Vibrational Mapping at the Mixed-Valence, Localized-to-Delocalized Transition

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In the initial classification scheme by Robin and Day, mixed-valence compounds were grouped as Class I (no electronic interaction), Class II (electronic interaction, localized oxidation states), and Class III (delocalized).[1] For ligand-bridged complexes in solution such as $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ (pz = pyrazine), it is becoming increasingly clear that such descriptions are inadequate.[2,3] These are complex molecules with multiple orbital interactions having both solvent and intramolecular coordinate changes coupled to the internal electronic distribution that defines their mixed-valence character. We report here an example at the localized-to-delocalized transition *in which vibrational measurements in the infrared provide evidence for both localization and delocalization.*

The complexes, *cis,cis*-$[(bpy)_2(Cl)Os^{II}(BL)Os^{II}(Cl)(bpy)_2]^{2+}$ (bpy is bipyridine, BL is the bridging ligand 4,4′-bipyridine (**1**, 4,4′-bpy) or pyrazine (**2**, pz)) were prepared and characterized previously.[4] In cyclic voltammograms in CH_3CN, 0.1 M in [N(*n*-

4,4'-bpy   pz
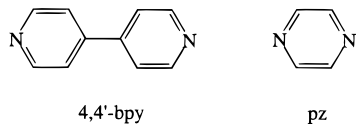
$C_4H_9)_4](PF_6)$ containing **1**, a single wave appears at $E_{1/2} = +0.37$ V vs SSCE. For this wave, $\Delta E_p = 90$ mV, consistent with closely spaced one-electron waves for the expected $Os^{III/III}-Os^{III/II}$ and $Os^{III/II}-Os^{II/II}$ couples. For **2**, one-electron waves appear at +0.42 and +0.61 V ($\Delta E_{1/2} = 190$ mV).

The $Os^{III}-Os^{III}$ forms of **1** and **2** were generated by Ce^{IV} oxidation, and the mixed-valence forms $[(bpy)_2(Cl)Os(BL)-Os(Cl)(bpy)_2]^{3+}$ (**1**(MV), BL = 4,4′-bpy and **2**(MV), BL = pz) were obtained by mixing the $Os^{III}-Os^{III}$ and the $Os^{II}-Os^{II}$ forms in CH_3CN.[4]

Oxidation of Os^{II} to Os^{III} results in loss of characteristic $Os^{II} \rightarrow$ bpy, $Os^{II} \rightarrow$ BL metal-to-ligand charge transfer (MLCT) bands in the visible (at 700, 510, 430 nm for **1** and 755, 690, 560, 490, 430 nm for **2**).[4] In the mixed-valence forms **1**(MV) and **2**(MV) new bands appear in the near-infrared (NIR) and infrared (IR). The spectra of **1**(MV) from 3500 to 10 500 cm^{-1} and **2**(MV) from 1300 to 11 000 cm^{-1} in CD_3CN are presented in Figure 1. Spectra for both **1**(MV) and **2**(MV) in the region of 1400−1500 cm^{-1} are shown in Figure 2.

For **1**(MV) there is evidence for localized Os^{II} and Os^{III} oxidation states. The UV−vis spectrum of **1**(MV) (see the Sup-
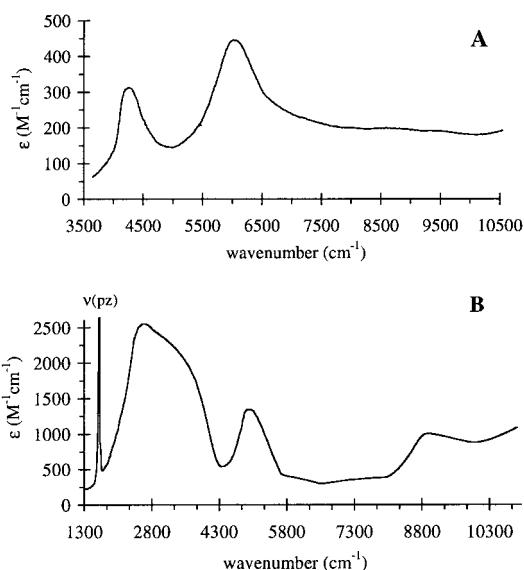

Figure 1. Near-infrared spectra of $[(bpy)_2(Cl)Os(4,4′-bpy)Os(Cl)-(bpy)_2]^{3+}$, **1**(MV) (A) from 3500 to 10 500 cm^{-1} and, of $[(bpy)_2(Cl)-Os(pz)Os(Cl)(bpy)_2]^{3+}$, **2**(MV) (B) from 1500 to 11 000 cm^{-1} in CD_3CN. Solvent overtone bands are not shown in spectrum B.
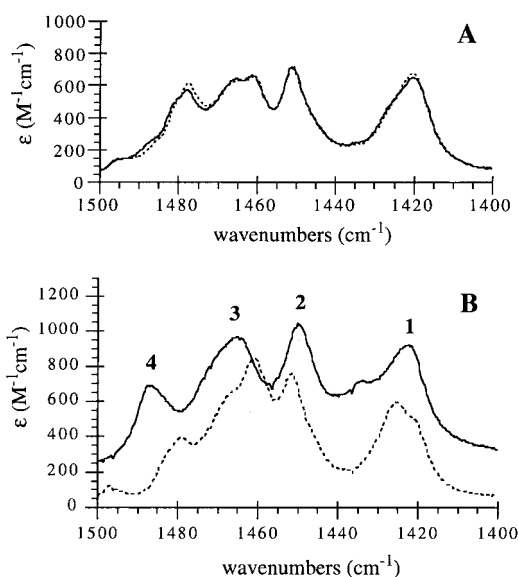

Figure 2. Infrared spectra of $[(bpy)_2(Cl)Os(4,4′-bpy)Os(Cl)(bpy)_2]^{3+}$, **1**(MV) (A, — experimental, - - - calculated), and $[(bpy)_2(Cl)Os(pz)-Os(Cl)(bpy)_2]^{3+}$, **2**(MV) (B, — experimental, - - - calculated)) from 1400 to 1500 cm^{-1} in CD_3CN. The calculated spectra are the sum of one-half of the spectra of the +2, $Os^{II}-Os^{II}$, and +4, $Os^{III}-Os^{III}$, ions.

porting Information) is the average of the spectra of the $Os^{II}-Os^{II}$ and $Os^{III}-Os^{III}$ forms. In the NIR region, distinct bands appear at 4200 cm^{-1} (2380 nm, $\epsilon = 310$, $\Delta \bar{\nu}_{1/2} \sim 550$ cm^{-1}) and 6000 cm^{-1} (1667 nm, $\epsilon = 450$, $\Delta \bar{\nu}_{1/2} \sim 650$ cm^{-1}), which can be assigned to the expected two $d\pi \rightarrow d\pi$ transitions at $d\pi^5$ Os^{III} (Figure 1A).[4a-6] There is also a broad, underlying absorption from ∼5000−10 000 cm^{-1} of significant intensity ($\epsilon \approx 200-250$ M^{-1} cm^{-1}) presumably arising from at least two of the

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expected three intervalence transfer (IT) bands.[5] The expected third IT band may be obscured because it overlaps with intense $Os^{II} \rightarrow$ (4,4′-bpy, bpy) bands at higher energy,[5a] the lowest lying of which appears at 14 290 cm^{-1} (700 nm, $\epsilon \approx 8000$).

Developing an appropriate description for **2**(MV) is less straightforward. Its NIR−IR spectrum is complex (Figure 1B). The low-energy bands that appear below 5800 cm^{-1} are narrow (see below) and solvent independent in acetonitrile, dimethyl sulfoxide, acetone, and dichloromethane. In the mid-IR a symmetric ν(pz) stretch appears at 1599 cm^{-1}. In the series, *cis,cis*-$[(bpy)_2(Cl)Ru(pz)Ru(Cl)(bpy)_2]^{4+/3+/2+}$, ν(pz) is observed only for the mixed-valence form and has been used as a marker for localization.[7] In **2**(MV) the appearance of ν(pz) *provides an oxidation state marker and evidence for localized oxidation states*, but it is of unusual intensity with $\epsilon = 2600$ M^{-1} cm^{-1}. It does not appear or is of negligible intensity in the Os^{II}−Os^{II} or Os^{III}−Os^{III} forms. For comparison, ν(pz) in *cis*-$[Os^{II}(bpy)_2(Cl)(pz)]^+$ appears at 1584 cm^{-1} with $\epsilon = 600$ M^{-1} cm^{-1}.

With the assumption of localized oxidation states in **2**(MV), it is possible to assign the NIR−IR spectra as follows: (1) Deconvolution of the composite band at ∼2700 cm^{-1} in Figure 1B, but with the spectrum rescaled as $\int \epsilon(\bar{\nu}) d\bar{\nu}/\bar{\nu}$,[8] gives components with $\bar{\nu}_{max} = 3590$ cm^{-1} ($\epsilon = 1340$, $\Delta\bar{\nu}_{1/2} = 835$ cm^{-1}) and $\bar{\nu}_{max} = 2620$ cm^{-1} ($\epsilon = 2300$, $\bar{\nu}_{1/2} = 1150$ cm^{-1}). If the band at 4960 cm^{-1} ($\epsilon = 1400$) is assigned to the highest energy $d\pi \rightarrow d\pi$ transition, one of these components, presumably the band at 3590 cm^{-1}, is the lower energy $d\pi \rightarrow d\pi$ transition.[4a,6] The $d\pi \rightarrow d\pi$ bands are enhanced in intensity and shifted to lower energy compared to **1**(MV) because Os^{III}−Os^{II} electronic coupling through pyrazine mixes IT character with the $d\pi \rightarrow d\pi$ transitions.[2,3a,b,9] (2) If this assignment is correct, the component at 2620 cm^{-1} can be assigned to the lowest energy IT band, IT(1), arising from excitation from the highest $d\pi$ level at Os^{II}, $d\pi_3(Os^{II})$, to the hole in Os^{III}, $d\pi_3(Os^{III})$.[3b] (3) The band at 8900 cm^{-1} ($\epsilon \approx 1100$) is the lowest energy $Os(d\pi) \rightarrow pz(\pi^*)$ band to give a largely triplet MLCT excited state. (4) The bands at 6000 and 7500 cm^{-1} ($\epsilon \geq 300$) may arise from IT(2) and IT(3). By comparison, in the spectrum of *cis,cis*-$[(bpy)_2(Cl)Ru^{III}(pz)Ru^{II}(Cl)(bpy)_2]^{3+}$, there is a single, unresolved IT band at 7690 cm^{-1} ($\epsilon = 455$).[7]

The intensity of IT(1) arises by cross-bridge $d\pi_3(Os^{III})$−$\pi,\pi^*(pz)$−$d\pi_3(Os^{II})$ mixing.[3b,9] Its narrow bandwidth and solvent independence point to a time scale for $Os^{II} \leftrightarrow Os^{III}$ intramolecular electron transfer that is rapid on the time scale for solvent dipole reorientation (∼1−10 ps).[10] Solvent averaging between the limiting polarizations for Os^{III}−Os^{II} and Os^{II}−Os^{III}, and the absence of a significant solvent reorganizational energy contributes to the low energy for IT(1) compared to IT(1) and IT(2)

for **1**(MV). On the basis of an equation derived by Hush[8,11] and the properties of IT(1), the resonance energy from $d\pi_3$−$\pi,\pi^*(pz)$−$d\pi_3$ mixing by using an Os^{III}−Os^{II} separation distance of 6.9 Å[12] is,

$$H_{DA}(1) = ((4.2 \times 10^{-4})\epsilon_{max}\Delta\bar{\nu}_{1/2}\bar{\nu}_{max}/d^2)^{1/2} = 247 \text{ cm}^{-1}$$

(ϵ_{max} is the molar extinction coefficient of the band scaled as $\int\epsilon(\bar{\nu}) d\bar{\nu}/\bar{\nu}$ at the maximum in M^{-1} cm^{-1}, $\Delta\bar{\nu}_{1/2}$ is the bandwidth at half-height in cm^{-1}, $\bar{\nu}_{max}$ is the absorption maximum in cm^{-1}, and d is the metal−metal distance in Å). This is a lower limit because, as noted by Hupp, electronic coupling across the bridge decreases the true charge-transfer distance from the geometrical distance.[13]

The bands that appear in the mid-IR in Figure 2 from 1400 to 1500 cm^{-1} arise from ν(bpy) ring stretching modes.[14] They are sensitive to oxidation state with two sets of four bands appearing in the spectrum of **1**(MV). The agreement between the experimental and calculated spectra in Figure 2A shows that there are separate Os^{II} and Os^{III} sites in the mixed-valence ion.

By contrast, the experimental and averaged spectra for **2**(MV) in Figure 2B are distinctly different. In a band-for-band comparison (see the Supporting Information), band energies are the *average* of those for Os^{II}−Os^{II} and Os^{III}−Os^{III}. For the bands labeled **1**−**4**, the band energies are as follows (Os^{II}−Os^{II}, mixed-valence, Os^{III}−Os^{III} (in cm^{-1})): **1** 1421, 1423, 1426; **2** 1447, 1450, 1451; **3** 1461, 1465, 1469; **4** 1480, 1487, 1497.[15] This provides clear evidence that these ν(bpy) modes experience an averaged electronic environment and that $Os^{II} \leftrightarrow Os^{III}$ electron transfer is rapid on the vibrational time scale.

There is an extraordinary ambiguity posed by the separate measurements of the ν(pz) and ν(bpy) vibrations. The solvent appears to be averaged. A barrier to intramolecular electron transfer may still exist, arising from coupled, low-frequency metal−ligand vibrations.[10a,16] From the unusually high intensity for ν(pz), it may be a non-Condon vibration coupled to a change in electronic distribution across the pz bridge.

Supporting Information Available: UV−vis, NIR, and mid-IR spectra for Os^{II}−Os^{II} mixed-valence, and Os^{III}−Os^{III} forms in CH$_3$CN for complexes **1** and **2** (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(15) In KBr, the band energies for these bands are (Os^{II}−Os^{II}, mixed-valence, Os^{III}−Os^{III} (in cm^{-1})): **1** 1420, 1421, 1426; **2** 1447, 1448, 1450; **3** 1460, 1459, 1468; **4** 1478, 1475, 1485. For **2**(MV) in KBr, the broad composite band due to overlapping IT(1) and the lowest-lying $d\pi \rightarrow d\pi$ transition appears in the range 4200−1500 cm^{-1}.

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