

Communications to the Editor

Electrochromism in the Near-Infrared Absorption Spectra of Bridged Ruthenium Mixed-Valence Complexes

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Many experimental and theoretical approaches have been developed to characterize the chemical and physical properties of mixed-valence complexes.^{1,2} These molecules may possess metals in differing oxidation states which participate in intervalence charge-transfer transitions. In principle, these transitions should be strongly affected by an external electric field. Such electrochromism can provide a direct and sensitive approach to investigating the electronic properties of molecules.³ We report the first measurements of the effects of an externally applied electric field on the near-infrared absorption spectra of $[(\text{NH}_3)_5\text{Ru}]_2\text{L}^{5+}$ (L = pyrazine or 4,4'-bipyridine). Significant differences are observed between the two complexes, illustrating the range of electronic interactions between the metal centers.

When an external electric field (F_{ext}) is applied to a nonoriented and immobilized sample of absorbing molecules, the change in the absorption spectrum, $\Delta A(\nu)$, can often be described as a linear combination of zeroth, first, and second derivatives of the absorption band, $A(\nu)$:^{3,4}

$$\Delta A(\nu) = \{A_{\chi}A(\nu) + B_{\chi}\nu[A(\nu)/\nu]'/15h + C_{\chi}\nu[A(\nu)/\nu]''/30h^2\} \cdot F_{\text{int}}^2 \quad (1)$$

h is Planck's constant, χ is the experimental angle between F_{ext} and the electric polarization of light at the frequency ν used to probe the effect, and $F_{\text{int}} = f \cdot F_{\text{ext}}$.⁵ A_{χ} and B_{χ} are fully described elsewhere;^{3,4} roughly, A_{χ} provides information on the transition moment polarizability and hyperpolarizability, and B_{χ} provides information on the change in polarizability ($\Delta\alpha$) associated with an electronic transition. $C_{\chi} = \{5|\Delta\mu_A|^2 + (3\cos^2\chi - 1)[3(\mathbf{p}\cdot\Delta\mu_A)^2 - |\Delta\mu_A|^2]\}$, where \mathbf{p} is a unit vector along the transition moment and $\Delta\mu_A$ is the change in permanent dipole moment associated with the transition. In principle, a decomposition of the ΔA spectrum into its component derivatives with their χ -dependences provides quantitative estimates of these molecular properties and their projections onto \mathbf{p} . The Stark effect and electrochromism have been applied to the study of metal-to-ligand charge-transfer transitions in only a few inorganic complexes;⁶⁻¹⁰ however, only

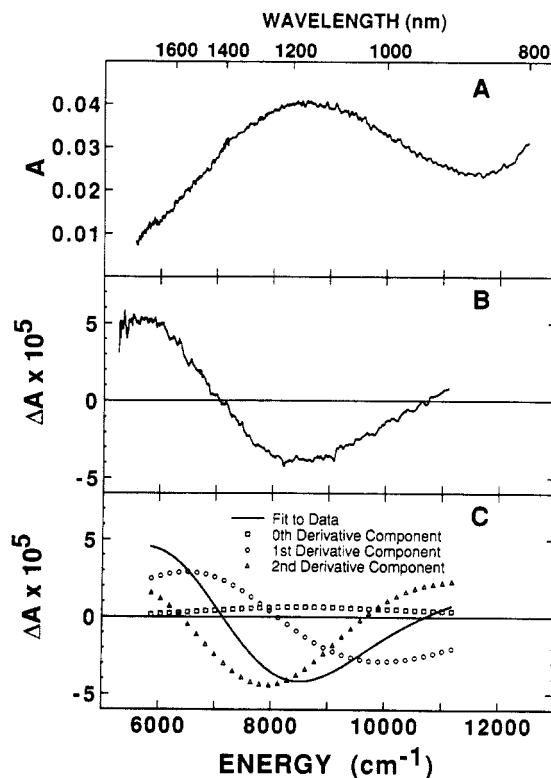


Figure 1. (A) Absorption, (B) electrochromism, and (C) fit of the electrochromism to eq 1 showing the individual derivative components of the fit for $[(\text{NH}_3)_5\text{Ru}]_2(4,4'\text{-bpy})^{5+}(\text{Br}^-)_5$ in 50% (v/v) glycerol/ D_2O at 77 K. $F_{\text{ext}} = 4 \times 10^5$ V/cm; $\chi = 90^\circ$. From the fit, $A_{\chi} = 1.1 \times 10^{-19}$ (m/V)², $B_{\chi} = 5.0 \times 10^{-37}$ J (m/V)², and $C_{\chi} = 3.4 \times 10^{-56}$ J² (m/V)², where $\chi = 90^\circ$.

indirect measurements of these properties exist for mixed-valence complexes.¹¹

All complexes were synthesized by literature methods¹²⁻¹⁴ and were kindly provided by Dr. Sano in Professor Taube's laboratory. The spectrophotometer and the basic technique have been described.^{4,15} Samples were dissolved in 50% (v/v) glycerol- d_3 / D_2O and immersed in liquid nitrogen to form clear 25- μm -thick glasses between semitransparent Ni electrodes. A Ge photodiode detector (Judson J16) was used to record the signal. To obtain the derivatives necessary to analyze the $\Delta A(\nu)$ spectra according to eq 1, the absorption spectra were fit to sums of skewed Gaussian components containing cubic and quartic terms in the exponent.¹⁶

The absorption and electrochromic spectra for the intervalence band of $[(\text{NH}_3)_5\text{Ru}]_2(4,4'\text{-bpy})^{5+}$ are shown in Figure 1. As shown in panels B and C, a linear combination of derivatives of the observed absorption band closely models the $\Delta A(\nu)$ line shape.¹⁷ The second derivative component dominates the $\Delta A(\nu)$

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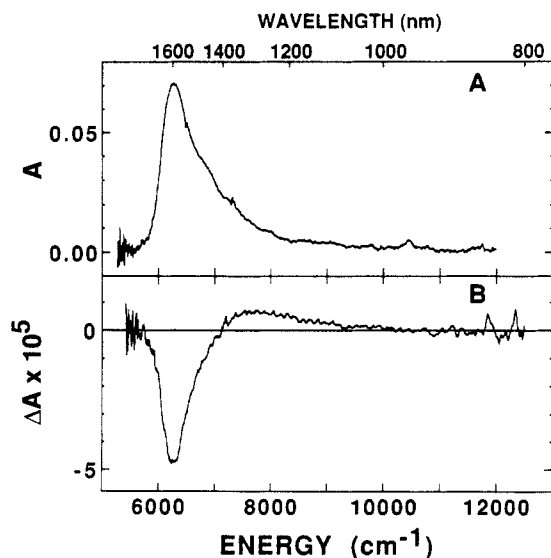


Figure 2. (A) Absorption and (B) electrochromic spectra for $[(\text{NH}_3)_5\text{Ru}]_2\text{pz}^{5+}(\text{C}_7\text{H}_7\text{SO}_3^-)_3$ in 50% (v/v) glycerol/ D_2O , 77 K. $F_{\text{ext}} = 4 \times 10^5$ V/cm; $\chi = 90^\circ$.

spectrum, though the zeroth and first derivatives also contribute, indicating that the transition moment and polarizability changes are non-negligible. $|\Delta\mu_A|$ calculated from this analysis is $(28 \pm 2)/fD$ (debye), and $\mathbf{p} \cdot \Delta\mu_A = (27 \pm 2)/fD$, indicating that $\Delta\mu_A$ and the transition dipole moment are essentially collinear.

The near-infrared absorption and electrochromic spectra of $[(\text{NH}_3)_5\text{Ru}]_2\text{pz}^{5+}$ are shown in Figure 2. The electric field causes the low-energy side and the peak of the absorption band to decrease in a manner that is well modeled by a negative zeroth derivative, while the high-energy side of the absorption increases in a field. The $\Delta A(\nu)$ spectrum does not satisfactorily decompose into a simple linear combination of derivatives of the overall absorption band. Qualitatively, however, there is little evidence that a second derivative and hence $\Delta\mu_A$ contributes significantly to the $\Delta A(\nu)$ line shape, especially on the low-energy side which lacks the large, positive signature of the second derivative.

A large $\Delta\mu_A$ should accompany a true intervalence transition involving a large redistribution of electronic charge density from one metal center to the other. In $[(\text{NH}_3)_5\text{Ru}]_2(4,4'\text{-bpy})^{5+}$, the observed $|\Delta\mu_A|$ of $28/fD$ indicates that the states involved are highly dipolar and the unpaired electron is substantially localized. For the limiting case of full charge transfer over 11.3 Å (the Ru-Ru distance),² $|\Delta\mu_A|$ will be 54 D. While very large, the experimentally measured value of $|\Delta\mu_A|$ is significantly smaller than this upper limit.¹⁸ This difference suggests that the limiting case is an over-simplification and that metal-ligand and metal-metal interactions may be more complex and significant than initially thought.^{2,11}

The absence of an observable contribution by $|\Delta\mu_A|$ to the $\Delta A(\nu)$ spectrum for the near-IR band of $[(\text{NH}_3)_5\text{Ru}]_2\text{pz}^{5+}$ indicates that there is little net movement of the centers of charge associated with this transition. This result directly demonstrates that the metal centers are so strongly coupled to each other that the unpaired electron is delocalized over both, even at 77 K; this description is consistent with a large body of indirect experimental evidence for this complex.^{1,2,11,19,20} The low-energy portion of the absorption band decreases in intensity in an electric field, indicating an effect solely due to a perturbation of the transition dipole moment. At higher energies, the band behaves in a com-

plicated manner, suggesting that multiple bands exist that behave differently in a field. Variations across the near-IR band have also been noted in MCD spectra at low temperature;²¹ electrochromism is likewise often useful for selectively detecting weak transitions which are sensitive to an electric field.

Electrochromism offers a wealth of information on the changes in electrostatic properties associated with transitions between states in mixed-valence complexes. In tandem with a detailed theoretical analysis,²² these will be explored more fully in a subsequent paper covering both metal-to-ligand and intervalence charge-transfer transitions of mono- and binuclear ruthenium complexes.

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Solvation-Controlled Diastereofacial Selectivity in Alkylations of Bicyclic Lactam Enolates

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Recent work by the Meyers group has suggested the possibility of stereoelectronic effects playing a role in diastereofacially selective alkylations of the enolate carbon in the bicyclic [3.3.0] lactam **1**.¹ Meyers describes numerous cases where alkylation leads to impressive endo selectivity (Figure 1).² Careful examination of the geometry of **1**, by molecular modeling techniques, suggests that the two faces are sterically very similar with the endo face slightly less accessible. The origin of the observed endo selectivity is therefore unclear.

One possibility that has been presented invokes stereoelectronic control via the Cieplak effect.^{3,4} This effect, which is purported to occur in σ bond forming reactions, involves stabilization of the transition state in question via orbital mixing of the incipient σ^* orbital with a proximal electron-rich σ bond. Although work done by le Noble et al. on adamantyl systems has suggested that this type of stereoelectronic control is real, the magnitude and generality of this effect remain incompletely documented.^{5,6} Moreover, other work done by Meyers on systems very similar to the lactam **1** has yielded results that are inconsistent with the Cieplak model.¹

Our goal was to use molecular orbital techniques to examine the lactam **1** in alkylation reactions in order to determine the nature of the facial bias. Semiempirical calculations (AMPAC)⁷ were chosen since the number of atoms preclude a complete ab initio study of the reaction surface. The AM1 Hamiltonian⁸ was used in all cases except those where a lithium counterion was used. In these cases MNDO⁹ was applied.

We examined the reaction surfaces for the endo and exo monoalkylation of methyl iodide to the naked enolate of **1** (no

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