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Direct Measurement of Excited-State Intervalence Transfer in $[(tpy)Ru^{III}(tppz^{\bullet -})Ru^{II}(tpy)]^{4+}*$ by Time-Resolved Near-Infrared Spectroscopy

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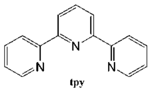
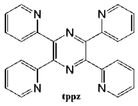
Mixed-valence compounds containing transition metals in more than one oxidation state have provided a useful experimental probe of the relationship between optical and thermal electron transfer, solvent effects on electron transfer, and the localized-to-delocalized transition between Class II and Class III in the Robin and Day classification scheme.[1−9] Recently, a new class, Class II−III, has been identified in which oxidation states are localized and the solvent averaged.[9−11] We describe here a direct approach to the study of mixed-valence molecules created by charge-transfer excitation by application of transient near-infrared (TRNIR) spectroscopy.

The mixed-valence complex $[(tpy)Ru(tppz)Ru(tpy)]^{5+}$ (**1**, tpy is 2,2′:6′,6″-terpyridine, tppz is 2,3,5,6-tetrakis(2-pyridyl)pyrazine) is characterized by the appearance of an intense, $Ru^{II} \rightarrow$ tppz metal-to-ligand charge transfer (MLCT) absorption band at $\lambda_{max} = 548$ nm ($\epsilon = 2.4 \times 10^4$ M^{-1} cm^{-1}; 298 K in acetonitrile), chemically reversible $Ru^{III/II}$ couples at $E_{1/2} = +1.40$ and $+1.71$ V (0.1 M in CH_3CN vs SSCE at 298 K)[12] and an intense mixed-valence band, Figure 1A. The latter appears at 6550 cm^{-1} ($\epsilon_{max} = 7560$ M^{-1}cm^{-1}; 298 K in CD_3CN).[13−17] The band is narrow with a bandwidth at half-maximum of $\Delta\bar{\nu}_{1/2} = 970$ cm^{-1}, and the band energy is relatively independent of solvent in CD_3CN, *d*-DMSO, CD_2Cl_2, *d*-acetone, and *d*-nitrobenzene. Assuming localized oxidation states and Class II−III behavior (see below), this band arises from the intervalence transfer (IT) transition in eq 1.





$$[(tpy)Ru^{III})(tppz)Ru^{II}(tpy)^{5+} \xrightarrow[E_{IT} = 6550\ \mathrm{cm}^{-1}]{h\nu} [(tpy)Ru^{II}(tppz)Ru^{III}(tpy)]^{5+} \quad (1)$$

The visible spectrum of the Ru^{II}-Ru^{II} form of **1**, $[(tpy)Ru^{II}(tppz)Ru^{II}(tpy)]^{4+}$ (**2**), in CH_3CN is dominated by an intense, $Ru^{II} \rightarrow$ tppz MLCT band at 548 nm ($\epsilon = 3.6 \times 10^4$ M^{-1} cm^{-1}; 298 K in CH_3CN), eq 2.[12,14] Excitation into this band results in the formation of a tppz-based MLCT excited state (**3**) which could be localized as shown in eq 2 or delocalized, $[(tpy)Ru^{II.5}(tppz^{\bullet -})Ru^{II.5}(tpy)]^{4+}*$.

$$[(tpy)Ru^{II}(tppz)Ru^{II}(tpy)]^{4+} \xrightarrow{h\nu} [(tpy)Ru^{III}(tppz^{\bullet -})Ru^{II}(tpy)]^{4+}* \quad (2)$$

Laser flash photolysis of **2** ($\sim 1 \times 10^{-5}$ M in CH_3CN, bubble degassed with Argon) at 548 nm with an apparatus described previously[18] results in the appearance of a transient which decays with $\tau = 82 \pm 2$ ns ($k = 1.20 \pm 0.03 \times 10^7$ s^{-1}), independent of monitoring wavelength from 370 to 600 nm. In the transient absorption difference spectrum, a bleach appears at ~550 nm due to the loss of ground-state $Ru^{II} \rightarrow$ tppz and $Ru^{II} \rightarrow$ tpy MLCT bands and an absorption appears at ~450 nm due to a $\pi^* \rightarrow \pi^*$ absorption at $tppz^{\bullet -}$, both consistent with formation of **3**.

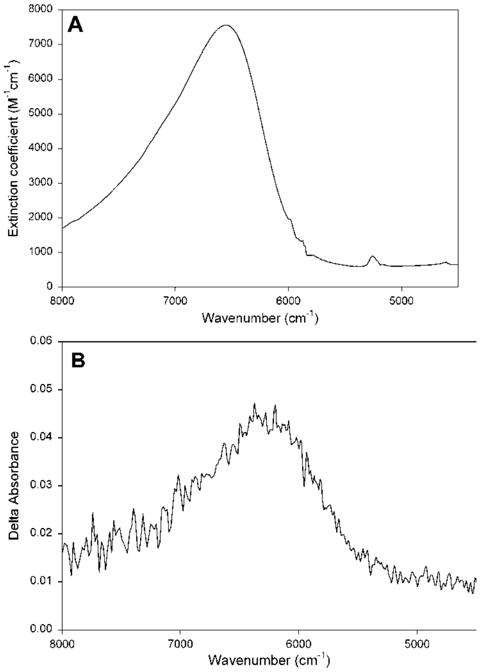


Figure 1. (**A**) Near-infrared absorption band for $[(tpy)Ru(tppz)Ru(tpy)]^{5+}$ from 4500 to 8000 cm^{-1} in CH_3CN at 298 K. (**B**) Transient absorption near-IR (TRNIR) difference spectrum obtained 20−40 ns after laser flash excitation (500 μJ/pulse) of $[(tpy)Ru^{II}(tppz)Ru^{II}(tpy)]^{4+}$ at 548 nm in CD_3CN at 298 K. Samples were purged with Ar prior to measurement.

MLCT excitation of **2** creates a mixed valency at the metals, eq 2, and raises the interesting possibility of observing a mixed-valence band in the excited state.[19] To explore this possibility, we have extended previous transient measurements in the IR region into the near-IR by modification of a step-scan FT-IR instrument.[20−25] These measurements were performed by using a Bruker IFS 66V/s step-scan FTIR spectrometer with a NIR (tungsten) source and a Quartz I beam splitter. In the experiment, the molecule is first excited with a pump beam at 548 nm from a Continuum Surelite Nd:YAG OPO combination described elsewhere.[26] The transients produced are probed by using broad-band NIR light with detection by a liquid N_2-cooled mercury−cadmium−telluride (MCT) detector with a face-mounted band-pass filter which limits the spectral observation region to 2600−8400 cm^{-1}.[26]

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As shown in the transient near-infrared (TRNIR) difference spectrum in Figure 1B, obtained 20−40 ns after laser photolysis of **2** at 548 nm in CD_3CN at 298 K, a new absorption feature appears in excited state **3** at $\bar{\nu}_{max} = 6300$ cm^{-1} with $\Delta\bar{\nu}_{1/2} = 1070$ cm^{-1} with evidence for a shoulder on the high energy side. The band energy is nearly solvent-independent with $\bar{\nu}_{max} = 6300$ cm^{-1} in CD_3CN, 6310 cm^{-1} in CD_2Cl_2, 6100 cm^{-1} in *d*-DMSO, and 6230 cm^{-1} in d-nitrobenzene. In CD_3CN at 298 K with **3** at ~3 mM, this band has a maximum ΔOD of ~0.04 at 6300 cm^{-1} from which it can be estimated that $\epsilon_{max} \geq 3300$ M^{-1}cm^{-1}.[27] The decay of the transient is exponential independent of monitoring wavelength from 5000 to 8000 cm^{-1} with $\tau \approx 130$ ns. This is in reasonable agreement with τ obtained by transient absorption decay given the uncertainties in the transient TRNIR measurements arising from deconvolution of the instrument response function.

The observation of a mixed-valence band or bands for **3** provides an unprecedented opportunity to compare mixed-valence properties between **1** and **3** which differ by a single electron and to compare tppz and tppz$^{\bullet -}$ in their abilities to promote electronic coupling between the metals. Assuming localization, the IT transition that gives rise to the mixed-valence band in **3** is shown in eq 3.

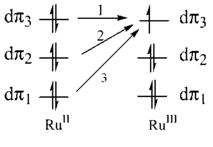
$$[(tpy)Ru^{III}(tppz^{\bullet -})Ru^{II}(tpy)]^{4+*} \xrightarrow{h\nu} [(tpy)Ru^{II}(tppz^{\bullet -})Ru^{III}(tpy)]^{4+*} \quad (3)$$

Energies and bandwidths for the ground- and excited-state mixed-valence bands are comparable with evidence for a shoulder on the high-energy side in both cases. Molar extinction coefficients are within a factor of 2. This suggests that electronic coupling and reorganizational energies for tppz^0 and tppz$^{\bullet -}$ as bridges are comparable in magnitude.

Even so, the detailed orbital interactions that dominate through-bridge electronic coupling may be different for the two. There is extensive $d\pi(Ru^{III})-\pi^*(tppz^{\bullet -})$ mixing in the excited state which probably dominates $d\pi(Ru^{II})-d\pi(Ru^{III})$ coupling across the bridge. In **1**, there is extensive $d\pi(Ru^{II})$ mixing with low-lying π^*(tppz) levels which may dominate through-bridge coupling.

The absence of a solvent dependence and the narrow bandwidths in both **1** and **3** point to Class II−III or Class III behavior in both. In Class III, as defined by Robin and Day, oxidation states are delocalized, and the solvent, molecular structure, and coupled vibrations are averaged.[2] In Class II−III, the oxidation states and structure are localized and the solvent averaged.[9−11]

If **1** and **3** are in Class III, the mixed-valence band at 6300 cm^{-1} and the higher-energy shoulder have their origin in Ru−tppz−Ru-based transitions between delocalized bonding and antibonding levels analogous to $\pi \rightarrow \pi^*$ transitions in organic molecules.[9] If they are in Class II−III, the bands arise from two of the expected three IT transitions illustrated below.



By comparison, for $[(bpy)(Cl)Ru^{II}(tppz)Ru^{III}(Cl)(bpy)]^{3+}$ in CD_3CN a structured IT band appears at 6070 cm^{-1} similar to the bands in **1** and **3**. It is independent of solvent with $\Delta\bar{\nu}_{1/2} = 1500$ cm^{-1}. In addition, a low energy, low intensity band appears at 3500 cm^{-1} that *is* solvent dependent.[9] This band has been assigned to IT(1), $(d\pi_3(Ru^{II})) \rightarrow (d\pi_3(Ru^{III}))$ with the solvent dependence pointing to Class II. The overlapping bands at higher energy have been assigned to the excited-state transitions IT(2) $(d\pi_2(Ru^{II})) \rightarrow (d\pi_3(Ru^{III}))$ and IT(3) $(d\pi_1(Ru^{II})) \rightarrow (d\pi_3(Ru^{III}))$. The greatly enhanced absorptivities for IT(2) and IT(3) compared to IT(1) can be explained by assuming that $d\pi_3(Ru^{II})$ is largely d_{xy} (defining the molecular *z* axis to fall along the Ru−tppz−Ru molecular axis) and to zero-order, orthogonal to π,π^*(tppz) and $\pi,\pi^*(tppz^{\bullet -})$.

If the same orbital scheme holds for **3**, the band at 6300 cm^{-1} and high energy shoulder arise from IT(2) and IT(3). There may be a band at lower energy for IT(1). We did extend the TRNIR measurements further into the IR but a third IT band was not observed. It may be of low intensity and there are interfering absorptions arising from ν(C−H) and ν(O−H) overtone bands in this region.

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Supporting Information Available: Additional figure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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