (F−C) energy has a significant contribution from nonspecific solvation and as a result E_A, C_A, and S' provide a better fit than the donor number scale. The small R^2 value (0.85) for the USM fit is a consequence of the small range in the values that are fit (0.11).

The extent to which real effects are averaged out in the one parameter plots is illustrated by the observation that, contrary to expectations, subtracting two straight line plots of energies (E_{IT} and $\Delta E_{1/2}$) vs donor numbers from each other does not give a straight line. Thus, the deviations in the donor number plots are significant but are hidden in the statistics. In contrast, not only are the E_{FC} values fit to USM but subtracting the E_A^* and C_A^* and W parameters for $\Delta E_{1/2}$ from E_{IT} gives parameters that are within the error limit of the E_{FC} fit. This is a very positive feature of the USM model compared to DN.

Our explanation of the origin of changes in the Franck−Condon barrier as a function of solvent differs from that offered by Chang et al.[6] They attribute the changes in the barrier to bond length variations resulting from the donor strength of the solvent hydrogen bonding to coordinated ammonia. The parameters from the USM analysis indicate that the dominant contribution is from nonspecific solvation, *i.e.* the PS' term. The USM view is in keeping with the expected dominance of the dielectric continuum contribution when metal−ligand bond length changes are small for redox couples.

Solvent Effects for Symmetrical Binuclear Mixed-Valence Compounds. As a measure of solvent polarity, S' has both dispersion and dipolar contributions contained in the single parameter. The values for S' are derived to a large extent from data for charge-transfer transitions in which the magnitude of the molecular dipole moment is different for the ground state and the excited state. As a result, the differences in S' are dominated by the dipolar term. Therefore, the S' parameterization is not necessarily valid in the special case of transitions with no change in the magnitude of the molecular dipole moment. Such a transition is more dependent on the solvent dispersion interaction with the solute than the S' parameter differences are. It was asserted in the previous section that eq 3 is useful for separating specific and nonspecific solvation terms in unsymmetrical bridged binuclear complexes. However, eq 3 is not expected to provide such a separation for related cases where dispersion forces dominate the nonspecific interaction and S' is inappropriate, *i.e.*, for symmetrical bridged binuclear complexes, where the magnitude of the dipole moment does not change following the electron-transfer event.

Much the same situation applies for the dielectric continuum model often used in fitting spectroscopic data for these systems. For symmetrical mixed-valence binuclear complexes, a term proportional to $1/D_S$ that applies for unsymmetrical binuclear complexes drops out since the IT transition does not change the magnitude of the dipole moment. Only a term proportional to $(1/\eta^2 - 1/D_S)$ remains when $\Delta E = 0$.

The term $(1/\eta^2 - 1/D_S)$, referred to as the Marcus−Hush function, has been used successfully[8] to fit the solvent dependence of E_{IT} for related symmetrical mixed-valence compounds. The quality of the fit can be improved by applying a variety of corrections, but even the simple plot of E_{IT} vs $(1/\eta^2 - 1/D_S)$ usually yields straight lines with relatively little scatter. Two symmetrical binuclear complexes related to the unsymmetrical complexes discussed above, $[Ru(NH_3)_5(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$ and $[(bpy)_2ClRu^{II}(pyz)Ru^{III}Cl(bpy)_2]^{3+}$, will be discussed to provide a more complete treatment of solvent influence. Both are valence localized ions with strongly solvent dependent E_{IT} values. In the case of the latter ion, donor-acceptor interactions with solvent are minimal. A good fit to $(1/\eta^2 - 1/D_S)$ results, and, as expected from the lack of correlations of S' with $(1/\eta^2 - 1/D_S)$, eq 1 does not fit the E_{IT} values for this symmetrical mixed-valence ion. In $[Ru(NH_3)_5(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$, significant hydrogen bonding by donor solvents to ammonia occurs in the first coordination shell. The data are poorly fit by eq 3 or by DN. The solvent dependence of E_{IT} is well fit[10] by $(1/\eta^2 - 1/D_S)$ and the contribution from the donor−acceptor interactions is negligible.

Given the extensive donor interactions between ruthenium-bound ammonias and donor solvents, it is initially surprising that the E_{IT} for the decaammine mixed-valence complex above does not correlate well with measures of solvent polarity and donor properties.[10] Neither DN or E, C, and S' provide data fits. Instead, the correlation with the Marcus−Hush function $(1/\eta^2 - 1/D_S)$ is strong, and when reasonable values are assigned to the transition dipole length and an ellipsoidal cavity model is used, the quantitative agreement between the model solvent shifts and experiment is good.[13] A simple model described below provides a qualitative explanation for the lack of a significant role for solvent polarity and donor-acceptor interactions in the intervalence transition energies for some symmetrical binuclear systems.

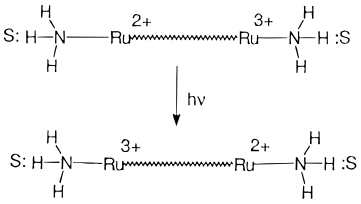
For a simple symmetrical mixed-valence binuclear ion without specific, orienting interactions with solvent, e.g. $[(bpy)_2(Cl)Ru(pyz)Ru(bpy)_2Cl]^{3+}$, the origin of the $(1/\eta^2 - 1/D_S)$ dependence on solvent is easily understood. The rapid electron promotion of the optical intervalence transition leads to a charge transfer from one center to the other, and the only portion of the dielectric continuum polarization that can follow the transition is the electronic polarization. Of the total Born dielectric solvation energy, const × $(1 - 1/D_S)$, the electronic energy component is equal to const × $(1 - 1/\eta^2)$. Thus, the remaining energy barrier to the transition is const × $[(1 - 1/D_S) - (1 - 1/\eta^2)]$, or const × $(1/\eta^2 - 1/D_S)$. This term then reflects the contributions of "orientational" polarization to the energetics. For the polar solvents involved in the studies treated here, $1/D_S$ is small compared to $1/\eta^2$ and the Marcus−Hush solvent dependence of E_{IT} is determined mostly by the refractive index.

(12) Equation 2 has mainly been applied to 1:1 adducts. Since it accommodates the specific hydrogen bonding interaction for both $\Delta E_{1/2}$ and E_{IT} for all solvents, this would imply that either the same number of solvent molecules are specifically interacting or that the number varies in a regular fashion with donor strength. Furthermore, the effect of coordinating the first and the following solvent molecules has the same proportionate influence on coordinating subsequent molecules in the second coordination sphere for all solvents.

(13) Hupp, J. T.; Doug, Y.; Blackbourn, R. I.; Lu H. *J. Phys. Chem.* **1993**, *97*, 3278.

Now consider the case of a complex ion that orients the solvent in the first solvation shell, e.g., due to specific ion−dipole interactions. Since a large fraction of the energy barrier to charge transfer arises from this first shell,[14] we must incorporate the restriction of solvent orientation into the model. The effect is often modeled by the assumption of dielectric saturation in the immediate vicinity of the ion, where the reduced orientational component to the solvent polarization near the ion results in a lower effective D_S value, and a lower Born energy (const × $(1 - 1/D_S)$) for the ion. However, the general dependence on the Marcus−Hush function using the bulk D_S value will be retained if the effective $1/D_S$ values are still relatively small compared to $1/\eta^2$ for a mixed-valence complex. Apparently, this is the case in $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$.

Finally, allowing for specific interactions of the donor-acceptor type will not change the above rationale for symmetrical binuclear complexes. Qualitatively, the charge transfer process can be largely followed by the electronic bonding components as shown schematically:



For clarity, only one solvent−ammine interaction is shown, and it is assumed that the number of bound solvents is similar for both oxidation states of the complex. Therefore, the lost donor−acceptor interaction on the side that is "reduced" in the transition is compensated for in this model by increased solvent binding energy at the other end of the binuclear complex. No dependence on the donor ability of the solvent is predicted, and the Marcus−Hush function $(1/\eta^2 - 1/D_S)$ can still be useful although dielectric saturation is certainly present in the first solvation shell. It is noted, however, that Lau et al.,[10] find that the situation is more complicated than expected for symmetrical end capping groups, and the relative importance of factors that influence the solvent-dependence of IT transitions is not easily predicted.

In considering symmetrical mixed-valence compounds, it is noted that variable fits of E_{IT} values to the $(1/\eta^2 - 1/D_S)$ function can arrive from experimental artifacts. Hendrickson and co-workers[15] showed conclusively that the energies of intervalence band maxima for biferrocenium cations are strongly dependent on concentration as a result of ion-pairing. Thus, reported[16] solvent dependence for such E_{IT} data supporting the Marcus−Hush function are only reliable if the band energies are extrapolated to infinite dilution, as done[8] in the study of E_{IT} values for $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$. Good fits of data for symmetrical complexes to solvent models that embody both specific and nonspecific effects (such as eq 3) could be successful because the ion-pairing propensity in various solvents is modeled well.[2d] It was suggested in an earlier report on application of the USM to ferrocene−ferrocenium electron-transfer kinetics that ion-pairing may contribute to the energetics of those reactions.[2f] The limited number and limited range of solvents reported for the biferrocenium IT band precludes a meaningful comparison with S' and $(1/\eta^2 - 1/D_S)$. Analysis of the limited data shows that charge transfer complexation and hydrogen bonding are noted in the S' fit of the E_{IT} bands consistent with earlier[2f] conclusions for ferrocene electron transfer kinetics.

Solvatochromism in $Ru(NH_3)_{6-X}L_X$ Complexes. The metal ligand charge-transfer transition in $Ru^{II}(NH_3)_{6-X}(L_X)^{2+}$ and the ligand to metal transition in $Ru^{III}(NH_3)_4(L_2)^{3+}$ complexes are very solvent dependent.[9] On the basis of correlations with donor numbers, it was concluded that specific hydrogen bonding of donor solvents to coordinated ammonia changes the redox asymmetry $\Delta E_{1/2}$ (estimated as $E_{1/2}$ (Ru) − $E_{1/2}$(L acceptor)) and causes the spectral shift.

Representative complexes are fit to eq 3 leading to an estimate of the specific and nonspecific components of the solvent effect. The data are shown in Table 3. The MLCT transition for $Ru^{II}(NH_3)_5C_5H_4N^{2+}$(**I**) produces an excellent fit. Specific solvation causes the decrease in the transition energy. The specific hydrogen bonding interaction of the solvent with coordinated NH_3 stabilizes the Ru(III) excited state, more than the ground state, thereby decreasing the transition energy. Contributions from the nonspecific term PS' are small and not statistically different from zero. This is expected since nonspecific effects arise from solvation of a large cation consisting of the complex ion and solvent specifically interacting in the second coordination sphere.

The specific hydrogen bonding interaction has substantial contributions in the same direction from both the electrostatic and covalent components of the interaction. The direction of the shifts from specific interactions are in the same direction as those recently determined from INDO calculations.[17] The value of W (28.34×10^3 cm^{-1}) corresponding to the nonsolvated ion in a solvent with $E_B = C_B = S' = 0$ is considerably lower than the gas phase value of 40.49×10^3 cm^{-1} from theory. (Note that $S' = 0$ is not necessarily appropriate for the gas phase.)

The fit of ν to S' for the complex $[Ru^{II}(NH_3)_5(4\text{-}CNC_5H_4\text{-}NCH_3+)]^{3+}$(**II**) is poor unless aromatic solvents are omitted. Deviations from S' by aromatic solvents arise when specific charge-transfer interactions exist.[3a] In this system the transition energy is decreased by this specific interaction. Such a change would occur if metal−ligand π-back-bonding were decreased when coordinated pyridinium forms a charge transfer complex with a π-solvent. The values for P in all these systems is zero within experimental error. The fit of $\Delta E_{1/2}$ for this complex is also good with the hydrogen bonding to coordinated NH_3 by more basic solvents making the complex easier to oxidize. The E_A, C_A, P, and W values are 0.324, 0.098, 0.059, and −2.281 respectively.

The fit of data for $[Ru^{II}(NH_3)_5(N\text{-}CH_3\text{-}4,4\text{-bipyridinium}^+)]^{3+}$ and the corresponding tetrammine derivative also gives a poor fit to eq 3 unless the aromatic solvents are omitted. Charge transfer complexation of the π-solvent and the coordinated N-CH_3-4,4′-bypyridine ligand occurs, again decreasing the energy of the transition. In contrast to the complexes containing cationic ligands, B, and in accord with complex **I**, $[Ru(NH_3)_4(bipyridyl)]^{2+}$ is well-behaved in aromatic solvents. The specific interaction is in the same direction as in $[Ru(NH_3)_5C_5H_5N]^{2+}$.

The ligand to metal charge transfer transition in $[Ru^{III}(NH_3)_5NC_5H_4N(CH_3)_2]^{3+}$ (where the ligand is 4-(*N*,*N*-dimethylamino)-pyridine) leads to a decrease in the metal charge in the excited state. The ground state is stabilized more by hydrogen bonding to ammonia and the $\pi \rightarrow$d transition energy is increased. The nonspecific solvation contribution is slight and the sign suggests solvent is properly oriented in the ground state to more effectively solvate the charged 4-(*N*,*N*-dimethylamino)pyridinium ion in the excited state decreasing the transition energy.

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Summary

The extension of the *E* and *C* model for specific interactions and the unified solvation model for nonspecific interaction is reported for redox potentials and electronic transitions of a series of ruthenium complexes. The binuclear complexes $[(bpy)_2Ru(Cl)(pyz)Ru(NH_3)_4B]^{4+}$ are analyzed as B is varied in CH_3CN and DMF solvent.

The solvent variation of $(bpy)_2Ru(Cl)(pyz)(NH_3)_5L^{4+}$, in which $L = NH_3$ or pyridine, is found to be dominated by the specific hydrogen-bonding interaction of the donor solvent with the coordinated ammonia. Data fits of $\Delta E_{1/2}$ and E_{IT} lead to potential energy surfaces in which the ground and excited states are dominated by the tendencies of the bases to undergo electrostatic bonding with the coordinated ammonias. The USM fits the Franck−Condon energies, and the FC barrier is found to have a substantial contribution from nonspecific solvation. The DN does not correlate this quantity. This difference provides strong support for the analysis of both nonspecific and specific interactions.

The inability of USM to fit solvent-dependent measurements for symmetrical mixed-valence complexes reflects the near absence of influences from the static dielectric constant and dominance by the solvent refractive index, $1/\eta^2$. Donor−acceptor and ion−dipole interactions that are lost in the electron transfer transition state on the side that is "reduced" are compensated by increased binding energy on the "oxidized" side.

The charge transfer transitions of a series of monomeric $Ru(NH_3)_{6-x}L_x^{n+}$ complexes are influenced predominantly by specific solvation. Charge transfer interactions between aromatic solvents and cationic ligands, L, are detected. Opposite signs are found for the influence of hydrogen bonding on the MLCT and LMCT transitions of $[Ru(NH_3)_5C_5H_4N]^{2+}$ and $[Ru(NH_3)_5NC_5H_4N(CH_3)_2]^{3+}$ respectively.

This understanding of second-sphere hydrogen-bonding interactions and nonspecific solvation contributions on the potential energy surfaces is not available from data fits that treat both interactions with a single parameter. The ability of the unified solvation model to fit this new class of compounds producing signs for E_A*, C_A* and *P* that are consistent with those predicted from qualitative bonding considerations builds confidence in this method of analysis. This confidence enables one to attribute deviation in data fits to the existence of more complex interactions and enables one to design experiments to find the nature of the interactions. This approach is to be contrasted with searching the literature for accommodating parameters which are poorly understood, complex mixtures of specific and nonspecific interactions.

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