# Electroabsorption and Related Spectroscopic Studies of Bimetallic Tetraiminoethylenedimacrocyclic Complexes: Corroboration of Valence Electron Delocalization

# Laba Karki, Robert D. Williams, and Joseph T. Hupp\*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

# Christian B. Allan and Larry O. Spreer

Department of Chemistry, University of the Pacific, Stockton, California 95211

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# Introduction

Mixed-valence complexes (chemical species containing multiple metal centers that exist formally in more than one oxidation state) represent ideal models for testing and understanding optical and thermal electron transfer.<sup>1</sup> Though the prototypical mixed-valence ion, the Creutz–Taube ion, was first studied over 25 years ago,<sup>2</sup> new mixed-valence complexes continue to be made and studied. Among the more interesting of these new complexes are a series of bimetallic tetraiminoethylenedimacrocycles (M<sub>2</sub>TIEDL<sub>4</sub>, where L is CH<sub>3</sub>CN, dimethylformamide (DMF), or Cl<sup>-</sup>, and M is Fe or Ru), **1**, first reported by Spreer and co-workers.<sup>3</sup>



These molecules have been characterized both electrochemically and optically. For example, two oxidation waves were found in the cyclic voltammetry of  $[Fe_2TIED(CH_3CN)_4]^{n+}$ , indicating that the molecule has three accessible metal-based oxidation states (analogous to the Creutz–Taube complex,  $[(NH_3)_5Ru-pyrazine-Ru(NH_3)_5]^{4+/5+/6+})^{.3b}$  The fully reduced, isovalent (II,II) form has an electronic absorption spectrum consisting of bands at 240, 340, and 874 nm. The longest wavelength band has been assigned as a particularly low energy metal-to-ligand charge transfer (MLCT) transition. In the mixed-valent (formally II,III) form the 340 nm band shifts, the 874 nm band disappears, and new bands appear at ~500 and 970 nm.<sup>3c</sup> Results of a Hush type analysis<sup>4</sup> of the 970 nm band, assigned as an intervalence transition, indicate that the mixed-valent state is best described as valence delocalized (Robin and Day class III<sup>5</sup>), a conclusion which is supported by the huge electrochemical comproportionation constant (ca. 10<sup>11</sup>), as well as Mossbauer spectroscopy<sup>3c</sup> of the Fe species and X-ray photoelectron spectroscopy of the Ru analogue.<sup>3d</sup>

Despite this body of work, there has remained some question as to the nature of the electronic transitions in these complexes. The transition assigned as MLCT in the II,II form is very low in energy for complexes of this type,<sup>3b,6</sup> and an MLCT for the mixed-valent state has not been assigned. Given these uncertainties, we believed that electroabsorption (electronic Stark effect) spectroscopy and resonance Raman spectroscopy of these low-energy transitions could be instructive.

Electroabsorption spectroscopy directly measures the absolute difference in dipole moment ( $|\Delta \mu|$ ) between a ground electronic state and a specified excited state. As such, it offers a quantitative means for assessing effective one electron transfer distances. A large  $|\Delta \mu|$  or transfer distance would be expected for a transition that involved a significant degree of charge transfer (such as a class II intervalence transition), while a transition that involved little net movement of charge (such as a class III intervalence transition) would be expected to have a small  $|\Delta \mu|$ . To the best of our knowledge, electroabsorption spectroscopy has been applied to just four other mixed-valence systems, three of them class II<sup>7,8</sup> and one of them class III.<sup>8</sup> In this study, we report that intervalence excitation of the mixedvalent, diruthenium form of 1 is accompanied by essentially no change in molecular dipole moment, consistent with the previous description of the system as a fully delocalized assembly.9

We additionally performed near-infrared resonance Raman experiments with isovalent and mixed-valent diiron species. The results of these experiments provide further support for a delocalized mixed-valence ion description; they also provide some insight into the apparent mechanism for electronic delocalization.

# **Experimental Section**

[Ru<sub>2</sub>TIEDCl<sub>4</sub>](PF<sub>6</sub>), Fe<sub>2</sub>TIEDCl<sub>4</sub>, and [Fe<sub>2</sub>TIEDCl<sub>4</sub>](PF<sub>6</sub>) were synthesized and characterized according to literature methods.<sup>3a,d</sup> Absorption and electroabsorption studies were performed on a 5:1 (v:v) 2-methyltetrahydrofuran/acetonitrile mixture at 77 K. The sample was dissolved in a deoxygenated solvent matrix, then loaded rapidly into the Stark cell, and immersed in liquid nitrogen. The electroabsorption procedure used here was similar to the method described in detail elsewhere.<sup>7</sup> Briefly, however, measurements were performed with an Olis modified Cary-14 spectrophotometer in single-beam mode. A large, oscillating electric field ( $\sim 10^7$  V/m) was applied across the

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- (9) Unfortunately, electroabsorption studies of the Fe analogues were precluded by lack of solubility.

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sample, and the field dependent and independent transmittance signals were detected with a Hamamatsu silicon photodiode (S 5591). The field dependent signal was demodulated by using a lock-in amplifier (Stanford Research Systems SRS 850) locked at twice the field modulation frequency of (typically) 200 Hz.

If the external field is uniform, the sample is isotropic, and the molecular dipoles have frozen orientations, then the electroabsorption signal ( $\Delta A(\nu)$ ) can be quantitatively represented as the following linear combination of zeroth, first, and second derivatives of the absorption band,  $A(\nu)$ :<sup>10</sup>

$$\Delta A(\nu) = \left\{ A_x A(\nu) + \frac{B_x}{15hc} \frac{\nu d[A(\nu)/\nu]}{d\nu} + \frac{C_x}{30h^2c^2} \frac{\nu d^2[A(\nu)/\nu]}{d\nu^2} \right\} \mathbf{F}_{\text{int}}^2$$
(1)

where  $\mathbf{F}_{int}$  is the internal electric field (i.e., the field actually experienced by the chromophore),<sup>11</sup>  $\nu$  is the frequency of the absorbed light, *h* is Planck's constant, and *c* is the speed of light. *A<sub>x</sub>* provides information about the transition moment polarizability and hyperpolarizability. *B<sub>x</sub>* describes the difference in polarizability ( $\Delta \alpha$ ) between the final and initial electronic states along the charge transfer axis. *C<sub>x</sub>* gives the absolute difference in dipole moment ( $|\Delta \mu|$ ) between the states.

Raman samples were prepared by saturating deoxygenated acetonitrile (Fisher, distilled over CaH<sub>2</sub>) with the compound ( $\sim$ 1 to 5 mM) and then passing the solution through a micron filter (Aldrich). Exposure to air was minimized during these manipulations. The Raman excitation source was a Nd:YAG laser (Lee Laser 712ST) operating at 1064 nm; its output was mechanically chopped prior to irradiation of the sample. The scattered light was focused into a Spex 1403 double monochromator equipped with gratings blazed at 1200 nm (600 gr/ mm). Detection was achieved with a liquid nitrogen cooled Ge photodiode (4  $\times$  4 mm; North Coast model EO817L) whose output was coupled to a lock-in amplifier (Stanford Research Systems SR 530).

#### Results

The low-temperature absorption spectrum of [Ru<sub>2</sub>TIEDCl<sub>4</sub>]- $(PF_6)$  is shown in the top panel of Figure 1. The energy maximum ( $\nu_{max}$ ) and the bandwidth at half-maximum ( $\Delta \nu_{1/2}$ ) at 77 K did not shift appreciably from their values at ambient temperature. The absorption line shape is fairly asymmetric with a shoulder in the higher energy region, indicating the existence of another vibronic or electronic transition higher in energy than the main (0,0) transition.<sup>12</sup> The dotted lines represent a Gaussian deconvolution of the spectrum into transitions at 12 400 and 12 900 cm<sup>-1</sup>. The middle panel of Figure 1 shows the electroabsorption response at angles,  $\gamma$ , of 90° (solid line) and 55° (dashed line) at a field strength of 6.0  $\times$  10<sup>7</sup> V/m. ( $\chi$  is the angle between the electric polarization vector of the incident light and the applied, external field.) The bottom panel of Figure 1 shows the fit to the overall electroabsorption spectrum at 90° using a six-parameter function ( $A_x$ ,  $B_{\rm r}$ , and  $C_{\rm r}$  for each of the two transitions). From this fit and an additional fit to the 55° spectrum, both the difference in the dipole moment and the trace of the polarizability difference (Tr- $(\Delta \alpha)$ ) between the ground and excited states were determined. The absolute dipole moment differences were found to be 0.4  $\pm$  0.2 and 0.55  $\pm$  0.3 D for the lower and higher energy



- (11)  $\mathbf{F}_{\text{int}} = f \cdot \mathbf{F}_{\text{ext}}$  where *f* is the local field correction factor, taken to be 1.3.
- (12) A similarly peculiar line shape has also been found for the Creutz– Taube molecule.<sup>2</sup> Both magnetic circular dichroism (Krausz, E. R.; Mau, A. W. H. *Inorg. Chem.* **1986**, 25, 1484) and electroabsorption experiments<sup>8</sup> on the complex have suggested electronic or vibronic heterogeneity in the intervalence spectrum.



**Figure 1.** Top panel: The absorption spectrum of  $Ru_2TIEDCl_4^+$  in the near-IR at 77 K (solid line). The dotted lines represent the Gaussian deconvolution of the overall transition into two components which fit the overall line shape (open circles) remarkably well. Middle panel: The Stark spectra at the two angles of 90° (solid line) and 55° (dashed line). Bottom panel: The fit (solid line) to the Stark signal at 90° (open circles).



**Figure 2.** Upper spectrum: The 1064 nm excited Raman spectrum of Fe<sub>2</sub>TIEDCl<sub>4</sub>. Bottom spectrum: The 1064 nm excited Raman spectrum of Fe<sub>2</sub>TIEDCl<sub>4</sub><sup>+</sup>. Inset: The absorbance spectra of Fe<sub>2</sub>TIEDCl<sub>4</sub> (solid line) and Fe<sub>2</sub>TIEDCl<sub>4</sub><sup>+</sup> (dashed line). Peaks due to the solvent are marked with an asterisk.

transitions, respectively. The corresponding Tr( $\Delta \alpha$ ) values were  $3 \pm 2$  and  $-0.6 \pm 0.5$  Å<sup>3</sup>.

Shown in Figure 2 are resonance and near resonance Raman spectra for  $Fe_2TIEDCl_4^{(+/0)}$  obtained with 1064 nm excitation. The bottom spectrum (mixed-valence species) reveals that at least six vibrations (530, 634, 886, 992, 1042, and 1592 cm<sup>-1</sup>) are coupled to the intervalence transition (starred peaks are due to solvent vibrations). Possible assignments include a C=N stretch for the 1592 cm<sup>-1</sup> mode and a totally symmetric breathing motion of the cyclam framework for the high-intensity

## Notes

532 cm<sup>-1</sup> mode. Conversely, the lack of detectable lowfrequency (<500 cm<sup>-1</sup>) activity indicates an absence of appreciable coupling to metal-ligand stretches. The isovalent form of the complex (top spectrum) yields a remarkably similar pattern of vibrational scattering intensities. Qualitatively, this indicates that similar molecular charge redistributions and similar coordinate displacements accompany the two optical transitions. Nevertheless, differences exist: the number of observable modes increases substantially upon conversion of the mixed-valence species to its isovalent form, and the intensities of several vibrations increase considerably relative to those of the solvent. From the inset in Figure 2, both effects appear to be associated with differences in enhancement at 1064 nm for scattering from the mixed-valent complex ( $\lambda_{max} = 985$  nm) versus the isovalent complex ( $\lambda_{max} = 883$  nm). As a control, the same samples were also excited with 1320 nm radiation. Only the  $532 \text{ cm}^{-1}$  mode (with very little intensity) was seen with the isovalent species, and no scattering was observed from the mixed-valent species. These studies verified that the Raman scattering described in Figure 2 was resonantly enhanced.<sup>13</sup>

## Discussion

Perhaps the most striking experimental observations in the current investigations are the overall near zero values for  $|\Delta \mu|$ upon intervalence excitation of Ru<sub>2</sub>TIEDCl<sub>4</sub><sup>+</sup>. These indicate that essentially no net transfer of charge occurs between metal centers. This, in turn, can be taken as compelling evidence for very strong coupling between metal centers, such that the odd electron is completely delocalized even at liquid nitrogen temperatures.<sup>14</sup> An examination of the actual electroabsorption spectral fits also gives some insight into the nature of the transitions. If only three parameters are used (i.e., if the lowenergy band is treated as a single transition), the fit diverges considerably from the experimental spectrum, especially at higher energy (see Figure S1 in the Supporting Information). On the other hand, if the spectrum is first deconvoluted into two Gaussians and then fitted with six parameters (Figure 1), excellent agreement is obtained. Interestingly, the two deconvolved transitions are separated in energy by 500 cm<sup>-1</sup>, which is roughly the energy of the most intense Raman mode (532  $cm^{-1}$ ). In all likelihood, therefore, the absorbance structure is vibronic in origin. Further, the displacement of the 532 cm<sup>-1</sup> mode is apparently quite small, given that the lower energy (0,0)component is twice as intense as the higher energy component of the abbreviated progression.

While the electroabsorption measurements confirm the class III nature of the mixed-valence species, they provide little direct insight into the chemical or molecular-orbital basis for electronic delocalization. To further our understanding, it may be useful to compare two limiting theoretical descriptions of mixed-valency and optical intervalence transfer. The first is a two-state vibronic coupling model originally developed by Piepho, Krausz, and Schatz,<sup>15</sup> which has been applied extensively to weakly coupled (class II) as well as strongly coupled mixed-valence systems. The second, a three-site bonding picture first

Scheme 1



developed by Ondrechen and co-workers has been applied primarily to strongly coupled class III intervalence transitions.<sup>16</sup> In the Ondrechen model, interaction between the two metal centers and the bridging ligand (the macrocylic framework in this case) results in the formation of three molecular orbitals in the complex having bonding, nonbonding, and antibonding character. As shown in Scheme 1, the intervalence transfer is then a bonding to nonbonding transition, while the nominal MLCT excitation becomes a two-center nonbonding to threecenter antibonding transition.

Since the nonbonding orbital formally involves only the metals, small perturbations of the parent metal orbital energies will result in shifts of both the intervalence transition and MLCT transition, but in opposite directions. A qualitative indication of metal orbital energy shifts is available from solvent dependent formal potential measurements. For example, for Fe<sub>2</sub>TIED<sup>4+</sup> the first metal-centered oxidation occurs at 0.7 V in DMF, but at 1.2 V in CH<sub>3</sub>CN, where the unusually large shift is clearly a consequence of axial ligation of solvent.3b In any case, consistent with Scheme 1 and the electrochemical data, the corresponding intervalence band for the 5+ form of the ion moves from 940 nm in CH<sub>3</sub>CN to 883 nm in DMF, while the MLCT band for the isovalent form is at 874 nm in CH<sub>3</sub>CN and 1075 nm in DMF.<sup>3b</sup> This behavior may be contrasted with the predictions of the two-state description. There, upper and lower states would be equally affected by the changes in metal redox potential and no net shift in transition energy would be expected. In fact, the energy shifts would derive only from reorganization effects; note, however, that the negligible degree of charge transfer also implies a negligible outer-sphere reorganization energy. In addition, the available Raman scattering and electronic absorption data indicate both a lack of metal-axial ligand activity<sup>13</sup> and an overall absence of substantial vibrational (inner-sphere) reorganizational demands.

Returning to the three-center description, this treatment predicts that the MLCT transition will shift in the opposite direction from the intervalence transition upon alteration of the nominally metal centered redox potential. A candidate MLCT transition would be the relatively intense and previously unassigned absorption near 500 nm. Consistent with the three-

<sup>(13)</sup> Scattering spectra similar to that for the isovalent Fe<sub>2</sub>TIEDCl<sub>4</sub> species were obtained with [Fe<sub>2</sub>TIED(CH<sub>3</sub>CN)<sub>4</sub>](PF<sub>6</sub>)<sub>4</sub> and [Fe<sub>2</sub>TIED(DMF)<sub>4</sub>]-(PF<sub>6</sub>)<sub>4</sub>, where excitations were into the red tails of the near-IR transitions (see ref 3b for absorption spectra). In addition, several lines from a Ti:sapphire laser were used to achieve resonant near-infrared excitation of the *mixed-valent* Ru<sub>2</sub>TIEDCl<sub>4</sub><sup>+</sup> complex; again, very similar Raman spectra were obtained.

<sup>(14)</sup> If a full unit of charge were transferred through a distance equal to the metal-metal separation distance, the change in dipole moment would be close to 34 D (7 e Å).

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center model, this band is found at higher energy in CH<sub>3</sub>CN than DMF. Seemingly arguing *against* the MLCT assignment is the tremendous difference in energy between this transition and the previously assigned near-infrared MLCT transition observed in the isovalent (II,II) form of the complex. We suggest, however, that the apparently anomalous energy shift is a necessary consequence of strong electronic coupling and multisite orbital mixing. In the Ondrechen description (Scheme 1), the II,II form of the complex has two electrons in the nonbonding orbital (i.e., the HOMO). Electron–electron repulsion will raise the energy of the HOMO with respect to the antibonding LUMO, and the MLCT transition will lie at relatively low energy. Since the repulsion term is lacking for the singly occupied HOMO of the mixed-valent complex, the MLCT will lie at relatively high energy.<sup>17</sup>

With the three-center model in mind, we return to the electroabsorption data, in particular, the excited-state/groundstate polarizability differences,  $Tr(\Delta \alpha)$ . The observed small or even negative polarizability changes for intervalence excitation are unusual.<sup>18</sup> One usually expects polarizability changes to be large and positive (i.e., the excited state to be more polarizable than the ground state) simply because of the greater importance in the excited state of configuration interactions with yet higher lying states.<sup>19</sup> A counterbalancing factor here, however, is the unusual pattern of charge redistribution upon intervalence excitation in the absence of configuration interactions. From Scheme 1, the ground state of the mixed-valent form features a doubly occupied bonding orbital that distributes charge simultaneously across both of the metals and the ligand. The mixed-valence excited state, on the other hand, concentrates charge primarily on the metals, at the expense of the bridge, thereby diminishing the molecular polarizability.

Turning to the resonance Raman data, an unambiguous analysis of the electronic origin of the scattering would necessitate assigning the modes. Unfortunately, this is precluded by our lack of either a normal coordinate analysis of these compounds or the availability of deuterated derivatives.<sup>20</sup> However, on the basis of the work of Gamelin et al.<sup>21</sup> and Petrov et al.<sup>22</sup> on other delocalized, dinuclear mixed-valence metal complexes in which totally symmetric vibrations are strongly activated (as predicted by the three-center model), it is probable that several of the modes (most notably, those at 532 and 626 cm<sup>-1</sup>) are totally symmetric vibrations of the cyclam framework.

- (17) A contrary piece of evidence comes from X-ray absorption near-edge spectroscopy (XANES) on the Fe analogues with chloride axial ligands (Spreer, L. O., unpublished work). These studies show a very small change in iron edge level in going from the isovalent to the mixed-valent oxidation state, indicating that there is little change in the charge on the metals as the compound is oxidized. This result implies that the Ondrechen model may be oversimplified and that, in addition to bridging ligand π<sup>\*</sup> orbitals, bridging ligand π participation may need to be taken into account. Indeed, Piepho (J. Am. Chem. Soc. 1990, 112, 4197) has successfully modeled a class III system using a more sophisticated model which explicitly includes the bridging-based π orbitals (so that the HOMO is no longer purely metal based). Despite these complications, it should be noted that a two-site description is even less capable of accommodating the XANES results.
- (18) These effects are unusual, but not unprecedented. For example, Shin et al. (Shin, Y. K.; Brunschwig, B. S.; Creutz, C.; Sutin, N. J. Phys. Chem. 1996, 100, 8157) and Boxer<sup>8a</sup> have reported negative polarizability changes for MLCT excitation of several members of a series of monomeric Ru ammine compounds.
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The two-state mixing picture<sup>15</sup> would predict the dominant vibrations to have metal—ligand character, and indeed the low-frequency (246 and 288 cm<sup>-1</sup>) modes observed for the isovalent compound are probably these metal—ligand stretches. However, their intensity is dwarfed by the symmetric vibrations, again in accord with a three-center picture. Leaving the assignments aside, it is not surprising that the same vibrations are activated by the two different types of transitions, given the similarity between intervalence excitation and MLCT excitation (the former moves electron density from the bridge to the metals, while the latter moves density from the metals to the bridge). In the absence of additional data,<sup>23</sup> we find the Raman data to be most consistent with an Ondrechen type description of the electronic transitions.

#### Conclusions

Extremely small absolute changes in the dipole moment accompany the near-infrared excitation of  $Ru_2TIEDCl_4^+$ , corroborating a previous interpretation of the near-IR feature as a delocalized intervalence transition. Near-IR resonance Raman evaluation of the corresponding diiron complex indicates that many vibrations activated by excitation into the intervalence absorption band of the mixed-valent compound are also activated by excitation into the MLCT absorption band of the isovalent compound. These findings are interpreted in terms of the threecenter bonding picture for class III chromophores proposed by Ondrechen. This model adequately explains the anomalous polarizability results from the electroabsorption and indicates that the previously assigned blue-green electronic absorption band in the mixed-valent complex arises from MLCT excitation.

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**Supporting Information Available:** A figure showing an attempted fit of the experimental electroabsorption spectrum to a three-parameter (single electronic/vibronic transition) expression (1 page). Ordering information is given on any current masthead page.

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- (20) A search of the literature reveals several reports on the Raman spectroscopy of cyclam-containing complexes, though none have explicitly assigned vibrations within the cyclam framework. (Cyclam, or 1,4,8,11-tetraazacyclotetradecane, is a precursor in the synthesis of these compounds.) For instance, Bakac et al. (J. Am. Chem. Soc. 1995, 117, 6483) report a Raman spectrum of Cr(cyclam)<sup>3+</sup> with modes at 449, 517, 764, 804, 842, 864, 995, 1033, 1059, 1082, and 1134. These, however, are simply assigned as "cyclam vibrations". Another group has reported Raman spectra of cyclam-containing zeolites (DeVos, D. E.; Vanoppen, D. L.; Li, X.-Y.; Libbrecht, S.; Bruynseraede, Y.; Knops-Gerrits, P.-P.; Jacobs, P. A. Chem. Eur. J. 1995, 1, 144). A third has reported (cyclamH<sub>4</sub>)CuCl<sub>6</sub> Raman data (McDonald, R. G.; Hitchman, M. A. Inorg. Chem. 1989, 28, 3996). A fourth has reported on an  $I_3^-$  complex of cyclam (Nour, E. M.; Abdel-Wahed, G.; Abdel-Khalik, S. Indian J. Chem., Sect. A 1990, 29A, 73)
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- (23) We were unable to prepare mixed-valent samples of the Fe complexes with L = CH<sub>3</sub>CN or DMF, nor was an isovalent Ru complex prepared.