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# Resonance Raman and Semiempirical Electronic Structure Studies of an Odd-Electron Dinickel Tetraiminoethylenedimacrocyclic Complex

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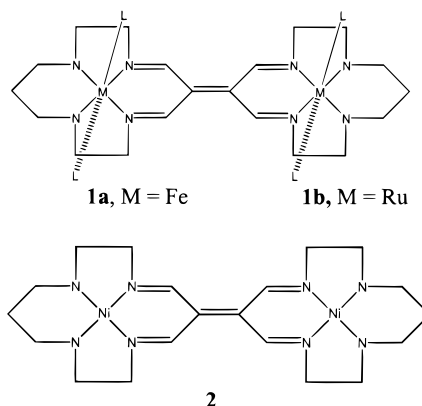
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Resonance Raman studies of  $\text{Ni}_2\text{TIED}^{3+}$  (TIED = tetraiminoethylenedimacrocyclic) reveal that many modes couple to the intense electronic transition centered at 725 nm, a feature that is nominally similar to the intense delocalized intervalence absorption bands observed in the same region for  $\text{Fe}_2(\text{TIED})\text{L}_4^{5+}$  and  $\text{Ru}_2(\text{TIED})\text{L}_4^{5+}$  (L is any of several axial ligands). Time-dependent spectral modeling of the Raman and absorption spectra for the nickel compound was undertaken to understand the electronic transition. We were unable to model the Raman and absorption spectra successfully with a single electronic transition, suggesting that the absorption band is made up of two overlapping transitions. Semiempirical electronic structure calculations corroborate the suggestion. Additionally, these calculations indicate that the transitions are in fact ligand-localized transitions, with little metal involvement and no charge-transfer character. Furthermore, the ground-state electronic structure is best described as an identical pair of  $\text{Ni}^{\text{II}}$  centers bridged by a radical anion rather than a three-site mixed-valence assembly. Previous EPR studies (McAuley and Xu, *Inorg. Chem.* **1992**, *31*, 5549) had indicated primarily ligand character for the radical. The assignments are consistent with the resonance Raman results where the dominant modes coupled to the transitions are assigned as totally symmetric bridge vibrations.

## Introduction and Background

Mixed-valence complexes represent ideal models for testing and understanding optical and thermal electron transfer and bridge-mediated electronic coupling.<sup>1–3</sup> An interesting pair of mixed-valence complexes first reported by Spreer and co-workers are the bimetallic tetraiminoethylenedimacrocycles **1a** and **1b** ( $\text{M}_2\text{TIEDL}_4$ , where M is Fe or Ru, L is solvent or halide, and TIED is tetraiminoethylenedimacrocyclic).<sup>4–8</sup> Cyclic voltammetry indicates that these compounds can exist in three oxidation states: isovalent II–II (4+), isovalent III–III (6+), and the nominally mixed-valent (5+) forms. In the “mixed-valent” form of either complex a strongly allowed intervalence transition is seen in the near-infrared region. In both cases, the shape and intensity of the intervalence absorption band are consistent with a valence-delocalized (Robin and Day class III<sup>9</sup>) electronic structural assignment. The assignments are supported by the observation of huge comproportionation constants<sup>5,6</sup> and



by results from resonance Raman,<sup>10</sup> Mossbauer,<sup>6</sup> X-ray photoelectron,<sup>4</sup> and electroabsorption<sup>10</sup> spectroscopy measurements.

In contrast to the diiron and diruthenium species, the analogous square planar nickel complex, **2**<sup>4+</sup>, displays a single two-electron oxidation, thus skipping the 5+ mixed-valent form. The compound does, however, undergo stepwise one-electron reductions. The electronic absorption spectrum of the singly reduced (3+) form features an intense band ( $\epsilon = 13\,000\text{ M}^{-1}\text{ cm}^{-1}$ ) at 724 nm and thus superficially resembles the spectra of the Ru and Fe mixed-valence complexes. The absorption at 724 nm has been tentatively assigned as a ligand-to-metal charge transfer (LMCT) transition.<sup>11</sup> Electron paramagnetic resonance spectroscopy indicates that the odd electron resides mostly on the ligand with little metal involvement. This type of ground-state bonding is consistent with a molecular orbital scheme

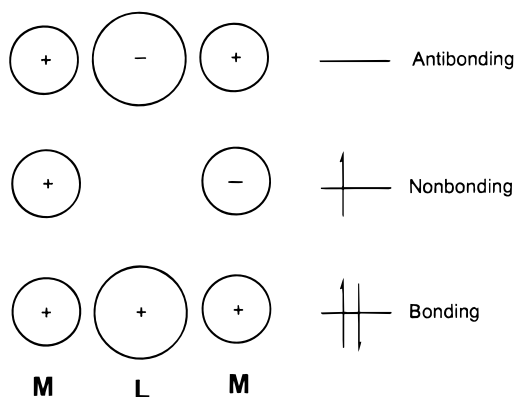
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Chart 1



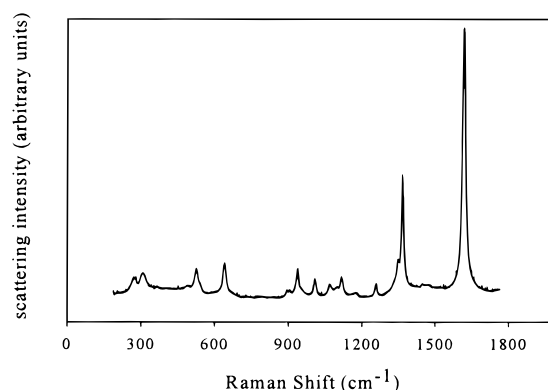
developed by Ondrechen and co-workers<sup>12</sup> for class III mixed valence complexes. In the Ondrechen model, intervalence excitation involves excitation from a three-center “bonding” orbital to a delocalized two-center nonbonding orbital with a node on the bridge (Chart 1). Thus, the intervalence transition can be thought of as a symmetrical LMCT transition, with charge moving from the bridge equally to both metals. We could also consider one limiting description of the ground state as a pair of oxidized metal ions bridged by a radical anion. While the Ondrechen model clearly does capture the essence of the electronic structure and behavior of **1a** and **1b**, the degree of applicability, if any, to **2<sup>3+</sup>** has yet to be established.

To interrogate further the electronic nature of the ground-state **2<sup>3+</sup>** species, as well as the character of the excited state arising from the intense near-infrared absorption, we performed resonance Raman and semiempirical electronic structure calculations. Together, these support the idea that despite the superficial similarity to **1a<sup>5+</sup>** and **1b<sup>5+</sup>**, a class III mixed-valence description is not appropriate.

## Experimental Section

The perchlorate salt of **2<sup>4+</sup>** was prepared according to literature methods.<sup>11</sup> *Caution: perchlorate salts of transition metals are known to be potentially explosive and should be handled only in small amounts and with extreme caution.* **2<sup>3+</sup>** was prepared by chemical reduction of the 4+ form using tetrabutylammonium iodide in acetonitrile as solvent or ascorbic acid in aqueous solutions (0.18 M H<sub>2</sub>SO<sub>4</sub> or 0.24 M HClO<sub>4</sub>; acidic aqueous solutions were used because of the decomposition of the compound in neutral water). Raman samples were prepared by nearly saturating the deoxygenated solvent with **2<sup>4+</sup>**, then adding the appropriate reducing agent until a deep-green solution resulted. The reduced solution (ca. 1 mM in **2<sup>3+</sup>**) was passed through a micrometer filter and into an NMR tube, which was sealed to limit exposure to oxygen to prevent the facile oxidation of **2<sup>3+</sup>** by dissolved oxygen. Instrumentation and experimental protocols for the Raman measurements have previously been described.<sup>13</sup>

Electronic structure calculations were performed using the semiempirical ZINDO/S method with configuration interaction in the Hyperchem program, version 5.02 (Hypercube Inc., Gainesville, FL). The reported crystal structure for the perchlorate salt of **2<sup>4+</sup>** was used as the geometry for the calculation of **2<sup>3+</sup>** because attempts to perform a geometry optimization of **2<sup>3+</sup>** at the ZINDO/1 level failed, and the **2<sup>4+</sup>** was judged to be the best approximation available. Three occupied and three virtual orbitals were judged to be sufficient for the CI calculation; use of more orbitals did not significantly change the results.



**Figure 1.** Uncorrected resonance Raman spectrum of **2<sup>3+</sup>** in 0.24 M HClO<sub>4</sub> based on 725 nm excitation.

## Results and Discussion

**Raman Spectra.** Shown in Figure 1 is the resonance Raman spectrum obtained from **2<sup>3+</sup>** in 0.24 M HClO<sub>4</sub> with 725 nm excitation. Corrected relative scattering intensities as well as depolarization ratios are given in Supporting Information. For A-term resonance Raman scattering, depolarization ratios of less than 0.75 are expected for totally symmetric modes, as is experimentally observed for all modes. The spectrum reveals that many modes are coupled to the transition, the most intense appearing at 1617 and 1367 cm<sup>-1</sup>. Plausible assignments are a C=N stretch for the 1617 cm<sup>-1</sup> mode, C=C stretches for the 1350 and 1367 cm<sup>-1</sup> modes,<sup>11</sup> totally symmetric breathing motions of the cyclam framework for the 527 and possibly 641 cm<sup>-1</sup> modes,<sup>10</sup> and metal–ligand stretches for the 271 and 310 cm<sup>-1</sup> modes. That the observed scattering is resonantly enhanced was confirmed by also exciting off-resonance (532 nm). Under these off-resonance conditions, scattering was sufficiently weak that only the 1617 and 1367 cm<sup>-1</sup> modes were observable.

**Excitation Profiles.** Excitation profiles were generated by recording Raman spectra with various excitation wavelengths from 710 to 810 nm, initially in aqueous solution. The modes observed and the pattern of scattering intensities (*relative* intensities) were similar over this range. It should be noted that for accurate excitation profiles an internal standard is generally necessary. The standard also allows the calculation of absolute scattering cross sections. Unfortunately, in acidic aqueous solutions, the expected modes of SO<sub>4</sub><sup>2-</sup> or ClO<sub>4</sub><sup>-</sup>, possible internal standards, were not seen evidently because of efficient absorption of the scattered radiation by the strongly chromophoric **2<sup>3+</sup>**. Instead, a few sets of spectra were taken with acetonitrile as the solvent and ν<sub>CN</sub> was used as an internal standard.<sup>14</sup> The scattering cross section of ν<sub>CN</sub> was obtained from extrapolation from previously reported UV Raman measurements.<sup>16</sup> The excitation profile for each of the enhanced modes shows a maximum in the 770–790 nm wavelength range. Notably, these maxima are significantly to the red of the absorption maximum (724 nm).

(14) The concentration of the essentially neat acetonitrile is high enough for its Raman spectrum to be seen without difficulty. The differential cross sections were then converted to total cross section by using known procedures (ref 15). The excitation profile of the 1617 cm<sup>-1</sup> mode was determined in acetonitrile assuming a depolarization ratio of 0.33. A total scattering cross section of  $3.4 \times 10^{-8}$  Å<sup>2</sup>/molecule was found for 725 nm excitation. Absolute Raman cross sections for the remaining modes of **2<sup>3+</sup>** were then evaluated from spectra obtained in aqueous solutions by referencing to the 1617 cm<sup>-1</sup> mode. The excitation profiles were then calculated assuming a depolarization ratio of 0.33 for the remaining modes. The protocol assumes that the absolute scattering cross section for the 1617 cm<sup>-1</sup> mode is unaffected by replacement of acetonitrile by water as solvent.

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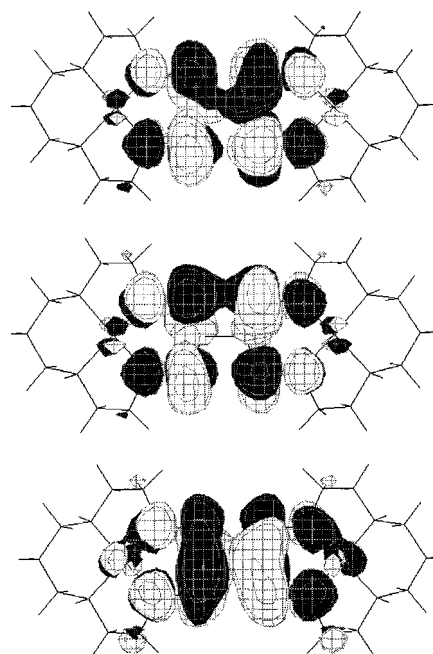
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**Symmetry Information.** Resonance Raman data give insight into the type of transition by showing which vibrational modes are coupled to the electronic transition. Coupling of totally symmetric bridging modes to an LMCT transition is forbidden in a symmetric dimetal complex if only a single metal is involved but would be permitted if charge were transferred symmetrically to both metals, as in Chart 1. This aspect has been validated experimentally for four class III compounds—**1a**<sup>5+</sup>, **1b**<sup>5+</sup>,<sup>10</sup> the Creutz–Taube ion ((NH<sub>3</sub>)<sub>5</sub>Ru–pyrazine–Ru–(NH<sub>3</sub>)<sub>5</sub><sup>5+</sup>),<sup>17,18</sup> and a symmetrically substituted derivative of the Creutz–Taube ion<sup>19</sup>—via intervalence-enhanced resonance Raman spectroscopy. Consistent with the three-site model (but see below), the Raman spectrum of the nickel compound includes a peak at 530 cm<sup>−1</sup>, where this has been assigned elsewhere<sup>10</sup> as a totally symmetric vibration of the cyclam framework. A much more intense vibration in the resonance Raman spectrum of **2**<sup>3+</sup>, however, is the mode at 1617 cm<sup>−1</sup>. This illustrates a difference between the Ni case and the Fe and Ru cases: For **1a**<sup>5+</sup> and **1b**<sup>5+</sup>, almost no Raman activity is seen above 1300 cm<sup>−1</sup>. Given the differences, an attractive alternative interpretation is that scattering by **2**<sup>3+</sup> is resonantly enhanced by a transition at  $\lambda = 724$  nm that lacks LMCT character but is instead completely symmetrical-ligand-centered.

**Spectral Modeling.** To quantify the vibrational mode displacements accompanying optical excitation, attempts have been made to fit the absolute resonance Raman scattering intensities and the near-infrared absorption spectrum of **2**<sup>3+</sup> via a standard time-dependent theory of spectroscopy.<sup>15</sup> Despite numerous attempts using a variety of parameters, poor fits to the absorption spectrum were obtained from the time-dependent analysis. In addition, all attempts at spectral modeling resulted in excitation profile maxima that were located 20–50 nm to the blue of the absorption maximum, the reverse of what is seen experimentally. Since the model assumes only one resonant state, this result, together with the results of the electronic structure calculation, strongly suggests that the observed absorption is composed of two overlapping absorption bands with the red shift of excitation profiles due to a second weaker absorbing and lower energy state.

To estimate excited-state displacements, we assumed, possibly incorrectly, that most of the Raman intensity obtained from excitation at 725 nm is due to the higher energy transition.<sup>20</sup> Since the higher energy portion of the spectrum should be least contaminated by the lower energy transition, we used the time-dependent analysis to fit the absolute Raman scattering spectrum and the high-energy side and peak region of the room-temperature absorption spectrum (see Supporting Information).

**Electronic Structure Calculations. 1. State Energies and Transition Intensities.** Consistent with the results from spectral modeling, ZINDO/S electronic structure calculations yielded two electronic transitions in the region of interest: one at 741 nm with an oscillator strength of 0.016 and a second at 649 nm with an oscillator strength of 0.15. The lower energy transition is mostly (~90%) a transition from orbital 87 to orbital 89, while



**Figure 2.** Electron density of ZINDO/S molecular orbitals 87 (bottom), 88 (middle), and 89 (top). Symmetries are A, A, and B, respectively. 741 nm ( $f = 0.016$ ): 87  $\rightarrow$  89. 649 nm ( $f = 0.15$ ): 87  $\rightarrow$  88.

the higher energy transition is mostly (~90%) from orbital 87 to orbital 88. Figure 2 shows calculated wave functions for orbitals 87, 88, and 89. No lower energy transitions were found in the calculation. Other transitions found in the calculation were higher in energy and not of interest.

**2. Identities of the Electronic Transitions.** As suggested by Figure 2, the two lowest energy transitions are similar, in both cases consisting of mainly bridge-centered  $\pi$  type transitions, with very little involvement of the metals. In Figure 1, the observation for the dinickel complex of substantial Raman activity in the 1350–1650 cm<sup>−1</sup> region contrasts with the absence of detectable activity in this region for the analogous Fe<sub>2</sub> and Ru<sub>2</sub> complexes **1a**<sup>5+</sup> and **1b**<sup>5+</sup>. In light of the ZINDO calculations, appreciable differences in vibrational activity are to be expected. In addition, according to the calculations, and consistent with the earlier EPR study,<sup>11</sup> ground-state **2**<sup>3+</sup> is best viewed as a pair of Ni(II) ions bridged by a radical anion. The appearance of significant metal–ligand stretching activity in the resonance Raman spectrum of **2**<sup>3+</sup> is interpreted not as a partial change in valence of the Ni atoms upon optical excitation but as an effect due to changes in charge density on the nitrogen atoms that coordinatively bind the Ni<sup>II</sup> centers. In contrast, the ground electronic states of **1a**<sup>5+</sup> and **1b**<sup>5+</sup> involve a three-center bonding interaction (metal–ligand–metal), and optical “intervalence” excitation involves a symmetrical transfer of charge from the ligand to both metal centers.

## Conclusions

Resonance Raman studies of **2**<sup>3+</sup> indicate some similarities but also some differences in comparison to Raman spectra for the class III mixed-valence iron and ruthenium analogues **1a**<sup>5+</sup> and **1b**<sup>5+</sup>. The observation of resonance enhancement of totally symmetric modes of the TIED bridge is consistent with a three-center/three-orbital delocalized (class III) “intervalence” excitation scheme but is also consistent with a purely ligand-centered absorption scheme. The results are inconsistent, however, with a ligand-to-single-metal charge-transfer. Modeling of the resonance Raman excitation profiles and the electronic absorption

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spectrum indicates that the absorption band is composed of two separate overlapping transitions. This is supported by semiempirical electronic structure calculations. These calculations also enable one to choose between the two possibilities suggested by resonance Raman measurements for the intense electronic transition. The transitions clearly are best described as ligand-based transitions rather than LMCT or class III intervalence transitions.

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comments. We also thank the U.S. Department of Energy, Office of Science (Grants DE-FG02-87ER13808 for J.T.H. and DE-FG02-91ER14228 for K.G.S.) for financial support.

**Supporting Information Available:** Absorption spectra of  $2^{3+}$  and  $1b^{5+}$ , excitation profiles of  $2^{3+}$ , and results of the time-dependent analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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