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# SOLVENT AND TEMPERATURE EFFECTS IN MIXED-VALENCE CHEMISTRY

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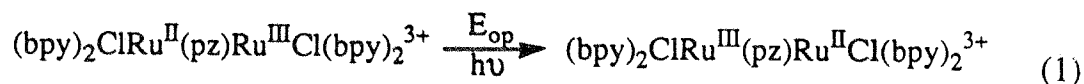*Chapel Hill, North Carolina 27599-3290*

## Abstract

A temperature dependence has been observed for the intervalence transfer absorption band in an unsymmetrical, ligand-bridged complex of ruthenium. The dependence has been analyzed by a free energy surfaces approach introduced by Marcus and Sutin or by a quantum mechanical approach. In a related, unsymmetrical, complex containing Os and Ru, it has been shown that solvent changes can be used to induce intramolecular electron transfer. If pyrazine is the bridging ligand, the mixed-valence isomers $Os^{III}$-$Ru^{II}$ and $Os^{II}$-$Ru^{III}$ have different properties. In the isomer $Os^{III}$-$Ru^{II}$, the absorption band energy is not solvent dependent but spectral markers point toward localized oxidation states. In both this and the related Creutz and Taube ion, it is suggested that there is significant electronic coupling but localized valences, and that intramolecular electron transfer is sufficiently rapid that the solvent is delocalized.

## Introduction

Complexes of Ru and Os have played an important role in mixed-valence chemistry because of the coordinative stability that exists in oxidation states $M^{II}$ ($d^5$) and $M^{III}$ ($d^6$). A number of issues have been explored in this chemistry by using such complexes as $[(NH_3)_5Ru(L)Ru(NH_3)_5]^{5+}$ (L= pz, 4,4'-bipyridine) (2,3) or $[(bpy)_2ClRu(L)RuCl(bpy)_2]^{5+}$ (4,5) They include (6): 1) the role of electronic delocalization and how it affects chemical and physical properties, 2) the utilization of

Intervalence Transfer (IT) band shapes, eq 1, to extract parameters for calculating electron
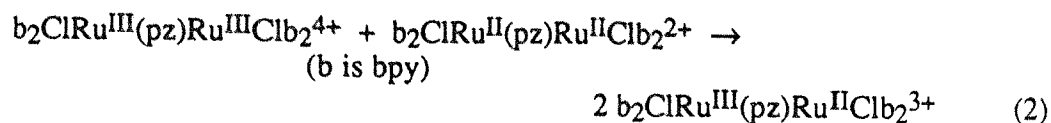
$$(bpy)_2ClRu^{II}(pz)Ru^{III}Cl(bpy)_2{}^{3+} \xrightarrow[h\upsilon]{E_{op}} (bpy)_2ClRu^{III}(pz)Ru^{II}Cl(bpy)_2{}^{3+} \qquad (1)$$

transfer barriers, 3) the effects of molecular size, the solvent, electronic structure, or the distance of charge transfer on band shapes. (6-8)



(pz)          (4,4'-bpy)          (bpy)
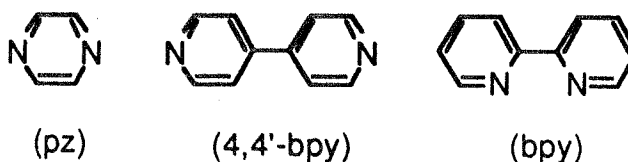
Even though considerable insight has emerged from these studies, a number of outstanding issues either remain to be resolved or are in need of further investigation. They include: 1) Extending the original Hush analysis of intramolecular vibrations.(9,10) Which modes are involved? Can information about these modes be used to calculate the barrier to intramolecular electron transfer?(11) 2) Developing a clearer view of the localized to delocalized transition.(12) What actually happens at the molecular level, when this transition occurs? 3) Describing the role of the solvent by using a model that goes beyond dielectric continuum theory. Is there any way to deal with specific solvent effects?(13) 4) Utilizing molecular, mixed-valence complexes and mixed-valence properties in possible device-like applications.

## Mixed-Valence Chemistry: A Background

In mixed-valence complexes, an estimate of the magnitude of the electronic coupling between metal sites across a ligand bridge is available from electrochemical measurements. For the complex in eq 1, $Ru^{III/II}$ couples are observed at 0.89 V and 1.01 V vs. SSCE in $CH_3CN$, $\mu = 0.1\ M$ in voltammetric experiments. The difference, $\Delta E_{1/2} = E_{1/2}(2)-E_{1/2}(1)$, gives the free energy of comproportionation, $\Delta G°_{com}$, eq 2.

$$b_2ClRu^{III}(pz)Ru^{III}Clb_2{}^{4+} + b_2ClRu^{II}(pz)Ru^{II}Clb_2{}^{2+} \rightarrow$$
$$(b \text{ is bpy})$$
$$2\ b_2ClRu^{III}(pz)Ru^{II}Clb_2{}^{3+} \qquad (2)$$

$$\Delta G°_{com}(eV) = -[(E_{1/2}(2) - E_{1/2}(1)] = -0.12\ eV$$

The stabilization of the mixed-valence complex comes from a statistical factor of 4, a favorable difference in solvation energies, and delocalization of the odd electron. Although it is not always possible to separate these terms, comparative data, Table 1, clearly reveal the importance of electronic delocalization. The comparison between $[(NH_3)_5M(pz)M(NH_3)_5]^{5+}$, M=Ru or Os, is especially striking since the complexes are of the same size and the enhanced value of $\Delta G°_{com}$ for M=Os must arise because of greater electronic delocalization. These comparisons illustrate the importance of d orbital mixing with appropriate orbitals in the intervening ligand bridge.[14] For example, delocalization in $[(bpy)_2ClRu(pz)RuCl(bpy)_2]^{3+}$ is less extensive than in $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ because of competitive $d\pi$-$\pi^*$ backbonding with bpy.

TABLE 1.  Stabilization of Mixed-Valence Complexes

| Complex | Medium | $-\Delta G°_{com}$,eV | Ref |
|---------|--------|------------------------|-----|
| $(NH_3)_5Ru^{III}(4,4'\text{-bpy})Ru^{II}(NH_3)_5{}^{5+}$ | 0.1 $M$ HCl | 0.08 | 3 |
| $(bpy)_2ClRu^{III}(pz)Ru^{II}Cl(bpy)_2{}^{3+}$ | CH$_3$CN (0.1 $M$, TBAH) | 0.13 | 5 |
| $(NH_3)_5Ru(pz)Ru(NH_3)_5{}^{5+}$ | 0.1 $M$ HCl | 0.39 | 2 |
| $(NH_3)_5Os(pz)Os(NH_3)_5{}^{5+}$ | 0.1 $M$ HCl | 0.76 | 15a |
| $(NH_3)_5Os(N_2)Os(NH_3)_5{}^{5+}$ | 0.1 $M$ HCl | 1.20 | 16a |

A second important theme in mixed-valence chemistry has been the utilization of the theories originally devised by Hush to obtain electron transfer parameters from the shapes of IT bands. For a symmetrical case, such as the one in eq 1, $\Delta G°$, $\Delta E° = 0$, and the relationships shown in eq 3-5 have been derived.[9,10]

$$E_{op} = \chi_i + \chi_o = \chi \qquad (3)$$

$$\chi_i = \sum_j S_j h\nu_j \qquad (4)$$

$$\chi_o = e^2\left(\frac{1}{a} - \frac{1}{d}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_S}\right) \qquad (5)$$

$$E_a = E_{op}/4 \qquad (6)$$

In these equations $E_{op}$ is the absorption band energy, $\chi_i$ is the intramolecular reorganizational energy, $\chi_o$ is the solvent or outer-sphere reorganizational energy and $E_a$ is the energy of activation. The $S_j$ are electron-vibrational coupling constants for the vibrational modes that contribute to the band shape. These are the modes for which there is a change in equilibrium displacement or frequency between the initial and final states. The electron-vibrational coupling constant for mode j is related to the change in equilibrium displacement, $(\Delta Q_{e,j})$, the reduced mass $(M_j)$ and the angular frequency $(\omega_j = 2\pi\nu_j)$ as shown in eq 7.

$$S_j = \frac{1}{2}\left(\frac{M_j \omega_j}{\hbar}\right)(\Delta Q_{e,j})^2 \qquad (7)$$

In the expression for the solvent reorganizational energy, eq 5, d is the internuclear distance separating the redox sites, e is the unit electron charge, and $D_{op}$ and $D_S$ are the optical and static dielectric constants of the solvent. This equation was derived by assuming that the solvent could be treated as a dielectric continuum. It takes into account the barrier to electron transfer that arises from solvent dipole reorientations. At the molecular level these reorientations take place by activating librational modes of the solvent. Librations are rotational motions of the solvent molecules that are necessarily collective dipoles because of the condensed nature of the medium.

More generally, for electron transfer in an unsymmetrical complex, eq 8,

$$(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5^{4+} \xrightarrow{h\nu} (bpy)_2ClRu^{III}(pz)Ru^{II}(NH_3)_5^{4+} \qquad (8)$$
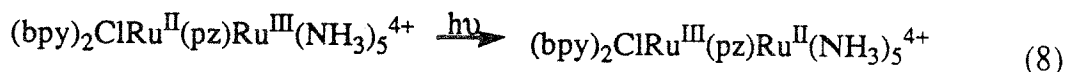
the relationships in eq 9 apply. The quantities that appear in these equations have the same meaning as in the previous equations.

$$E_{op} = \chi + \Delta E^{\circ} \qquad (9a)$$

$$E_a = E_{op}^2/4\chi \qquad (9b)$$

These relationships are only valid in certain limits: 1) The oxidation states must be localized and the electronic delocalization energy much smaller than $\chi$. 2) The existence of multiple IT transitions, which must exist given the low symmetries of the complexes, are neglected.(8a) 3) The quantum spacings and force constants of the molecular vibrations and librations in the surrounding solvent are the same before and after electron transfer occurs. 4) The band shapes are gaussian. 5) The vibronic contributors to the band shape can be treated as classical, harmonic oscillators.

The relationships in eq 6 and 9 provide a basis for calculating energies of activation based on a simple band shape analysis. Application of time dependent perbation theory and utilization of the Golden Rule result in the complete rate constant expression in eq 10. (17,18)

$$k = \frac{2\pi V^2}{h}\left(\frac{\pi}{\chi RT}\right)^{1/2}\exp(-E_{op}^2/4\chi RT) \qquad (10)$$

In eq 10 the quantity $V$ is the electron transfer matrix element. It has the form of a resonance energy and arises by electronic delocalization and coupling between the redox sites. Eq 10 is only valid in the limit that $V \ll \chi$. The pre-exponential term is applicable only in the nonadiabatic limit. In this limit, electronic coupling is weak and the actual electron transfer act slow on the timescales for vibrational equilibration or solvent dipole reorientation. If this condition is not met, the dynamics of electron transfer, and the pre-exponential term, will be determined by timescales associated with the intramolecular vibrational modes or the librational modes of the solvent. (19)

**Temperature Dependence. The Role of the Entropy Change**

In analyzing the relationship between optical and thermal electron transfer based on an approach that utilizes free energy surfaces, Marcus and Sutin have derived eq 11 and 12. (20)

$$E_{op} = \lambda + \Delta G^\circ \qquad (11)$$

$$\Delta G^* = E_{op}{}^2/4\lambda \qquad (12)$$

In these equations the internal energy quantities $\chi$ and $\Delta E^\circ$ are replaced by the corresponding free energy quantities $\lambda$ and $\Delta G^\circ$. The two sets of equations are similar in form, but there is a considerable difference between them in a fundamental sense. One inference that can be drawn from eq 11 is that the measurement of an absorption band energy gives information about the free energy difference between the excited and ground states rather than about the internal energy difference between states as is the case for eq 9a. The difference between the two results is important for reactions where there are large entropic changes. An example is shown in eq 13, where py is pyridine. (21)

$$Ru^{III}(NH_3)_5(py)^{3+}, Fe^{II}(CN)_6{}^{4-} \rightarrow$$

$$Ru^{II}(NH_3)_5(py)^{2+}, Fe^{III}(CN)_6{}^{3-} \qquad (13)$$
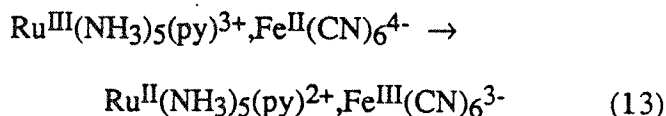
In this case, electron transfer is accompanied by a considerable decrease in charge density because of the lowering of the electrostatic charge on the ions in the products. This leads to a large, positive entropic change ($\Delta S^\circ = 40$ eu at 298 K) and a considerable difference between $\Delta H^\circ$ and $\Delta G^\circ$ since $\Delta G^\circ - \Delta H^\circ = -T\Delta S^\circ$. In the absence of pressure-volume work, $\Delta H^\circ = \Delta E^\circ$.

A significant question then arises concerning the band shape equations for IT transitions, and for molecular-level, electronic transitions, in general. Are the appropriate parameters that appear in these equations the internal energy quantities of eq 9 or the free energy quantities of eq 11?

We have attempted to resolve this question experimentally.(22) The experiments were conducted on the mixed-valence complex in eq 8. Two types of measurements were made. In one, the temperature dependences of the individual $Ru^{III/II}$ couples were measured by using the non-isothermal cell arrangment of Weaver and co-workers. (23) The first oxidation occurs at -$Ru(NH_3)_5{}^{2+}$ and the second at -$RuCl(bpy)_2{}^+$. From temperature dependent redox potential measurements, $\partial(\Delta E_{1/2})/\partial T \sim \Delta S$. (24)

The temperature dependence of the energy of the IT band, $E_{op}$, was also measured. The experiments were conducted over a wide range of temperatures in either methanol or a 48:52 (V:V) propionitrile: n-butyronitrile solvent mixture. In methanol the temperatures

ranged from 180 to 300 K.

According to eq 11, a temperature dependence in $E_{op}$ could arise in either, or both, $\lambda$ and $\Delta G°$. The relevant relationships are shown in eq 14-17,

$$(\partial \lambda_i/\partial T) \sim 0 \qquad (14)$$

$$(\partial \lambda_o/\partial T) \; \alpha \; \left[\partial\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)\partial T\right] \qquad (15)$$

$$(\partial \Delta G°/\partial T) = -\Delta S° \qquad (16)$$

$$(\partial E_{op}/\partial T) = (\partial \lambda_o/\partial T) - \Delta S° \qquad (17)$$

The force constants and quantum spacings for the intramolecular vibrations that contribute to the electron transfer barrier are typically, insensitive to temperature. A dependence of the solvent reorganizational energy is predicted to exist by dielectric continuum theory through the temperature dependences of $D_{op}$ and $D_s$.

The temperature dependences obtained from the electrochemical and spectral measurements in $CH_3OD$ are summarized in Table 2.

TABLE 2. Temperature Dependences in $CH_3OD$, 35 m$M$ in [NEt$_4$](PF$_6$)   (22)

| Complex | e.u. $(\partial \Delta E_{1/2}/\partial T)$ | e.u. $-(\partial E_{op}/\partial T)$ |
|---|---|---|
| $(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5^{4+}$ | $21 \pm 5$ | $29 \pm 6$ |
| $(bpy)_2ClRu^{II}(pz)Ru^{III}Cl(bpy)_2^{3+}$ | -- | $-3 \pm 3$[a] |
| $(NH_3)_5Ru^{II}(4,4'\text{-}bpy)Ru^{III}(NH_3)_5^{5+}$ | -- | $5 \pm 3$[a] |

[a]In 48:52 (V:V) propionitrile: $n$-butyronitrile

Data are included in Table 2 for the unsymmetrical complex in eq 8 and for the corresponding, symmetrical, mixed-valence complexes. For the symmetrical complexes, $\Delta S° = 0$ and the temperature dependence of $E_{op}$ must arise solely in $\lambda_o$.

Several interesting conclusions can be drawn from the data in Table 2. The entropic changes implied by the temperature dependences of the electrochemical and spectral

quantities are large and positive. This is qualitatively what is expected for the reaction in eq 8. The conversion to the high-energy, oxidation state isomer, $[(bpy)_2ClRu^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$, is accompanied by a decrease in charge at the smaller - $Ru(NH_3)_5$ site from +3 to +2. This decreases interactions with the solvent including a loss of specific interactions through H-bonding. (13) Qualitatively, this leads to an increase in entropic content due to a decreased "electrostriction" in the surrounding solvent. The decrease in charge density in the final state can also be viewed as decreasing the extent of interaction of the electrostatic field of the ion with the surrounding solvent dipoles. This leads to a decrease in force constant and quantum spacings for the solvent librations that contribute to the electron transfer barrier.

There does appear to be a temperature dependence for the symmetrical complexes although it is of smaller magnitude and nearly within the error of the experiment. If the difference in sign between the two cases is real, the temperature dependences can not be accounted for by dielectric continuum theory. According to eq 15, they should be the same for either complex.

When the apparent temperature dependence of $\lambda_o$ is included, the entropic change derived from the electrochemical measurement is within experimental error of the temperature dependence found for $E_{op}$. This agreement appears to validate the free energy surface analysis and equations such as 11 and 12 rather than eq 9.

The temperature dependence of absorption bands can also be treated by using a quantum mechanical approach and the method of moments developed by Lax and the generating function technique of Kubo. (25) In the quantum mechanical treatment, a temperature dependence is predicted if there are changes in frequencies for the intramolecular vibrations or solvent librations that respond to the change in electronic configuration. The relationship between $E_{op}$ and the first moment of the absorption band, $M_1$, is given in eq 18.(22) For a gaussian-shaped absorption band, $M_1 = E_{op}$.

$$E_{op} \sim M_1 = \Delta E^\circ + \sum_j \chi_j' + 1/2 \sum_j \hbar\Omega_j \coth(\beta_j/2) \qquad (18)$$

$$\chi_j' = S_j \hbar\omega_j' \qquad (18a)$$

$$\Omega_j = \frac{(\omega_j')^2 - (\omega_j)^2}{2\omega_j} \qquad (18b)$$

$$\beta_j = \frac{\hbar\omega_j}{k_B T} \qquad (18c)$$

The sums are over the participating intramolecular vibrations and librations of the solvent. The $\omega_j$ and $\omega'_j$ are the angular frequencies of these vibrations or librations in the initial and final states. In this treatment, the origin of the temperature dependence is found in the change in frequencies. With a decrease in frequency and the associated quantum spacing, the vibrational population is spread amongst a greater number of levels which increases entropic content. Once again, in the absence of pressure-volume work, $\Delta E^\circ = \Delta H^\circ$.

It is possible to relate the temperature dependent term that appears in eq 18 to the entropic change for the reaction. For an harmonic oscillator, the contribution to the entropy from mode j is given by eq. 19. (26)

$$S_j/k_B = \frac{\beta_j}{\exp\beta_j - 1} - \ln[1 - \exp\beta_j] \qquad (19)$$

In the limits that $h\omega_j'$, $h\omega_j << k_BT$ and $\Delta\omega_j = |\omega_j' - \omega| << \omega_j', \omega$, it can be shown that $T\Delta S^\circ$ is related to the third term on the rhs of eq. 18 by,

$$T\Delta S^\circ \sim -1/2\sum_j \hbar\Omega_j \coth(\beta_j/2) \qquad (20)$$

Based on this result it is possible to relate the first moment to $\Delta S^\circ$ as shown in eq 21.

$$E_{op} = \chi' + \Delta E^\circ - T\Delta S^\circ = \chi' + \Delta G^\circ \qquad (21)$$

This is an important result. It demonstrates that the quantum mechanical treatment of absorption band shapes also successfully predicts a temperature dependence. Based on this result, an entropic-like term will appear for any electronic transition in which there is a change in frequency in the vibrational and/or librational modes between the initial and final states.

The entropic change will be dominated by the librations of the solvent. For polar organic solvents, the quantum spacings for these modes are small, 1-10 cm$^{-1}$, based on dielectric loss measurements. With spacings of this magnitude, many levels will be populated at room temperature. For high frequency modes, frequency changes of 5-10% are common. However, when the quantum spacings are large, populations above $\upsilon = 0$ are small and their contribution to changes in entropic content are usually negligible.

The quantum mechanical analysis gives a result that is similar in form to that

obtained by the free energy surfaces approach. The agreement between the two reinforces the point that absorption (and emission) band energies contain information about free energy differences between states. In the quantum mechanical treatment, the temperature dependence arises from the entropic difference between states without having recourse to a dielectric continuum model for the solvent. Even with the agreement, there is a significant difference between the results of the two treatments that is yet to be reconciled. In the quantum mechanical treatment the reorganizational energy is the internal energy quantity, $\chi$. In the analysis based on free energy surfaces it is the free energy quantity, $\lambda$.

## Solvent-Induced, Intramolecular Electron Transfer

For the mixed-valence example in eq 8, the difference in ligand environments at the two Ru sites is sufficient to create an appreciable difference in redox potentials. This is caused by the stabilization of $Ru^{II}$ as $-Ru^{II}Cl(bpy)_2$, caused by back-bonding to the bipyridine ligands. This leads to the oxidation state distribution $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ in the mixed-valence ion.

In the mixed-metal complex, $[(bpy)_2ClOs^{II}(4,4'-bpy)Ru^{II}(NH_3)_5]^{3+}$, the compensating effect of exchanging $Os^{II}$ for $Ru^{II}$ at the bpy site makes the potentials for the $Os^{III/II}$ and $Ru^{III/II}$ couples nearly equal in magnitude. In coordinatively equivalent complexes of Ru and Os, the potentials for the $Os^{III/II}$ couples are lower by ~ 0.4-0.5 V . For the mixed complex in acetonitrile ($\mu = 0.1$ $\underline{M}$) the potentials for the $Os^{III/II}$ and $Ru^{III/II}$ couples are the same, ~ 0.53 V vs. SSCE.

The overlap in potentials exists in only a few, polar organic solvents. The $Ru^{III/II}$ couple is strongly solvent dependent but the $Os^{III/II}$ couple is not. The solvent dependence arises from strong, specific interactions between individual solvent molecules and the ammino groups in $-Ru^{III}(NH_3)_5$. The potentials of the $Ru^{III/II}$ couple in this and related complexes correlate linearly with the donor number (DN) of the solvent.(13,27) As defined by Gutmann, the donor number is the molar enthalpic change that occurs when a donor molecule forms a donor-acceptor complex with $SbCl_5$ in 1,2-dichloroethane as solvent.(28) Solvents that lie high on the donor number scale, e.g., DMF (DN = 26.6), are known to have high propensities to undergo H-bonding. On this scale, acetonitrile (DN = 14.1) is a solvent of intermediate donor number and nitromethane (DN = 2.7) is a solvent of low donor number.

Because of the difference in the response to solvent changes by the $Os^{III/II}$ and

$Ru^{III/II}$ couples, the oxidation state distribution between the mixed-valence isomers $[(bpy)_2ClOs^{III}(4,4'-bpy)Ru^{II}(NH_3)_5]^{4+}$ and $[(bpy)_2ClOs^{II}(4,4'-bpy)Ru^{III}(NH_3)_5]^{4+}$ is solvent dependent. By a combination of electrochemical and spectroscopic studies, it has been possible to show that: (1) The oxidation state distribution $Os^{II}$-$Ru^{III}$ is favored in solvents of high donor number where $Ru^{III}$ is stabilized by ammine-solvent interactions. (2) In acetonitrile there is an equilibrium distribution between the isomers. (3) In solvents of low donor number, the dominant isomer is $Os^{III}$-$Ru^{II}$. (27)

The assignment of oxidation states was made based on the spectral properties of the complex in the visible and near infrared (NIR). For example, in nitromethane, where the oxidation state distribution is $Os^{III}$-$Ru^{II}$, an intense absorption band is observed at ~520 nm, which can be assigned to a $Ru^{II} \rightarrow 4,4'$-bpy transition. In this spectrum there is no sign of the characteristic $Os^{II} \rightarrow$ bpy transitions. In DMF, characteristic $Os^{II} \rightarrow$ bpy bands appear at ~680, ~510, and ~430 nm and the $Ru^{II} \rightarrow 4,4'$-bpy transition is absent.

Based on the electrochemical measurements, the effect of solvent on the relative energies of the two mixed-valence isomers is considerable. In nitromethane, the isomer $Os^{III}$-$Ru^{II}$ is favored over $Os^{II}$-$Ru^{III}$ by 0.20 eV. In DMSO, the isomer $Os^{II}$-$Ru^{III}$ is favored over $Os^{III}$-$Ru^{II}$ by 0.38 eV.

In solvents of intermediate donor number it possible to adjust the equilibrium between isomers by utilizing solvent mixtures. In acetronitrile (DN = 14.1) the $Os^{III}$-$Ru^{II}$ isomer is dominant. In propylene carbonate (DN = 15.1) the $Os^{II}$-$Ru^{III}$ isomer is dominant. In mixtures of the two solvents the distribution between isomers can be tuned by varying the composition of the solvent. These experiments have been used to demonstrate that solvent effects can be utilized to induce intramolecular electron transfer.(27) For example, when an excess of propylene carbonate is added to an acetonitrile solution, the net electron transfer in eq 22 occurs as shown by spectrophotometric measurements.

$$(bpy)_2ClOs^{III}(4,4'-bpy)Ru^{II}(NH_3)_5^{4+} \rightarrow (bpy)_2ClOs^{II}(4,4'-bpy)Ru^{III}(NH_3)_5^{4+}$$

$$(22)$$
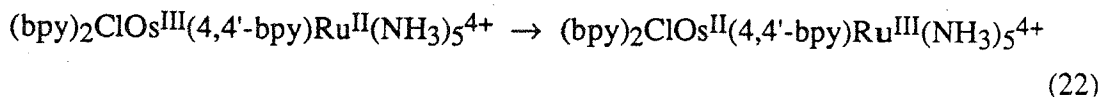
## Solvent-Induced "Delocalization" in $[(bpy)_2ClOs(pz)(Ru(NH_3)_5]^{4+}$

In the mixed-valence complex $[(bpy)_2ClOs(4,4'-bpy)Ru(NH_3)_5]^{4+}$, relatively weak

electronic coupling exists across the 4,4'-bipyridine ligand bridge. This is a Class II example in the Robin and Day classification scheme. (30) The redox sites are localized, and the IT transition can be described as a charge transfer between isolated redox sites that are weakly coupled electronically. In $[(NH_3)_5Os(L)Os(NH_3)_5]^{5+}$ (L = pz, $N_2$), the electronic properties of the molecules are consistent with strong electronic coupling (Table 1) and delocalization of the odd electron over both metal sites. (7a,15,16)

For the Creutz and Taube ion, $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ many studies have been conducted and different conclusions have been reached concerning localization or delocalization of the odd electron. (2,6,29) From the data in Table 1, the $\Delta E_{1/2}$ value for this complex is intermediate between those for $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$, where there is strong electronic coupling and $[(NH_3)_5Ru(4,4'-bpy)Ru(NH_3)_5]^{5+}$ where electronic coupling across the 4,4'-bpy bridge is weak. From the properties of the complex $[(bpy)_2ClOs(pz)OsCl(bpy)_2]^{3+}$ it appears to be an intermediate case as well.(31)

In the mixed complex, $[(bpy)_2ClOs(pz)Ru(NH_3)_5]^{4+}$, there is both a Creutz and Taube half and an Os half and its properties are unusual as well. For this complex it has also been possible to use the appearance of characteristic electronic transitions as oxidation state markers.(27) Especially revealing is the pattern of bands that appear in the near infrared (NIR) and how they are affected by solvent. In $d_6$-DMSO, (DN = 29.8) a broad, relatively weak IT band appears at 6600 cm$^{-1}$ with evidence for a second band at higher energy. These are IT bands that arise from $d\pi(Os^{II}) \rightarrow d\pi(Ru^{III})$ transitions from the two highest $d\pi$ levels at $Os^{II}$ to the $d\pi$ hole at $Ru^{III}$. The third transition, $d\pi_3(Os^{II}) \rightarrow d\pi(Ru^{III})$, occurs at higher energy and is obscured by $Os^{II} \rightarrow$ bpy bands.

In solvents of intermediate or low donor number such as $CD_3CN$, an intense, narrow absorption band appears at 8300 cm$^{-1}$ with a shoulder at ~9300 cm$^{-1}$. In addition, the $Os^{III}$-based $d\pi \rightarrow d\pi$ transitions $d\pi_1 \rightarrow d\pi_3$; $d\pi_2 \rightarrow d\pi_3$ are observed at 5770 cm$^{-1}$ and 4170 cm$^{-1}$. (8a,27) An additional, band of low intensity appears at 1600 cm$^{-1}$. The $d\pi \rightarrow$ $d\pi$ transitions at $Os^{III}$ are somewhat red-shifted and of noticeably higher intensity than the $d\pi \rightarrow d\pi$ transitions in related complexes such as $[Os^{III}(bpy)_2(pz)Cl]^{2+}$. (31) The energy of the band at 8300 cm$^{-1}$ is solvent independent in solvents of donor numbers that vary from 11.9 ($C_6H_5CN$) to 23.0 (O=P(OMe)$_3$).

The visible and NIR absorption features for $[(bpy)_2ClOs(pz)Ru(NH_3)_5]^{4+}$ in solvents of high donor number are consistent with the oxidation state distribution $[(bpy)_2ClOs^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$. The fact that the IT bands are of relatively low intensity, broad, and solvent dependent all point to their origin as IT transitions between localized

redox sites. From the electrochemical measurements the electronic delocalization energy is <0.05 eV.

The oxidation state markers in solvents of low or moderate donor number are consistent with the oxidation state distribution $[(bpy)_2ClOs^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$. The properties of the IT bands in these solvents differ in detail but are highly reminiscent of those found for the Creutz and Taube ion. They include the lack of a solvent dependence and band widths that are narrower by a factor of 2-3 than those predicted by the Hush bandshape analysis. (9,10) From the electrochemical measurements, the delocalization energy is ~0.16 eV.

In formamide (DN = 24.0) or trimethyl phosphate (DN = 23.0), measurements in the NIR provide evidence for the simultaneous existence of <u>both</u> isomers in solution. From temperature dependent absorption band measurements, $[(bpy)_2ClOs^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ is favored at high temperature consistent with a higher entropic content for this isomer.

The mixed-valence properties of $[(bpy)_2ClOs(pz)Ru(NH_3)_5]^{4+}$ are solvent dependent. The changes in properties that occur with solvent arise because there is a coupling between external solvent molecules and the internal, electronic structure of the ion. In solvents of high donor number, strong, specific interactions with the N-H bonds stabilize $-Ru^{III}(NH_3)_5^{3+}$ and the oxidation state isomer $Os^{II}-Ru^{III}$ by donation of electronic density. In solvents of lower donor number there is a switch to $Os^{III}-Ru^{II}$. In this isomer there is enhanced electronic delocalization and properties that reflect the delocalization.

According to the oxidation state markers, there are localized oxidation states in $[(bpy)_2ClOs^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ and, yet, from the absence of a solvent dependence on $E_{op}$, this isomer appears to be "delocalized". The two observations are not necessarily in conflict. They probe different things at the molecular level. The appearance of the $d\pi \rightarrow d\pi$ transitions is a probe of internal electronic structure. The variation in $E_{op}$ with solvent probes the solvent. When taken together, these two results point to the fact that there may be different degrees of "delocalization" in mixed-valence complexes. At one extreme are the complexes $[(NH_3)_5Os(L)Os(NH_3)_5]^{5+}$ (L = pz, $N_2$) where strong electronic coupling exists and the odd electron is completely delocalized.(15,16) In these complexes the force constants and quantum spacings for the intramolecular vibrations and solvent librations are those of an electronically delocalized system. At the other extreme are complexes such as $[(bpy)_2ClRu^{II}(pz)Ru^{III}Cl(bpy)_2]^{5+}$ where electronic coupling is weak, and the properties of the individual oxidation states, $Ru^{II}$ or $Ru^{III}$, are retained.

The properties of $[(bpy)_2ClRu^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ can be explained if <u>there are</u>

localized but electronically coupled oxidation states and the surrounding solvent is delocalized. With this interpretation, the three bands in the NIR arise from a lowest energy $d\pi_3(Ru^{II}) \rightarrow d\pi(Os^{III})$ IT transition and the two higher energy, $d\pi_1, d\pi_2(Ru^{II}) \rightarrow d\pi(Os^{III})$ transitions that are separated in energy by $\sim 1000$ cm$^{-1}$.(27)

Both $[(bpy)_2ClOs^{III}(pz)Ru^{II}(NH_3)_5]^{4+}$ and the Creutz and Taube ion may be intermediate cases where the solvent is delocalized, and there is considerable electronic coupling, but the oxidation states are still localized. This apparent dichotomy in behavior could have its origin in dynamics and the difference in timescales between vibrational equilibration and solvent dipole reorientation. In $[(bpy)_2ClOs(pz)Ru(NH_3)_5]^{4+}$ or the Creutz and Taube ion, electronic coupling is sufficient ($\sim 0.16$ and $\sim 0.30$ eV, respectively) to decrease greatly the barrier to electron transfer and ensure that electron transfer is adiabatic. If the timescale for intramolecular electron transfer becomes shorter than the timescale for solvent dipole reorientation, 1-10 ps for polar organic solvents, solvent dipoles would be unable to "keep up" with the switch in oxidation states induced by electron transfer. This would lead to averaged solvent dipole orientations and delocalization of the solvent . An intramolecular barrier to electron transfer must continue to exist based on the difference in the response of the intramolecular vibrations to the two different oxidation states.

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