in zeolite-Y.[16] [Note pentamethylbenzene with σ = 7.15 Å passes readily, whereas hexamethylbenzene with σ = 7.95 Å does not—despite its enhanced donor strength.] Once the arene has penetrated this window, a cavity dimension of ~13 Å is large enough to accommodate both MV^{2+} and anthracene (but not tetracene), as depicted in Figure 3. A similar shape selectivity is also observed with zeolite-X (of related dimensions to zeolite-Y)[17] but not with the more constricted 4.2 Å aperture in zeolite-A[18] or with completely amorphous silica alumina.

Owing to the wide structural variations that are allowed by different organic cations, we anticipate that shape selectivity can also be finely tuned in the formation of CT complexes with other types of hydrocarbon donors. We hope that further tests in progress will provide the requisite information for the detailed mapping of substrate access to various zeolite structures,[19] especially with regard to both their kinetic and thermodynamic properties in the liquid phase.

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Supplementary Material Available: Tables of data collection and processing parameters, atomic coordinates and isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters (4 pages). Ordering information is given on any current masthead page.

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Stark Effect Spectra of $Ru(diimine)_3^{2+}$ Complexes

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The metal-to-ligand charge-transfer (MLCT) states of $Ru(diimine)_3^{2+}$ and related complexes have been the subject of intense interest over the past 20 years in an effort to understand and potentially to exploit their photochemical properties.[1] Although the degree of charge separation between the metal and ligand is the distinguishing characteristic of these states, little quantitative experimental data exists.[2] We report here the magnitude of the difference between the electric dipole moments of the ground and excited states, $|\Delta\mu_A|$, associated with MLCT transitions in several $Ru(diimine)_3^{2+}$ complexes using Stark effect spectroscopy.

The effect of an applied electric field on the absorption spectrum (the Stark effect spectrum) has rarely been applied to the spectroscopy of transition-metal complexes; we are only aware of two examples in single crystals[3] and none in solid solution as discussed in this communication.[4] For a non-oriented sample in a rigid matrix, the change in absorbance, ΔA, due to $\Delta\mu_A$ is proportional to the second derivative of the absorption line shape, the square of the electric field felt by the chromophore, and $|\Delta\mu_A|^2$.[5]

The absorption, second derivative of absorption, and Stark effect spectra of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) at 77 K are shown

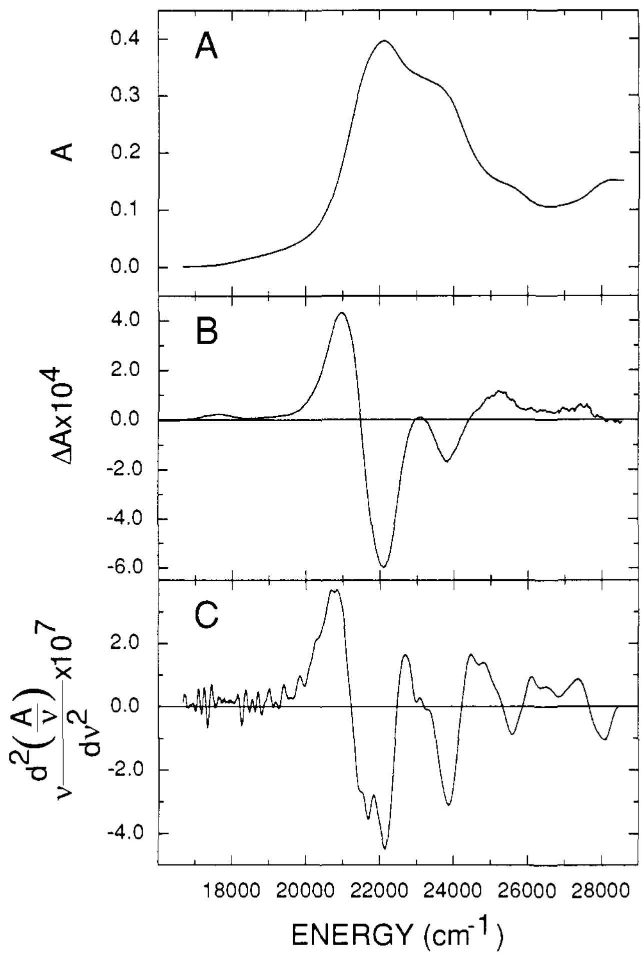

Figure 1. (A) Absorption spectrum of $Ru(bpy)_3^{2+}(PF_6^-)_2$ in PVA at 77 K. (B) Stark effect spectrum of $Ru(bpy)_3^{2+}$, $\boldsymbol{F}_{ext} = 6.43 \times 10^5$ V/cm; $\chi = 54.7°$.[5] (C) Second derivative of the absorption spectrum obtained by numerical differentiation. The Stark effect spectrum has the shape of the second derivative of the absorption spectrum in which each electronic absorption band is weighted by its appropriate value of $|\Delta\mu_A|^2$.[5]

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(2) The solvent dependence of absorption (or emission) band positions provides one approach to this problem. For example, see: Kober, E.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098-2104.

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(4) The molecule of interest is dissolved in a thin polymer film (typically 20-100 μm thick) that is coated with semitransparent electrodes across which an electric field is applied. For experimental details, see: Lockhart, D. J.; Boxer, S. G. *Biochemistry* **1987**, *26*, 664-668, 2958.

(5) More precisely

$$\Delta A(\nu) = \frac{C_\chi}{30h^2}\boldsymbol{F}_{int}^2\nu\,\frac{d^2(A/\nu)}{d\nu^2}$$

where $C_\chi = \Delta\mu_A^2[5 + (3\cos^2\chi - 1)(3\cos^2\zeta_A - 1)]$, χ is the angle between the applied electric field direction and the polarization vector of the probing beam, ζ_A is the angle between $\Delta\mu_A$ and the transition dipole moment being probed at energy $h\nu$, and $\boldsymbol{F}_{int}$ is the internal field related to the actual applied electric field, $\boldsymbol{F}_{ext}$, by the local field correction: $\boldsymbol{F}_{int} = f\boldsymbol{F}_{ext}$. (Mathies, R. Ph.D. Thesis, Cornell University, 1974: Liptay, W. *Ber. Bunsenges.* **1976**, *80*, 207-217.) The value of f is generally greater than unity (typically about 1.2 for the polymers used here[4]); although its value is uncertain, it is likely to be roughly the same for different complexes in the same matrix and for different electronic states within a complex. For MLCT transitions, we assume $|\Delta\mu_A|$ dominates any effect due to a change in polarizability between the ground and excited states. The overall similarity between the Stark effect and second derivative of absorption line shapes confirms this. Figure 1 and the values of $|\Delta\mu_A|$ in Table I were obtained at χ = 54.7° to minimize complications from variations in ζ_A due to overlapping bands, a problem that will be dealt with quantitatively elsewhere. The differential weighting of absorption bands by $|\Delta\mu_A|^2$ may help to reveal features that are obscured by overlapping bands. The signal-to-noise of the Stark data is far superior to that obtained by numerically differentiating the absorption spectrum.

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Table I. Values of $\Delta\mu_A$ for MLCT Transitions of Several Tris(diimine)ruthenium(II) Complexes Determined by Stark Effect Spectroscopy

complex[a]	λ (nm)	ν (cm^{-1})	$\lvert\Delta\mu_A\rvert$ (D)[b]
$Ru(bpy)_3^{2+}$	454	22026	$(8.8 \pm 0.7)/f$
	420	23810	$(5.3 \pm 0.4)/f$
$Ru(bpy)_2(biq)^{2+}$	532	18797	$(5.7 \pm 0.4)/f$
	441	22676	$(4.8 \pm 0.3)/f$
$Ru(biq)_3^{2+}$	510	19608	$(6.3 \pm 0.9)/f$

[a] All complexes are salts of PF_6^- in poly(vinyl alcohol) at 77 K. [b] $\chi = 54.74°$; $F_{ext} \simeq 6.5 \times 10^5$ V/cm; f is the local field correction;[5] D = Debye (3.34×10^{-30} C·m).

in Figure 1. Large features resembling a second derivative line shape, increasing quadratically with applied electric field, and corresponding to transitions assigned to singlet MLCT states (${}^1A_1 \rightarrow {}^1E$),[6,7] appear in the Stark effect spectrum (Figure 1B). If contributions to ΔA from overlapping bands in the spectrum are neglected, the apparent $|\Delta\mu_A|$ for the dominant band at 22026 cm^{-1} (454 nm) is $(8.8 \pm 0.7)/f$ D, where f is the local field correction.[5,8] This value represents the excited-state dipole moment if the ground state possesses true D_3 symmetry and thus no permanent dipole moment;[9] $|\Delta\mu_A|$ then corresponds to separation of a full charge by $1.83/f$ Å. The distance from the metal to the geometric center of a bipyridine ligand is 2.82 Å[10] and allows an estimate of $(65/f)$% of full charge-transfer character. Such a large value of $|\Delta\mu_A|$ is most consistent with work which indicated that the initially prepared ^{1}MLCT state is highly dipolar.[2] The transition at 23810 cm^{-1} (420 nm) also possesses a significant Stark effect, though comparison with the second derivative spectrum (Figure 1C) shows that the $|\Delta\mu_A|$ associated with this transition is smaller than that for the 22026-cm^{-1} transition. Direct excitation to the lowest triplet MLCT state of the complex results in the weak shoulder on the low-energy side of the main MLCT absorption band;[6] from the positive feature in the Stark effect spectrum at 17606 cm^{-1} (568 nm), we estimate $|\Delta\mu_A| \simeq 10/f$ D.[11] No significant Stark effect appears between 26000 and 29000 cm^{-1}, indicating that the excited states in this region are not highly dipolar.

The presence of only two bands in the visible region of the Stark effect spectrum due to large $|\Delta\mu_A|$ is consistent with the assignments of Ceulemans and Vanquickenborne, who predicted that only two of the four possible spin- and symmetry-allowed MLCT transitions to the lowest π^* orbitals of the complex should possess significant CT intensity.[7] Other work has suggested that three singlet MLCT transitions occur in the visible region.[12,13] The second derivative of the absorption spectrum does show an additional feature at ~21600 cm^{-1} (463 nm) which is absent in the Stark effect spectrum. While second derivative spectra with good signal-to-noise are difficult to obtain for the broad absorption bands found in these complexes, the 21600-cm^{-1} feature is reproducible and may reflect an electronic transition with significant oscillator strength but a relatively small excited state dipole moment. Alternatively, a third ^{1}MLCT band may lie too close in energy to the 22026-cm^{-1} band to be resolved in the Stark effect spectrum.

Data for $Ru(biq)_3^{2+}$ and $Ru(bpy)_2(biq)^{2+}$ (biq = 2,2′-biquinoline) have also been obtained for the principal ^{1}MLCT transitions (Table I). The ^{1}MLCT bands of $Ru(biq)_3^{2+}$ give smaller observed values of $|\Delta\mu_A|$ than those for $Ru(bpy)_3^{2+}$. This result presumably reflects the slightly greater metal-to-ligand distance in $Ru(biq)_3^{2+}$,[14] which diminishes overlap of metal and ligand orbitals, reducing CT and the magnitude of the excited state dipole. $Ru(bpy)_2(biq)^{2+}$ has C_2 molecular point symmetry and is of interest because transitions corresponding to CT to each type of ligand are distinguishable in the absorption spectrum.[15] Interestingly, $|\Delta\mu_A|$ measured for transitions to the bpy ligands (22676 cm^{-1}) are smaller than those for $Ru(bpy)_3^{2+}$. Possibly, a steric interaction between bpy and biq ligands suffices to diminish bpy overlap with metal orbitals relative to $Ru(bpy)_3^{2+}$.

Stark effect spectroscopy should be generally applicable to quantitatively characterizing the excited states of a wide range of transition-metal complexes. Even at a qualitative level variations in the degree of CT character associated with different transitions are immediately evident from the Stark spectra. Extensions of these measurements to the photochemically interesting emitting states of these complexes will be reported shortly.

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(9) The ground state is most likely only approximately D_3 due to static distortions of the complex in the PVA matrix and the influence of the PF_6^- counterions. For qualitative arguments, we assume that the ground-state dipole is negligible compared to the excited-state dipole.

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Synthesis and Reactivity of the First Structurally Characterized Heterobimetallic Complex Containing an Unsupported Bridging Sulfur Atom

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Studies of the reactivity of complexes containing sulfur atoms bridging two inequivalent transition metals are important in both biological[1] and heterogeneous catalytic (e.g., hydrodesulfurization[2]) systems. Although many bimetallic complexes and clusters containing double sulfido bridging units are known,[3] there is

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