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USING THE INTERVALENCE CHARGE TRANSFER BAND IN MIXED VALENCE MIXED PROTONATED METAL DITHIOLENE COMPLEXES TO FOLLOW GROUND STATE PROTON-COUPLED ELECTRON TRANSFER

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by

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ABSTRACT

Proton-coupled electron transfer (PCET) is an important phenomenon for controlling charge mobility in chemistry and biology because it allows the simultaneous movement of a proton and electron with a lower energy barrier than otherwise possible. Much work has been done on PCET systems, particularly for excited state processes in which charge mobility can be easily followed using pump-probe methods. However, while *excited state* PCET is utilized for the initial step of many solar energy-driven processes, including photosynthesis, *ground state* PCET is critical for all subsequent processes, including regeneration of solar cells. Homogeneous ground state PCET systems are of particular interest for this regeneration, but no convenient method exists for measuring parameters governing such reactions. Our work is directed toward understanding homogeneous ground state PCET reactions as probed using solution-phase steady-state methods.

In order to establish a probe for these homogeneous ground state PCET reactions, we design self-exchange model systems for PCET in analogy to classical electron transfer. With our first model system, [Ni(2,3-pyrazinedithiol)₂], we demonstrate that protonation of a mixed valence species, generating a mixed valence mixed protonated (MVMP) state, results in severe reduction of the electronic coupling intimately connected with electron transfer kinetics. This ligand-based mixed valence molecule can be asymmetrically protonated, rendering the MVMP state. We characterize the structural, electronic, vibrational, and magnetic properties of this complex in five different states, including the mixed valence and MVMP states, and then analyze the intervalence charge transfer (IVCT) band to demonstrate a five-fold reduction in electronic coupling upon protonation. We conclude that the reduction in electronic coupling is a result of the asymmetry of the electronic orbitals of the redox sites that results from the asymmetric protonation. As a result, the IVCT band is established as a probe for interrogating the electronic

coupling in the MVMP state, which reflects the change in the PCET potential energy landscape as a result of protonation. This conclusion suggests that many systems designed to link electron and proton transfer will also exhibit a decrease in electronic coupling upon protonation as the strength of the interaction between redox and protonation sites is increased.

After having established the MVMP state as a useful model system to study homogeneous ground state PCET, we explored structural modifications to control the communication between electron transfer and protonation sites. These studies allow for a more fine-tuned response to protonation in a series of metal dithiolene complexes when moving from the mixed valence to the MVMP state. We investigate the effect of changing the bridge between ligands simply by changing the metal center. In this study, we find nearly five-fold decreases in electronic coupling for both Ni and Pt, while, for the Pd complex, the electronic coupling is reduced to the point that the IVCT band is no longer observable. We ascribe the reduction in electronic coupling for the Pd complex is a result of greater energetic mismatch between ligand and metal orbitals, reflected in the smaller electronic coupling for the pure mixed valence state. This work demonstrates that the bridging metal center can be used to tune the electronic coupling in both the mixed valence and MVMP states, as well as the magnitude of change of the electronic coupling that accompanies changes in protonation state.

In addition, we explore 2,3-quinoxalinedithiol and 2,3-pyridinedithiol ligands, which are structurally altered versions of the above dithiolene ligands in which the aromatic rings are extended and the number of ring nitrogen atoms is reduced, respectively. With these complexes, we find that these modifications cause changes in the electronic coupling both in the mixed valence and MVMP states, and the degree of response to protonation, generating the MVMP state, is controlled as well. For [Ni(2,3-quinoxalinedithiol)₂], the only complex with the 2,3-quinoxalinedithiol ligand that reversibly generated its MVMP state, the IVCT band, and hence

the electronic coupling, disappeared upon protonation. This disappearance of electronic coupling resulted from additional electron density being placed on the ligands and not being channeled into ligand-ligand electronic coupling through the metal center. The complex [Ni(2,3-pyridinedithiol)₂] retained its IVCT band in the MVMP state, but with less electronic coupling than in the 2,3-pyrazinedithiol analogue. This lower value of electronic coupling is a result of higher energy ligand orbitals that overlap with the metal orbitals to a lesser extent.

Lastly, we explore the $[Au(2,3-pyrazinedithiol)_2]$ complex, which is appealing for the non-innocent character of its ligands. We report its synthesis and characterization, along with electrochemistry and spectrophotometric response to acid titration. This molecule did not exhibit generation of its singly oxidized mixed valence species, so it does not permit direct comparison to the mixed valence species of the other metal dithiolene compounds in this study.

Ultimately, our investigations of these metal dithiolene MVMP model systems allow for more informed control over PCET self-exchange transformations, as interrogated through their IVCT bands. The IVCT band is established as a probe for monitoring the effect of asymmetric protonation upon electronic coupling, seeking to extend classical electron transfer model systems into the domain of PCET. The interdependence of asymmetric protonation and electron transfer will allow for better control over PCET charge mobility through structural modifications, which will allow for more rational design of systems that undergo ground state PCET in device applications.

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Chapter 1

The Need for Model Proton-Coupled Electron Transfer Systems, in Analogy to Pure Mixed Valence Systems

Introduction to Proton-Coupled Electron Transfer (PCET)

Many energy conversion processes (fuel cells, dye-sensitized solar cells, many biological processes, artificial photosynthesis) rely on the transfer of electrons and protons.^{1–8} While the movements of each individual charged species are important for the operation of these important processes, they are often inhibited by at least one high energy intermediate and the need to move a larger counterion.^{1,6,7,9–12} Pairing the movements of electrons and protons results in a process referred to as proton-coupled electron transfer (PCET) that, when performed in a concerted manner, avoids the high-energy intermediates associated with sequential transfer of individual species caused by separation of charges.^{1–15}

Reactions and mechanisms that involve PCET have been known at least since the early studies on hydroquinone in which two protons are lost upon redox interconversion to quinone.¹⁶ Because the proton transfer in PCET mechanisms involves protonation and deprotonation, the overall reactions depends on pH. As such, the E_{1/2} redox potentials associated with the redox centers of electron transfer are pH-dependent, shifting to more positive potentials at lower pH.^{1,16} This effect is mirrored by the pK_a values of the basic sites as well. When comparing the pK_a values of singly reduced and oxidized species of a particular redox couple, the pK_a value of the oxidized species is lower than that of its reduced form. Consideration of the dependence of these values on one another results in a Pourbaix diagram, shown in Figure 1-1a.¹⁶ In this diagram, M^{III}L and M^{III}L are the two species in the redox couple, and M^{III}LH and M^{III}LH are the protonated

species of the former respective states. The PCET reaction is shown between $M^{II}L$ and $M^{II}LH$ in Equation 1-1 in which *n* is the number of electrons and *m* is the number of protons.

$$M^{III}L + ne^{-} + mH^{+} \rightleftharpoons M^{II}LH \tag{1-1}$$

The $E_{1/2}$ value for the protonated species is shifted to more positive potentials as compared to the deprotonated species, and the pK_a value is lower for the oxidized species as compared to the reduced species. The middle line in the diagram shows the shift in the above thermodynamic properties as the applied potential and pH are changed. The slope of the central region of this line is -59 mV/pH unit for a one-electron one-proton transformation as dictated by the Nernst equation, shown in Equation 1-2, where $E_{1/2}$ and $E_{1/2}^{\circ}$ are the measured potential and formal potential, respectively.

$$E_{1/2} = E_{1/2}^{\circ} - \frac{0.0591m}{n} \log \frac{[M^{II}LH]}{[M^{III}L]} - \frac{0.0591m}{n} pH$$
(1-2)

Outside of this central region, marked by the horizontal and vertical lines, the redox potentials and pK_a values do not depend on one another.

These Pourbaix diagrams are often viewed as predominance diagrams in which the four species (cross-combinations of reduced/oxidized and protonated/non-protonated) are the predominant species in solution in their respective regions of the diagram. From the information provided in these diagrams, square schemes can be constructed that illustrate the interconversion between all four species, shown in Figure 1-1b.^{3,14,16} The vertical transformation represents the redox event, the horizontal transformation represents the protonation event, and the diagonal transformation represents thermodynamic PCET.



Figure 1-1. (a) Pourbaix diagram showing the dependence of the $E_{1/2}$ redox potential on pH for a redox couple and their protonated states. The four redox and protonation states are shown in their respective regions of predominance, with a diagonal line through the middle of the diagram. (b) Square scheme illustrating the four charge configurations and their relation by thermodynamic parameters. Figure adapted from reference 16.

While the thermodynamic PCET perspective is useful for describing changes in redox potentials and pK_a values, it does not appropriately capture molecular-scale movement of the proton and electron. In the same way in which molecular-scale pure electron transfer rates^{17–27} are discussed in the study of a wide range of redox phenomena, molecular-scale understanding of PCET kinetics is likewise important for full understanding of PCET reactions.

Importance of Ground State PCET

Common energy conversion devices that aim to utilize PCET, such as solar cells, are inspired by photosynthesis, in which plant life captures solar energy and stores it in chemical bonds.^{1,9,10,28–32} As such, the natural focus of study of PCET in these systems is excited state processes,^{15,33–35} and excited state PCET is studied to understand how to better optimize these systems. Transient absorption techniques for these excited state PCET processes are extremely valuable for such excited state reactions because they provide a means to follow PCET

transformations as they occur. By tracking the decay of an absorption signal from a short-lived intermediate, information on PCET reaction mechanisms and rates can be obtained. As such, transient absorption techniques have been utilized for a large number of PCET reactions^{15,36–46} and hold promise to help design more efficient light-harvesting devices. However, regeneration of these light-harvesting systems is necessary for continual device operation, which occurs in the ground state.^{47–50} Drawing another analogy from pure electron transfer systems, the regeneration of dye-sensitized solar cells is often limited by the ground state regeneration of the dye.^{48,50–55} As a result, ground state PCET will play a large role in energy capture and conversion as well.

Heterogeneous Ground State PCET

Ground state PCET systems can be further separated into homogeneous and heterogeneous PCET. Heterogeneous ground state PCET has been well-studied using electrochemistry because the driving force can be easily controlled through applied potentials. Kinetic information can then be obtained from the resulting current density.^{12,13,56–59} In addition, electrochemical techniques can be used to determine the contributions of each possible mechanism (stepwise electron-proton transfer, stepwise proton-electron transfer, or concerted transfer of both species).^{12,56,60,61} In these experiments, the anodic and cathodic peak separation of a particular redox couple is monitored as a function of scan rate across a range of pH values. Figure 1-2a shows a sample plot for an osmium aquo/hydroxo compound from the literature, $[Os(2,2'-bipyridine)_2(H_2O)(pyridine)](PF_6)_2$, at pH 5.^{12,56,60,61} From this data over a range of pH values, an apparent rate constant k_{ap} can be extracted using Equation 1-3^{12,56,60,61}

$$\frac{i}{FSC^0} = k_{ap} \exp\left[\frac{F}{2RT} \left(E - E_{ap}^0\right)\right] \left[\frac{\sum red}{C^0} - \frac{\sum ox}{C^0} \exp\left(-\frac{F}{RT} \left(E - E_{ap}^0\right)\right)\right]$$
(1-3)

where i is the current, S is the electrode surface area, F is the Faraday constant, C⁰ is the total concentration of redox-active species in solution, R is the ideal gas constant, T is the temperature, Σ red is the sum of concentrations of all reduced species at the electrode, and Σ ox is the sum of concentrations of all oxidized species at the electrode. The apparent rate constant is also a sum of the three rate constants associated with the three respective mechanisms, shown in Equation 1- $4^{12,56,60,61}$

$$k_{ap} = k_{CPET} \sqrt{[B][B-H^+]} + k_{EPT} \sqrt{\frac{[H^+]}{K_{0x-H^+}}} + k_{PET} \sqrt{\frac{K_{red-H^+}}{[H^+]}}$$
(1-4)

where k_{CPET} , k_{EPT} , and k_{PET} are the rate constants for the three respective mechanisms, concerted PCET, stepwise electron-proton transfer, and stepwise proton-electron transfer, [B] is the concentration of free base, $[B-H^+]$ is the concentration of protonated base, $[H^+]$ is the concentration of free protons, K_{ox-H^+} is the acid equilibrium constant for the oxidized species, and K_{red-H}^{+} is the acid equilibrium constant for the reduced species. Plotting the log of the observed rate constant kap against pH allows for visualization of the region of dominance of each mechanism, as shown in Figure 1-2b for the same above compound. The solid line represents theoretical treatment in which only the stepwise rate constants are considered, which trade off (indicating that the electron and proton switch which species transfers first) at roughly neutral pH values. The concerted mechanism is indicated by deviations from these fits, which are usually manifested by less steep slopes in these plots due to few stepwise PCET charge conformers, reducing the effect of pH on the overall rate constant. The compound represented by Figure 1-2b exhibits a tradeoff between stepwise mechanisms because the data closely matches the solid line.^{12,56,60,61} Overall, as a result of the ability to determine the mechanism within these PCET reactions and their tradeoff as a function of pH, electrochemical measurements are gaining prominence in studying PCET reactions.



Figure 1-2. (a) Variation of anodic (above) and cathodic (below) peak potentials with scan rate for an osmium aquo/hydroxo compound, $[Os(2,2'-bipyridine)_2(H_2O)(pyridine)](PF_6)_2$, at pH 5. (b) Upon acquiring many plots such as the one shown in (a), the apparent rate constant k_{ap} can be extracted, which is shown as a function of pH. This variation of k_{ap} with pH is used to determine the mechanism of overall PCET. Figure adapted from reference 60.

Homogeneous Ground State PCET

In contrast to excited state PCET and heterogeneous ground state PCET, homogeneous ground state PCET does not *yet* have a convenient method to follow the charge exchanges as they occur. Kinetic and mechanistic information for PCET must be obtained from stopped flow methods of mixing reagents which do not permit the study of intramolecular self-exchange or extremely rapid exchanges.^{62–65} In the stopped flow experiments, two reagents that are poised to undergo intermolecular electron transfer and proton transfer are quickly mixed, and the absorbance of one species is monitored over time. In contrast, intramolecular PCET occurs by self-exchange between alternate PCET configurations within the same molecule, which is appealing for the incorporation of these molecules into devices, allowing them to control overall charge mobility. The stopped flow methods of monitoring PCET reactions are restricted to outer sphere self-exchange and prevent the study of dynamic PCET, a process which will grant

fundamental insight into how to control PCET charge mobility. Because of the lack of an available method to follow such dynamic transformations and the difficulty in using stopped flow techniques, homogeneous ground state intramolecular PCET reactions are less studied despite their clear importance to energy conversion devices and prevalence in chemical reactions.

Borrowing Inspiration from Classical Model Electron Transfer Systems

We aim to establish a method to follow homogeneous ground state intramolecular PCET reactions, ideally through the use of widely available steady-state spectroscopic techniques. For this, we draw inspiration from the fields of classical electron transfer. For decades, electron transfer reactions were at the forefront of chemical research, and elegant theoretical descriptions were constructed for such systems.^{17–27} A critical breakthrough in this field was the analysis of intramolecular electron transfer self-exchange of two identical metal centers through an organic bridge in a system known as the Creutz-Taube ion,^{66–68} shown in Figure 1-3. Redox chemistry is used to singly oxidize this compound to generate a mixed valence system in which the two metal centers possess different formal oxidation states. The identities of these redox sites may be exchanged *via* the transfer of an electron between them, and, by studying the properties of the system that influence this electron transfer, we gain insight into how intramolecular electron transfer proceeds. The importance of controlling this electron transfer for device applications has led to the study of a large number of mixed valence complexes.^{27,69–82}



Figure 1-3. Structure of the Creutz-Taube ion.⁶⁶ This structure is the archetypal mixed valence complex, with two ruthenium centers with asymmetric formal oxidation states, linked by an organic bridge. Figure from reference 27.

Marcus-Hush Theory

These Creutz-Taube mixed valence systems are readily described by Marcus-Hush theory.^{17–27} In this description, two charge transfer conformers are represented by potential energy wells as shown by the parabolas in Figure 1-4. Each redox state consists of the entire system (solvent included) possessing the electron localized on either side of the molecule. The xaxis represents movement of the electron from one redox state to the other, and it is known as the electron transfer collective solvent coordinate. Three classes, first proposed by Robin and Day,⁸³ are then used to describe three regimes of electronic coupling (mixing between these potential energy surfaces) for these systems. Class I is the case in which no electronic coupling is present, with the electron localized on one redox site or the other, reverting the description to that of formal oxidation states. In Class II systems, the potential energy surfaces mix to a moderate extent. The previous diabatic states give rise to two adiabatic states after electronic coupling is introduced. The electronic coupling is determined by the electronic coupling parameter H_{AB} , which results from diagonalizing the potential energy surfaces. Electronic coupling at their intersection results in ground and excited state potential energy surfaces. In Class II systems, two distinct potential energy minima are still present, and the electron is primarily localized to one redox site. The electron is allowed to thermally traverse the energy barrier of ΔG^{\ddagger} at the saddle

point to transfer to the other redox site. The system can also undergo optical excitation in which the electron transfers to the excited state potential energy surface (this portion of the surface is formerly associated with the product potential energy well before mixing). Upon relaxation back to the ground state at the saddle point, the electron can subsequently transfer to the ground potential energy well associated with the product configuration. The optical excitation is termed intervalence charge transfer (IVCT), and it is often observed in electronic spectra of mixed valence compounds.^{26,27} In addition, upon optical excitation, the system (now on the product excited state potential energy surface) finds itself in a solvent dielectric medium that is wellsuited for the reactant. As such, the energy for the optical excitation is also the energy required for the solvent to reorient itself to accommodate this new configuration, known as the reorganization energy, given as λ . For a symmetrical system with no change in free energy between the reactant and product minima, the activation barrier to electron transfer is given by Equation 1-5.^{21,23,26,84}

$$\Delta G^{\ddagger} = \frac{(\lambda - 2H_{AB})^2}{4\lambda} \tag{1-5}$$

Note that in Class I systems or in cases with very small H_{AB} values, Equation 1-5 collapses to give a value of ΔG^{\ddagger} equal to $\lambda/4$. Using Equation 1-5 for the activation energy gives Equation 1- $6^{19,21,23,25}$ for k_{ET} , the rate constant of electron transfer, in cases of small H_{AB} values

$$k_{ET} = \frac{2H_{AB}^2}{h} \left[\frac{\pi^3}{\lambda RT}\right]^{1/2} \exp\left[\frac{(\lambda - 2H_{AB})^2}{4\lambda RT}\right]$$
(1-6)

where h is Planck's constant. From this analysis, the rate of electron transfer is related to the degree of electronic coupling.



Figure 1-4. The three classes for assigning extent of electronic coupling in mixed valence compounds in the Robin-Day classification scheme.⁸³ In Class I systems, minimal electronic coupling is present, resulting in potential energy surfaces that do not interact. In Class II systems, a small amount of electronic coupling is present, resulting in a mixing of the potential energy surfaces. The electron is then partially localized to one redox state and can then transfer either thermally or optically. In Class III systems, the electronic coupling is large, resulting in a large degree of mixing between potential energy surfaces and delocalization of the electron. Figure adapted from reference 27.

Lastly, Class III systems involve a large degree of electronic coupling such that a single potential energy minimum is present. In this case, the electron is delocalized across both redox sites, no net movement of the electron occurs, and the redox sites are described using half-integer oxidation states. The IVCT optical excitation to the excited state still occurs, however, only simply with no net change in electron position. Because the IVCT is observed through bands in electronic spectra, the assignment of class can be determined through the shape, position, and intensity of these bands.^{26,27} In particular, the molar absorptivity at the wavelength of maximum absorbance, ε_{max} , of the IVCT band is given by Equation 1-7²⁶

$$\varepsilon_{max} = \frac{2.36 x \, 10^3 H_{AB}^2 r_{AB}^2}{v_{max} \Delta v_{1/2}^0} \tag{1-7}$$

where r_{AB} is the separation distance of charge donor and acceptor, v_{max} is the wavelength of maximum absorbance, and $\Delta v^{0}_{1/2}$ is the full width of the band at half height. Equation 1-7 shows that the IVCT band gains intensity directly from the magnitude of the electronic coupling. This

analysis has granted significant insight into how to control ground state electron mobility through steady-state electronic spectroscopy techniques.

Theoretical Description of PCET

An analogous theoretical description has been developed for PCET processes as well.^{5–8,85–88} Here, a proton transfer collective solvent coordinate is added to the electron transfer collective solvent coordinate established in the theory of pure electron transfer. This additional coordinate results in the potential energy paraboloid surfaces shown in Figure 1-5a for the reactant and product PCET diagonal wells. Four total charge configurations are present, resulting from the cross-combinations of the electron and proton occupying the reactant and product sites for their respective coordinates (Figure 1-5b). Then, coupling of all four paraboloids can result in the case in which the ground state potential energy surface possesses four minima, as shown in Figure 1-5b.



Figure 1-5. (a) Paraboloids for the PCET transformation resulting from addition of a proton transfer coordinate to the previous electron transfer coordinate. (b) Four charge configurations are created, and the paraboloids associated with each charge configuration can mix together to give a ground state potential energy surface. Each configuration represents a cross-combination of redox and protonation states. The diagonal transformation represents the PCET transformation. Figure adapted from reference 6.

In the quantum mechanical description of the PCET reaction, a major factor in determining whether PCET will occur is the proton wavefunction overlap between reactant and product states.^{6–8} Figure 1-6 shows the cross-section of the potential energy paraboloids, which collapse to parabolas along the diagonal PCET transformation. Because protons are much more massive than electrons, it is the overlap of the proton vibrational wavefunctions (shown in the insets along the pure proton transfer coordinate) that ultimately limits the rate of PCET. In order for the proton to transfer, the system must reach the saddle point, at which point the proton wavefunction overlap must be sufficient for the proton to transfer to the product potential well. In addition, upon excitation, the Franck-Condon overlap of the proton wavefunctions (the overlap of the reactant ground state proton wavefunction and the product excited state proton wavefunction) is also important for placing the system on the excited potential energy parabola of the product well. This scheme of four configurations and the proton vibrational wavefunction overlap upon IVCT excitation is especially useful to us as we strive to provide a handle to follow the movement of species across this potential energy landscape in the ground state.



Figure 1-6. Cross-section of the potential energy paraboloids for the diagonal PCET transformation. The insets show the potential energy surfaces of the proton transfer (without the associated electron transfer) at the given configuration within the paraboloid, along with the vibrational ground state wavefunction of the proton. The overlap of the reactant and product proton wavefunctions is shown at the saddle point of the diagonal PCET transformation. Figure adapted from references 6-8.

A Steady-State Spectroscopic Approach to Following Homogeneous Ground State PCET Reactions

Observing the Response of the IVCT Band to Protonation

In order to provide a steady-state handle on ground state homogeneous PCET processes, we aim to utilize the IVCT band, arising from the optical excitation shown in Figure 1-4. Given that the IVCT band has emerged as the dominant probe of electronic coupling in systems undergoing electron transfer, we felt that it would also provide insight into charge mobility in PCET systems. While the attempted intersection of PCET and classical electron transfer has been pursued before, model systems for this involve hydrogen-bonded mixed valence dimers that transfer electrons in an intermolecular fashion.^{89–94} In these studies, generation of mixed valence monomers induces dimerization through hydrogen bonds, and electronic delocalization between the dimers stabilizes the mixed valence dimer. This increased stabilization of the mixed valence dimer is manifested in electrochemical comproportionation constants, and the extent of electronic coupling can be extracted from the resulting IVCT bands. As a result, mixed valence dimers are created that depend on the strength of hydrogen bonding, a process termed proton-coupled mixed valence.

In our systems, we seek to establish intramolecular electron transfer self-exchange that explicitly depends on the presence of a proton at a basic site.^{95–97} The model system that we envision is a mixed valence compound that possesses asymmetrically protonated basic sites, in addition to the asymmetric redox states. We have termed such complexes mixed valence mixed protonated (MVMP), and an example of such a complex is shown in Figure 1-7. In a similar manner to the study of pure electron transfer, we aim to study the impact of adding asymmetric protonation upon the mobility of the electron, as probed by the IVCT band. As such, we will gain understanding of how the PCET potential energy landscape is interconnected with the electron

transfer component by constructing a possible proton transfer coordinate and investigating the effect of the presence of a proton on the electron movement in the MVMP state as compared to the pure mixed valence state. It should also be mentioned that, despite IVCT optical excitation to an excited state potential energy surface, the excited state potential energy surface arises from coupling of a formerly ground state potential energy surface. Thus, the optical excitation reflects the degree of electronic coupling in the ground state.



Figure 1-7. Schematic of $[Ni(2,3-pyrazinedithiol)_2]$ undergoing PCET self-exchange. Upon either intramolecular electron transfer or proton transfer to two external bases through the complex, the system will respond by reconfiguring to the other PCET state. In our studies, we found that the proton did not in fact transfer between external bases, but we did explore the effect of a *possible* proton transfer coordinate on the intramolecular electron transfer.

Metal Dithiolene Complexes as Model Systems for Ligand-to-Ligand Electron Transfer

To accomplish the goal outlined above, we have chosen the metal dithiolene class of complexes as our model system. Metal dithiolene complexes were the first example of complexes containing redox non-innocent ligands.^{98–105} Non-innocent ligands create ambiguity in the oxidation state of the metal center upon coordination, often through favorable orbital mixing.^{105–107} This sharing of redox activity often manifests itself through the presence of single-electron redox events that occur primarily on the ligand sites.^{101,103,105,108–111} An example of the single-electron redox events for dithiolene ligands is shown in Figure 1-8. The non-innocent

character of the ligands has led to the use of metal dithiolenes in a number of applications involving electron transport.^{112–122} The mixed valence states of metal dithiolenes also can be readily generated, and they exhibit prominent IVCT bands in their electronic spectra.^{98,101,102,123–126} In fact, the dithiolene ligands can be viewed as the redox sites in these mixed valence states with the metal center acting as the bridge.^{101,126,127} However, metal dithiolene complexes are not usually discussed from the mixed valence perspective, although much work has been performed to characterize the non-innocent nature of the ligands.^{100,101,105} In addition, the generally electron-rich nature of these complexes makes them appealing for use as hydrogen reduction catalysts for storage of chemical fuels.^{125,128–133} The particular metal dithiolene complexes that we chose to study also possess basic nitrogen sites, which can be protonated to allow us to selectively generate the MVMP state, allowing us to study the effect of protonation on the electronic coupling. While the protonation of metal dithiolene complexes has been studied for closed shell systems,^{123,134–141} the MVMP state has not yet been examined.



Figure 1-8. Single-electron redox events of dithiolene ligands, interconverting between the dithione, semithionate, and dithionate forms. A large degree of orbital mixing between the ligands and metal center lends non-innocent character to the distribution of electron density, allowing for such redox events. Figure from reference 110.

Inspiration for Using the Ligand Linkage to Control PCET

A previous study has previously sought to explore the effect of protonation on the mixed valence state of a metal dithiolene complex.¹²⁴ We used this study as inspiration for obtaining the MVMP state in which we see a large response of the mixed valence state to protonation. Figure

1-9 shows the spectrophotometric acid titration experiment on the nickel pyridine dithiolene complex with a "dangling pyridine" connection. In this experiment, the IVCT band is present in the electronic spectrum; upon protonation, the IVCT band does not change significantly, indicating that the electronic coupling is not significantly affected. This minimal effect of protonation is thought to occur because of the dangling connection of the protonation site, which is known to twist out of the plane of conjugation. Because the protonation site is not strongly tied into the electronic center of the mixed valence state, little effect is observed on the IVCT band. Furthermore, the MVMP state is not well-defined in this study because two protonation events occur during the acid titration, as indicated by two sets of isosbestic points. Isosbestic points in a spectrophotometric titration are points at which the absorbance does not change when converting between two species. In addition, the spectrum of the singly protonated state is not clearly obtained in this study. We choose to focus on fused ring dithiolene ligands with nitrogen sites, which includes 2,3-pyrazinedithiol (also shown in Figure 1-7), 2,3-quinoxalinedithiol, and 2,3pyridinedithiol. In these sets of complexes, the protonation event is expected to be more intimately tied into the mixed valence electronic center because of increased conjugation and planarity between the protonation and redox sites. We also strive to unambiguously capture the steady-state spectra of the MVMP states of these complexes to report on the change in electronic coupling due to the presence of a single proton.


Figure 1-9. Spectrophotometric acid titration of $[Ni(4-pedt)_2]$. The IVCT band was minimally affected, indicating that the site of protonation and site of mixed valence electron transfer did not communicate efficiently, likely due to the twisting nature of the "dangling pyridine" group. Figure adapted from reference 124.

Dissertation Overview

Within this dissertation, we highlight our efforts toward establishing a steady-state spectroscopic probe for following homogeneous ground state PCET reactions. For the metal dithiolene complexes investigated, we obtained electronic spectra, electron paramagnetic resonance (EPR) spectra, and electrochemical data in different redox and protonation states. The electronic spectra permit observation of the IVCT bands, the EPR spectra allows the identification of paramagnetic species, and the electrochemical measurements permit generation of the mixed valence species. In addition, we report the syntheses of many novel metal dithiolene complexes, as well as novel states of several previously reported complexes. Chapter 2 focuses on first establishing the MVMP state as a valid means to follow the change in electronic coupling

upon protonation. This first study involves the nickel 2,3-pyrazinedithiol complex in various redox and protonation states. The change in electronic coupling is then discussed in terms of the alteration to the PCET potential energy landscape due to the presence of a proton, and thus a possible proton transfer coordinate. Chapter 3 focuses on the same ligand, but with changes to the metal center bridge, by exploring the palladium and platinum analogues. The changes in electronic coupling in the mixed valence state and the MVMP state are then compared between all three sets of complexes (including nickel as well). Chapter 4 focuses on complexes of two different sets of ligands, the 2,3-quinoxalinedithiol and 2,3-pyridinedithiol ligands, to investigate changes in ligand orbital energy and geometry on the change in electronic coupling. Chapter 5 focuses on the gold 2,3-pyrazinedithiol complex, which is important for tuning electronic properties of metal dithiolene complexes.

The IVCT band is ultimately a useful probe for interrogating the degree of electronic coupling in the MVMP state. The presence of a possible proton transfer event in the MVMP state changes the potential energy landscape, which is reflected in the changes to the IVCT bands. While we have studied predominantly fused ring structures up to this point, future work will seek to establish a measure of refined control over the electronic coupling, especially when moving between the mixed valence and MVMP states. Structural changes that are envisioned to impart this level of control are discussed herein, along with progress toward their synthesis. This work will then lead to rational control of electronic coupling in mixed valence systems due to protonation in general, and control of electron and proton mobility interdependence in ground state PCET systems. As a result, any device that utilizes PCET, even excited state processes that need to be regenerated, will benefit from informed control over PCET within these metal dithiolene model systems.

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Chapter 2

Effect of Protonation upon Electronic Coupling in the Mixed Valence and Mixed Protonated Complex, [Ni(2,3-pyrazinedithiol)2]

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Introduction

The recognition of the importance of proton-coupled electron transfer (PCET) has inspired a great deal of research.^{1–13} As a result, there is a good understanding of the parameters that govern PCET^{2–10,14–18} and the features of PCET that are unique from those of pure electron transfer (ET). For example, the kinetics of PCET can depend on the Franck-Condon overlap between proton vibrational wavefunctions.^{3,4,7,9} Nevertheless, there are many aspects of PCET that remain to be studied. In particular, we are interested in determining the impact that protonation of redox active sites has upon the electronic coupling between adjacent redox sites. This electronic coupling is intimately tied to the electron mobility, and understanding how protonation affects electron mobility has clear implications for PCET systems.

Our approach to studying the impact of protonation is to use the intervalence charge transfer (IVCT) band (see Chapter 1), stemming from optical excitation in mixed valence compounds, as a probe for determining the electronic coupling upon protonation. The IVCT band has emerged as the most common gauge of ground state electron transfer dynamics within (and even between) molecules,^{19–24} as the shape, intensity, and position of the bands associated with

the IVCT transition provide insight into the electronic coupling between redox states, which in turn impacts the rate of thermal (ground state) electron transfer.^{23,25,26} Thus, to the extent that the overall mobility of an electron can be broken down into elementary steps of single electron transfers, analysis of the IVCT band has provided great insight into how electron mobility can be controlled *via* the nature of both the bridge and redox sites across a wide variety of organic and inorganic species.^{27–38}

As a model system for connecting ET and proton transfer (PT) events, we designed a mixed valence complex that, upon protonation, occupies a mixed valence mixed protonated (MVMP) state that is expected to exhibit proton-coupled mixed valency.³⁹⁻⁴³ The term MVMP indicates a complex that contains at least two distinct redox centers and at least two distinct basic sites, giving rise to at least four different charge transfer configurations (two redox isomers and two protonation isomers for each redox isomer). By comparing the properties of the mixed valence and MVMP states, we can determine the manner in which protonation of a pure ET system results in changes to the electronic coupling that underlies ET in PCET complexes. Specifically, analysis of changes to the shape, intensity, and position of the IVCT band²³ enables us to quantify changes in electronic coupling that are brought about by this protonation.

In this chapter, we investigate the impact of protonation of the $[Ni(pdt)_2]$ (pdt = 2,3pyrazinedithiol) complex (1), shown in Figure 2-1. This dithiolene molecule is borrowed from the literature of non-innocent ligands, which create ambiguity in the oxidation state of the metal center upon coordination.^{44,45} This ambiguity arises from strong electronic coupling between the ligand and the metal. For pdt, the redox unit is the thiolene (S-C=C-S) moiety, which can be singly oxidized. Due to the redox activity of the ligands, 1 possesses three accessible redox states, which we term 1, 2, and 3 (Figure 2-1). In the open shell state (2), the unpaired electron is shared between both dithiolene ligands, rendering a state that could be classified as a strongly coupled mixed valence species,^{44–53} though dithiolene complexes are not usually discussed within the mixed valence context. The choice of the nickel metal center imparts square planar geometry to the molecule, allowing for maximum coupling of ligand electronic states. Consistent with classification as mixed valence species, the open shell states of these complexes possess a low-energy electronic transition that can be viewed as an IVCT band,^{51,54–58} which should provide the means to follow the effect of asymmetric protonation upon the electronic coupling.^{55,59–61} The nitrogen atoms of the ligands in **1** function as the basic sites and allow for three easily accessible protonation states. The combination of these states results in nine non-degenerate protonation/redox states (Figure 2-1) for this complex. Of these nine states, two (**2** and **2-2H**) are pure mixed valence, while one (**2-H**) is a MVMP state (shown explicitly in Figure 2-1).



Figure 2-1. Structure of $[Ni(pdt)_2]$, depicted in the mixed valence mixed protonated (MVMP) state (left). Square scheme demonstrating the electron and proton transfer events that generate the nine possible states for the complex. In addition, we provide labels for all states, denoting in bold the five states that were found to be stable under laboratory conditions and that are discussed in this chapter.

Of the states shown in Figure 2-1, we find that five are stable under laboratory conditions: 1, 1-H, 1-2H, 2, and 2-H. We report the structural and spectroscopic properties of these five states, and we find that the electronic properties of both the closed shell dianion 1 and the mixed valence monoanion 2 are affected by the protonation of the ligands. Of particular

interest, we observe changes in the IVCT band when going from the pure mixed valence state (2) to the MVMP state (2-H), which is associated with changes in the electronic coupling. Using analysis of this IVCT band, we demonstrate a steady-state spectroscopic approach for the study of ground state PCET while also providing guidance for the design of chemical systems that rely upon ground state PCET.

Experimental

Materials and Methods

NaSH • xH₂O, NiCl₂, and Bu₄NBr were purchased from Sigma Aldrich, and 2,3dichloropyrazine was purchased from TCI. NaOEt was purchased from Strem Chemicals, and I₂ was purchased from Acros. Anhydrous sodium sulfate was purchased from EMD, and TsOH • H₂O was purchased from Fisher Scientific. All solvents were ACS grade and were used without further purification. IR spectra were recorded on a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer equipped with an ATR accessory. Near-infrared (NIR) spectra were recorded on the same instrument, but in transmission mode, using a quartz cuvette. Raman spectra were recorded using a Renishaw inVia Raman Microscope equipped with a Leica DM2500 M integral microscope. Samples were excited with a 647 nm, 70 mW CrystaLaser CL-2000 diode pumped laser of model DL647-070. Samples were dissolved and transferred to a 1 mm path length glass cell for spectral acquisition. ¹H NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer in CDCl₃ or d_6 -DMSO using the residual solvent peak as the internal standard. Electron paramagnetic resonance (EPR) spectra were recorded using a Bruker ELEXSYS E 580 spectrometer with samples dissolved in tetrahydrofuran (THF) at 35 K. Electronic absorption spectra in the UV-vis region were acquired using an Agilent 8453 spectrometer with a 1 cm path length quartz cell. Cyclic voltammetry (CV) measurements were made using a Pine WaveNow potentiostat under inert atmosphere using a Pt wire as the working electrode, a Pt wire as the auxiliary electrode, and a Ag/Ag⁺ wire as a pseudo-reference electrode. 0.1 M tetra-butyl ammonium hexafluorophosphate was used as the electrolyte in N,N'-dimethylformamide (DMF), and the Fc/Fc^+ redox couple was used as an internal standard. Spectroelectrochemical (SEC) measurements were made under inert atmosphere using a 1 mm path length quartz cell. A gold honeycomb electrode card (Pine Instrument Company) was used as the working and counter electrodes, and a Ag/Ag^+ wire was used as a pseudo-reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate was used as the electrolyte in DMF. Crystals for compounds 1 and 2 were grown as described later, and their X-ray structures were determined using a Bruker SMART APEX CCD area detector equipped with a graphite monochromator, a Monocap collimator, and a MoK_{α} fine-focus sealed tube. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The structures were solved and refined using the Bruker SHELXTL (Version 6.1) software package. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of 2, 3-Pyrazinedithiol (pdt)

2,3-Pyrazinedithiol (pdt) was synthesized according to a literature procedure.^{35,62–65} 2,3-Dichloropyrazine (12.0247 g, 0.0766774 mol) was dissolved in 200 mL MeOH under inert atmosphere. NaSH • xH₂O (23.49 g, 0.2133 mol) was dissolved in 100 mL H₂O under inert atmosphere. The solutions were combined, and the yellow reaction mixture was brought to reflux at 90 °C for 15 hrs. 100 mL of a 1.21 M HCl (aq) solution was slowly added to the reaction mixture. The mixture slowly turned red, and some dark red precipitate was visible. The mixture was cooled to -20 °C for 3 hrs, after which the precipitate (4.972 g, 42.7 %) was filtered and washed with cold MeOH. ¹H NMR (CDCl₃): 13.50 ppm (2H), 6.85 ppm (2H). IR (neat): *v*/cm⁻¹ = 3083, 2893, 1630, 1547, 1528, 1480, 1316, 1290, 1148, 1133, 1071, 1051, 852, 828, 820, 803, 726, 668, 623. Anal. Calcd for H₄C₄N₂S₂: H, 2.80; C, 33.31; N, 19.42; S, 44.47. Found: H, 2.83; C, 32.92; N, 19.05; S, 44.23.

Synthesis of $(Bu_4N)_2[Ni(pdt)_2]$ (1)

The complex (Bu₄N)₂[Ni(pdt)₂] was synthesized according to a literature procedure.^{35,66} 2,3-Pyrazinedithiol (4.9366 g, 0.033939 mol) was dissolved in 300 mL MeOH containing NaOEt (4.74 g, 0.0652 mol). Anhydrous NiCl₂ (2.2346 g, 0.017372 mol) was added while stirring, and the mixture turned dark red. The mixture was left to stir for 3 h, and the solvent was removed in vacuo. The resulting orange solid was redissolved in 200 mL EtOH and filtered. The solvent was again removed in vacuo. 5.3537 g of the solid was dissolved in 500 mL water and transferred to a separatory funnel. A solution of Bu₄NBr (6.5320 g, 0.020346 mol) was prepared in 100 mL CHCl₃. The product was extracted using the CHCl₃ solution (5 x 20 mL), and the combined organic layers were washed 3 times with water (20 mL). The organic layers were dried over Na_2SO_4 , and the solvent was removed *in vacuo* to give an orange solid (7.6476 g, 53.57%). The product was recrystallized by slow evaporation of a solution in acetone open to air. ¹H NMR (d₆-DMSO): 7.24 ppm (s, 4 H), 3.24 ppm (t, 16 H), 1.55 ppm (m, 16 H), 1.30 ppm (m, 16 H), 0.93 ppm (t, 24 H). IR (neat): $v/cm^{-1} = 3070, 3019, 2959, 2926, 2869, 1490, 1476, 1456, 1409,$ 1387, 1313, 1297, 1281, 1147, 1140, 1066, 1043, 928, 880, 811, 737, 644. Anal. Calcd for H₇₆C₄₀N₆S₄Ni: H, 9.25; C, 58.02; N, 10.15; S, 15.49. Found: H, 9.24; C, 58.28; N, 10.10; S, 15.21.

1 (0.4243 g, 0.5124 mmol) was dissolved in 30 mL MeOH. I₂ (0.1302 g, 0.5130 mmol) was dissolved in 30 mL MeOH, which was added to the original solution. Upon addition of I₂, the solution turned from orange to green, indicating the formation of **2**. The solvent was removed *in vacuo*, and a column was performed using 4:1 EtOAc / MeOH as eluent. The solvent was removed *in vacuo*, resulting in a black solid (0.1439 g, 47.96%). Single crystals for X-ray structure determination were obtained by slow evaporation of a solution of **2** in 1:1 MeOH / H₂O. IR (neat): $v/cm^{-1} = 3476$, 3210, 2957, 2872, 1672, 1521, 1473, 1453, 1415, 1339, 1317, 1177, 1143, 1109, 1085, 1053, 981, 922, 896, 880, 842, 814, 736, 668. Anal. Calcd for H₄₀C₂₄N₅S₄Ni: H, 6.89; C, 49.23; N, 11.96; S, 21.90. Found: H, 6.81; C, 48.96; N, 11.65; S, 21.64.

Computational Methods

Time-dependent density functional theory (TDDFT)⁶⁷ calculations were performed using the GAUSSIAN 09 package.⁶⁸ The CAM-B3LYP functional⁶⁹ and the 6-31+G(d,p) basis set were used. The solvent was described with the polarizable continuum model (PCM)⁷⁰ using the defaults in Gaussian 09. To be consistent with the experiments, the solvent was chosen to be THF, which has dielectric constants of $\varepsilon_0 = 7.4257$ and $\varepsilon_{\infty} = 1.974025$. For calculations of the vertical excitation energies at the Franck-Condon geometry, we used nonequilibrium linearresponse PCM solvation.⁷¹ Spin-unrestricted calculations were carried out for open shell species.

Results

The results that we present focus on the five protonation/redox states of [Ni(pdt)₂] that are stable at room temperature. Below, we report the structural, electronic, vibrational, and magnetic properties observed for each of these states. Because our focus is on the effects of protonation, we will reference the results with respect to the unprotonated forms of the closed shell (1) and the mixed valence (2) states. Due to the multiple charge states that we explore, change in solubility is a recurring theme, and no single solvent proved ideal for all states under consideration. Throughout, we strive to make clear any changes in solvent that were necessitated by these changes in solubility.

Crystal Structures of 1 and 2

Of the five redox/protonation states discussed in this chapter, we were able to obtain crystals for **1** and **2** that were suitable for X-ray diffraction. While we were unable to determine the structure of any of the protonated states of this molecule, we note that an ethylated analogue of **1-2H** (ethyl groups on the available carbons of the pyrazine ring) was previously synthesized, isolated, and characterized,⁵⁸ and, for that compound, protonation occurs at the nitrogens. An analogue of **1** in which the pyrazine rings are fully substituted with cyano groups has been synthesized previously as well.^{72,73}

Crystals of **1** were obtained by slow evaporation of an acetone solution of **1**, which yielded orange, block-like crystals. The crystal structure can be seen in Figure 2-2, and data refinement parameters are reported in Table 2-1. Selected bond lengths and angles, as well as the shortest S•••S and C•••C distances across the Ni center, are reported in Table 2-2. While this is the first example of crystals of the *tetra*-butylammonium salt of this compound, the *tetra*-

ethylammonium salt is known.^{74,75} As expected, our compound exhibits a very similar structure to that of previous compounds. Here, we briefly highlight the most pertinent features.



Figure 2-2. ORTEP plot of the dianion [Ni(pdt)₂]²⁻ in 1. H atoms are omitted for clarity.

	1	2	
empirical formula	$C_{20}H_{38}N_3Ni_{0.50}S_2$	$C_{24}H_{40}N_5NiS_4$	
formula weight and crystal system	414.01, monoclinic	585.58, triclinic	
color and habit	orange, block	brown, needle	
Temp (K)	298(2)	298(2)	
λ (Å)	0.71073, Μο Κα	0.71073, Mo Kα	
crystal size (mm ³)	0.16 x 0.21 x 0.28	0.29 x 0.03 x 0.01	
space group	$P 2_1/n$	P -1	
a (Å)	7.9683(19)	9.8856(13)	
b (Å)	20.411(5)	10.1476(13)	
<i>c</i> (Å)	14.249(4)	15.386(2)	
α (°)	90	72.931(2)	
β (°)	97.122(5)	79.621(2)	
γ (°)	90	89.431(2)	
$V(\text{\AA}^3)$	2299.5(10)	1449.8(3)	
Z	4	2	
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.196	1.341	
$\mu \text{ (mm}^{-1}$)	0.637	0.979	
no. of reflens collected	15449	13550	
no. of reflens with $I > 2\sigma(I)$	3041	4784	
no. of independent params	236	314	
GOF on F^2	0.996	1.031	

 Table 2-1. Crystallographic data for compounds 1 and 2.

	1		
Ni1-S1	2.1823(10)	C2–C3'	1.418(5)
Ni1-S2	2.1687(9)	S1S2	3.038
S1-C2	1.722(4)	C2•••C3	6.056
S2-C3	1.742(4)		
S1-Ni1-S1'	180.00(2)	S1'-Ni1-S1-C2	-3(100)
S2-Ni1-S2'	180.00(3)	S2'-Ni1-S2-C3	41(100)
S1-Ni1-S2	88.55(4)	N1-C2-S1-Ni1	179.6(2)
S1-Ni1-S2'	91.45(4)	N2-C3-S2-Ni1	-177.4(3)
	2		
Ni1–S1	2.1765(10)	S4C7	1.728(3)
Ni1–S2	2.1587(9)	C5–C7'	1.433(4)
S1C1	1.737(3)	Ni1Ni2	8.36(1)
S2-C2	1.713(4)	S1•••S2'	3.008
C1–C2	1.422(5)	S3•••S4	3.033
Ni2-S3	2.1765(8)	C1•••C2'	6.008
Ni2-S4	2.1752(9)	C5•••C7	6.034
S3C5	1.717(3)		
04 X74 044	100.000(1)		100(100)
SI-NII-SI'	180.000(1)	SI'-NII-SI-CI	132(100)
S2-N11-S2'	180.0	N1-C1-C2-S2	175.1(3)
S1-Ni1-S2	92.13(3)	S1C1C2N2	175.3(2)
S1-Ni1-S2'	87.87(3)	N2-C2-S2-Ni1	-177.8(2)
S3-Ni2-S3'	180.00(5)	N1C1S1Ni1	-175.6(3)
S4-Ni2-S4'	180.00(5)	S4'-Ni2-S4-C7	-28(100)
S3-Ni2-S4'	91.64(3)	S3'-Ni2-S3-C5	120(100)
S3-Ni2-S4	88.36(3)	N4-C7-S4-Ni2	-174.8(2)
S2'-Ni1-S2-C2	-55(100)	N3-C5-S3-Ni2	178.9(2)

 Table 2-2. Selected bond lengths (Å) and angles (deg) for 1 and 2.

Compound 1 exhibits an approximate D_{4h} symmetry about the Ni atom. The deviation from D_{4h} stems from the fact that each dithiolene exhibits two distinct Ni–S bond lengths, which differ by 0.0136 Å between syn Ni–S bonds on the same ligand. This difference is essentially identical to that found for the *tetra*-ethylammonium salt.^{74,75} Recently, several metal dithiolene complexes were synthesized that utilized coordination of Na⁺ cations with the pyrazinic N atoms to form supramolecular structures.^{74,75} This coordination resulted in deviations from planarity in the complexes. In our case, the steric bulk of the cations presumably prevents such coordination, preserving the overall planarity of the complex. The bond distances around the aromatic rings of the complexes exhibit a short-long-short pattern, consistent with a semithionate ligand.^{76,77} Such semithionate character is unusual for a closed shell metal dithiolene, although the coupling between dithiolene ligand and metal is very strong for the case of nickel, and the emergence of semithionate character may simply reflect a large degree of charge donation from the ligand to the metal. However, overall, we find our structure to be consistent with a Ni^{II} center coordinated by two largely unoxidized ligands.

The monoanion salt of $[Ni(pdt)_2]$, compound 2, was synthesized by oxidation with I₂, and crystals suitable for X-ray diffraction were obtained by evaporation of a 1:1 MeOH/H₂O solution. The crystal structure can be seen in Figure 2-3, and data refinement parameters are reported in Table 2-1. Selected bond lengths and angles, as well as the shortest S•••S and C•••C distances across the Ni center, are presented in Table 2-2. Compound 2 exhibits two crystallographically independent monoanion species in [Ni(pdt)₂], as seen in Figure 2-3. Both species possess approximately square planar Ni geometries, with centers of symmetry located at the Ni metal center. One of the monoanion complexes shows a Ni-S bond length difference of 0.002 Å on each dithiolene unit, while the other monoanion complex shows a Ni-S bond length difference of 0.017 Å. Thus, there is a significant difference between the two Ni complexes contained in the unit cell. Within either complex, the two pdt ligands are related by C₂ symmetry, consistent with delocalization of the unpaired electron over both pdt ligands. In addition, neither monoanionic complex exhibits deviations from planarity. As was the case for 1, the bulky tetrabutylammonium cations prevent significant interactions between the monoanions, enforcing a Ni•••Ni distance of 8.36 Å between inequivalent nickel centers.⁷⁷ The bond distances around the aromatic rings exhibit a short-long-short pattern for both crystallographically distinct species of 2, which is consistent with a semithionate.76,77



Figure 2-3. ORTEP plot of the two crystallographically independent [Ni(pdt)₂] monoanions in **2**. H atoms are omitted for clarity.

Comparing **1** to **2**, we find that oxidation of **1** resulted in a decrease of the average C–S bond length, which is expected because of the increased thione character.^{62,78} The C–C bond length of the dithiolene moiety increased with oxidation because of the decreased alkene character.^{55,62} However, these changes in bond length are rather small, consistent with the known behavior of benzenoid-type metal dithiolenes, which tend to resist changes in structure in a redox series.⁵¹ This resistance to structural change is thought to be connected to the strong electronic coupling present in the Ni^{II} dithiolene compounds.

Electrochemistry and pH-Dependent Redox Potentials

The CV of **1** in DMF contains two redox events, as shown in Figure 2-4. A reversible wave is observed at $E_{1/2} = -0.570$ V vs. Fc/Fc⁺, while an irreversible oxidation is observed at $E_{pa} = +0.399$ V vs. Fc/Fc⁺. The reversible event is assigned to the $[Ni(pdt)_2]^{2-/1-}$ couple (conversion between **1** and **2**), and the irreversible oxidation event is assigned to the formation of the unstable neutral species.⁷⁷ The reversible $[Ni(pdt)_2]^{2-/1-}$ couple was previously reported in MeCN.³⁵ Compared to the ethylated analogue of **1**,⁵⁸ the **1**^{2-/1-} couple is shifted to more positive potentials,

fully consistent with the fact that our pyrazine rings do not possess these electron-donating groups.



Figure 2-4. Cyclic voltammograms of **1** in DMF at a scan rate of 100 mVs⁻¹ using 0.1 M Bu_4NPF_6 as electrolyte showing shift with appropriate number of equivalents of aqueous HCl to generate **1-2H**.

Given the square scheme presented in Figure 2-1, it was natural to attempt to generate a Pourbaix diagram for our complex. This diagram requires the acquisition of proton-dependent redox potentials *via* electrochemical titration experiments.⁷⁹ Due to issues of solubility of **1-H** and **1-2H** in water, these experiments were performed in DMF with the addition of aqueous HCl. In general, we found that the redox couples did experience a more positive shift during titration. However, the irreversible event associated with generation of the neutral species from the mixed valence monoanion was quickly pushed outside the solvent window of DMF, forcing us to focus on the $[Ni(pdt)_2]^{2-/1-}$ couple. The endpoint of this titration (**1-2H**) gave well-behaved electrochemistry with $E_{1/2} = -0.065$ V vs. Fc/Fc⁺ (Figure 2-4), and the redox couple of interest was shifted by +0.505 V upon double protonation. The behavior of the electrochemistry at the intermediate states was complex and resulted in CVs with poorly resolved waves (Figure A-1a). Nevertheless, we made an attempt to extract a Pourbaix diagram from the data (Figure A-1b).

Oxidative titration with I₂ was used to follow the conversion from **1** to **2** in THF. The spectra obtained during this conversion are presented in Figure 2-5. We can reproduce the behavior shown in Figure 2-5 using spectroelectrochemical techniques in DMF (Figure A-2). This series of spectra displays isosbestic points, consistent with clean conversion from **1** to **2**. TDDFT calculations were performed to aid in assignment of electronic transitions (see below). The lowest energy band in the electronic absorption spectrum of **1** in DMF is observed at 498 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). In the electronic spectrum of **2** in THF, this band is positioned at higher energy ($\lambda_{max} = 469 \text{ nm}$) with decreased intensity ($\varepsilon = 0.57 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and is discussed as the IVCT transition associated with the mixed valence state. This assignment is consistent with other nickel dithiolene complexes.^{51,55} We also found that the absorbance of all bands scaled linearly with concentration,⁵⁸ indicating that there is no dimerization of this compound.



Figure 2-5. UV-visible spectra during the oxidative titration from 1 to 2 in THF using I_2 as oxidant.

The protonated forms of **1** were found to be insoluble in water, so we performed the titrations in DMF with acid, exploring the use of hydrochloric, trifluoroacetic, and tosylic acids. For the titration of **1**, aqueous HCl gave clean results, and the change in the UV-vis spectrum of **1** upon titration with HCl can be seen in Figure 2-6. Two clean sets of isosbestic points were observed, consistent with two consecutive protonation events. This is also consistent with the behavior of the ethylated analogue of **1**.⁵⁸ The first protonation event generates **1-H** (Figure 2-6a) and results in a large bathochromic shift of the lowest energy band from 498 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^-$ tcm⁻¹) to 610 nm ($\varepsilon = 0.50 \times 10^4 \text{ M}^-$ tcm⁻¹). This band also possesses a shoulder observed at 680 nm ($\varepsilon = 0.34 \times 10^4 \text{ M}^-$ tcm⁻¹). Upon the second protonation event generating **1-2H** (Figure 2-6b), the transition at 610 nm undergoes a hypsochromic shift to $\lambda = 578$ nm ($\varepsilon = 0.97 \times 10^4 \text{ M}^-$ tcm⁻¹), although the energy of this transition is still lower than that found in **1**. Finally, we note that generation of **1-H** results in the appearance of a weakly absorbing peak at 875 nm which remains even after the second protonation event. Due to its location, this band is likely due to a small presence of the oxidized compound **2**.



Figure 2-6. UV-visible spectra taken during spectrophotometric titration of (a) 1 to 1-H and (b) 1-H to 1-2H in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in the plots shown in panels (a) and (b), respectively.

Spectrophotometric titration was performed on 2 as well, following its *in situ* generation. In this case, the spectral response in DMF using aqueous HCl was not well-behaved, but was well-behaved in THF with tosylic acid monohydrate (TsOH \bullet H₂O) as the titrant. One set of isosbestic points is present (Figure 2-7), consistent with clean conversion from the parent mixed valence species 2 to the neutral MVMP state 2-H. During titration, new bands grew in at 622 nm $(\varepsilon = 0.80 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1})$ and 580 nm ($\varepsilon = 0.93 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Of particular note is the shift in the IVCT band from 866 nm ($\epsilon = 1.0 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$) to lower energy at 907 nm ($\epsilon = 0.096 \text{ x } 10^4$ M⁻¹cm⁻¹), accompanied by a drastic decrease in extinction coefficient, upon protonation. This behavior is in sharp contrast to the titration of another open shell nickel dithiolene, one bearing a pyridyl ligand attached to the dithiolene core by a single C-C linkage (denoted 'dangling pyridine').⁵⁵ Although it is unclear in Ref. 55 if the singly protonated (MVMP) state is generated or if titration results directly in the doubly protonated mixed valence system, protonation of this complex results in almost no change to the IVCT band. However, some impact of protonation upon the IVCT band might be expected, and the lack of response to protonation is surprising. It seems likely that this insensitivity to protonation would originate from poor communication between the dithiolene units and the pyridine ring, which might be expected because such indirect attachment of aromatic ligands often results in non-planarity of the molecule. The direct fusing of the nitrogen bases to the dithiolene unit in 2 in our study signifies that strong communication should exist between the basic site and the redox active site, which may account for the larger response of this complex to protonation.

In Figure 2-7, the IVCT band appears to first decrease and then shift to lower energy, which might suggest two separate transformations. However, the appearance of these two stages is an artifact of the large difference in ε_{max} for the IVCT band in 2 and 2-H, and simulation of the conversion between 2 and 2-H (using only spectra for 2 and 2-H) results in reproduction of the spectra obtained during titration (Figure A-3). The implications of this change in the IVCT band

for the electronic coupling in the MVMP state are addressed in the discussion. Lastly, the doubly protonated species was inaccessible in titration experiments. Presumably, our inability to obtain this species is due to a relatively low pK_a associated with this protonation event.



Figure 2-7. UV-visible spectra during spectrophotometric titration of **2** to **2-H** in THF using a solution of TsOH • H_2O in THF as titrant following generation of **2** with I_2 *in situ*.

Solvatochromism of the Electronic Bands

We also acquired electronic spectra of all states (with the exception of 2-H) in multiple solvents, which are presented in the Supporting Information (Figures A-4 – A-7). In all cases, 1 or 2 were dissolved in each solvent, and appropriate equivalents of aqueous HCl were added to generate the species of interest. Although multiple solvents were examined, we only report the results for solvents in which clean isosbestic points were observed. In the case of 2-H, we attempted to add appropriate equivalents of TsOH • H₂O, as well as aqueous HCl, to determine solvent dependence, but only titration in THF showed clean generation of 2-H and retention of the IVCT band.

For the symmetrically protonated/deprotonated states (1, 2, and 1-2H), the only large solvatochromism is a bathochromic shift that accompanies a change from aprotic to protic

solvents. For **2**, this behavior is only observed for the transitions that are not the IVCT transition. We observed no solvatochromism for the IVCT band of **2** (Figure A-7), indicating that there is no change in dipole moment, a hallmark for delocalized (Class III) mixed valence systems. For all other bands associated with the symmetric states, if the identity of the solvent is changed, while maintaining protic or aprotic character, little to no solvatochromism is observed. We calculated values for the ground and excited state dipole moments (Table 2-3), which indicate no change in dipole moment for any of the transitions of these symmetric states. From these observations, it seems likely that the change in energy of these transitions stems from specific chemical interactions (i.e., hydrogen bonding) that stabilize the excited state relative to the ground state, rather than from a solvent response to a change in dipole moment.

If protonation of **1** (or **2**) results in an electronic asymmetry, we would expect a dipole moment for these species, and we might expect an associated solvatochromism in their low energy transitions as seen in the changes in dipole moments associated with these transitions in Table 2-3. The electronic transitions found for the asymmetrically protonated state **1-H** (Figure A-8) display larger solvatochromic responses than the transitions for the symmetrically protonated/deprotonated species. Once again, we find a different response for protic and aprotic solvents, although this is now convoluted by the fact that changing the identity of the aprotic solvent, in particular, results in a solvatochromic response of its own. Interestingly, this response is negative (increasing the polarity of the solvent gives rise to a hypsochromic shift), suggesting that the dipole moment in the excited state associated with these transitions is smaller than the dipole moment of the ground state. This further implies that there must be a permanent dipole moment in the ground state of **1-H**, as would be expected given its asymmetric protonation, which is consistent with our TDDFT calculations.

To aid in the assignment of the electronic transitions upon protonation and oxidation, we performed TDDFT calculations on all five stable states of $[Ni(pdt)_2]$. Molecular orbital calculations for the non-protonated monoanion **2** (but not the protonated form **2-H**) have been reported previously.^{74,75,78} The electronic transitions with non-negligible oscillator strength are listed in Table 2-3. The natural transition orbitals (NTOs) corresponding to these electronic transitions are depicted in Figure 2-8. The isosurfaces of electronic density difference between the ground and excited electronic states are shown in Figure A-8. Spin density plots corresponding to the IVCT transition in compounds **2** and **2-H** are depicted in Figures A-9 and A-10, respectively. Calculated electronic spectra are presented in Figure A-11 in the Supporting Information. The majority of experimental wavelengths were determined for the compounds dissolved in DMF solution, with the exceptions of **2** and **2-H**, which are from spectra acquired in THF solution (titration of **2** to **2-H** is well-behaved in THF and not in DMF). All calculations were performed in THF solution using the nonequilibrium linear response PCM formalism at the CAM-B3LYP/6-31+G(d,p) level of theory. In general, we find reasonable qualitative agreement between the energies of our calculated and experimentally observed transitions.

Compound	λ/nm (calcd)	$\epsilon/10^4 M^{-1} cm^{-1}$ (calcd)	<s<sup>2></s<sup>	$ \mu $ (D)	λ/nm (exp)	$\epsilon/10^4 \mathrm{M}^{-1} \mathrm{cm}^{-1}$ (exp)
				0.0		
1	344	2.86	0.000	0.0	498	1.0
				15.4		
1-H	428	1.57	0.000	6.3	610	0.50
	343	0.80	0.000	6.2	416	0.56
				0.0		
1-2H	406	2.78	0.000	0.0	578	0.97
	329	0.75	0.000	0.0	345	1.9
				0.0		
2	699	0.68	0.795	0.0	866	1.0
	619	0.39	0.785	0.0	469	0.57
				14.4		
2-Н	1106	0.23	0.784	7.5	907	0.096
	673	0.33	0.866	16.4	622	0.80
	582	0.21	1.068	12.0	580	0.93

Table 2-3. Selected calculated and experimental electronic transitions for states of [Ni(pdt)₂].

Note: Experimental transitions were determined in DMF solution for 1, 1-H, and 1-2H, and in THF solution for 2 and 2-H. The calculations were carried out in THF solution using the nonequilibrium linear response PCM formalism with the CAM-B3LYP/6-31+G(d,p) level of theory. Only transitions with calculated excitation wavelengths greater than 320 nm are listed. Note that the last two transitions for 2-H exhibit significant spin contamination. For each compound, the first row in the dipole moment column is the ground state dipole moment, while the other rows in the dipole moment column are excited state dipole moments. The origin used for the dipole moment calculations is the center of nuclear charge. Lorentzian functions with a FWHM of 0.4 eV were used to convolute the calculated line spectra and obtain the molar absorptivity (ϵ) values (Figure S11).



Figure 2-8. Natural transition orbitals representing the dominant electronic transitions of compounds 1, 1-H, 1-2H, 2, and 2-H in solution. These orbitals were obtained with the nonequilibrium LR-PCM TDDFT/CAM-B3LYP/6-31+G(d,p) level of theory at the ground state equilibrium geometries. The natural transition orbitals represent more than $\sim 80\%$ of the transition matrix for each state. Only transitions with calculated excitation wavelengths greater than 320 nm are shown.

We begin the analysis with the electronic transitions for the closed shell states. For 1, the orbital from which the excitation occurs is comprised of the out-of-phase combination of dithiolene ligands, mediated by the d_{xz} and d_{yz} orbitals of the nickel. This type of orbital is the one from which the lowest energy excitation occurs for all closed shell species, and is also the β orbital to which excitation occurs for all of the open shell mixed valence species. For 1, the orbital to which excitation occurs is the symmetric combination of the π^* orbitals of the pyrazine ring, without any contribution from orbitals on the Ni and minimal contribution from the S atoms. Upon the first protonation, leading to 1-H, the degeneracy of the π^* orbitals of the pyrazine rings is broken, with the orbital on the protonated ligand reduced in energy. The second protonation

event (generating 1-2H) re-establishes the symmetry, and the degeneracy of the π^* orbitals of the pyrazine rings is restored. The second transition for 1-H and 1-2H involves excitation from an orbital that is the symmetric combination of the ligand π -system (predominantly on the C-S bonds) out of phase with the metal d_{xz} and d_{yz} orbitals, although the electron density is significantly biased on the protonated ligand in the case of 1-H. The orbital to which excitation occurs remains the same as in the lowest energy transition.

In contrast to 1, 1-H, and 1-2H, the lowest energy transition in the oxidized species 2 involves excitation from an orbital with large π -delocalization over the metal and the S atoms of both dithiolene ligands. Protonation of 2, leading to 2-H, results in this orbital becoming localized on the unprotonated dithiolene ligand. The second transition for 2 involves excitation from an orbital that is an antisymmetric combination of the ligand π -system (predominantly on the C-S bonds). For 2-H, the second and third transitions involve excitation from an orbital with similar character but with more contribution from the metal p_z orbital and negligible electron density on one of the S atoms of the protonated ligand. As mentioned previously, for all dominant transitions of 2 and 2-H, the orbital to which excitation occurs is comprised of the out-of-phase combination of dithiolene ligands, mediated by the d_{xz} and d_{yz} orbitals of the nickel.

Vibrational Spectroscopy: Solution-Phase Raman Spectra of Titration Endpoints

Raman spectra were collected for all five states, and IR spectra were collected for 1 and 2. The use of aqueous titrations prevented the collection of meaningful IR spectra of the protonated species; however, we could still collect their Raman spectra. In order to reduce the number of vibrational bands from the solvent, we focused on using MeOH as a solvent for the Raman studies (in place of DMF or THF) when possible. However, 2-H could only be formed using TsOH • H₂O as titrant in THF. In addition, generation of 1-2H was clean in DMF using

aqueous HCl, while generation of **1-2H** in MeOH was not clean. All Raman spectra of these states in varying solvents are presented in Figure A-12, along with spectra of the pure solvents. IR spectra were collected on neat samples of **1** and **2**, and these spectra are presented in Figure A-13. The most important observation from the study of the vibrational spectra is the lack of splitting in the bands associated with the ligands for **2**. This indicates that the ligands are structurally identical, consistent with the structure reported above and an assignment of electronic delocalization of the unpaired electron, as seen in the change in spin density of **2** upon IVCT excitation (Figure A-9) and the solvent independence of the IVCT band (Figure A-7).

Magnetic Spectroscopy and Shift in g Values upon Protonation

Compound 2 gave a rhombic-type EPR signal when dissolved in THF at 35 K, which can be seen in Figure 2-9. Anisotropic g values were present for this complex, with $g_1 = 2.246$, $g_2 = 2.044$, and $g_3 = 2.021$. These results for 2 are typical for open shell metal dithiolene species.^{46,51,55} We also obtained the EPR spectrum of 2-H, generated by titration of 2 with TsOH • H₂O in THF, which was confirmed by UV-vis spectroscopy prior to acquisition of the EPR spectrum. The protonated complex 2-H exhibited a rhombic-type signal similar to that of 2. The g values of 2-H were found to be $g_1 = 2.237$, $g_2 = 2.044$, and $g_3 = 2.016$. The values of g_1 and g_3 were shifted to slightly lower g values compared to 2, but the value of g_2 remained identical. Addition of aqueous NaOH to a solution of 2-H allowed us to recover the signal associated with 2, confirming the reversibility of the $2 \rightarrow 2$ -H transformation. We note that protonation of 2 results in smaller changes to the diagonal elements of the g-tensor than observed for protonation of other open shell dithiolene complexes.⁵⁵ The origin of this difference in g-shift is unknown.



Figure 2-9. EPR spectra of 2 and 2-H dissolved in THF at 35 K. 2-H was generated by addition of TsOH \cdot H₂O in THF.

Finally, we note that we are able to obtain reasonable NMR spectra of states 1, 1-H, and 1-2H, but not of states 2 or 2-H. This supports the assignment of 1, 1-H, and 1-2H as closed shell systems and 2 and 2-H as open shell systems.

Discussion

The goal of this work was to generate a complex with both mixed valence and MVMP states so that the electronic coupling in these two states could be compared *via* analysis of their IVCT bands. To this end, we begin the discussion by demonstrating that we have made the MVMP state. (Recall that the pure mixed valence state **2** was crystallized.) We then discuss the degree of electronic coupling for the pure mixed valence state **2** and the MVMP state **2-H**, where we conclude that the electronic coupling is severely curtailed upon protonation of the mixed valence state. Finally, we discuss the possible origins of this loss of electronic coupling.

Generation of 2-H

Though we have been unable to structurally characterize the MVMP state (2-H), the evidence that we have generated it *in situ* is compelling. This evidence begins with the EPR spectra (Figure 2-9), which clearly indicate that the new state generated by addition of TsOH \bullet H₂O to **2** retains unpaired spin. In addition, we reiterate that **2-H** does not yield an NMR spectrum. Together, these observations restrict the possible identity of the new state to the second row of the square scheme (Figure 2-1). We note that the EPR intensity of the protonated species is significantly decreased from that of the monoanion **2**. It is tempting to interpret the reduction in signal intensity in the EPR as the fact that protonation results in two species, only one of which is EPR-active. However, we note that our UV-vis titration yielded clean isosbestic points, and addition of base to a solution of **2-H** will reclaim both the starting UV-vis and EPR spectra associated with **2**. Thus, we conclude that it is more likely that a single species (**2-H**) is made, and that this simply has reduced intensity in the EPR.

Moving on to the spectrophotometric titration of **2** generated from oxidative titration of **1** with I_2 *in situ* (Figure 2-7), we observe a single set of isosbestic points during this titration, consistent with clean conversion between two species. This titration is also reversible. Given the manner in which our titrations were performed, their reversibility indicates that the product of this titration is stable on a timescale of hours. In addition, the electronic spectra of all five states (Figure 2-6) confirm that the product of the titration of **2** is also distinct from the other states that we were able to generate in a clean and reversible manner,⁵⁸ making it clear that addition of TsOH • H₂O to **2** generates a species that is distinct from **1**, **1-H**, **1-2H**, or **2**. Moreover, the retention of the IVCT band, albeit shifted to 907 nm, attests to the continued presence of the mixed valence species. Finally, we note that the observed electronic spectra are qualitatively consistent with the calculated spectra (Figure A-11).

Examining the literature, it is possible that we could be protonating the S atoms of the dithiolene core during the titration experiments.^{53,80-82} In order to rule this out, we performed identical titration experiments on the mixed valence complex $(Bu_4N)[Ni(bdt)_2]$ (bdt = benzenedithiol), which does not possess nitrogen basic sites.^{53,83} The IVCT band of this complex remained unchanged upon addition of acid (Figure A-14), indicating that the nitrogen sites are needed to observe the spectral changes in **2**. In total, all of this evidence implies that we have generated **2-H**, in which a single nitrogen site is protonated, and we move on to quantification of the effects of protonation upon electronic coupling when moving from **2** to **2-H**.

Electronic Coupling in State 2

We will discuss the properties of the mixed valence states within the confines of the twostate Marcus-Hush treatment of inner sphere electron transfer.⁸⁴⁻⁸⁹ Our determination of electronic coupling comes from the analysis of the IVCT band at 866 nm in THF solution for **2** (Figure 2-5). As illustrated in Figure A-7, the position of this IVCT band is invariant with changes in solvent. Based upon the solvent independence, an assignment to Robin-Day Class III, or a delocalized electronic state, seems appropriate for **2**.⁸⁸ Such an assignment is supported by the shape and intensity of the IVCT band, which presents very asymmetric character and consists of at least two components.⁸⁶ There are two possible sources for this asymmetry: either it results from vibronic progression in a single transition, or it results from multiple overlapping transitions. However, either origin of asymmetry is consistent with Class III assignment.

It is worth noting that there is an intermediate class between Class II and Class III – the so-called Class II-III that contains those complexes that have features of both delocalized and localized electrons.^{23,86,90,91} This intermediate class arises for systems in which the timescale of the solvent dipolar relaxation is much slower than the timescale of the internal molecular

vibrations, and the ET occurs on an intermediate timescale in between these two timescales. In such a case, the complex would possess a solvent-independent IVCT band (Class III behavior), while simultaneously displaying vibrational modes associated with both oxidized and non-oxidized redox sites (Class II behavior). However, our vibrational spectra do not support assignment of localized charge on the vibrational timescale. Thus, the solvent independence of the IVCT band, the presentation of the IVCT band, and the vibrational spectrum support the assignment of **2** as a Class III, fully delocalized, mixed valence state.

The assignment of **2** as Class III within the Robin-Day scheme allows for straightforward determination of the magnitude of electronic coupling (H_{AB}) using Equation 2-1:⁸⁶

$$H_{AB} = \frac{v_{max}}{2} \tag{2-1}$$

where v_{max} is the energy associated with the maximum absorption of the IVCT band. We find that the electronic coupling for **2** is equal to 5800 cm⁻¹ in THF. This value of electronic coupling is quite large, but it is consistent with that found for other Class III systems.^{42,43,92,93} In addition, such a large value of the electronic coupling is logical given the fact that the "bridge" is a single Ni atom.

Electronic Coupling in State 2-H

The IVCT band of **2-H** can also be used to determine the magnitude of the electronic coupling in this complex. However, because we are dealing with the MVMP state, we must consider the asymmetry of the complex. In particular, if the Franck-Condon principle holds, then the electronic transition will proceed without a change in the position of the nuclei, including the proton attached to the nitrogen base. This, in turn, means that the two redox states involved in transfer of an electron are no longer energetically degenerate (Figure 2-10). The electrochemical data (Figure 2-4) shows an increase in redox potential of ~0.5 V upon protonation, so we can

provide a zeroth-order estimate that the energetic asymmetry between redox isomers is also ~ 0.5 V. Although this is a crude approximation, similar analysis has been performed for other mixed valence systems.⁹⁴



Figure 2-10. Free energy surfaces (diabatic surfaces are shown in black and adiabatic surfaces are shown in red) involved in electron transfer for both the (a) mixed valence and (b) MVMP states. The primary difference is that the asymmetric protonation in the MVMP state creates an energetic difference between the product and reactant wells, which affects the IVCT transition.

The asymmetric character of the ground state free energy surface has several important implications. Even in the delocalized limit, the free energy surface will be asymmetric, meaning that the complex will have a permanent dipole moment. Thus, for Classes I, II, and III, we expect that the IVCT transition will proceed with a change in dipole moment, and solvent independence of the IVCT band is no longer a requirement for asymmetric Class III molecules. In addition, because the ground and excited state minima can be offset from one another (Figure 2-10b), we do not necessarily expect asymmetric IVCT bands. Thus, an asymmetric IVCT band is also no longer a requirement of asymmetric mixed valence systems as Class III. In total, this situation conspires to make assignment of the complex as Class II or Class III difficult, and perhaps even meaningless, for mixed valence complexes with large energetic asymmetries.

Nevertheless, we can analyze the IVCT band to obtain estimates of the electronic coupling using Equation 2-2:⁸⁶

$$H_{AB} = \frac{|\mu_{12}|}{er_{ab}} \nu_{max}$$
(2-2)

where $|\mu_{I2}|$ is the transition dipole moment of the IVCT band, which can be obtained from the integrated intensity, *e* is the elementary charge of an electron, and r_{ab} is the distance between the two redox sites. Equation 2-2 is valid for both symmetric and asymmetric complexes, spanning Class II and Class III systems. However, the use of this equation requires an estimation for the distance between redox sites r_{ab} , a quantity that is notoriously difficult to estimate.⁸⁶ Fortunately, given the similarities between the complexes **2** and **2-H**, we can use our analysis of **2** to provide an estimation of this distance. To do so, we use the value of H_{AB} obtained from Equation 2-1 to solve for r_{ab} in **2**, using Equation 2-2. This requires a value for $|\mu_{I2}|$, which can be obtained by integration of the IVCT band (Figure A-15) and was found to be 8.5 x 10⁻²⁸ Cm. This approach provides a value of 4.94 Å for r_{ab} , which is fully consistent with assignment of the dithiolene carbons across the nickel are 3.021 Å and 6.021 Å, respectively. Using this value of r_{ab} , we then use Equation 2-2 to solve for H_{AB} for the complex **2-H**, providing a value of 1200 cm⁻¹, which is almost a factor of five smaller than that observed for **2**. Thus, we conclude that protonation of the complex results in a significant curtailing of the electronic coupling between pdt ligands.

Impact of Protonation upon Electronic Coupling

The reduction of electronic coupling upon protonation deserves further comment. There are two potential reasons why one might expect this result. The first possibility is that the IVCT excitation is accompanied by PT, therefore comprising a PCET process. Such a transition would result in a small Franck-Condon overlap between the initial proton vibrational wavefunction on the reactant electronic diabat and the final proton vibrational wavefunction on the product

electronic diabat. The small Franck-Condon overlap would then reduce the effective coupling in the system, which would result in a decrease in the intensity of the IVCT absorption band, as shown in Equation 2-3:⁹⁵

$$V_{AB} = \int \psi_A^* H \psi_B d\tau \approx \int \psi_A^{el*} H^{el} \psi_B^{el} d\tau_e \int \psi_A^{p*} \psi_B^p d\tau_p = H_{AB} S_{AB}$$
(2-3)

where ψ_i , ψ_i^{el} , and ψ_i^p are the *i*th vibronic, electronic, and proton vibrational wavefunctions, respectively, *H* is the vibronic Hamiltonian, H_{AB} remains the electronic coupling, and S_{AB} is the Franck-Condon overlap between the proton vibrational wavefunctions. Thus, the Franck-Condon overlap for PT could *potentially* influence the apparent electronic coupling affecting the IVCT band.

In order to test the validity of this explanation, we calculated the proton potentials associated with the ground and IVCT adiabatic electronic states, which provide insight into the corresponding diabatic electronic states (Figure 2-11, as well as Figure A-16). Here, the proton is transferring from the protonated nitrogen to a hydrogen-bonded water molecule. We found that the proton potentials are very similar for the ground and excited electronic adiabatic states, implying that the proton potentials for the corresponding electronic diabats will also be very similar at the equilibrium ground state geometry in solution. As a result, the Franck-Condon overlap between the ground proton vibrational states of the two diabatic electronic states will be nearly unity. Therefore, we conclude that PT is not involved in the vertical IVCT excitation, and the Franck-Condon overlap associated with PCET is a negligible source of the change in the IVCT band and corresponding electronic coupling.


Figure 2-11. Proton potentials for the ground (dashed) and excited (solid) electronic adiabatic states at the equilibrium ground state geometry in solution calculated by moving the proton bonded to nitrogen to a hydrogen-bonded water molecule with all other nuclei fixed and either one (red) or three (blue) explicit water molecules.

In the absence of PCET, the IVCT transition involves only ET, and the free energy surfaces associated with this transition are those shown in Figure 2-10b. The most striking aspect of these surfaces is the large energetic asymmetry between the diabatic states, brought about by asymmetric protonation of the complex. This energetic asymmetry is also associated with an asymmetry in electron density, which can be seen in Figure 2-8, as well as Figures A-9 and A-10. The asymmetry in electron density, in turn, will result in a decrease in electronic wavefunction overlap between the diabatic states and a decrease in the electronic coupling. Thus, we conclude that, for **2-H**, the proton creates a large electronic asymmetry that results in a 5-fold decrease in electronic coupling, producing the observed loss in the intensity of the IVCT transition.

The previously studied nickel dithiolene complex with a dangling pyridyl group attached to the dithiolene unit also has a protonated mixed valence state.⁵⁵ In comparison to the behavior of that complex, the observed change in IVCT band intensity for **2** is extremely large. Indeed, the IVCT band of the dangling pyridyl complex displayed almost no change upon protonation, indicating virtually no loss in electronic coupling upon protonation. More work will need to be done to definitively establish the origin of this difference in behavior; however, it seems likely

that the separation of the basic site from the redox active site by a C-C linkage effectively decouples the protonation event from the redox center, allowing the complex to preserve electronic coupling upon protonation.

Given the above discussion, we return to the inspiration for the work: understanding the effect of protonation upon electronic coupling in systems capable of electron transfer. Given that electron mobility is tied to electronic coupling and that electron and proton mobility are interdependent in PCET complexes, the above analysis leads to a prescription for promoting charge mobility in PCET systems. Namely, it would be wise to decouple the electron and proton transfers to some extent. Thus, there should be some optimal strength of coupling between electron and proton transfers that will lead to the greatest mobility of these charges. Future work from our laboratory will be directed toward the design and synthesis of molecules that will maximize charge mobility in these complexes.

Conclusions

Understanding the behavior of systems undergoing ground state PCET will be critical for the design and manufacture of devices built upon such processes. In this chapter, we have presented the synthesis and characterization of five redox/protonation states of the complex [Ni(pdt)₂]. This complex functions as a simple molecular model for examining the impact of protonation upon the electronic coupling that controls electron transfer dynamics in both mixed valence and PCET complexes. For all five states we examined, we presented electrochemistry, as well as UV-vis, EPR, and calculated absorption spectra supporting our ability to generate these states. The focus of our work was on comparing the properties of the pure mixed valence (2) and MVMP (2-H) states, especially with respect to electronic coupling. We find that, while the Class III mixed valence state, 2, presents a strong IVCT transition associated with strong electronic coupling between the redox sites, generation of **2-H** results in a drastic reduction in the electronic coupling (which is indicated by a red-shift and a decrease in intensity for the IVCT band). Consideration of the most likely explanations for this reduction in electronic coupling suggests that asymmetric protonation lends asymmetry to the free energy surfaces and electronic orbital distributions, thereby decreasing the apparent electronic coupling. The extent of the asymmetry is expected to be directly related to the degree to which the redox and protonation events are energetically interdependent. This result suggests that, when attempting to maximize charge mobility in systems involving proton-coupled electron transfer, a balance must be struck between coupling of the electron and proton transfers and the charge pinning that results from this coupling.

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Appendix A: Supporting Information for [Ni(pyrazinedithiol)₂]



Figure A-1. (a) Change in the -2/-1 redox wave upon protonation of **1** following addition of aqueous HCl. Trials were performed in DMF at a scan rate of 100 mVs⁻¹ using 0.1 M Bu₄NPF₆ as electrolyte. (b) Pourbaix diagram of the -2/-1 redox wave of **1** following addition of aqueous HCl. pH was used as an indicator of acid content despite the solvent consisting of predominantly DMF. A kink in the diagram indicates the difficulty in resolving multiple redox events.



Figure A-2. Electrochemical conversion from 1 to 2 using 0.1 M Bu_4NPF_6 as electrolyte in DMF.



Figure A-3. Simulated conversion of 2 to 2-H using combined percentages of the endpoint spectra (2 and 2-H) in THF.



Figure A-4. Spectra of 1 dissolved in various solvents.



Figure A-5. Spectra of 1-H dissolved in various solvents.



Figure A-6. Spectra of 1-2H dissolved in various solvents.



Figure A-7. Spectra of 2 dissolved in various solvents.



Figure A-8. For the five accessible states of $[Ni(pdt)_2]$, isosurfaces of electronic density differences between the lowest-lying excited electronic states and the ground state. The electronic densities were obtained with the PCM DFT/CAM-B3LYP/6-31+G(d,p) method for the ground state and the nonequilibrium LR-PCM TDDFT/CAM-B3LYP/6-31+G(d,p) method for the excited states. The isosurfaces of 0.001 and -0.001 Bohr⁻³ are depicted in turquoise and violet, respectively. For compound 1, λ_{exc} =344 nm for the depicted isosurface. The depicted isosurfaces (from top to bottom) correspond to λ_{exc} values of 428 nm and 343 nm for compound 1-H, 406 nm and 329 nm for compound 1-2H, 699 nm and 619 nm for compound 2, and 1106 nm, 673 nm and 582 nm for compound 2-H.



Figure A-9. For compound 2, the change in spin density upon IVCT excitation at a calculated wavelength of 699 nm.



Figure A-10. For compound **2-H**, the change in spin density upon IVCT excitation at a calculated wavelength of 1106 nm.



Figure A-11. Calculated spectra of closed shell (a) and open shell (b) species of different protonation states, and experimental spectra of closed shell (c) and open shell (d) species. Experimental closed shell species were studied in DMF, and experimental open shell species were studied in THF. All transitions with oscillator strength greater than 0.025 and with negligible spin contamination were used to calculate the convoluted spectra.



Figure A-12. Raman spectra of states of $[Ni(pdt)_2]$ dissolved in (a) MeOH. (b) THF, and (c) DMF, and Raman spectra of pure solvents (d).



Figure A-13. IR spectra of 1 and 2.



Figure A-14. UV-visible titration of $(NBu_4)[Ni(bdt)_2]$ in THF with aqueous HCl. Minimal change is observed in the IVCT band.



Figure A-15. Integration of the IVCT band was done by plotting the experimental spectra in terms of molar extinction coefficient as a function of wavenumber. We then fit this experimental spectra (solid black) to three Gaussian bands (Gaussian1, Gaussian2, and Gaussian 3). The sum of these bands is labeled Sum (solid red line) and provides the value for the integration of the band. The residuals (solid green line) between the sum and the experimental data shows the quality of fit, and resulting integration.



Figure A-16. Proton potentials calculated by moving the proton bonded to the nitrogen atom to a hydrogen-bonded water molecule with all nuclei except hydrogen atoms fixed for the ground (dashed) and excited (solid) electronic adiabatic states with either one (red) or three (blue) explicit water molecules at the equilibrium ground state geometry in solution.

Chapter 3

Steady-State Spectroscopic Analysis of Proton-Dependent Electron Transfer on Pyrazine-Appended Metal Dithiolenes [Ni(pdt)₂], [Pd(pdt)₂], and [Pt(pdt)₂] (pdt = 2,3-pyrazinedithiol): Effect of Changing Bridging Metal Center

This chapter is adapted from:

Kennedy, S. R.; Kozar, M. N.; Yennawar, H. P.; Lear, B. J. Inorg. Chem. 2016, Submitted.

Introduction

In the ground state, the compound poised to undergo PCET¹⁻⁹ will necessarily exist as an asymmetrically protonated mixed valence species, a state we have termed MVMP.¹⁰ Together, the mixed valence/MVMP states of molecules function as a model system for understanding one aspect of PCET: the effect that asymmetric protonation has on ground state electron mobility. We have just seen that the IVCT band for both mixed valence^{11–20} and MVMP states is a useful probe of electronic coupling for determining the impact of asymmetric protonation. We found that asymmetric protonation drastically reduces the electronic coupling,¹⁰ but we have not yet seen how control over this change in electronic coupling can be influenced by the design of the MVMP system.

In mixed valence chemistry, structural changes, either through changes to the bridge or redox sites, can modulate the electronic coupling.^{18,20–26} In a similar fashion, we propose that modifications to the bridge of MVMP molecules used to study ground state PCET will result in analogous control of PCET properties. In essence, we seek to establish the IVCT band, with a

possible proton transfer coordinate imposed by the MVMP state, as a probe for interrogating the changes in electronic coupling in the MVMP state arising from structural modification of the bridge.



Figure 3-1. (left) Structure of $[M(pdt)_2]$ where M = Ni, Pd, and Pt. (right) Square scheme of two redox events and two protonation events for $[M(pdt)_2]$.

Because our prior work showed that protonation^{27–32} of pyrazine-appended metal dithiolene complexes (Figure 3-1) changed the electronic coupling between ligands,¹⁰ we sought to understand the role of the mediating bridge in controlling this change in electronic coupling³³⁻³⁵ by extending our studies on the Ni complex (1) to the analogous Pd and Pt complexes (2) and (3), respectively. In dithiolene complexes, the metal center functions as this bridge between the redox-active ligands,³⁶ which allows for the study of alternate bridges simply by synthesizing complexes with different metal centers. Specifically, we hypothesize that complexes with greater electronic coupling between ligands in the pure mixed valence state would more strongly resist changes to electronic coupling upon protonation. In this chapter, we describe our efforts to test this hypothesis by studying the behavior of the IVCT bands of the Pd and Pt complexes in their mixed valence and MVMP states.

Experimental

Materials and Methods

NaSH • xH₂O, PdCl₂, PtCl₂, and Bu₄NBr were purchased from Sigma Aldrich, and 2,3dichloropyrazine was purchased from TCI. NaOEt was purchased from Strem Chemicals, and I_2 was purchased from Acros. Anhydrous sodium sulfate was purchased from EMD, and TsOH • H₂O was purchased from Fisher Scientific. All solvents were used without further purification. IR spectra were acquired using a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer equipped with an ATR accessory. NIR spectra were recorded on the same instrument, but in transmission mode, using a quartz cuvette. ¹H NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer in d_6 -DMSO, and the residual solvent peak was used as the internal standard. EPR spectra were recorded using a Bruker ESP 300 spectrometer with samples dissolved in tetrahydrofuran (THF) at 35 K. Protonated samples were obtained by titration with TsOH • H₂O in THF and were monitored by UV-visible spectroscopy prior to acquisition of EPR spectra. UV-visible spectra were acquired using an Agilent 8453 spectrometer with a 1 cm path length quartz cell. Electrochemical measurements were made in N,N'-dimethylformamide (DMF) using a Pine WaveNow potentiostat under inert atmosphere. A Pt wire was used as the working electrode, a separate Pt wire was used as the auxiliary electrode, and a Ag/Ag⁺ wire was used as the pseudo-reference electrode. 0.1 M tetra-butyl ammonium hexafluorophosphate was used as the electrolyte, and the Fc/Fc^+ redox couple was used as an internal standard. Crystals for compounds 2 and 3 were grown as described below, and the structure of $(Bu_4N)_2[Ni(pdt)_2]$ (1) was reported previously.¹⁰ The X-ray structures were determined using a Bruker SMART APEX CCD area detector equipped with a graphite monochromator, a Monocap collimator, and a MoK $_{\alpha}$ fine-focus sealed tube. A narrow-frame integration algorithm with the Bruker SAINT software

package was used to integrate the frames. Structures were solved and refined using the Bruker SHELXTL (Version 6.1) software package. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of $(Bu_4N)_2[Pd(pdt)_2]$ (2)

2.3-pyrazinedithiol was synthesized according to existing literature procedures as well as our previous description^{10,37–41} The Pd complex (Bu₄N)₂[Pd(pdt)₂] (2) was synthesized according to a modified literature procedure analogous to the Ni complex.^{10,40,42} 2,3-pyrazinedithiol (0.5123 g, 3.552 mmol) was dissolved in 250 mL MeOH containing NaOEt (0.49 g, 7.2 mmol). PdCl₂ (0.3169 g, 1.787 mmol) was added while stirring, and the mixture turned brown-yellow. The mixture was left to stir for 2 hrs, and the solvent was removed *in vacuo*. The resulting solid was redissolved in 200 mL EtOH and filtered. The solvent was again removed in vacuo. The solid was dissolved in 80 mL water and transferred to a separatory funnel. A solution of Bu4NBr (1.1523 g, 3.574 mmol) was prepared in 100 mL CHCl₃. The product was extracted using the $CHCl_3$ solution (5 x 20 mL), and the combined organic layers were washed with water (3 x 20 mL). The organic layers were dried over Na_2SO_4 , and the solvent was removed *in vacuo* to give an orange solid. The solid was recrystallized from acetone by slow evaporation to give orange, needle-like crystals (0.9377 g, 59.91%). ¹H NMR (*d*₆-DMSO): 7.46 ppm (s, 4 H), 3.16 ppm (t, 16 H), 1.56 ppm (m, 16 H), 1.31 ppm (m, 16 H), 0.94 ppm (t, 24 H). IR (neat): $v/cm^{-1} = 2960, 2871$, 1463, 1405, 1381, 1313, 1295, 1274, 1144, 1065, 1045, 881, 814, 738. Anal. Calcd for H₇₆C₄₀N₆S₄Pd: H, 8.75; C, 54.86; N, 9.60; S, 14.65. Found: H, 8.70; C, 54.85; N, 9.63; S, 14.62.

Similarly to the Pd complex, the Pt complex (Bu₄N)₂[Pt(pdt)₂] (3) was also synthesized according to a modified literature procedure analogous to the Ni complex.^{10,40,42} 2.3pyrazinedithiol (0.5929 g, 4.111 mmol) was dissolved in 250 mL MeOH containing NaOEt (0.56 g, 8.2 mmol). PtCl₂ (0.5506 g, 2.070 mmol) was added while stirring, and the mixture turned dark red. The mixture was left to stir for 2 hrs, and the solvent was removed in vacuo. The resulting brown solid was redissolved in 200 mL EtOH and filtered. The solvent was again removed in vacuo. The solid was dissolved in 100 mL water and transferred to a separatory funnel. A solution of Bu₄NBr (1.1358 g, 3.523 mmol) was prepared in 100 mL CHCl₃. The product was extracted using the CHCl₃ solution (5 x 20 mL), and the combined organic layers were washed with water (3 x 20 mL). The organic layers were dried over Na₂SO₄, and the solvent was removed in vacuo to give a brown solid (1.5585 g, 78.07%). Crystals suitable for single crystal X-ray structure determination were obtained by slow evaporation of acetone. ¹H NMR (*d*₆-DMSO): 7.47 ppm (s, 4 H), 3.16 ppm (t, 16 H), 1.55 ppm (m, 16 H), 1.28 ppm (m, 16 H), 0.91 ppm (t, 24 H). IR (neat): $v/cm^{-1} = 2959$, 2872, 1468, 1405, 1380, 1312, 1294, 1141, 1068, 1045, 882, 813, 739. Anal. Calcd for H₇₆C₄₀N₆S₄Pt: H, 7.94; C, 49.82; N, 8.71; S, 13.30. Found: H, 7.68; C, 49.45; N, 8.52; S, 13.36.

Results

Crystal Structures of 2 and 3

While the [Ni(pdt)₂] complex has been previously crystallized with *tetra*-ethylammonium counterions by others^{43,44} and with *tetra*-butylammonium counterions by ourselves,¹⁰ the Pd and Pt versions of this complex are not presented in the literature. However, the ethyl-substituted

analogue for both metals^{32,45} and the cyano-substituted analogue for Pd^{46,47} have been previously described.

Crystals of **2** and **3** were obtained by evaporation of acetone solutions of each compound. Compound **2** gave orange, needle-like crystals, while compound **3** gave red, rod-shaped crystals. The crystallographic data collection parameters are shown in Table 3-1, and selected bond lengths and angles are shown in Table 3-2. ORTEP diagrams of **2** and **3** can be seen in Figures 3-2a and 3-2b, respectively.

	2	3
empirical formula	$C_{20}H_{38}N_3Pd_{0.50}S_2$	$C_{40}H_{76}N_6PtS_4$
formula weight and crystal system	437.88, monoclinic	964.41, monoclinic
color and habit	orange, needle	red, rod
Temp (K)	298(2)	298(2)
λ (Å)	0.71073, Mo Ka	0.71073, Μο Κα
crystal size (mm ³)	0.22 x 0.07 x 0.02	0.27 x 0.18 x 0.12
space group	$P 2_1/n$	$P 2_1/n$
a (Å)	8.0923(8)	8.2394(15)
<i>b</i> (Å)	20.2213(19)	20.015(4)
<i>c</i> (Å)	14.3201(14)	14.350(3)
α (°)	90	90
β (°)	98.568(2)	99.736(4)
γ (°)	90	90
V (Å ³)	2317.1(4)	2332.3(7)
Z	4	2
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.252	1.33
$\mu (\text{mm}^{-1})$	0.614	3.219
no. of reflens collected	22114	15944
no. of reflexs with $I > 2\sigma(I)$	3777	2939
no. of independent params	236	234
GOF on F^2	1.071	0.965

Table 3-1. Crystallographic data for Compounds 2 and 3.

		2					
	Pd1-S1	2.2909(11)	S2-C2	1.734(5)			
	Pd1-S2	2.3015(12)	C2–C3'	1.416(6)			
	S1-C3	1.746(5)					
	S1-Pd1-S1'	180.00(3)	S1'-Pd1-S1-C3	-114(80)			
	S2-Pd1-S2'	180.000(1)	S2'-Pd1-S2-C2	128(95)			
	S1-Pd1-S2	91.09(4)	N2-C3-S1-Pd1	-177.6(3)			
	S1-Pd1-S2'	88.91(4)	N1-C2-S2-Pd1	179.6(3)			
3							
	Pt1-S1	2.294(2)	S2-C2	1.757(9)			
	Pt1–S2	2.2892(19)	C1–C2'	1.400(11)			
	S1-C1	1.746(8)					
	S1-Pt1-S1'	180.00(5)	S1'-Pt1-S1-C1	179(100)			
	S2-Pt1-S2'	180.0	S2'-Pt1-S2-C2	-13(91)			
	S1-Pt1-S2	91.02(7)	N2-C1-S1-Pt1	-179.9(5)			
	S1-Pt1-S2'	88.98(7)	N1-C2-S2-Pt1	-178.2(7)			

Table 3-2. Selected bond lengths (Å) and angles (deg) for 2 and 3.



Figure 3-2. ORTEP plots of the dianion $[M(pdt)_2]^{2-1}$ in **2** (a) and **3** (b). H atoms are omitted for clarity.

Both **2** and **3** possess D_{4h} symmetry around the central metal atom. For both compounds, the asymmetric fragment is represented by one side of the mirror plane that bisects the pyrazine rings through the metal atoms. Each S-M-S bond across the metal atom is 180°, and the metal dithiolene core shows no deviation from planarity. Adjacent S-M-S angles show slight variations around the metal center, with angles of 91.09° and 88.91° in **2** and 91.02° and 88.98° in **3**. Average C-S bond lengths are 1.740 Å in **2** and 1.752 Å in **3**, fully consistent with the presence of

dithiolate character in metal dithiolene dianions.^{10,33} For comparison, the average C-S bond length in **1** is 1.732 Å,¹⁰ indicating that dithiolate character is increasing moving down the group, reflecting the decrease in Lewis acidity of the metal center.

Electrochemistry and Group Trends

Cyclic voltammograms (CVs) of 1,¹⁰ 2, and 3 in DMF are shown in Figure 3-3. All three CV's show two redox events, consistent with the capability of metal dithiolenes to undergo multiple redox events. The peak-to-peak separation for these events is consistent with the assignment of these events as involving single electron transfer, and we find that the redox event associated with the [M(pdt)₂]^{2-/1-} couple is reversible in all cases (1, 2, and 3), while the redox event associated with the [M(pdt)₂]^{1-/0} couple is irreversible in all cases.



Figure 3-3. Cyclic voltammograms of **1**, **2**, and **3** in DMF at a scan rate of 100 mVs⁻¹ using 0.1 M Bu₄NPF₆ as electrolyte. The cyclic voltammogram of **1** is included for comparison from ref 10.

In comparing redox potentials, we only consider the reversible $[M(pdt)_2]^{2-/1-}$ couples, the potentials of which are reported in Table 3-3. The previously measured value for the redox

potential of **1** is $E_{1/2} = -0.570$ V vs. Fc/Fc⁺.¹⁰ The Pd complex **2** gave $E_{1/2} = -0.288$ V vs. Fc/Fc⁺ for conversion to the monoanion, and the Pt complex **3** gave $E_{1/2} = -0.437$ V vs. Fc/Fc⁺. The $[M(pdt)_2]^{2-/1-}$ couple follows the order of metal center as Ni<Pt<Pd, indicating that the HOMO is most stabilized by the Pd metal center and least stabilized by the Ni metal center.^{33,48} This trend is consistent with the electronic spectra obtained for these complexes, as described next.

Compound	-2/-1 $E_{1/2}$ /V vs. Fc/Fc ⁺	IVCT λ_{max}/nm	IVCT $\epsilon/10^4 M^{-1} cm^{-1}$	H_{AB}/cm^{-1}	r _{ab} /Å	$ \mu_{12} /C^{*}cm$
1	-0.570	866	1.0	5800	4.94	4.0 x 10 ⁻²⁷
2	-0.288	1119	1.0	4500	6.47	5.2 x 10 ⁻²⁷
3	-0.437	876	1.6	5700	6.10	4.9×10^{-27}
1-H ⁰		907	0.096	1200	4.94	8.5 x 10 ⁻²⁸
2-H ⁰		_	_	_	_	_
3- Н ⁰		877	0.27	1200	6.10	1.1 x 10 ⁻²⁷

Table 3-3. Redox potentials of the reversible -2/-1 couple and electronic absorption parameters for the IVCT bands of the MV and MVMP states of 1, 2, and 3.[†]

Electronic Spectroscopy: Spectrophotometric Acid Titrations

In order to gain insight into the effects of protonation upon the closed shell states of the complexes, we performed spectrophotometric acid titration experiments on **2** and **3** using aqueous HCl in DMF (Figures B-1 and B-2, respectively). The spectra for each protonation state are shown in Figure 3-4, where they are also compared to the spectrum of **1**, which was obtained previously.¹⁰ During titration, both compounds **2** and **3** gave two sets of clean isosbestic points, consistent with two protonation events throughout the titration, as seen for the ethyl-substituted analogues.³² The electronic spectrum of the Pd complex **2**²⁻ (Figure 3-4a) exhibits an absorbance at 438 nm ($\varepsilon = 1.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), which is assigned as the HOMO \rightarrow LUMO transition.^{10,33,49} After the first protonation event to generate **2-H**⁻, two absorbance bands are present at 384 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 526 nm ($\varepsilon = 0.69 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) (Figure 3-4b). The second protonation

event shows the low energy band in **2-H**⁻ shifting to higher energy and partially resolving into two bands at 491 nm ($\epsilon = 1.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 520 nm ($\epsilon = 1.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) as **2-2H**⁰ is formed (Figure 3-4c).



Figure 3-4. (a) UV-visible spectra of 1^{2-} , 2^{2-} , and 3^{2-} dissolved in DMF. Upon spectrophotometric titration using aqueous HCl, we acquire spectra for (b) 1-H⁻, 2-H⁻, and 3-H⁻, followed by (c) 1-2H⁰, 2-2H⁰, and 3-2H⁰. Spectra of 1 were originally reported in ref. 10 and are included to facilitate comparison.

The behavior of 3^{2-} upon acid titration in DMF is similar to that of 2^{2-} . The HOMO \rightarrow LUMO transition absorbance band of 3^{2-} is at 486 nm ($\varepsilon = 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), which also possesses a shoulder around 424 nm (Figure 3-4a). The spectrum of 3^{2-} also possesses a low energy absorbance at 881 nm, which increases slightly throughout the titration experiment. It seems reasonable to assign this transition as residual 3^{-} resulting from slight oxidation of 3^{2-} because this band is similar in energy to the IVCT band of 3^{-} (see below, Figure 3-5b) and the oxidation potential for this couple is relatively low. The spectrum of $3-\text{H}^{-}$ shows two absorbance bands at 387 nm ($\varepsilon = 0.91 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 579 nm ($\varepsilon = 0.69 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) (Figure 3-4b). The second protonation event generating $3-2\text{H}^{0}$ results in two unresolved absorbance bands at 554 (ε = 1.1 x 10⁴ M⁻¹\text{cm}^{-1}) and 576 nm ($\varepsilon = 1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), along with a shoulder around 489 nm (Figure 3-4c). Despite having previously reported the spectra for 1, we summarize the spectra here for ease of comparison with 2 and 3. We find that the HOMO \rightarrow LUMO transition of 1²⁻ occurs at 498 nm ($\varepsilon = 1.0 \ge 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Upon the first protonation event, two bands are present at 610 nm ($\varepsilon = 0.50 \ge 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 416 nm ($\varepsilon = 0.56 \ge 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The second protonation event also results in two bands present at 578 nm ($\varepsilon = 0.97 \ge 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 345 nm ($\varepsilon = 1.9 \ge 10^4 \text{ M}^{-1}\text{cm}^{-1}$).

Comparing 1²⁻, 2²⁻, and 3²⁻, the ordering of the HOMO \rightarrow LUMO transition energy in DMF (Figure 3-4a) follows the order of Ni<Pt<Pd. This trend is consistent with our electrochemical results that the HOMO is stabilized to the largest extent in the Pd complex. Interestingly, the ordering of the Ni and Pt absorbance energies is inconsistent with those of similar complexes,^{33,49} although our energy values for the complexes of these two metals are fairly close to one another. In addition, the energetic ordering of these complexes does match that of the ethyl-substituted analogues.³²

Electronic Spectroscopy: Oxidative Titrations, Generation of MVMP States, and Group Trends

We also performed oxidative spectrophotometric titrations of **2** and **3**, in THF using I_2 as oxidant (Figure B-3). THF was used in place of DMF because we found that subsequent acid titration following the oxidative titration yielded clean isosbestic points in THF (Figure B-4) but not in DMF. Slight deviations at the expected isosbestic points at high energy are likely due to absorption by I_2 . In these experiments, a solution of I_2 dissolved in THF was added to the metal dithiolene dianion dissolved in THF until no further change in the IVCT band was observed, indicating full conversion to the mixed valence monoanions. Initial spectra of the dianions in THF are shown in Figure 3-5a, and the final spectra of the mixed valence states are shown in Figure 3-5b. The spectra for 1^{2-} and 1^{-} were also previously reported.¹⁰ The full IVCT band for

 2^{-} is shown in the inset in Figure 3-5b, as the UV-visible and NIR spectra were acquired using different instruments.



Figure 3-5. (a) UV-visible spectra of $1^{2^{\circ}}$, $2^{2^{\circ}}$, and $3^{2^{\circ}}$ dissolved in THF. (b) UV-visible spectra of states 1, 2, and 3 in THF, which were obtained by titration using a solution of I₂ in THF. The inset shows the NIR spectrum of 2 obtained using a NIR spectrometer. (c) UV-visible spectra of $1-H^{0}$, $2-H^{0}$, and $3-H^{0}$, which were obtained by titration using TsOH • H₂O in THF following generation of the mixed valence monoanions. Spectra of 1 are included for comparison from ref. 10.

The initial spectra of 1^{2-} , 2^{2-} , and 3^{2-} in THF (Figure 3-5a) possess slight differences compared to their spectra in DMF (Figure 3-4a), which we ascribe to solvatochromism. The Pd complex 2^{2-} possesses its HOMO \rightarrow LUMO transition at 432 nm ($\varepsilon = 1.2 \times 10^4 \text{ M}^{-1}\text{ cm}^{-1}$) in THF solution. Upon oxidation (Figures 3-5b and B-3a), this band shifts to lower energy and lower intensity, becoming a shoulder to the increasing band at 364 nm that is likely due to residual I₂. In addition, the IVCT band grows in at 1119 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{ cm}^{-1}$). The maximum wavelength and extinction coefficient of all of the IVCT bands are collected in Table 3-3. Turning to the electronic spectrum of 3^{2-} (Figure 3-5a), we observe the HOMO \rightarrow LUMO transition at 477 nm ($\varepsilon = 0.98 \times 10^4 \text{ M}^{-1}\text{ cm}^{-1}$) in THF. This band also possesses a shoulder on the high energy side at about 420 nm. Oxidation of 3^{2-} (Figures 3-5b and B-3b) results in a similar change to this absorbance band in that it decreases in intensity and shifts to 494 nm ($\varepsilon = 0.51 \times 10^{-1}$) 10⁴ M⁻¹cm⁻¹). The IVCT band grows in at 876 nm ($\epsilon = 1.6 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and a small band arises at 635 nm ($\epsilon = 0.25 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Similarly, I₂ seems to be responsible for the growth of the absorbance band at 364 nm. Lastly, 1²⁻ possesses its HOMO \rightarrow LUMO transition at 488 nm ($\epsilon = 0.83 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$) in THF. Upon oxidation to 1⁻, this band shifts to 469 nm ($\epsilon = 0.57 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and the IVCT band arises at 866 nm ($\epsilon = 1.0 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$).¹⁰

Of all of these spectroscopic features, it is the IVCT band of the mixed valence states that is of greatest interest, as this feature can be used to calculate the electronic coupling for the mixed valence species. In these complexes, the IVCT band is also assigned as the SOMO - $1 \rightarrow$ SOMO transition.³⁶ We find that the energy of this transition follows the trend of Ni>Pt>Pd, which is the inverse of the trend for the HOMO \rightarrow LUMO transition in the dianion states. However, the energy difference between the IVCT bands for the Ni and Pt species is extremely small (132 cm⁻¹) compared to the energy difference between the Pt and Pd complexes (2480 cm⁻¹). Another interesting aspect of the IVCT bands is their shape. The IVCT band for 1⁻ is very asymmetric, with a long shoulder at high energy. Previously, we were unable to assign this asymmetry as arising from additional nearby electronic transitions, or as vibronic features. However, the IVCT bands for both 2⁻ and 3⁻ are symmetric and lack this shoulder. At the same time, they do possess additional transitions near the energy of the shoulder for 1⁻. Thus, it is likely that the shoulder observed for the IVCT band of 1⁻ is also due to additional electronic transitions, rather than vibronic features.

Finally, as the goal of this chapter is to examine the effects of protonation upon electronic coupling, we needed to generate the MVMP states of the three compounds in the series. Figure B-4 shows the acid titrations of 2^{-} and 3^{-} with TsOH • H₂O in THF following their *in situ* generation with I₂ (directly following Figure 3-5b). The endpoint spectra of these titration experiments are collected in Figure 3-5c. For generation of the Pd complex 2-H⁰, two bands appear at 499 nm ($\varepsilon = 1.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 534 nm ($\varepsilon = 1.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The IVCT band in

the NIR region for 2⁻ is observed to disappear entirely upon acid titration (Figures 3-5c and B-4a). It is important to note that the isosbestic points observed here are not as clean as for the other transformations presented. For generation of the Pt complex **3-H**⁰, again we observe two absorbance bands arise at 572 nm ($\varepsilon = 0.90 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 605 nm ($\varepsilon = 0.95 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). However, the IVCT band for this complex behaves differently from that for **2-H**⁰. In the Pt complex **3-H**⁰, the IVCT band is drastically reduced in intensity upon addition of acid solution (Figures 3-5c and B-4b). Even upon addition of excess acid, the IVCT transition never fully disappears, similar to the behavior of **1-H**⁰ (Figure 3-5c).¹⁰ Also, for this transition, the observed isosbestic points were not as clean as for the other transformations. The energy of the transition is nearly constant throughout the experiment, with a very slight shift from 876 nm to 877 nm ($\varepsilon = 0.27 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$).

Lastly, we note that, despite the lack of perfectly clean isosbestic points, addition of aqueous basic solution following these titration experiments quantitatively recovers the IVCT bands associated with 2^{-} and 3^{-} , demonstrating that the titrations are reversible, and suggesting that the acid titration experiments occur exclusively on the open shell species.

Magnetic Spectroscopy of Paramagnetic Species

EPR spectra for 1⁻ and 1-H⁰ were previously reported.¹⁰ The spectrum of 1⁻ displayed a rhombic-type signal with g values of $g_1 = 2.246$, $g_2 = 2.044$, and $g_3 = 2.021$. Upon protonation, the rhombic nature of the signal was retained, but the intensity was reduced, and two of the resonance positions were shifted, giving g values of $g_1 = 2.237$, $g_2 = 2.044$, and $g_3 = 2.016$.

EPR spectra were acquired for all of the open shell states of 2^{-} , 2- H^{0} , 3^{-} , and 3- H^{0} at 35 K in THF solution, shown in Figure 3-6. All species were generated during spectrophotometric titration experiments, and they were monitored using UV-visible and NIR spectroscopy. 2^{-}

exhibits a rhombic signal typical for mixed valence metal dithiolene complexes, and its *g* values are $g_1 = 2.090$, $g_2 = 2.051$, and $g_3 = 1.944$. **2-H**⁰ did not yield an observable EPR spectrum, which might be expected given its loss of IVCT band, though addition of base did reclaim the EPR spectrum associated with **2**⁻. The fact that acid/base titrations can be used to exchange **2**⁻ and **2**-**H**⁰ suggests that the oxidation state of the complex is maintained. We are unable to provide an explanation for the loss of EPR spectra for **2-H**⁰. Though spin pairing in a dimer of **2-H**⁰ might seem a likely explanation, concentration-dependent UV-visible spectroscopy performed on **2-H**⁰ maintained a linear trend between absorbance and concentration of **2-H**⁰, leaving little evidence for the formation of a dimer.



Figure 3-6. EPR spectrum of **2** (a) and **3** and **3-H**^{0} (b) dissolved in THF at 35 K. **2** and **3** were generated by addition of I₂ to compounds **2**^{2} and **3**^{2} in THF, respectively, and **3-H**^{0} was generated by subsequent addition of TsOH • H₂O to **3** as determined by UV-visible spectroscopy.

The Pt complex 3⁻ exhibits a rhombic signal with g values of $g_1 = 2.277$, $g_2 = 2.048$, and $g_3 = 1.784$. Compound 3⁻ also exhibits hyperfine coupling in g_2 and g_3 . Upon protonation to generate 3-H⁰, little change is observed in the EPR spectrum. None of the g values shift position, although the relative intensity of g_1 is reduced, similar to observations for 1⁻.¹⁰

Discussion

Determination of H_{AB} Values for the Mixed Valence and MVMP States

As we are interested in determining the impact of protonation upon electronic coupling in the mixed valence complexes, we begin by calculating the electronic coupling parameter, H_{AB} , for the pure mixed valence states of all three complexes. In our previous work, we assigned 1⁻ as Class III within the Robin-Day classification scheme,⁵⁰ based on the shape and solvent independence of its IVCT band. As such, H_{AB} was calculated using Equation 2-1¹⁸ and was found to be 5800 cm^{-1 10} using the wavelength of maximum absorbance for the IVCT band. Based upon the similarity between the complexes, we also treat 2⁻ and 3⁻ as Class III mixed valence complexes. Again using Equation 2-1, we find H_{AB} values of 4500 cm⁻¹ and 5700 cm⁻¹ for 2⁻ and 3⁻, respectively. We note that the lower energy IVCT transition of 2⁻ is consistent with similar dithiolene complexes in the literature.³⁶

The trend in electronic coupling is explained using the ordering of metal orbitals and is reflected in the electrochemical behavior of the complexes. The d orbitals on the Ni and Pt metal centers are higher in energy (due to higher effective nuclear charge and relativistic effects) and allow for stronger mixing with the ligand orbitals when forming the SOMO (the accepting molecular orbital of the IVCT transition) of the complexes.³⁶ Here, the effective nuclear charge is simply an empirical parameter used in spin-orbit calculations when simulating electronic coupling and does not necessarily reflect the traditional shielding effect.^{36,51} Because the metal-ligand orbital interaction is antibonding in nature, the stronger metal-ligand mixing in the Ni and Pt complexes raises the energy of the SOMO. In addition, from a molecular orbital perspective, the IVCT band is assigned to the SOMO - $1 \rightarrow$ SOMO transition.³⁶ A blue-shift in the IVCT band results from higher energy metal orbitals contributing to the SOMO energy level and

improved energetic alignment between metal and ligand orbitals. This stronger metal-to-ligand donation of electron density also gives rise to more negative redox potentials for the Ni and Pt mixed valence complexes (Figure 3-3). Thus, the electrochemistry also suggests better alignment in energy between the ligand and metal center orbitals that form the frontier orbitals of the complexes. Since we can view the coupling in the mixed valence states as interligand coupling mediated by a metal bridge,³⁶ we also expect that better energetic alignment between the metal and ligand orbitals will result in stronger coupling, producing the observed blue-shift of the IVCT transition for 1^{-} and 3^{-} relative to the Pd complex $2^{-.18,36}$

We next calculated H_{AB} values for the MVMP states. Assignment of the MVMP states within the Robin-Day scheme is ambiguous for strongly asymmetric complexes. As such, Equation 2-1 is not appropriate for obtaining the magnitude of electronic coupling from the IVCT bands of the MVMP states. Previously, we showed that we could use Equation 2-2, which applies equally to mixed valence systems spanning Class II and III as well as to symmetric and asymmetric systems, for analysis of the MVMP states.^{10,18} The value of v_{max} , the maximum wavelength of absorption of the IVCT band, can be taken directly from the IVCT band maximum, and the transition dipole moment of the IVCT transition, $|\mu_{12}|$, can be obtained from integration of the IVCT band. An experimental value for the distance of ET within the structure of the molecule, r_{ab} , is more difficult to obtain. However, we can assume that the molecular structure, and hence the electron transfer distance, does not vary substantially when moving from the mixed valence state to the MVMP state (i.e., $1^- \rightarrow 1$ - H^0). Working from this assumption, we can use Equation 2-1 to calculate a value of r_{ab} for the Class III pure mixed valence complexes and then use this value of r_{ab} to find H_{AB} for the MVMP states using Equation 2-2.

The results of our calculations for r_{ab} are presented in Table 3-3. We find values of 4.94 Å, 6.47 Å, and 6.10 Å for 1⁻, 2⁻, and 3⁻, respectively. While these distances are different from one another, we do note that all of the r_{ab} values lie between the S-S and C-C distances across the

metal center in the crystal structures of the closed shell dianions (the S-S distances are 3.038 Å, 3.278 Å, and 3.270 Å, respectively, and the C-C distances are 6.056 Å, 6.255 Å, and 6.266 Å, respectively). Thus, in all cases, the values of r_{ab} , which are closer to the C-C distances, are consistent with the dithiolene core as the redox unit. Thus, the differences in r_{ab} values are not a major concern for our analysis.

With values of r_{ab} in hand, we then used Equation 2-2 to find the electronic coupling in the MVMP state for all three complexes. Prior application of this approach for **1-H**⁰ gave a value of $H_{AB} = 1200 \text{ cm}^{-1}$.¹⁰ The effect of protonation upon the IVCT bands for compounds **2-H**⁰ and **3-H**⁰ can be seen in Figures 3-5b-c and B-4. From the final spectra, the H_{AB} value of **3-H**⁰ was calculated to be 1200 cm⁻¹, identical to that for **1-H**⁰. As noted above, the Pd complex **2-H**⁰ did not exhibit an IVCT band in its UV-vis-NIR spectrum. This lack of observed IVCT band is either due to complete loss of coupling in the complex or transformation to a non-mixed valence species. The presence of isosbestic points (albeit rough) in the titration of **2**⁻ to **2-H**⁰, as well as the reversibility of this titration, indicate that there is no drastic change in the nature of the state. As such, we conclude that we are observing the loss of electronic coupling in the MVMP state.

Degree of Change in Electronic Coupling upon Protonation and Effect of Changing Bridging Metal Center

In our previous work on the PCET potential energy surface of $1-H^0$, we proposed that the drastic decrease in H_{AB} most likely arose from a decrease in energy of the diabatic potential surface associated with the electron primarily occupying the protonated ligand.¹⁰ Under this interpretation, the similar results for $1-H^0$ and $3-H^0$ are expected because the HOMO energy and mixed valence electronic coupling of the Pt complex are very similar to those of the Ni complex. Moreover, the UV-visible spectra of states 1^{2-} , 2^{2-} , and 3^{2-} (Figures 3-4a and 3-5a) show that the

HOMO-LUMO gap is similar between the Ni and Pt complexes, but much larger for the Pd complex.³⁶ The fact that the bridging metal orbital (used to construct the SOMO) in the Pd complex is positioned at much lower energy (resulting in reduced metal-ligand orbital overlap) means that the resulting energy gap between the metal and orbitals of the protonated ligand is even larger in the MVMP state. Following from the reasoning given for the Ni complex,¹⁰ the energetic asymmetry in the MVMP state appears to result in complete pinning of the charge in the MVMP state of the Pd complex, and electronic coupling is not observed by analysis of an IVCT band. In other words, the energetic asymmetry is large enough that **2-H⁰** becomes a Class I mixed valence compound.

The above reasoning is consistent with our observations and the original hypothesis that the energy of the bridging species (in this case the metal center) can be used to control the response of mixed valence systems to asymmetric protonation. In particular, weaker electronic coupling in the pure mixed valence state indicates that there will be greater loss of electronic coupling upon asymmetric protonation. In this case, we do not observe fine gradations in the loss of the electronic coupling, which was either about 5-fold (Ni, Pt) or complete (Pd). Future work from our group will focus on fine-tuning the energetic alignment between the ligands and the metal centers in order to obtain improved control over the response of these MVMP complexes.

Conclusions

Based on the reduction in electronic coupling that we observed in the mixed valence mixed protonated state of [Ni(pdt)₂] upon protonation, we sought to extend our studies to the Pd and Pt analogues by varying the metal bridge. We were able to relate trends that we observed in the mixed valence mixed protonated states within this series of complexes to trends that were previously known for the closed shell and mixed valence states. Analysis of the IVCT band of the Pt complex, before and after protonation, indicates that the change in H_{AB} mirrors that of the Ni complex, with a reduction in H_{AB} from 5700 cm⁻¹ to 1200 cm⁻¹ upon protonation. The IVCT band of the Pd complex was red-shifted in comparison to the other two complexes, which reflects decreased coupling in of **2**⁻, a result of a larger gap between the ligand and bridging metal orbitals. Upon protonation, the IVCT band of this complex disappeared, which we interpret as the generation of a charge-localized Class I mixed valence state. This study shows that changing the metal bridge, which changes the molecular electronic structure, can result in drastic changes to the electronic coupling in mixed valence and MVMP states and suggests a means to tune the behavior such states.

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Figure B-1. Spectrophotometric titration of 2^{2} in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in Figures (a) and (b), respectively.



Figure B-2. Spectrophotometric titration of 3^{2-} in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in Figures (a) and (b), respectively.


Figure B-3. Oxidative titration from 2^{2-} to 2^{-} (a) and from 3^{2-} to 3^{-} (b) in THF using I₂ as oxidant. The inset in (a) shows the IVCT band in the NIR region for 2^{-} . Note that the UV-vis and NIR experiments were performed on different instruments.



Figure B-4. Spectrophotometric titration from 2^{-} to $2-H^{0}$ (a) and from 3^{-} to $3-H^{0}$ (b) in THF using a solution of TsOH • H₂O in THF as titrant following generation of 2^{-} and 3^{-} , respectively, with I₂ *in situ*. The inset in (a) shows the loss of the IVCT band in the NIR region for $2-H^{0}$. Note that the UV-vis and NIR experiments were performed on different instruments.

Chapter 4

Effect of Ligand Energy and Orbital Overlap on Control of Electronic Coupling in Mixed Valence Mixed Protonated States of Metal Dithiolenes

Introduction

Our work thus far has explored model systems for homogeneous ground state PCET.^{1–13} Specifically, we have studied the effect of asymmetric protonation on the electronic coupling in the MVMP states of pdt-containing metal dithiolene complexes, as probed by the IVCT band.^{14,15} The electronic coupling was described using classical Marcus-Hush theory,^{16–25} and the reduction in the electronic coupling when moving from the mixed valence state to the MVMP state was ascribed to partial confinement of the electron to one ligand. These systems allow us to probe the effect of asymmetric protonation on the intramolecular electron mobility, and, to the extent that systems undergoing PCET will necessarily have asymmetrically protonated sites, such insight is applicable to understanding the behavior of ground state PCET.²⁶⁻³⁰

During our studies of the pdt-containing dithiolene complexes, we discovered a dependence of the electronic coupling on the energetic alignment and orbital overlap of the ligand and metal states.^{14,15} As we changed the metal center of the complexes (thereby changing the bridge between redox sites³⁰⁻³⁷), the electronic coupling changed both in the mixed valence state and the MVMP state. Because of the decreased metal-ligand orbital overlap in the Pd complex [Pd(pdt)₂], this complex exhibited lower ligand-ligand electronic coupling in its mixed valence state, as indicated by its IVCT band.¹⁵ In addition, the reduction of electronic coupling upon protonation was larger for [Pd(pdt)₂], which we interpreted as arising from this decreased metal-

ligand orbital overlap. These previous studies therefore highlight the importance of considering the energetics of the metal center and the ligands in both mixed valence and MVMP states.

Of course, changes to the central metal are not the only means by which to adjust this energy gap. In this chapter, we report research efforts that explore the possibility of changing the energy of the aromatic ring through the use of alternate aromatic ligands. Specifically, we use 2,3-quinoxalinedithiol (qdt) species, which, due to their larger aromatic structure, possess decreased HOMO energies relative to their pdt counterparts. Likewise, decreasing the number of ring nitrogen atoms through the use of 2,3-pyridinedithiol (pdt) species raises the energy of the HOMO relative to pdt-containing species. Despite both qdt and pydt ligands (Figure 4-1) being well-established in the dithiolene literature,^{36,38-42} the mixed valence and MVMP states of these compounds are not well-explored,³⁹ and the change in electronic coupling between the ligands when moving between the mixed valence and MVMP states of these compounds is completely unknown. Next, we report how changes in ligand set allow us to control the electronic coupling and response to protonation in mixed valence and MVMP complexes formed with these ligands.



Figure 4-1. Structures of [M(qdt),] (left) and [M(pydt),] (right) where M = Ni, Pd, or Pt.

Experimental

Materials and Methods

All reagents were purchased from commercial sources, and all solvents were ACS grade and used without further purification. 2,3-Dichloroquinoxaline and I₂ were purchased from Acros Organics, and NaSH • xH₂O, 2,3-dichloropyridine, sodium 2-propanethiolate, NiCl₂, Bu₄NBr, and metallic Na were purchased from Sigma Aldrich. PdCl₂ was purchased from Matrix Scientific, and PtCl₂ was purchased from TCI. NiCl₂ • 6H₂O was purchased from Alfa Aesar, and NaOEt was purchased from Strem Chemicals. IR spectra were collected on a PerkinElmer Spectrum 400 FT-IR/NIR instrument with an ATR attachment. NIR spectra were collected on the same instrument without the ATR attachment and with a quartz cuvette. ¹H NMR spectra were recorded on a Bruker Avance CDPX-300 spectrometer in either CDCl₃ or d_6 -DMSO. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ESP 300 spectrometer. Electronic absorption spectra were collected using an Agilent 8453 spectrometer with a quartz cell with a path length of 1 cm. Electrochemical data was acquired with a Pine WaveNow potentiostat using a Pt wire as the working electrode, a Pt wire as the counter electrode, and Ag/Ag⁺ as the pseudo-reference electrode. All cyclic voltammograms (CVs) were referenced to the Fc/Fc⁺ redox couple, and 0.1 M *tetra*-butylammonium hexafluorophosphate was used as the electrolyte in N,N'-dimethylformamide (DMF). X-ray structures were determined using a Bruker SMART APEX CCD area detector equipped with a graphite monochromator, a Monocap collimator, and a MoK $_{\alpha}$ fine-focus sealed tube. Using Olex2,⁴³ the structures were solved with the ShelXS⁴⁴ structure solution program using Direct Methods and refined with the XL⁴⁴ refinement package using Least Squares minimization. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of 2,3-Quinoxalinedithiol (qdt)

2,3-quinoxalinedithiol has been synthesized previously, 38,40,45 and it has been synthesized here according to a modified literature procedure for the synthesis of 2,3-

pyrazinedithiol.^{34,46} 2,3-Dichloroquinoxaline (10.5474 g, 0.05299 mol) was dissolved in 300 mL MeOH under inert atmosphere. NaSH • xH₂O (15.16 g, 0.1377 mol) was dissolved in 150 mL H₂O under inert atmosphere. The solutions were combined, and the mixture turned dark red with a large amount of yellow precipitate. The precipitate redissolved in the reaction mixture to give a dark red solution, which was brought to reflux at 90 °C for 15 hrs. The mixture was acidified with HCl (aq) and cooled to 0 °C. An orange precipitate formed, which was filtered and washed with H₂O followed by cold MeOH. The product was redissolved in NaOH (aq) and filtered to give an orange solution. This solution was reacidified with HCl (aq) and cooled to 0 °C. The precipitate had formed again, which was filtered and washed with H₂O followed by cold MeOH to give an orange solutio (8.3588 g, 81.19%). ¹H NMR (*d*₆-DMSO): 7.43 ppm (m, 2H), 7.28 ppm (m, 2H). IR (neat): *v*/cm⁻¹ = 3086, 2963, 2907, 2802, 2690, 1664, 1630, 1609, 1561, 1503, 1482, 1429, 1358, 1324, 1251, 1142, 1092, 1059, 1031, 928, 897, 830, 738, 657, 621, 593. Anal. Calcd. for H₆C₈N₂S₂: H, 3.11; C, 49.46; N, 14.42; S, 33.01. Found: H, 3.31; C, 49.14; N, 14.14; S, 33.09.

Synthesis of $(Bu_4N)_2[Ni(qdt)_2]$ (1)

 $(Bu_4N)_2[Ni(qdt)_2]$ has been synthesized previously,^{38,39,47–53} many times as the Bu₄N⁺ salt.^{38,52,53} Our synthesis procedure follows from analogous procedures for $(Bu_4N)_2[Ni(pdt)_2]$.⁴⁶ 2,3-Quinoxalinedithiol (3.2348 g, 0.01665 mol) was dissolved in 160 mL MeOH containing NaOEt (2.27 g, 0.0334 mol). Anhydrous NiCl₂ (1.0790 g, 0.008326 mol) was added while stirring, and the mixture turned dark pink. The mixture was left to stir for 2 hrs, and the solvent was removed *in vacuo*. The resulting pink solid was redissolved in 250 mL EtOH and filtered. The solvent was again removed *in vacuo*. The dark pink solid was taken up in 120 mL water and transferred to a separatory funnel. A solution of Bu₄NBr (5.3673 g, 0.01665 mol) was prepared

in 100 mL CHCl₃. The product was extracted using the CHCl₃ solution (5 x 20 mL), and the combined organic layers were washed 3 times with water (20 mL). The organic layers were dried over Na₂SO₄, and the solvent was removed *in vacuo* to give a dark pink solid (4.2509 g, 55.01%). Crystals for single crystal X-ray structure determination were obtained by evaporation of a solution of acetone. ¹H NMR (d_6 -DMSO): 7.45 ppm (dd, 4 H), 7.21 ppm (dd, 4 H), 3.16 ppm (t, 16 H), 1.58 ppm (m, 16 H), 1.33 ppm (m, 16 H), 0.91 ppm (t, 24 H). IR (neat): $\nu/\text{cm}^{-1} = 3055$, 2960, 2872, 1555, 1470, 1412, 1360, 1257, 1164, 1118, 1068, 1018, 937, 881, 791, 748, 598. Anal. Calcd for H₈₀C₄₈N₆S₄Ni: H, 8.69; C, 62.12; N, 9.05; S, 13.82. Found: H, 8.75; C, 61.79; N, 8.66; S, 13.43.

Synthesis of $(Bu_4N)_2[Pd(qdt)_2]$ (2)

The Pd complex (Bu₄N)₂[Pd(qdt)₂] has been synthesized fewer times by comparison.^{38,54} Our procedure for synthesis follows in an analogous fashion from that of the Ni complex. 2,3-Quinoxalinedithiol (0.2876 g, 1.449 mmol) was dissolved in 150 mL MeOH containing NaOEt (0.20 g, 2.9 mmol). Anhydrous PdCl₂ (0.1326 g, 0.7478 mmol) was added while stirring, and the mixture appeared yellow-orange. The mixture was left to stir for 15 hrs, and the solvent was removed *in vacuo*. The resulting solid was redissolved in 150 mL EtOH and filtered, resulting in a yellow-brown filtrate. The solvent was removed *in vacuo*. The solid was taken up in 40 mL water and transferred to a separatory funnel. A solution of Bu₄NBr (0.4823 g, 1.496 mmol) was prepared in 60 mL CHCl₃. The product was extracted using the CHCl₃ solution (2 x 30 mL) and again with pure CHCl₃ (30 mL). The combined organic layers were washed 3 times with water (20 mL). The organic layers were dried over MgSO₄, and the solvent was removed *in vacuo* to give an orange-brown solid (0.2082 g, 28.53 %). Crystals for single crystal X-ray structure determination were obtained by evaporation of a solution of acetone. ¹H NMR (*d_e*-DMSO): 7.51 ppm (dd, 4 H), 7.25 ppm (dd, 4 H), 3.18 ppm (t, 16 H), 1.55 ppm (m, 16 H), 1.29 ppm (m, 16 H), 0.91 ppm (t, 24 H). IR (neat): v/cm⁻¹ = 3055, 2960, 2870, 1555, 1469, 1361, 1256, 1162, 1115, 1017, 881, 792, 748, 598. Anal. Calcd for H₈₀C₄₈N₆S₄Pd: H, 8.26; C, 59.08; N, 8.61; S, 13.14. Found: H, 8.04; C, 59.27; N, 8.70; S, 13.17.

Synthesis of $(Bu_4N)_2[Pt(qdt)_2]$ (3)

The Pt complex has been synthesized previously as well,^{38,40,41} and its synthetic procedure here also follows in analogy to that of the Ni complex. 2,3-Quinoxalinedithiol (0.3056 g, 1.590 mmol) was dissolved in 150 mL MeOH containing NaOEt (0.22 g, 3.2 mmol). Anhydrous PtCl₂ (0.2116 g, 0.7955 mmol) was added while stirring, and the mixture turned dark red. The mixture was left to stir for 15 hrs, and the solvent was removed *in vacuo*. The resulting red solid was redissolved in 150 mL EtOH and filtered, resulting in a dark red filtrate. The solvent was removed in vacuo. The red solid was taken up in 40 mL water and transferred to a separatory funnel. A solution of Bu₄NBr (0.5129 g, 1.591 mmol) was prepared in 60 mL CHCl₃. The product was extracted using the CHCl₃ solution (2 x 30 mL) and again with pure CHCl₃ (30 mL). The combined organic layers were washed 3 times with water (20 mL). The organic layers were dried over MgSO₄, and the solvent was removed *in vacuo* to give a red solid (0.3465 g,40.91 %). Crystals for single crystal X-ray structure determination were obtained by evaporation of a solution of acetone. ¹H NMR (d_6 -DMSO): 7.51 ppm (dd, 4 H), 7.24 ppm (dd, 4 H), 3.16 ppm (t, 16 H), 1.55 ppm (m, 16 H), 1.29 ppm (m, 16 H), 0.94 ppm (t, 24 H). IR (neat): $v/cm^{-1} =$ 3059, 2960, 2872, 1558, 1471, 1361, 1258, 1163, 1116, 1017, 881, 792, 748, 599. Anal. Calcd for H₈₀C₄₈N₆S₄Pt: H, 7.58; C, 54.16; N, 7.89; S, 12.05. Found: H, 7.62; C, 54.18; N, 7.42; S, 11.99.

2,3-Bis(isopropylthio)pyridine was synthesized according to a literature procedure.⁵⁵ 2,3-Dichloropyridine (1.2226 g, 8.262 mmol) was dissolved in 40 mL DMF and added to sodium 2-propanethiolate (3.21 g, 32.7 mmol) under inert atmosphere. The light yellow mixture was heated to 80 °C for 15 hrs. The mixture was allowed to cool, and it was transferred to a separatory funnel with the aid of 25 mL water. The product was extracted with ether (3 x 20 mL), and the combined organic phases were washed with water (2 x 15 mL) and dried over MgSO₄. Solvent was removed *in vacuo* to give a colorless oil (1.664 g, 88.60 %). ¹H NMR (*d*₆-DMSO): 8.33 ppm (1H), 7.70 ppm (1H), 7.10 ppm (1H), 3.93 ppm (1H), 3.52 ppm (1H), 1.33 ppm (6H), 1.23 ppm (6H). IR (neat): $v/cm^{-1} = 2962$, 2932, 2867, 1650, 1559, 1496, 1439, 1389, 1255, 1154, 1136, 1100, 1062, 787, 759, 742, 660.

Synthesis of 3-Thio-pyridine-2(1H)-thione (pydt)

3-Thio-pyridine-2(1H)-thione was also synthesized according to a literature procedure.⁵⁵ A solution of 2,3-bis(isopropylthio)pyridine (1.6537 g, 7.273 mmol) in 25 mL hexamethylphosphoramide (HMPA) was prepared and placed under inert atmosphere. Small pieces of sodium (0.47 g, 20 mmol) were added to a separate flask containing 15 mL HMPA. The sodium began to dissolve, creating a blue mixture. Under inert atmosphere, the initial pyridine solution was transferred to the sodium mixture, which gradually became dark red. The mixture was heated to 120 °C for 3 hrs, after which it was allowed to cool. Residual sodium present in the mixture was worked down using sequential addition of isopropanol, ethanol, methanol, and water. The solution was acidified using 200 mL of a pH=1 HCl (aq) solution. The solution was transferred to a separatory funnel, and the product was extracted using ether (4 x 25

mL). The combined organic phases were washed with water (2 x 25 mL), dried over MgSO₄, and solvent was removed *in vacuo*, yielding an orange solid (0.3356 g, 43.57 %). ¹H NMR (CDCl₃): 7.61 ppm (1H), 7.38 ppm (1H), 6.67 ppm (1H). IR (neat): *v*/cm⁻¹ = 2961, 2924, 2863, 2807, 1601, 1558, 1461, 1429, 1374, 1312, 1265, 1238, 1196, 1139, 1124, 1065, 1054, 1038, 983, 891, 764, 752, 709, 657.

Synthesis of $(Bu_4N)[Ni(pydt)_2]$ (4)

While the established literature procedure for this compound utilizes the dimeric, Slinked ligand,⁴² our synthesis utilizes the monomeric ligand pydt. In addition, we aim to synthesize the Bu_4N^+ salts of all metal complexes, while only the Pd complex $(Bu_4N)_2[Pd(pydt)_2]$ was synthesized in the established report.⁴² For the Ni complex, both the protonated and deprotonated Et_4N^+ salts were synthesized in these reports.^{42,56} In all other respects, our synthetic procedure follows from that for the deprotonated salt with an extraction and column work-up procedure performed at the end.

3-Thio-pyridine-2(1H)-thione (0.3939 g, 2.750 mmol) was added to 24 mL 10% NaOH (2.42 g NaOH in 24 mL H₂O). NiCl₂ • $6H_2O$ (0.3267 g, 1.374 mmol) was added, and the mixture turned reddish-brown with some brown solid visible. The mixture was brought to reflux at 110 °C for 15 hrs. Upon cooling, the brown solid was filtered off, leaving an orange-yellow filtrate. The filtrate was acidified with 110 mL 1.0 M HCl (aq), and a red precipitate formed, which was filtered and washed with H₂O. A solution of NaOH (aq) was prepared (3.9814 g in 100 mL H₂O), and it was added to the red solid in the filter. The solid redissolved and was filtered using the NaOH (aq) solution, regenerating the orange-yellow filtrate. A solution of Bu₄NBr (0.8861 g, 2.749 mmol) was prepared in 60 mL CHCl₃. The product was extracted using the CHCl₃ solution (3 x 20 mL). The combined organic layers were washed with H₂O (2 x 20 mL) and dried over

MgSO₄, and solvent was removed *in vacuo*. A column was performed on the resulting solid using 7:3 EtOAc / MeOH as eluent. The leading red fraction was collected, and solvent was removed *in vacuo* to give a black solid (0.0653 g, 7.91 %). IR (neat): $v/cm^{-1} = 3425$, 3019, 2961, 2923, 1617, 1555, 1528, 1425, 1373, 1333, 1285, 1222, 1205, 1139, 1026, 835, 768, 728, 704, 674, 650.

Synthesis of $(Bu_4N)_2[Pd(pydt)_2]$ (5)

Our synthetic procedure for this Pd complex also follows from the literature report for the Bu₄N⁺ salt.⁴² 3-Thio-pyridine-2(1H)-thione (0.4143 g, 2.893 mmol) was added to 26 mL 10% NaOH (2.62 g NaOH in 26 mL H₂O). PdCl₂ (0.2563 g, 1.445 mmol) was added, and the mixture turned brown with some brown solid visible. The mixture was brought to reflux at 110 °C for 15 hrs. Upon cooling, the brown solid was filtered off, leaving a bright orange filtrate. The filtrate was acidified with 100 mL 1.0 M HCl (aq), and an orange precipitate formed, which was filtered and washed with H_2O . A solution of NaOH (aq) was prepared (3.9641 g in 100 mL H_2O), and it was added to the orange solid in the filter. The solid redissolved and was filtered using the NaOH (aq) solution, regenerating the bright orange filtrate. A solution of Bu₄NBr (0.9322 g, 2.892 mmol) was prepared in 60 mL CHCl₃. The product was extracted using the CHCl₃ solution (3 x 20 mL). The combined organic layers were washed with H_2O (2 x 20 mL) and dried over MgSO₄, and solvent was removed *in vacuo* to give a red solid (0.0879 g, 6.96 %). ¹H NMR (d₆-DMSO): 8.22 ppm (1 H), 7.97 ppm (1 H), 7.46 ppm (1 H), 6.83 ppm (1 H), 6.67 ppm (1 H), 6.42 ppm (1 H), 3.16 ppm (t, 16 H), 1.56 ppm (m, 16 H), 1.30 ppm (m, 16 H), 0.92 ppm (t, 24 H). IR $(neat): v/cm^{-1} = 2961, 2873, 1545, 1482, 1429, 1362, 1261, 1128, 1102, 1055, 1029, 882, 799,$ 776, 737, 652.

Our synthetic procedure for the Pt complex follows from the above literature report, although they do not synthesize the dianionic complex.⁴² 3-Thio-pyridine-2(1H)-thione (0.3080 g, 2.151 mmol) was added to 23 mL 10% NaOH (2.35 g NaOH in 23 mL H₂O). PtCl₂ (0.2861 g, 1.076 mmol) was added, and the mixture turned yellow-brown with some brown solid visible. The mixture was brought to reflux at 110 °C for 15 hrs. Upon cooling, the brown solid was filtered off, leaving a yellow filtrate. The filtrate was acidified with 100 mL 1.0 M HCl (aq), and a brown precipitate formed, which was filtered and washed with H₂O. A solution of NaOH (aq) was prepared (4.0474 g in 100 mL H_2O), and it was added to the brown solid in the filter. The solid redissolved and was filtered using the NaOH (aq) solution, regenerating the yellow filtrate. A solution of Bu_4NBr (0.6930 g, 2.150 mmol) was prepared in 60 mL CHCl₃. The product was extracted using the CHCl₃ solution (3 x 20 mL). The combined organic layers were washed with H₂O (2 x 20 mL) and dried over MgSO₄, and solvent was removed *in vacuo* to give a black solid (0.0381 g, 3.68 %). ¹H NMR (*d*₆-DMSO): 8.03 ppm (1 H), 7.69 ppm (1 H), 7.37 ppm (1 H), 6.60 ppm (1 H), 6.37 ppm (1 H), 6.11 ppm (1 H), 3.16 ppm (t, 16 H), 1.55 ppm (m, 16 H), 1.29 ppm (m, 16 H), 0.92 ppm (t, 24 H). IR (neat): $v/cm^{-1} = 2960, 2932, 2873, 1564, 1465, 1379, 1260,$ 1133, 1069, 1039, 881, 796, 772, 738, 666.

Results

Crystallographic Characterization of Compounds 1-3

Because of the widespread study of the $[M(qdt)_2]^{2-}$ complexes, crystals of $[Ni(qdt)_2]$,^{38,48,57,58} $[Pd(qdt)_2]$,³⁸ and $[Pt(qdt)_2]^{38,40}$ molecules have been obtained in several

syntheses. However, crystallization is often used as a purification method in these procedures, and not as a means of characterization, so few crystal structures have been reported. In the products that were reported for $[Ni(qdt)_2]$, the crystal structures that were reported are those of the tetraethylammonium salt of the dianion, $(Et_4N)_2[Ni(qdt)_2]$, the doubly protonated complex, $[Ni(Hqdt)_2]$, and the doubly oxidized complex $[Ni(qdt)_2]$.^{48,57,59} Here, we report the crystal structures of the tetrabutylammonium salts of the dianions of $(Bu_4N)_2[Ni(qdt)_2]$ (1), $(Bu_4N)_2[Pd(qdt)_2]$ (2), and $(Bu_4N)_2[Pt(qdt)_2]$ (3).

Crystals of 1, 2, and 3 were grown by controlled evaporation of a solution of the dianion complexes dissolved in acetone. In all crystal structures obtained, one acetone molecule of crystallization was present for each unit cell. The unit cell also possessed two inequivalent dianionic complexes in the crystals of 1 and 3. The crystal structures obtained for each unit cell for 1, 2, and 3 are shown in Figure 4-2, data collection parameters are shown in Table 4-1, and selected bond lengths and angles are shown in Tables C-1 – C-3. The structures of all three compounds possess slightly distorted D_{4h} symmetry. The Ni atom in compound 1 induces a slightly shorter average M-S bond length, with a value of 2.179 Å, relative to the other two compounds, which have average bond lengths of 2.3009 Å and 2.293 Å, respectively. The Pt complex 3 possesses the longest average C-C bond length of 1.49 Å and the shortest average C-S bond length of 1.72 Å, reflecting the largest degree of dithione character. The average C-C bond lengths for 1 and 2 are 1.444 Å and 1.460 Å, respectively, and the average C-S bond lengths for 1 and 2 are 1.735 Å and 1.737 Å, respectively.



Figure 4-2. ORTEP plots of the inequivalent dianions of $[M(qdt)_2]^{2^-}$ in $1 \cdot C_3H_6O(a)$, $2 \cdot C_3H_6O(a)$, 2

	1 • C ₃ H ₆ O	2 • C ₃ H ₆ O	3 • C ₃ H ₆ O
empirical formula	C51H86N6NiOS4	$C_{51}H_{86}N_6OPdS_4$	$C_{102}H_{172}N_{12}Pt_2O_2S_8$
formula weight and crystal system	986.21, triclinic	1033.88, triclinic	2245.22, triclinic
color and habit	red, block	orange, block	red, cubical
Temp (K)	298(2)	298	298(2)
λ (Å)	0.71073, Mo Ka	0.71073, Mo Kα	0.71073, Mo Kα
crystal size (mm ³)	0.28 x 0.20 x 0.16	0.18 x 0.18 x 0.06	0.19 x 0.16 x 0.15
space group	P -1	P-1	P 1
a (Å)	11.7459(18)	11.830(4)	11.829(2)
b (Å)	14.274(2)	14.302(5)	14.312(3)
c (Å)	18.084(3)	18.091(7)	18.038(3)
a (°)	67.942(3)	67.933(6)	67.824(3)
β (°)	81.703(3)	81.948(6)	81.658(3)
γ (°)	86.684(3)	86.441(7)	86.523(4)
$V(\text{\AA}^3)$	2780.5(7)	2808.5(17)	2798.0(9)
Z	2	2	1
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.178	1.220	1.332
$\mu (\text{mm}^{-1})$	0.539	0.518	2.696
no. of reflens collected	19726	26670	20528
no. of reflens with $I > 2\sigma(I)$	4657	13527	11477
no. of independent params	1155	589	1155
GOF on F^2	1.018	1.055	0.975

Table 4-1. Crystallographic data for compounds **1** • C₃H₆O, **2** • C₃H₆O, and **3** • C₃H₆O.

Crystals of $(Bu_4N)_2[Ni(pydt)_2]$ (4), $(Bu_4N)_2[Pd(pydt)_2]$ (5), and $(Bu_4N)_2[Pt(pydt)_2]$ (6) were not obtained despite many attempts. The crystal structure of (5) has been reported previously, however, in addition to the tetraethylammonium salt of (4) and the doubly protonated species of 4-2H⁰, 5-2H⁰, and 6-2H⁰.⁴² From the structural work on the metal complexes containing pydt²⁻, we proceed with the assumption that the *anti* isomers formed in our syntheses.⁴²

Electrochemistry and Trends in Metal and Ligand

The CV's of the [M(qdt)₂] species **1**, **2**, and **3** are shown in Figure 4-3. As is typical for metal dithiolene complexes, these compounds possess one-electron redox processes.^{14,30,31,35,36,60} Electrochemical data for this series of compounds has been obtained in various manners previously,^{38–40,61} and we present our electrochemical results to complete the picture and make comparisons between compounds, although portions of our work are qualitatively similar to those reported previously. For the Ni compound **1**, a reversible one-electron oxidation event assigned to the [Ni(qdt)₂]^{2/1-} redox couple is observed at $E_{1/2} = -0.337$ V vs. Fc/Fc⁺ in DMF. The analogous redox couple for the Pt compound **3** is quasi-reversible, as the anodic and cathodic currents are dissimilar. The $E_{1/2}$ value for this redox event is measured at -0.266 V vs. Fc/Fc⁺. For the Pd compound **2**, this redox event is not reversible; the peak potential value of this event is measured at $E_{pa} = -0.020$ V vs. Fc/Fc⁺. The irreversibility of the oxidation event for **2** precludes the generation of its mixed valence compound. The ordering of these three oxidation events (Ni < Pt < Pd) is consistent with the ordering observed for the similar [M(pdt)₂] compounds.¹⁵ This ordering arises from the higher effective nuclear charges (see Chapter 3 discussion) of Pt and Ni,

which raises the HOMO energies in these complexes, causing oxidation to occur at less positive potentials.³¹ All three of the $[M(qdt)_2]$ compounds also possess an irreversible oxidation peak at more positive potentials, assigned to oxidation to the neutral species. This E_{pa} value falls at 0.597 V, 0.565 V, and 0.513 V vs. Fc/Fc⁺ in for **1**, **2**, and **3**, respectively.



Figure 4-3. Cyclic voltammograms of 1, 2, and 3 in DMF at a scan rate of 100 mVs⁻¹ using 0.1 M Bu_4NPF_6 as electrolyte.

Turning to the pyridine-containing dithiolene compounds **4**, **5**, and **6**, the CV's of which are shown in Figure 4-4 and reported previously for **4** and **5**,⁴² the oxidation events are qualitatively similar to those of the $[M(qdt)_2]$ complexes in that all compounds exhibit oneelectron oxidations and an irreversible oxidation at more positive potentials. The first oxidation assigned to the $[M(pydt)_2]^{2/-}$ redox couple is quasi-reversible for **4** and reversible for **5**, which is measured at $E_{1/2} = -0.757$ V vs. Fc/Fc⁺ for **4** and at $E_{1/2} = -0.582$ V vs. Fc/Fc⁺ for **5**. The analogous irreversible oxidation event for **6** occurs at a significantly more positive potential than expected ($E_{pa} = -0.232$ V vs. Fc/Fc⁺), given the above inspection of the $[M(qdt)_2]$ series and the previously studied $[M(pdt)_2]$ series.¹⁵ We would have expected that the oxidation of **6** should occur at potentials intermediate to that of **4** and **5**. However, this is not the case, as the potential is shifted to more positive values. The irreversibility of this redox event also precludes the study of the mixed valence state of **6**. All three complexes in the pydt series also exhibit irreversible redox events assigned to the $[M(pydt)_2]^{-/0}$ redox couple. These events occur at $E_{pa} = 0.192$ V vs. Fc/Fc^+ , $E_{pa} = 0.128$ V vs. Fc/Fc^+ , and $E_{pa} = 0.402$ V vs. Fc/Fc^+ for **4**, **5**, and **6**, respectively.



Figure 4-4. Cyclic voltammograms of **4**, **5**, and **6** in DMF at a scan rate of 100 mVs⁻¹ using 0.1 M Bu_4NPF_6 as electrolyte.

Since the electrochemical data for the $[M(pdt)_2]$, $[M(qdt)_2]$, and $[M(pydt)_2]$ series has been clearly established, we can compare the redox potentials for the first oxidation event. Figure C-1 shows the CV's of the first oxidation event of the Ni complexes of these three ligands, also plotted with the CV of $(Bu_4N)[Ni(bdt)_2]$.⁶² Comparing these four oxidation potentials, the $[Ni(xdt)_2]^{2-/-}$ redox couple becomes more positive with increasing number of ring N atoms. In addition, the redox potential is also pushed toward more positive values with extension of the pyrazine ring to a quinoxaline ring. This trend reflects the electron-withdrawing ability of the N atoms and the increased stability afforded by the extended aromatic ring. The tendency for each complex to oxidize during synthesis is then put into perspective when considering that the [Ni(bdt)₂] and [Ni(pydt)₂] complexes form as the monoanionic, singly oxidized states, and the [Ni(pdt)₂] and [Ni(qdt)₂] complexes form as the dianionic states.

While we are interested in the effect of protonation for these complexes, we expect a shift in redox potential to more positive values upon protonation.^{14,63} A positive shift in redox potential was observed previously for 1,³⁹ although it was assigned to the oxidation potential of the quadruply protonated complex. As discussed below, we and others⁴¹ have not observed the quadruply protonated complex in our spectrophotometric titrations. For the [Ni(pdt)₂] complex, we observed a similar shift toward more positive potentials for the doubly protonated complex.¹⁴

Electronic Spectroscopy: Spectrophotometric Acid Titrations of Closed Shell [M(qdt)₂] *Complexes*

We begin our presentation of the electronic spectra by considering the response of each closed shell dianionic complex to protonation during spectrophotometric titration. All closed shell protonation states of our complexes are stable in DMF solution. Many of the spectra are presented elsewhere, which includes the dianionic compounds in various solvents,^{38–41,47,52} and, particularly, the spectrophotometric titration of 3^{2-} to $3-2H^{0}$.^{40,41} Nevertheless, we present all spectra here, for ease of comparison between complexes.

The spectra of the closed shell states of 1, 2, and 3 are shown in Figure 4-5. The spectra shown in Figures 4-5b and 4-5c are the spectra of the singly and doubly protonated states, respectively, and were acquired during spectrophotometric titration of 1, 2, and 3 in DMF using aqueous HCl solution. Complete sets of the spectra acquired during the titration are shown in Figures C-2 – C-4 for 1, 2, and 3, respectively. The series of spectra for each compound exhibit two sets of clean isosbestic points throughout the titrations, indicating two protonation events.

Previous work determined that protonation occurs at the N atoms, not at the metal or S atoms.^{14,40,41} Addition of acid to solutions of $[Ni(bdt)_2]^-$ (bdt = 1,2-benzenedithiol) shows little change in its electronic spectrum,⁶² indicating that the N atoms of the qdt ring are required for the spectral changes.



Figure 4-5. UV-visible spectra of various states of 1, 2, and 3 dissolved in DMF (a-c). The dianionic $X^{2^{-}}$ states are shown in (a), the singly protonated states X-H⁻ are shown in (b), and the double protonated states X-2H⁰ are shown in (c). These states were obtained by spectrophotometric titration using aqueous HCl, and the spectra shown in (b) were taken at the change in isosbestic points during titration.

For all three compounds, the spectrum of the dianion (unprotonated state) contains two resolved bands in the visible region of the spectrum. In protic media such as MeOH, these bands are unresolved.^{40,41,61} Our use of an aprotic solvent in DMF allows for the bands to be resolved. These bands are presented at 533 nm ($\varepsilon = 2.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 560 nm ($\varepsilon = 2.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **1**², at 461 nm ($\varepsilon = 3.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 489 nm ($\varepsilon = 3.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **2**², and at 514 nm ($\varepsilon = 2.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 550 nm ($\varepsilon = 2.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **3**². The lowest energy band is assigned to the HOMO \rightarrow LUMO transition in which the HOMO consists of a mixture of metal and ligand character and the LUMO consists of predominantly ligand character.^{14,40,41,64,65} The ordering of the energies of the bands follows the trend of Ni<Pt<Pd, which is consistent with the trend for similar complexes, as well as with the electrochemical data.^{15,40,64}

Upon single protonation, an asymmetry in ligand energy levels is established, which is reflected by the initial HOMO \rightarrow LUMO transition being split into multiple bands.^{14,41} The new spectral features are present at 443 nm ($\varepsilon = 0.87 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 468 nm ($\varepsilon = 0.80 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and 650 nm ($\varepsilon = 0.90 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **1-H**⁻, at 408 nm ($\varepsilon = 1.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 432 nm ($\varepsilon = 1.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and 548 nm ($\varepsilon = 1.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **2-H**⁻, and at 436 nm ($\varepsilon = 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 621 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **3-H**⁻. Upon the second protonation event, the symmetry between ligands is restored, merging the separate transitions back into a single HOMO \rightarrow LUMO transition, albeit at lower energies than with the dianionic compounds, which reflects the lowering of the ligand-based orbitals that form the LUMO of the transition.^{14,41} The new spectral features are present at 599 nm ($\varepsilon = 1.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 656 nm ($\varepsilon = 1.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **1-2H**⁰, at 518 nm ($\varepsilon = 2.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 549 nm ($\varepsilon = 3.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **2-2H**⁰, and at 581 nm ($\varepsilon = 1.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 627 nm ($\varepsilon = 1.9 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for **3-2H**⁰.

Electronic Spectroscopy: Oxidative Titration and Generation of MVMP State of $[M(qdt)_2]$ Complexes

We now turn to spectrophotometric oxidation titrations using I₂ dissolved in tetrahydrofuran (THF) as titrant for the series of compounds **1**, **2**, and **3**. THF is used as a solvent here because the subsequent acid titration is better behaved in THF solution, rather than in DMF solution. The open shell state of **1**⁻ has been generated previously,³⁹ but the electronic spectrum has not been presented. The final spectra for **1**⁻ and **3**⁻ are shown in Figure 4-6, and the complete oxidative titrations for these species are shown in Figure C-5. As the oxidation for **2** was irreversible, we simply report the spectrum for **2**²⁻ dissolved in THF for completeness in Figure C-6. The starting spectra of the dianionic complexes in THF are slightly different from their spectra in DMF. In THF solution, bands are presented at 522 nm ($\varepsilon = 1.9 \times 10^4 \text{ M}^{-1}\text{ cm}^{-1}$) and 550

nm ($\varepsilon = 2.2 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$) for 1², at 456 nm ($\varepsilon = 2.6 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 482 nm ($\varepsilon = 2.7 \text{ x } 10^4 \text{ M}^{-1}$ 1 cm⁻¹) for **2**², and at 505 nm ($\varepsilon = 2.1 \times 10^{4} \text{ M}^{-1}$ cm⁻¹) and 539 nm ($\varepsilon = 2.0 \times 10^{4} \text{ M}^{-1}$ cm⁻¹) for **3**². Oxidative titration to generate 1⁻ displayed a clean set of isosbestic points, and an IVCT band was observed to arise at 873 nm ($\varepsilon = 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) with a shoulder at 802 nm. In addition, the previous HOMO \rightarrow LUMO transition shifted to 519 nm ($\varepsilon = 1.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Oxidative titration to generate 3^{-} also displayed a clean set of isosbestic points. However, addition of slight excess of I₂ caused the IVCT band to decrease (after reaching a maximum absorption value) while the other bands continued to increase. The spectrum of 3^{-1} reported in Figure 4-6 was taken at the point of maximum absorbance of the IVCT band. As a result, we have less confidence in the extinction coefficients for 3^{-} . This variability in observing the rise of the IVCT band is likely due to the quasi-reversible nature of the oxidative redox couple in the electrochemical data (see above). Overall, the IVCT band for 3⁻ was observed at 909 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and the previous HOMO \rightarrow LUMO transition shifted to 552 nm ($\epsilon = 0.86 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$). In comparing the positions of the IVCT bands in 1⁻ and 3⁻, the IVCT band of the Ni complex occurs at slightly higher energy than that of the Pt complex, as has been observed for similar open shell metal dithiolenes, including the $[M(pdt)_2]^-$ complexes.^{15,31}



Figure 4-6. Spectra of **1** and **3** in THF following spectrophotometric titration using a solution of I_2 in THF. While the IVCT band for **1** reached a maximum and leveled off, the IVCT band for **3** decreased with additional I_2 added. The maximum IVCT band absorbance for **3** is shown.

Spectrophotometric acid titration experiments of the open shell species to generate the MVMP states were performed using TsOH • H₂O in THF solution as titrant following previous generation of the mixed valence complexes using I₂ in THF solution, shown in Figure 4-7. For the Ni complex **1-H**⁰, a clean set of isosbestic points was observed, and the IVCT band disappeared completely. Two bands arose at 613 nm ($\varepsilon = 1.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 678 nm ($\varepsilon = 1.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Upon addition of aqueous base, the IVCT band reappeared, showing that the previous acid titration consisted of conversion between two open shell states. For the Pt complex **3-H**⁰, isosbestic points were not clean. This lack of clean isosbestic points is again likely due to the quasi-reversible nature of the electrochemical oxidation. The IVCT was observed to disappear completely as well, and two other bands arose at 597 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 646 nm ($\varepsilon = 1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Addition of aqueous base regenerated the IVCT band associated with **3**, although the back-conversion was not as clean as that for the Ni complex.



Figure 4-7. Spectrophotometric titration from **1** to **1**-**H**⁰ (a) and from **3** to **3**-**H**⁰ (b) in THF using a solution of TsOH • H₂O in THF as titrant following generation of **1** and **3**, respectively, with I₂ *in situ*.

Electronic Spectroscopy: Spectrophotometric Acid Titrations of Closed Shell [*M*(*pydt*)₂] *Complexes*

We now turn our attention to the pydt-containing complexes 4, 5, and 6, beginning with the acid titrations of the closed shell states. For these compounds, the spectra of $4-2H^0$, $5-2H^0$, and $6-2H^0$ were presented previously.⁴² While we isolated 4 in the open shell monoanionic state, we did not generate the closed shell state for this complex, and our work on the acid titrations of the closed shell states focus on 5 and 6. The complete sets of spectra obtained during the titrations of 5 and 6 are shown in Figures C-7 and C-8, respectively.

In the spectrophotometric titration of **5**, two sets of clean isosbestic points are present, indicating clean conversion between 5^{2-} , $5-H^{-}$, and $5-2H^{0}$. The spectrum of as-synthesized 5^{2-} in DMF solution exhibits two absorbance bands at 362 nm ($\varepsilon = 0.78 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 403 nm ($\varepsilon =$ $0.78 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Due to the similarity to the pdt-containing complexes, it was expected that only one absorbance band (the low-energy band in this case) would be present, representing the HOMO \rightarrow LUMO transition. As such, it was suspected that the higher-energy band represented the presence of a partial amount of the singly protonated species. Addition of aqueous base solution to a starting solution of as-synthesized **5** resulted in Figure C-9, in which the low-energy band increased in intensity and the high-energy band decreased in intensity. However, the conversion to the non-protonated state **5**²⁻ was not complete, as indicated by the persistence of the high-energy band with addition of excess base. Upon addition of acid solution to as-synthesized **5**²⁻, the high-energy band increased in intensity, and a separate band arose. These two bands are presented at 358 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 489 nm ($\varepsilon = 0.35 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Addition of a second proton to generate **5-2H**⁰ resulted in the appearance of another band at 468 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), which matches well with the previously reported spectrum.⁴²

Spectrophotometric acid titration of **6** also contains two clean isosbestic points (Figure C-8). Again, two sets of clean isosbestic points were observed. The starting spectrum of **6**²⁻ shows two shoulders on a high-energy absorption feature. The shoulders are present at 308 nm ($\varepsilon = 1.1$ x 10⁴ M⁻¹cm⁻¹) and 363 nm ($\varepsilon = 0.69$ x 10⁴ M⁻¹cm⁻¹). Upon generation of **6-H**⁻, the shoulder features shift to 312 nm ($\varepsilon = 1.1$ x 10⁴ M⁻¹cm⁻¹) and 430 nm ($\varepsilon = 0.32$ x 10⁴ M⁻¹cm⁻¹). Upon addition of the second proton to generate **6-2H**⁰, a shoulder is present at 310 nm ($\varepsilon = 1.0$ x 10⁴ M⁻¹cm⁻¹), and a new band arises at 392 nm ($\varepsilon = 0.59$ x 10⁴ M⁻¹cm⁻¹). The spectrum of **6-2H**⁰ matches closely to the reported literature spectrum with the exception that our spectrum is lacking an additional low-energy absorbance feature at 542 nm.⁴² It is unclear why this discrepancy is present, especially considering that the other absorbance features match very closely.

Electronic Spectroscopy: Oxidative Titrations and Generation of MVMP State of $[M(pydt)_2]$ Complexes

We next investigated the open shell states of the pydt-containing complexes as well. Given that the electrochemistry of 6 was irreversible, we report only the behavior of 4 and 5.

Once again, slight differences are present in the spectrum of 5^{2-} in DMF and THF solutions. Because **4**[•] was isolated as the monoanionic open shell species, no oxidative titration was necessary to generate the mixed valence state for this complex. Oxidative titration of 5^{2-} to generate **5**[•] is shown in Figure C-10. The starting spectrum of 5^{2-} in THF solution possesses bands at 366 nm ($\varepsilon = 1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 398 nm ($\varepsilon = 1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Upon addition of I₂ in THF solution, the IVCT band arises at low energy, which is captured in the inset of Figure C-10 through the use of a separate NIR spectrometer. Similar changes in the UV-visible spectral region are present as well. The IVCT band is present at 1100 nm ($\varepsilon = 1.9 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), and other absorbance bands are present at 355 nm ($\varepsilon = 1.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The final spectrum of this titration and the spectrum of **3**⁻. The spectrum of **4**⁺ possesses an IVCT band at 870 nm ($\varepsilon = 0.43 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and other absorbance features at 363 nm ($\varepsilon = 0.52 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 522 nm ($\varepsilon = 0.22 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). Similarly to the [M(pdt)₂]⁻ complexes, the IVCT band of the Ni complex **4**⁻ occurs at significantly higher energy than that of **5**⁻.



Figure 4-8. Spectra of 4° and 5° in THF. While 4° was isolated as the monoanion, the spectrum of 5° was obtained following spectrophotometric titration using a solution of I_2 in THF. The inset shows the spectrum of 5° obtained with a separate NIR instrument.

Following acquisition of the spectra of the mixed valence states for **4**[•] and **5**[•], spectrophotometric acid titration was performed on each species using TsOH • H₂O in THF solution as titrant to generate its respective MVMP state, shown in Figure 4-9. In the titration of **4**[•], the IVCT band of **4**[•] is observed to initially shift to lower energy. However, as the titration proceeds with a clean set of isosbestic points, the IVCT band maximum energy shifts back to higher energy. Then, once it stabilizes at a particular energy, it continues to decrease in intensity until the endpoint of the titration is reached. This endpoint is indicated by the lack of response to addition of excess acid. In this titration experiment, the IVCT band for **4-H**⁰ came to rest at 874 nm ($\varepsilon = 0.12 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), a net shift of 4 nm from its original position for **4**[•]. Additional absorbance bands were present at 521 nm ($\varepsilon = 0.46 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 554 nm ($\varepsilon = 0.53 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). This shift toward low energy and decrease in intensity is also consistent with that observed for the [Ni(pdt)₂]⁻ and [Pt(pdt)₂]⁻ complexes.^{14,15} In the titration to generate the MVMP state of **5-H**⁰, the IVCT band was observed to disappear completely. Clean isosbestic points were present, and an additional absorbance feature was exhibited at 480 nm ($\epsilon = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).



Figure 4-9. Spectrophotometric titration from **4** to **4**-**H**^{0} (a) and from **5** to **5**-**H**^{0} (b) in THF using a solution of TsOH • H₂O in THF as titrant. While **4** was isolated as the monoanion, the spectrum of **5** was obtained following spectrophotometric titration using a solution of I₂ in THF. The inset shows the titration of **5** performed using a separate NIR instrument.

Magnetic Spectroscopy of Paramagnetic Species

EPR spectra of the mixed valence states were obtained in THF solution at 35 K following generation of the mixed valence states through addition of I_2 dissolved in THF, which was monitored through UV-visible spectroscopy. As we have previously observed that the lack of an IVCT band in the MVMP states leads to a loss of EPR signal,¹⁵ we focus here only on MVMP states that retain their IVCT bands. As such, we report the EPR spectrum of the MVMP state **4**-**H**⁰, which was generated by addition of TsOH • H₂O in THF solution and monitored using UV-visible spectroscopy.

The EPR spectra of 1⁻ and 3⁻ are shown in Figure C-11. The EPR spectrum of 1⁻ has been previously reported, and our results are similar.³⁹ The spectrum of 1⁻ displays a rhombic-type

signal, with $g_1 = 2.311$, $g_2 = 2.057$, and $g_3 = 2.037$. The EPR spectrum of the mixed valence state **3**⁻ also exhibits a rhombic-type signal, but it also shows splitting of the central spectroscopic feature. While this compound does exhibit hyperfine coupling due to the Pt nucleus, multiple central features of the spectrum might reflect some degradation, as suggested by the lack of complete reversibility in its electrochemistry. The *g* values for **3**⁻ were measured as $g_1 = 2.279$, $g_2 = 2.044$, and $g_3 = 1.774$.

The EPR spectra of the mixed valence state **4**⁻ and its associated MVMP state **4**-**H**⁰ and the EPR spectrum of the mixed valence state **5**⁻ are shown in Figure C-12. The spectrum of **4**⁻ also exhibits a rhombic-type signal, with $g_1 = 2.214$, $g_2 = 2.045$, and $g_3 = 2.010$. Upon generation of **4**-**H**⁰, a decrease in overall signal intensity and shift in one g value occurred, similar to the analogous [Ni(pdt)₂] states.¹⁴ The g values for the spectrum of **4**-**H**⁰ are measured as $g_1 = 2.214$, $g_2 = 2.045$, and $g_3 = 2.014$, with the shift occurring in g_3 . Lastly, the EPR spectrum of **5**⁻ exhibits a rhombic-type signal, with $g_1 = 2.082$, $g_2 = 2.049$, and $g_3 = 1.944$.

Discussion

Our overall goal is to explore the effect of protonation when moving from the mixed valence state to the MVMP state. We previously established that a reduction in electronic coupling accompanies titration from the mixed valence state to the MVMP for similar metal dithiolene complexes,^{14,15} but that the reduction in electronic coupling is sensitive to the HOMO-LUMO spacing as modulated by changes in the metal center. The qdt and pydt ligands in this study present an opportunity to investigate changes in the ligand and metal orbital overlap that affects the electronic coupling. The oxidation potentials of the dianion states, which become more positive as C atoms on the rings are substituted by N atoms, reflect the electronic.

withdrawing nature of the N atoms (Figure C-1). In addition, the qdt ligand lowers the HOMO in the closed shell state relative to the pdt-containing and pydt-containing complexes.

Calculation of H_{AB} Values

The effects that changes in ligand identity have upon the electronic coupling are readily seen in the pure mixed valence state, which is typically discussed within the Robin-Day classification scheme.⁶⁶ Based on the shape, position, intensity, and solvent independence of the IVCT bands of similar benzenoid-type metal dithiolenes, we assign the mixed valence complexes in this study to the Class III, fully delocalized case.^{14,31} In the Class III regime, the electronic coupling parameter H_{AB} can be conveniently calculated from the λ_{max} value of the IVCT band.^{23,25} Calculated H_{AB} parameters for these complexes, as well as the pdt-containing complexes^{14,15} and Bu₄N[Ni(bdt)₂],⁶² can be seen in Table 4-2. Because of the asymmetry induced in the MVMP states by the presence of a single proton, H_{AB} values must be calculated by integrating the IVCT bands for the MVMP states to obtain r_{ab} , the distance associated with the IVCT. In order to find r_{ab} , the transition dipole moment, $|\mu_{12}|$, must be obtained from integration of the IVCT band (see Equation 2-2). With r_{ab} in hand for the mixed valence state, the distance is assumed to be the same value for the MVMP state. By using the same value of r_{ab} and finding the MVMP $|\mu_{12}|$ for its IVCT band, the resulting value of H_{AB} can be found for the MVMP state.^{14,15} The MVMP HAB values for the complexes under study are collected in Table 4-2 as well.

Table 4-2. Oxidation potentials of the -2/-1 redox couple and electronic absorption parameters for the lowest energy bands of the dianionic closed shell state, monoanionic mixed valence state, and MVMP states of the metal dithiolene complexes under study. H_{AB} electronic coupling parameters are provided for open shell species with IVCT bands observable in electronic spectroscopy.

Compound	E1/2/V vs. Fc/Fc ⁺	$X^{2*}\lambda_{max}\!/nm$	$X^{2\text{-}}\epsilon/10^4M^{\text{-1}}\text{cm}^{\text{-1}}$	MV IVCT λ_{max}/nm	MV IVCT $\epsilon/10^4 M^{-1} cm^{-1}$	MV H _{AB} /cm ⁻¹	MVMP IVCT λmax/nm	MVMP IVCT ε/10 ⁴ M ⁻¹ cm ⁻¹	MVMP H _{AB} /cm ⁻¹
[Ni(pdt)2]	-0.570	488	0.83	866	1.0	5800	907	0.096	1200
[Pd(pdt)2]	-0.288	432	1.2	1119	1.0	4500	-	-	-
[Pt(pdt)2]	-0.437	477	0.98	876	1.6	5700	877	0.27	1200
[Ni(qdt)2]	-0.337	550	2.2	873	1.2	5700	-	-	-
[Pd(qdt)2]	-0.020 (irreversible)	482	2.7	_	-	-	-	-	-
[Pt(qdt)2]	-0.226	539	2.0	909	1.0	5500	-	-	-
[Ni(pydt)2]	-0.757	_	-	870	0.43	5700	874	0.12	820
[Pd(pydt)2]	-0.582	398	1.1	1100	1.9	4500	-	-	-
[Pt(pydt)2]	-0.232 (irreversible)	363	0.71	-	-	-	-	-	-
[Ni(bdt)2]	-1.010	-	-	868	0.44	5800	-	-	-

Oxidative titrations of 1^{2-} and 3^{2-} are shown in Figures 4-6 and C-5. The electrochemistry shows that oxidation of 2^{2} is irreversible, so this complex was excluded from the UV-visible chemical titrations. The H_{AB} values are 5700 cm⁻¹ for 1^{-} and 5500 cm⁻¹ for 3^{-} . The magnitudes of these H_{AB} values (and the positions of the λ_{max} values from which they were obtained) reflect the relative ordering of the accepting molecular orbital in the IVCT transition, which is higher in energy for the Ni complex compared to the Pt complex. Following the oxidative titrations, acid spectrophotometric titration was performed using TsOH • H₂O in THF solution. Figure 4-7 shows the IVCT band for both complexes decreasing completely, with no band present at the endpoint. While this result may be surprising for the MVMP state, we did previously observe complete disappearance of the IVCT band for the pdt-containing complex [Pd(Hpdt)(pdt)]^{0.15} The reversibility of the titration of $1-H^0$ with aqueous base solution is compelling evidence that the species is remaining in an open shell state despite the loss of electronic coupling. As a result, we assert that titration to 1-H⁰ forms a localized, Class I MVMP complex in which no electronic coupling is observed spectroscopically. In the case of complex 3-H⁰, clean isosbestic points were not observed. Again, it seems likely that the electrochemical transformation that is not fully reversible is causing the disruption of isosbestic points. However, we do note that the IVCT band does decrease completely as well.

Turning to the pydt-containing complexes 4, 5, and 6, we once again note that we are excluding oxidative titration of 6 due to its irreversible electrochemistry. As 4^{-} was found to form following column chromatography, it was unnecessary to perform oxidative titration in situ. These two complexes show a similar trend in IVCT band energy in that the band for 4⁻ is present at relatively high energy and that the IVCT band for 5^{-} is shifted to low energy, into the NIR region. The HAB values for the mixed valence states were found to be 5700 cm⁻¹ and 4500 cm⁻¹ for 4^{-} and 5^{-} , respectively. These values are nearly identical to those found for the pdt-containing complexes of the same metals, with the only difference arising from a value of 5800 cm⁻¹ for H_{AB} of [Ni(Hpdt)(pdt)]^{0.14} Upon acid titration following oxidative titration, the IVCT band of 5⁻ decreased completely, consistent with previous observations for the pdt-containing Pd complex (Figure 4-9). The IVCT band of 4^{-} shifted toward lower energy before shifting back toward higher energy and settling at a position of slightly lower energy than the starting mixed valence state 4^{-} , at drastically reduced intensity. Calculation of the H_{AB} value for the resulting MVMP state 4-H⁰ gives a value of 820 cm⁻¹, which is less than the value of 1200 cm⁻¹ for $[Ni(Hpdt)(pdt)]^{0.14}$ The shift in g values from 4⁻ to 4-H⁰ (Figure C-12) also indicates that a new state has formed. In this case, only one g value, g_3 , shifts; this value begins at 2.010 and shifts to 2.014. This shift is less prominent (only one g value changes in this case) than for the analogous [Ni(pdt)₂] states.

Summary of Complexes Retaining Their IVCT Bands in MVMP States

Of the four MVMP states investigated in this study, three were obtained reversibly and one $(3-H^0)$ lacked a clean set of isosbestic points. In addition, only a single MVMP state $(4-H^0)$ retained its IVCT band upon its generation. This configuration is the only MVMP state that was found to possess a degree of electronic coupling measurable by our UV-visible methods. All other MVMP states investigated here are assigned to Class I. The loss of electronic coupling in these Class I MVMP states likely results from the decrease in metal and ligand orbital overlap in the SOMO, which is the accepting orbital of the predominant IVCT transition.³¹ This decrease in orbital overlap is also accompanied by a decrease in SOMO energy, which can be seen from the electrochemistry of the mixed valence states. When moving from the mixed valence states to generate the asymmetric MVMP states, the complexes with higher energy SOMO's (and thus increased metal-ligand orbital overlap) retain intensity in their IVCT bands, which indicates a retention of electronic coupling. The complexes that have exhibited this IVCT band retention thus far are the pdt-containing Ni and Pt complexes and **4-H**⁰ ([Ni(Hpydt)(pydt)]⁰) in this study. While the aforementioned pdt-containing Ni and Pt complexes each exhibited H_{AB} values of 1200 cm⁻¹, **4-H**⁰ exhibits its H_{AB} value of 820 cm⁻¹ at slightly lower energy. This slight decrease of H_{AB} in the MVMP state is likely due to the slight increase in energy of the SOMO of the mixed valence state **4**, reflecting a lower degree of metal-ligand orbital overlap.

In the case of the mixed valence state 1^{-} , the IVCT band is at lower energy than in the $[Ni(pdt)_2]^-$ mixed valence state.¹⁴ Despite the qdt ligands' lowered relative energy (and better energetic alignment with the metal state), this complex exhibits slightly *less* electronic coupling than $[Ni(pdt)_2]^-$. This reduced electronic coupling must then reflect reduced orbital overlap of the ligand and metal states. Due to this reduced orbital overlap, the electronic coupling is completely removed upon generation of the MVMP state as observed through the complete disappearance of the IVCT band, rendering **1-H**⁰ a Class I state.

In this study, we have demonstrated a degree of control over the electronic coupling in the MVMP state by investigating two series of ligands. While we were able to establish an additional complex as containing persistent electronic coupling in its MVMP state, most complexes under study resorted to the Robin-Day Class I regime. A threshold still appears to be present for whether or not these benzenoid-type metal dithiolene complexes retain their electronic coupling in their MVMP states. Future work from our laboratory will seek to better understand the transition of degree of electronic coupling in MVMP states by controlling ligand and metal identities. This effect of protonation on the mixed valence states of complexes with non-innocent ligands will prove useful in following PCET reactions in the ground state. The potential selfexchange of configurations of these asymmetric complexes sheds light on the result of imposing a proton transfer coordinate on the electronic coupling. We have thus provided a probe *via* the IVCT band to exclusively interrogate electronic coupling in the potential energy landscape of PCET reactions.

Conclusions

We investigated the electrochemical and steady-state spectroscopic properties of two series of metal dithiolene complexes, $[M(qdt)_2]$ and $[M(pydt)_2]$ (M = Ni, Pd, Pt), (qdt = 2,3quinoxalinedithiol), (pydt = 2,3-pyridinedithiol). In analogy to the pdt-containing metal complexes (pdt = 2,3-pyrazinedithiol), we studied the effect of protonation on the electronic coupling in the mixed valence states. The electronic coupling parameter H_{AB} was found for all of the accessible mixed valence states, and trends within each ligand series match expectations based on metal-ligand orbital overlap. When moving from the mixed valence states to the asymmetrically protonated MVMP states, $[Ni(pydt)_2]$ retained a degree of electronic coupling; its H_{AB} value was decreased from 5700 cm⁻¹ to 820 cm⁻¹, a decrease of 86%. All other MVMP states resulted in no observable IVCT band, indicating localization of electron density and assignment to the Class I mixed valence regime. A threshold amount of metal-ligand orbital overlap appears to be required when generating the MVMP states from the initial mixed valence states. This asymmetric protonation gives a direct indication of the presence of a proton on the electronic coupling, giving information about the potential energy surfaces of PCET reactions in the ground

state.

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Appendix C: Supporting Information for [M(quinoxalinedithiol)₂] and [M(pyridinedithiol)₂] (M = Ni, Pd, Pt)

Ni1-S1	2.154(3)	S3-C10	1.713(9)
Ni1-S2	2.191(3)	S4–C9	1.722(9)
Ni1-S3	2.161(3)	S5-C17	1.744(10)
Ni1-S4	2.185(3)	S6-C18	1.729(10)
Ni2-S5	2.187(3)	S7-C26	1.770(9)
Ni2-S6	2.182(3)	S8–C25	1.746(10)
Ni2–S7	2.178(3)	C1–C2	1.414(13)
Ni2–S8	2.192(3)	C9–C10	1.475(11)
S1-C2	1.711(10)	C17–C18	1.476(13)
S2C1	1.745(10)	C25–C26	1.412(12)
S1-Ni1-S4	176.84(12)	S2-Ni1-S3-C10	140(5)
S2-Ni1-S3	178.45(14)	S3-Ni1-S2-C1	45(5)
S1-Ni1-S2	91.00(10)	N1-C1-S2-Ni1	-179.0(7)
S3-Ni1-S4	91.25(10)	N2-C2-S1-Ni1	-178.4(7)
S1-Ni1-S3	87.91(11)	N3-C9-S4-Ni1	-179.6(6)
S2-Ni1-S4	89.89(10)	N4-C10-S3-Ni1	177.8(6)
S5-Ni2-S7	177.70(2)	S5-Ni2-S7-C26	-33(3)
S6-Ni2-S8	177.57(13)	S7-Ni2-S5-C17	-145(3)
S5-Ni2-S6	91.17(11)	S6-Ni2-S8-C25	-139(3)
S7-Ni2-S8	91.08(10)	S8-Ni2-S6-C18	-43(3)
S5-Ni2-S8	87.05(11)	N5-C26-S7-Ni2	-179.7(6)
S6-Ni2-S7	90.74(10)	N6-C25-S8-Ni2	-175.4(6)
S1-Ni1-S4-C9	76(2)	N7-C18-S6-Ni2	-178.0(8)
S4-Ni1-S1-C2	108(2)	N8-C17-S5-Ni2	-178.6(6)

Table C-1. Selected bond lengths (Å) and angles (deg) for $1 \cdot C_3H_6O$.

Table C-2. Selected bond lengths (Å) and angles (deg) for $2 \cdot C_3H_6O$.

Pd1-S1	2.3061(15)	S2-C2	1.728(5)	
Pd1–S2	2.2938(15)	S3–C9	1.728(5)	
Pd1–S3	2.2945(15)	S4C10	1.744(4)	
Pd1–S4	2.3090(14)	C1–C2	1.460(6)	
S1C1	1.749(5)	C9–C10	1.460(6)	
S1–Pd1–S3	178.01(5)	S3-Pd1-S1-C1	-23.8(16)	
S2-Pd1-S4	177.72(5)	S2-Pd1-S4-C10	-45.6(13)	
S1-Pd1-S2	88.38(5)	S4-Pd1-S2-C2	-134.4(12)	
S3–Pd1–S4	88.62(5)	N1-C1-S1-Pd1	-179.6(3)	
S1–Pd1–S4	93.22(5)	N2-C2-S2-Pd1	179.3(3)	
S2-Pd1-S3	89.80(5)	N3-C10-S4-Pd1	179.8(3)	
S1-Pd1-S3-C9	-159.6(15)	N4-C9-S3-Pd1	-176.6(3)	
Pt1-S1	1	2.304(6)	S3–C9	1.76(2)
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Pt1-S2	2	2.282(7)	S4C10	1.754(16)
Pt1-S3	3	2.285(6)	S5-C17	1.66(2)
Pt1–S4	1	2.323(5)	S6C18	1.73(2)
Pt2-S5	5	2.284(7)	S7–C25	1.73(2)
Pt2–Se	5	2.285(7)	S8-C26	1.772(14)
Pt2–S7	7	2.287(6)	C1–C2	1.57(2)
Pt2–S8	3	2.306(5)	C9–C10	1.44(2)
S1C1		1.741(19)	C17–C18	1.53(2)
S2-C2		1.64(2)	C25–C26	1.43(2)
S1–Pt	l-S3	176.6(3)	S2-Pt1-S4-C10	-24(10)
S2–Pt1	l-S4	178.1(2)	S4-Pt1-S2-C2	-156(9)
S1–Pt	l-S2	88.6(2)	N1C1S1Pt1	-170.5(12)
S3–Pt1	l-S4	89.3(2)	N2-C2-S2-Pt1	-167.6(16)
S1–Pt	l-S4	93.2(2)	N3-C9-S3-Pt1	-171.2(11)
S2–Pt1	I-S3	88.9(2)	N4-C10-S4-Pt1	-179.8(16)
S5–Pt2	2–S8	178.3(2)	S5-Pt2-S8-C26	175(30)
S6–Pt2	2–S7	179.0(3)	S8-Pt2-S5-C17	11(12)
S5–Pt2	2–S6	87.7(2)	S6-Pt2-S7-C25	67(16)
S7–Pt2	2–S8	88.9(2)	S7-Pt2-S6-C18	123(16)
S5–Pt2	2–S7	92.7(2)	N5-C17-S5-Pt2	-179.3(16)
S6–Pt2	2–S8	90.6(2)	N6-C18-S6-Pt2	-166.8(13)
S1–Pt	l-S3-C9	-133(4)	N7-C25-S7-Pt2	-167.0(13)
S3–Pt	I-S1-C1	-38(5)	N8-C26-S8-Pt2	-177.7(12)

Table C-3. Selected bond lengths (Å) and angles (deg) for $3 \cdot C_3H_6O$.



Figure C-1. Cyclic voltammograms of $(Bu_4N)_2[Ni(pdt)_2]$ (pdt = 2,3-pyrazinedithiol),²⁸ **1**, **4**, and $Bu_4N[Ni(bdt)_2]$ (bdt = 2,3-benzenedithiol)⁶² in DMF at a scan rate of 100 mVs⁻¹ using 0.1 M Bu_4NPF_6 as electrolyte. The reversible or quasi-reversible redox events are shown for each compound. In all cases, the $[M(xdt)_2]^{2-/1-}$ couple is shown; this redox couple is not completely reversible in the case of **4**. In addition, the $[Ni(bdt)_2]^{1-/0}$ reversible redox event is shown for $Bu_4N[Ni(bdt)_2]$.



Figure C-2. Spectrophotometric titration of 1^{2-} in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in Figures (a) and (b), respectively.



Figure C-3. Spectrophotometric titration of 2^{2-} in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in Figures (a) and (b), respectively.



Figure C-4. Spectrophotometric titration of 3^{2-} in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in Figures (a) and (b), respectively.



Figure C-5. Oxidative titration from 1^{2-} to 1^{-} (a) and from 3^{2-} to 3^{-} (b) in THF using I_2 as oxidant. The IVCT band of 3^{-} was taken at its maximum value following titration.



Figure C-6. UV-visible spectrum of 2²⁻ in THF.



Figure C-7. Spectrophotometric titration of 5^{2-} in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in Figures (a) and (b), respectively.



Figure C-8. Spectrophotometric titration of 6^{2-} in DMF using aqueous HCl as titrant. Two sets of isosbestic points were present, resulting in Figures (a) and (b), respectively.



Figure C-9. UV-visible spectra of 5^{2-} after addition of aqueous NaOH solution. Slight changes to the initial bands resulted, indicating partial protonation of the starting compound in our acid titration experiments.



Figure C-10. Spectrophotometric titration from 5^{2-} to 5^{-} in THF using a solution of I₂ in THF as titrant. The inset shows the same titration performed on a separate NIR instrument.



Figure C-11. EPR spectra of 1⁻ (a) and 3⁻ (b) dissolved in THF at 35 K, generated after addition of a solution of I_2 dissolved in THF to the respective dianions. The oxidation was monitored using UV-visible spectroscopy.



Figure C-12. EPR spectra of 4⁻ and 4-H⁰ (a) and 5⁻ (b) dissolved in THF at 35 K. 4-H⁰ was generated by addition of a solution of TsOH • H₂O dissolved in THF to 4⁻, and 5⁻ was generated by addition of a solution of I₂ dissolved in THF to 5²⁻. The conversions were followed using UV-visible spectroscopy.

Chapter 5

Synthesis and Characterization of the Gold Dithiolene Monoanion, (Bu₄N)[Au(pdt = 2,3-pyrazinedithiol)₂]

This chapter is adapted from:

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Introduction

Metal dithiolene complexes have long been of interest for the non-innocent behavior of their ligands. One reason for the interest in non-innocent complexes is that the strong ligandmetal interaction allows for charge to be spread over large distances within the complex, stabilizing redox states that would not otherwise be accessible.^{1–12} As such, these complexes are valued for their rich electrochemical behavior and their multiple single-electron redox processes that occur predominantly on the ligands.^{5,8} Because the ligands are often the most redox-active unit in planar metal dithiolenes, the formal oxidation of a single ligand results in a state that can be described in the language of mixed valence chemistry, in which the ligands are modeled as two interacting redox sites, while the metal functions as the bridge. Thus, properties of mixed valence states should change with structural modification of the metal center or the ligands.

Recently, interest has grown in metal dithiolenes in which the carbon backbone of the dithiolene core is structurally modified.^{5,6,13} In particular, nitrogen-containing heterocyclic ligands allow for a wide variety of interactions, including their use as additional coordination modalities within metal-organic frameworks (MOFs).^{14,15} The nitrogen-containing portions also

allow structural modifications at the nitrogen sites to control structural and electronic properties throughout the entire molecule – for example, by protonation of the nitrogen bases.^{16,17} Thus, there is current interest in complexes of this type, as testified to by multiple theoretical studies examining the same molecule reported herein.^{18,19} These reports focused on the complex's possible uses in supramolecular assemblies, where the nitrogen bases might be used to tune the electronics of the complex. However, despite multiple such theoretical studies, the molecule remains to be synthesized, isolated, and studied experimentally.

We report efforts to examine the electronic properties of the gold complex $[Au(pdt)_2]$ (Figure 5-1) as a function of both redox and protonation state. Compared to the previous Ni, Pd, and Pt complexes that we have studied, the Au complex is expected to possess decreased electronic coupling in its mixed valence state as result of decreased effective nuclear charge of Au (see Chapter 3 discussion),⁷ thereby extending the range of our control over electronic coupling. In the series with Ni, Pd, and Pt pdt analogues, the Au complex should permit the least degree of metal-ligand interaction and the lowest energy IVCT band. Though this molecule is absent from the experimental literature, many close analogues of [Au(pdt)₂] have been synthesized, including the Se-containing $[Au(pds)_2]^-$ (pds = 2,3-pyrazinediselenolate),²⁰⁻²³ the cyano-substituted pyrazine dithiol complex [Au(dcdmp)₂]⁻ (dcdmp = 2.3dicyanodimercaptopyrazine),^{24,25} and the Cu-containing complex [Cu(pdt)₂]^{-,23,26-28} We report our synthesis and characterization of (Bu₄N)[Au(pdt)₂] (1), as well as our investigation of its electrochemistry, spectroelectrochemistry, and spectrophotometric response to acid titration. We find that a reversible reduction event occurs to generate the dianion. However, the oxidation to the neutral species is irreversible, precluding detailed analysis of that state. A spectral response to acid titration was observed in acetone, which we ascribe to generation of the singly protonated state.



Figure 5-1. Structure of [Au(pdt)₂]⁻.

Experimental

Materials and Methods

NaSH • xH₂O and Bu₄NBr were purchased from Sigma Aldrich, 2,3-dichloropyrazine was purchased from TCI, NaOEt was purchased from Strem Chemicals, and HAuCl₄ • 3H₂O was purchased from Acros. Anhydrous sodium sulfate was purchased from EMD. All commercial reagents and solvents were used without further purification. IR spectra were recorded on a PerkinElmer Spectrum 400 FT-IR spectrometer equipped with an ATR accessory. ¹H NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer in d_6 -DMSO and were referenced to the residual solvent peak. Electronic absorption spectra were recorded using an Agilent 8453 spectrometer and a 1 cm path length quartz cell. Electrochemical measurements were obtained using a Pine WaveNow potentiostat using a Pt wire as the working electrode, a Pt wire as the auxiliary electrode, and a Ag/Ag^+ wire as a pseudo-reference electrode. The electrolyte was 0.1 M tetra-butyl ammonium hexafluorophosphate in acetonitrile (MeCN). Measurements were referenced using the Fc/Fc^+ redox couple as an internal standard. Spectroelectrochemical (SEC) measurements were made in a similar fashion. The sample was electrolyzed under inert atmosphere in a 1 mm path length quartz cell. A gold honeycomb electrode card (Pine Instrument Company) was used as the working and counter electrodes, and the same Ag/Ag⁺ wire as before was used as the pseudo-reference electrode. The solvent was MeCN for the SEC measurements, and the electrolyte was 0.1 M tetra-butylammonium

hexafluorophosphate. A single crystal for X-ray structure determination was grown as described below. The crystal structure was obtained using a Bruker SMART APEX CCD area detector equipped with a graphite monochromator, a Monocap collimator, and a MoK_{α} fine-focus sealed tube. The collected frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The structure of **1** was solved and refined using the Bruker SHELXTL (Version 6.1) software package. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of $(Bu_4N)[Au(pdt)_2]$ (1)

2,3-Pyrazinedithiol (pdt) was synthesized according to a literature procedure.^{15,26-28} A solution of HAuCl₄ • $3H_2O$ (0.6161 g, 1.564 mmol) in 30 mL H₂O was prepared. 2,3-Pyrazinedithiol (0.4479 g, 3.127 mmol) was added to a separate solution of NaOEt (0.43 g, 6.3 mmol) in MeOH. A separate solution of Bu₄NBr (0.5039 g, 1.563 mmol) was prepared in 40 mL CHCl₃. The H₂O solution was transferred to a separatory funnel, and the CHCl₃ solution was added to phase transfer AuCl₄⁻. The orange CHCl₃ layer was drained directly into the stirring MeOH solution. The solution quickly turned green-brown, and a brown precipitate formed. The mixture was left to stir for 15 hrs, after which the precipitate had dissolved. Solvent was removed *in vacuo*. The remaining green solid was taken up in 100 mL CHCl₃ and transferred to a separatory funnel. The cHCl₃ solution was washed with H₂O (3 x 25 mL) and dried over Na₂SO₄. The solvent was removed *in vacuo*. The remaining green solid over the product was recrystallized from evaporating methanol to give silver, needle-like crystals (0.1794 g, 15.84%). Single crystals for X-ray structure determination were also obtained from controlled evaporation of a solution of **1** in methanol. ¹H NMR (*d₆*-DMSO): 8.00 ppm (s, 4 H), 3.15 ppm (t, 8 H), 1.54 ppm (m, 8 H), 1.30

ppm (m, 8 H), 0.91 ppm (t, 12 H). IR (neat): v/cm⁻¹ = 2962, 2873, 2345, 1486, 1461, 1416, 1383, 1328, 1283, 1182, 1139, 1063, 880, 847, 833, 802, 739. Anal. Calcd for H₄₀C₂₄N₅S₄Au: H, 5.57; C, 39.82; N, 9.68; S, 17.72. Found: H, 5.65; C, 40.10; N, 9.76; S, 17.99.

Results and Discussion

Crystal Structure of 1

Crystals of **1** were obtained from evaporation of a methanol solution. The crystal structure can be seen in Figure 5-2, and data collection parameters and selected bond lengths and angles can be seen in Tables 5-1 and 5-2, respectively. This is the first instance in which the $[Au(pdt)_2]^-$ unit has been characterized crystallographically. Several analogues of this compound exist in the literature, including the cyano-substituted pyrazine derivative $[Au(dcdmp)_2]^{24}$ and the selenium-containing analogue $[Au(pds)_2]$,²⁰ and calculations have previously been performed on $[Au(pdt)_2]$,^{18,19} all of which can be compared to our structure.



Figure 5-2. ORTEP plots of the two crystallographically inequivalent monoanions of $[Au(pdt)_2]^-$. The counterion (C₁₆H₃₆N) and the H atoms are omitted for clarity.

	1	
empirical formula	$C_8H_4AuN_4S_4$, $C_{16}H_{36}N$	
formula weight and crystal system	723.86, monoclinic	
color and habit	brown, block	
Temp (K)	298(2)	
λ (Å)	0.71073, Μο Κα	
crystal size (mm ³)	0.29 x 0.26 x 0.16	
space group	$P 2_1/c$	
a (Å)	17.920(3)	
b (Å)	9.8615(15)	
c (Å)	17.533(3)	
α (°)	90	
β (°)	106.409(3)	
γ (°)	90	
V (Å ³)	2972.2(8)	
Z	4	
$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.618	
$\mu \text{ (mm}^{-1}$)	5.252	
no. of reflens collected	24018	
no. of reflens with $I > 2\sigma(I)$	4386	
no. of independent params	314	
GOF on F^2	0.997	

 Table 5-1. Crystallographic data for compound 1.

Table 5-2. Selected bond lengths (Å) and angles (deg) for 1.

	• • •		
Au1-S1	2.3149(10)	S3–C8	1.742(4)
Au1-S2	2.3129(11)	S4–C5	1.756(4)
Au2-S3	2.3153(12)	C1–C4	1.412(5)
Au2-S4	2.3110(12)	C5–C8	1.407(5)
S1-C1	1.750(4)	Au1···Au2	8.960
S2-C4	1.749(4)		
S1-Au1-S1'	180.00(9)	S1'-Au1-S1-C1	-88(100)
S2-Au1-S2'	180.00(8)	S2'-Au1-S2-C4	42.63(11)
S1-Au1-S2	89.91(4)	N1-C1-S1-Au1	175.8(2)
S1-Au1-S2'	90.09(4)	N2-C4-S2-Au1	-174.6(3)
S3-Au2-S3'	180.00(6)	S3'-Au2-S3-C8	51(100)
S4-Au2-S4'	180.0	S4'-Au2-S4-C5	-66(100)
S3-Au2-S4	90.61(4)	N4-C8-S3-Au2	177.6(3)
S3-Au2-S4'	89.39(4)	N3-C5-S4-Au2	-175.4(3)

Two crystallographically distinct [Au(pdt)₂] monoanion complexes were present within the asymmetric unit cell (half unit cell) of **1**, with a Au•••Au separation distance of 11.708 Å between symmetry-related Au centers. Bond distances and angles do not deviate from typical expectations for gold dithiolene complexes. The complexes appear to deviate slightly from ideal square planar geometry, with adjacent S–Au–S angles differing by as much as 0.61° in one of the complexes (S3–Au2–S4). Opposing S–Au–S angles do not deviate from 180°, and the Au atoms occupy centers of inversion for their respective molecules. Most bond lengths compare very favorably with those of [Au(dcdmp)₂], as the average Au–S, dithiolene core C–N, and outer pyrazine ring N–C bond lengths are nearly identical for these complexes.²⁴ The inclusion of cyano groups seems to make the biggest difference on the dithiolene core C–C bond lengths; this distance changes from an average of 1.41 Å to 1.45 Å with inclusion of cyano groups. Interestingly, the electron-withdrawing cyano groups lengthen the C–C bond because of decreased electron density on the S atoms, which introduces more dithione character into the dithiolene core. In comparison with previous calculations, average bond lengths in **1** are shorter in all cases.^{18,19}

Vibrational Spectroscopy

The IR spectrum of **1** (Figure D-1) is similar to that of other monoanionic gold dithiolenes.^{19,29,30} The minimal changes in the IR spectrum reinforce the fact that benzenoid-type dithiolene structures tend to resist changes in vibrational energies. As such, vibrational markers for determining relative oxidation states of benzenoid-type metal dithiolenes remain elusive.^{19,29,31}

The cyclic voltammogram (CV) of **1** near the cathodic end of MeCN's electrochemical window is shown in Figure 5-3. Other scans in different regions of MeCN's electrochemical window can be found in Figure D-2. The only reversible redox event for $[Au(pdt)_2]$ is the one shown in Figure 5-3 (occurring at -1.665 V vs. Fc/Fc⁺), which is associated with the $[Au(pdt)_2]^{2/1-}$ couple. Consideration of the previously calculated molecular orbitals of **1** suggests that the electron is added to a LUMO comprised of a sigma antibonding combination of the dithiolene sulfur orbitals with the gold $5d_{xy}$ orbital.^{18,19} Relative to the analogous $[Ni(pdt_2)]^{2-}$, the large effective nuclear charge of the Au^{III} stabilizes the LUMO and results in a more positive reduction potential for **1** (the reduction of $[Ni(pdt)_2]^{2-}$ is not observed within the solvent window of MeCN).^{15,19} In comparison to the electrochemical behavior of **1**, the $[Au(dcdmp)_2]^-$ complex possesses a reversible reduction event at -0.604 V vs. Fc/Fc⁺ in MeCN due to stabilization by the electron withdrawing CN moiety, a large difference from observations of **1**.²⁴



Figure 5-3. Cyclic voltammogram of 1 in MeCN at a scan rate of 100 mVs⁻¹ using 0.1 M Bu_4NPF_6 as electrolyte.

In the anodic range, 1 shows two irreversible oxidation events at 0.73 V and 1.50 V vs. Fc/Fc⁺, which correspond to generation of the neutral and monocationic complexes, respectively (Figure D-2). The HOMO of 1 is the antisymmetric combination of the ligand S $3p_z$ orbitals and a small contribution from the gold $5d_{xz}$ orbital.¹⁹ In a similar manner to that of the LUMO, the HOMO of 1 is stabilized relative to its [Ni(pdt)₂]²⁻ analogue and has a smaller metal contribution to the HOMO in 1 (note that the metal contribution to the HOMO is of antibonding character).¹⁹ This stabilization results in a more positive oxidation potential required to generate the neutral species of 1.^{15,19} Interestingly, an additional redox event was visible upon the return cathodic scan. If the anodic scan proceeded only to generate the neutral complex, then this new redox event appears at -0.61 V vs. Fc/Fc⁺. If the full range is scanned to include the monocationic complex, the new redox event appears at -1.11 V vs. Fc/Fc⁺, indicating that this redox event requires that the oxidized species be formed first, and that it is dependent upon the degree of oxidation.

One of our interests in this molecule originally lay in generation of the neutral mixed valence state of **1**. Unfortunately, we are prevented from generating the neutral state of this molecule because it is unstable on the electrochemical time scale. Although generation of the dianion itself is reversible, the associated oxidation at -0.92 V vs. Fc/Fc^+ makes recovery of the monoanionic complex difficult, and we were unable to isolate this state for structural characterization.

Electronic Spectroscopy: Solvatochromism, Spectroelectrochemical Response, and Spectrophotometric Acid Titration

Figure 5-4 shows the UV-visible extinction spectrum of **1** in a series of solvents. Though other analogous complexes ($[Cu(pdt)_2]^-$) have transitions at lower energy, the transition at ca. 372

nm is the lowest energy transition that we observe (including the NIR region). Based upon prior calculations, the lowest energy transition should be predominantly a HOMO \rightarrow LUMO transition. While the pure HOMO \rightarrow LUMO transition is symmetry forbidden, this transition is observed in the copper analogue, due to contributions from other orbitals.²⁶ Prior calculations indicate that the HOMO-LUMO gap should be smaller in the gold complex, relative to the copper complex.¹⁹ Thus, if the HOMO \rightarrow LUMO transition were present for 1, we would expect it to be found at wavelengths much longer than 372 nm. Based upon this, we suspect that the HOMO \rightarrow LUMO transition is suppressed more strongly in 1, and we tentatively assign the intense absorbance band ca. 372 nm as predominantly the HOMO - 1 \rightarrow LUMO transition,²⁶ which occupies a spectral region similar to the absorbance of other monoanionic gold dithiolenes.^{29,32,33} However, we cannot conclusively exclude its identity as the HOMO \rightarrow LUMO transition.

This transition at ca. 372 nm displays significant solvatochromism. Within the series of aprotic solvents, we observe a negative solvatochromic response (Table 5-3). Negative solvatochromism indicates that the ground state has a larger dipole moment than the excited state, as the ground state is stabilized more than the excited state with increasing solvent polarity. This also means that 1 must possesses a permanent dipole moment in solution, which is an interesting result given its high symmetry in the crystal structure. While we cannot provide a definitive explanation for this ground state dipole moment, it seems likely that it should originate from the position of the counterion. When moving from aprotic to protic solvents (EtOH and MeOH), we observe a significant bathochromic shift. Given the presence of the nitrogen bases on the pdt ring, it seems reasonable to conclude that the excited state is stabilized relative to the ground state by hydrogen bonding to these nitrogen bases. A second absorbance band, assigned as predominantly the HOMO - 2 \rightarrow LUMO transition based upon prior calculations,²⁶ appears at higher energy. This band has minor shifts in various solvents, but no systematic solvatochromism trend exists.



Figure 5-4. UV-visible spectra of 1 in various solvents. Note that the spectrum of 1 in acetone extends only to 327 nm.

		Band 1		Band 2	
_	Solvent	λ_{max} / nm	$\epsilon / 10^4 M^{-1} cm^{-1}$	λ_{max} / nm	$\epsilon / 10^4 M^{-1} cm^{-1}$
-	THF	375	2.1	288	2.9
	acetone	372	2.2	_	_
	MeCN	370	2.2	285	2.9
	DMF	373	2.3	287	3.1
	EtOH	383	1.6	285	2.3
	МеОН	382	2.1	285	2.9

Table 5-3. Solvatochromic response of 1.

We also investigated the UV-visible spectroelectrochemical response of 1 during the generation of the dianion in MeCN. As shown in Figure 5-5, the spectrum changed slightly, with the HOMO - $1 \rightarrow$ LUMO band at 370 nm shifting to 373 nm and gaining a significant shoulder on the low energy side. The position of the higher energy band did not change, but also gained a low energy shoulder. The relatively small changes in the absorption spectra might be expected, as the electron density changes are largely confined to the gold and dithiolene sulfurs in the

LUMO. Upon re-oxidation of the complex, we regain the starting spectrum of the monoanion, indicating that this transformation is reversible at least on the timescale of minutes.



Figure 5-5. Spectroelectrochemical response of 1 to an applied potential of -2.25 V vs. Fc/Fc^+ in MeCN.

Finally, we acquired electronic absorbance spectra of **1** in acetone as a function of added HCl (aq). In acetone, the HOMO - 1 \rightarrow LUMO transition was present at 372 nm ($\varepsilon = 2.2 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$). As seen in Figure 5-6, addition of HCl (aq) presented new absorbance bands at 426 nm ($\varepsilon = 0.86 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 349 nm ($\varepsilon = 1.3 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$), with a shoulder at 381 nm ($\varepsilon = 0.88 \text{ x } 10^4 \text{ M}^{-1}\text{cm}^{-1}$). A set of clean isosbestic points is present, consistent with conversion from the unprotonated state to the singly protonated state. The larger response of the spectra to protonation (versus reduction) of **1** can be understood by the fact that the protonation should affect the electron density over the ligands, while the reduction is confined largely to the metal center. For the orbitals carrying contributions from the aromatic portions of the ligands, protonation should stabilize the orbital and create an asymmetry, in which the electron density is biased towards the protonated orbital. We note that the titration is also reversible upon the addition of aqueous base. Interestingly, the same experiment was performed in DMF solution,

but no spectral changes occurred during the addition of acid (Figure D-3). At present, we are unsure of the exact reason for this behavior, though we think it likely that the basicity of the solvent was greater than that of the complex, causing the solvent to be protonated before the complex.



Figure 5-6. Spectrophotometric titration of **1** in acetone as a function of the noted equivalents of aqueous HCl added.

Conclusions

The complex $(Bu_4N)[Au(pdt)_2]$ was synthesized and characterized for the first time. Its experimental study was conspicuously absent from the literature, although it was explored in several sets of calculations. Our results allow for direct comparison with many of these calculations, as well as to several related compounds. In addition, we find that $(Bu_4N)[Au(pdt)_2]$ possesses a reversible electrochemical generation of the dianion, and we obtained the UV-visible spectrum of the dianion using spectroelectrochemistry. The complex is sensitive to protonation in acetone solution, and the singly protonated state can be generated – a process we followed using UV-visible spectrophotometric titration. The electronic spectrum is much more sensitive to protonation than reduction, which we attribute to the fact that protonation directly affects the electron density over an entire ligand, while the reduction is mostly localized to the metal center. This study should help inform subsequent uses of this molecule, as proposed by previous theoretical studies.^{18,19}

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Appendix D: Supporting Information for [Au(pyrazinedithiol)₂]



Figure D-1. IR spectrum of 1.



Figure D-2. Various range cyclic voltammetry scans of **1** in MeCN at a scan rate of 100 mVs⁻¹ using 0.1 M Bu₄NPF₆ as electrolyte. Scans are referenced vs. Fc/Fc^+ .



Figure D-3. Spectrophotometric titration of 1 in DMF using aqueous HCl as titrant. No change is observed.

Chapter 6

Controlling Proton-Dependent Electron Transfer in Metal Dithiolenes: Conclusions and Outlook

Summary and Conclusions

The studies recorded in this thesis have demonstrated several important points about mixed valence chemistry, the effects of protonation, and implications for PCET reactions through the use of metal dithiolene model systems. Although all cases lacked explicit proton transfer, the mere occurrence of asymmetric protonation, which creates the possibility of proton transfer, induces changes in the electron transfer coordinate. This electron transfer was followed by monitoring the IVCT band using steady-state electronic spectroscopy, which we have established as a probe for extending pure electron transfer into the realm of PCET reactions. Changes to this IVCT band upon protonation are explained using changes to the underlying potential energy landscape of the PCET process. As a result, we have established an understanding of how to control the electron transfer and proton transfer interdependence through structural modification of the ligands in metal dithiolene complexes.

Exploring the MVMP State of [*Ni*(*pdt*)₂]

Understanding the mixed valence mixed protonated (MVMP) state is essential when studying PCET self-exchange in homogeneous ground state transformations. Because nickel 2,3pyrazinedithiolene, [Ni(pdt)₂], possesses a reversible single electron oxidation event¹ to generate its mixed valence state while also undergoing single protonation to give rise to the MVMP state, it acted as our first model system to study the MVMP state. Our study was the first instance in which the MVMP state was unambiguously identified and characterized. The closed shell states of this compound were fully characterized in terms of their electronic spectra,² and the crystal structures for the dianion and monoanion were reported. While interpretation of the proton-dependent electrochemistry is difficult due to overlapping redox events, we were able to observe clean and reversible changes in the steady-state electronic spectra and EPR spectra, indicating generation of a singly protonated paramagnetic species. As such, we conclude that we had successfully generated the MVMP state of [Ni(pdt)₂].

In addition, the degree of electronic coupling was quantified in both the mixed valence and MVMP states. The mixed valence complex exhibits a prominent IVCT band in its electronic spectrum, which allows the electronic coupling parameter, H_{AB} , to be calculated as 5800 cm⁻¹. Upon protonation, this IVCT band shifts to lower energy while decreasing in intensity. This shift in IVCT band was shown to be fully reversible and accompanied by a slight shift in two g values in the EPR spectrum of this compound. The value of H_{AB} for the MVMP state was calculated to be 1200 cm⁻¹, a five-fold decrease in electronic coupling. This drastic decrease in electronic coupling was interpreted as resulting from a partial localization of electron density to the protonated ligand. Another possibility for the decrease could be due to PCET self-exchange, which would have an associated Franck-Condon overlap of the wavefunctions associated with the reactant and product state potential energy surfaces. This possibility was ruled out, however, with the aid of proton potential calculations that showed the lack of proton transfer, leading us to conclude that the decrease in electronic coupling was due solely to localization of electron density. Regardless, through analysis of the IVCT band the presence of a proton informs us of the effect of a possible proton transfer on the electron transfer coordinate, an important effect for PCET transformations.

Following our work on [Ni(pdt)₂], we explored the effect of altering the bridging metal center by extending the above studies to the Pd and Pt analogues. Again, we provided full structural, electrochemical, and spectral characterization of these compounds, and we explored spectrophotometric titrations of all accessible redox and protonation states. This series of complexes allows us to easily explore how changes to the bridge could possibly affect PCET simply by synthesizing complexes with different metal centers. Additionally, our descriptions of the electronic spectra when moving from the mixed valence to the MVMP state connect the fields of non-innocent ligands and mixed valence chemistry, two fields which describe similar phenomena but use different approaches.

The Pt analogue, $[Pt(pdt)_2]$, was found to exhibit a response similar to that of the Ni complex when generating the MVMP state. The electronic coupling parameter was found to be 5700 cm⁻¹ in the mixed valence state, which also exhibited a drastic five-fold decrease to 1200 cm⁻¹ when protonated to generate the MVMP state. The IVCT band drastically decreased in intensity but barely shifted position, in contrast to the experiments on the Ni complex. In addition, the EPR spectrum of the Pt complex did not shift, but decreased in intensity. The Pd complex, $[Pd(pdt)_2]$, exhibited an IVCT band in the NIR region in the electronic spectrum of its mixed valence complex, which is positioned at significantly lower energy. Its value of H_{AB} was found to be 4500 cm⁻¹, which was found to result from a lower energy metal bridge state contributing to the mixing between ligand states.³ This lower energy IVCT band is also consistent with its higher energy HOMO \rightarrow LUMO transition and more positive oxidation potential. Upon generation of the MVMP state of the Pd complex, the IVCT band disappears entirely, without shifting, in contrast to both the Ni and Pt analogues which retained their IVCT bands. Due to a smaller degree of metal contribution to mediating the ligand-ligand coupling in

the Pd complex, we conclude that, upon protonation, the electronic coupling between ligands is removed entirely. Essentially, the electron density in the Pd complex was completely localized on the protonated ligand. This study demonstrates a simple means by which to control the electronic coupling in the MVMP state, which, for this series of complexes, either resulted in a five-fold reduction in electronic coupling (Ni and Pt) or complete electronic localization (Pd).

Ligand-Based Tools for Controlling Electronic Coupling in the MVMP State: Ligand Energy and Orbital Overlap

Next, we aimed to further control the change in electronic coupling when moving from the mixed valence to the MVMP state by investigating two other ligands, 2,3-quinoxalinedithiol (qdt) and 2,3-pyridinedithiol (pydt). The qdt ligand possesses four nitrogen atoms, similarly to pdt, but the aromatic rings are extended, lowering the ligand states. The pydt ligand possesses only two nitrogen atoms, causing its ligand states to be higher in energy relative to pdt. Considering the qdt series of complexes, we fully characterize the electrochemistry and electronic spectra of all five accessible redox and protonation states for each metal complex.⁴⁻⁷ The [Pd(qdt)₂] complex exhibited irreversible electrochemistry to generate its mixed valence state, while the [Pt(qdt)₂] complex did not exhibit clean isosbestic points when generating its MVMP state. In addition, the H_{AB} value of the mixed valence state of the [Pt(qdt)₂] complex was found to be 5500 cm⁻¹. The behavior of $[Ni(qdt)_2]$, however, was clean upon generating its MVMP state. For the $[Ni(qdt)_2]$ complex, its H_{AB} value was found to be 5700 cm⁻¹,⁵ slightly less than its pdt-containing analogue. Upon titration to its MVMP state, the IVCT band disappeared completely, indicating complete localization of electron density on the protonated ligand. The difference between the qdt and pdt Ni complexes ([Ni(pdt)₂] retained its IVCT band and electronic coupling in its MVMP state, with an H_{AB} value of 1200 cm⁻¹) arises from a difference in spatial orbital overlap between the ligand states and the metal bridge state. The IVCT band for the mixed valence state of $[Ni(qdt)_2]$ is positioned at lower energy, indicating lower electronic coupling, despite possessing lower energy ligand states as evidenced by the lower energy HOMO \rightarrow LUMO transition. As such, the electron density must be placed further toward the outer ring and play less of a role in coupling together the ligand states. When generating the MVMP state, this effect is further emphasized by the complete loss of electronic coupling.

When exploring the pydt series of complexes, no such effect of the extended aromatic rings drawing electron density away from the ligand-ligand coupling is present. Instead, the ligand states are present at higher energy relative to the pdt-containing series of complexes. We again performed electrochemical and spectroscopic measurements of all accessible redox and protonation states of the pydt complexes. Here, the mixed valence state of [Pt(pydt)₂] was inaccessible due to irreversible electrochemistry. Due to its relatively low oxidation potential, the mixed valence state of $[Ni(pydt)_2]$ was isolated after purification by column chromatography, in contrast to a previous synthetic procedure.⁸ Despite the relatively higher energy ligand states compared to $[Ni(pdt)_2]$, the electronic coupling in the mixed valence state of $[Ni(pydt)_2]$ was surprisingly similar, with a value of 5700 cm⁻¹ for H_{AB}. This electronic coupling value was also shown to decrease to 820 cm⁻¹ upon generation of its MVMP state. Additionally, the IVCT band of [Ni(pydt)₂] shifted slightly to lower energy and drastically decreased in intensity. While it initially shifted toward much lower energy during titration, it proceeded to shift back toward its original position toward the end of the titration, resulting in a net shift of 4 nm. During the titration, a clean set of isosbestic points was present. The lower electronic coupling in the MVMP state is likely due to slightly higher energy ligand states. In addition, the EPR spectrum shifted slightly upon generation of the MVMP state, similar to the [Ni(pdt)₂] complex, aiding assignment of the paramagnetic MVMP state. The Pd complex, [Pd(pydt)₂], exhibits an IVCT band in its mixed valence state at lower energy giving an H_{AB} value of 4500 cm⁻¹. Its IVCT band completely

disappeared upon protonation, which is consistent with previous observations of [Pd(pdt)₂]. These studies involving two different ligands demonstrates further refinement of the control of electronic coupling within the mixed valence and MVMP states of these dithiolene complexes. The pydt complexes behave as expected, with [Ni(pydt)₂] retaining intensity in its IVCT band upon generation of its MVMP state. Surprisingly, [Ni(qdt)₂] does not retain its IVCT band intensity, which is a result of the electron density being spatially oriented farther from the metal center.

An Additional Study of Metal Dithiolene Non-Innocence

Our work with the Au complex [Au(pdt)₂] sought to study the electronic structure and electronic spectroscopy of this compound in a similar way. This compound was explored computationally in simulations that utilized its nitrogen atoms in supramolecular assemblies.^{2,9} We report the synthesis and structure of this compound, as well as its response to protonation. Although it does not possess an oxidation to the mixed valence state, preventing direct comparison to other pdt-containing complexes, it does possess a reversible one-electron reduction event. Thus, it has the potential to be included in applications which seek to utilize non-innocence in metal dithiolene structures.

Summary

Throughout this work, we have established the MVMP state in metal dithiolene complexes as a means to study the effect of asymmetric protonation on the electronic coupling. The IVCT band, which is typically used to quantify ground state electronic coupling in pure mixed valence complexes, was extended to report on the incorporation of a set of PCET coordinates. As such, the alterations to the electronic potential energy surfaces due to the presence of a proton also report on changes to the potential energy surfaces of possible PCET coordinates. Consequently, this method is useful as a probe to monitor homogeneous ground state PCET self-exchange through steady-state spectroscopic methods, an approach that has previously only been attempted with hydrogen-bonded dimers.¹⁰ With the compounds investigated, we have found that three ([Ni(pdt)₂], [Pt(pdt)₂], and [Ni(pydt)₂]) retain their IVCT bands upon generation of the MVMP state. However, three compounds ([Pd(pdt)₂], [Ni(qdt)₂], and [Pd(pydt)₂]) lose their IVCT bands completely, indicating localization of electron density on the protonated ligands. This change in electronic coupling upon protonation has been explained in terms of their electronic structure. The electronic coupling also either decreases very significantly or disappears completely upon generation of the MVMP state. Future work will seek to study cases of intermediate coupling through which gradual structural modifications will allow refined rational control over the degree of electronic coupling.

Future Directions and Outlook

Controlling Proton-Dependent Electron Transfer Using the Linkage between Proton and Redox-Active Sites

All of the compounds studied in this work possess fused ring structures containing nitrogen atoms. Because of the planarity and conjugation, the electronic coupling in the mixed valence states is large, allowing for observation of the IVCT band in the electronic spectra and assignment as Class III delocalized systems.¹¹ In addition, the proximity of the basic nitrogen sites to the metal dithiolene core induces a large change in the electronic coupling upon protonation. With this geometrical arrangement, the proton and electron transfer interdependence

is quite large. In order to establish more refined control over this interdependence, we seek to study molecules that possess intermediate changes in electronic coupling upon protonation.

For these cases of intermediate electron and proton interdependence, we draw from a previous study that utilized a "dangling pyridine" connection, which is also shown in the center in Figure 6-1. For this compound, the MVMP state was not unambiguously identified, as the spectrophotometric titration proceeded with two protonation events. Nevertheless, the IVCT band observed for the mixed valence state in the UV-visible spectrum did not change appreciably with protonation.¹² This result suggests that, due to the twisting of the dangling connection, the protonation is not significantly tied into the electron transfer event.

Decreasing asymmetry in diabatic electronic states Increasing coupling between PCET states



Figure 6-1. Series of nickel dithiolene complexes with ligands designed to gradually separate the protonation site and electron transfer site. The linkages differ in their degrees of conjugation and planarity with the metal dithiolene core.

Based on this previous study, we seek to establish a means to control the protonation and electron transfer interdependence by modifying the linker between the dithiolene core and protonation sites. Controlling the way in which the protonation site is coupled into the electronic π system of the dithiolene core should exert control over the interdependence of electron transfer and asymmetric protonation. The molecules that we have chosen for this pursuit are shown in Figure 6-1, with the expected trend in protonation and electron transfer interdependence shown as well. The alkene-linked complex is expected to display the largest degree of protonation and electron transfer interdependence because the pyridine ring should be conjugated into the metal

dithiolene core. The alkyne linkage is known to possess a low energy barrier for rotation, so this linkage should further decrease the interdependence, creating an intermediate case between the alkene and direct linkages.^{13,14}

The synthesis of the nickel complex with the dangling pyridine connection, [Ni(4-pedt)₂], was achieved in a previous report.¹⁵ Syntheses of the alkene-linked and alkyne-linked nickel complexes are currently underway. It was previously thought that the complexes were obtained, but the electronic spectra of the products of both syntheses were featureless. To complicate matters, the redox state of the products is unknown, as the previously studied [Ni(4-pedt)₂] is singly oxidized and paramagnetic under atmospheric conditions. Electrochemistry of these products shows a reduction event at very low reduction potentials; if the compounds have been obtained, they do not possess an oxidation event, which prevents direct comparison to the dangling pyridine (singly oxidized) mixed valence state, or even the fused ring compounds represented in this study. Future work will seek to more rigorously establish the synthetic procedures for these compounds. Proposed synthetic schemes for both compounds are shown in Figures 6-2 and 6-3, respectively.¹⁶⁻²¹



Figure 6-2. Proposed synthetic scheme of the alkene-linked pyridine dithiolene ligand.¹⁶⁻²⁰



Figure 6-3. Proposed synthetic scheme of the alkyne-linked pyridine dithiolene ligand.^{16-18, 21}

The series of metal dithiolene complexes constructed from these ligands is expected to result in a gradual change in the degree of interdependence between the protonation event and electron transfer. While clearly demonstrating the utility of rational synthesis for imposing this control, these complexes will also illustrate the IVCT band as a tool to determine this degree of communication, at lower values of electronic coupling than discussed in this thesis. In total, these complexes will allow for the prediction of overall charge mobility based on the degree of communication between protonation and electron transfer sites, which is important for understanding how to control charge mobility in systems that undergo homogeneous ground state PCET. Once this measure of control over ground state PCET is established in these model systems, we can use this knowledge to inform control over charge mobility in device applications.

Concluding Remarks

Finally, we have explored the effect of protonation on the electronic communication within mixed valence metal dithiolene complexes. The addition of a possible proton transfer coordinate partially localizes the unpaired electron to one redox state in several cases. The change in electronic communication upon protonation is drastic in every case, with several systems retaining intensity in their IVCT bands, and other systems losing IVCT band intensity altogether. In the latter cases, the unpaired electron is completely localized to one ligand redox state. These systems have allowed us to explore the IVCT band as a probe to monitor the changes to the underlying PCET potential energy landscape, particularly as viewed through the electron transfer coordinate. These studies will inform future synthetic design of systems to control the extent of communication between the protonation and electron transfer sites within metal dithiolene systems. These synthetic designs are expected to grant insight into how to control overall charge mobility in PCET self-exchange model systems. Ultimately, we have established the IVCT band as an indicator of protonation and electron transfer interdependence, which will allow for control of charge mobility in homogeneous ground state systems that undergo PCET.

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- Kennedy, S. R.; Goyal, P.; Kozar, M. N.; Yennawar, H. P.; Hammes-Schiffer, S.; Lear, B. J. "Effect of Protonation upon Electronic Coupling in the Mixed Valence and Mixed Protonated Complex, [Ni(2,3-pyrazinedithiol)₂] *Inorg. Chem.*, 2016, 55, 1433-1445.

PRESENTATIONS

- Kennedy, S. R.; Kozar, M. K.; Yennawar, H.; Lear, B. J. "Using the IVCT Band in MVMP Dithiolene Complexes to Follow Ground State PCET" (*oral*) GRC for Photochemistry, Stonehill College, 2015
- Kennedy, S. R.; Kozar, M. K.; Yennawar, H.; Lear, B. J. "The Effect of Protonation on Electronic Communication of a Mixed Valence Dithiolene Complex" (*oral*) ACS national meeting, San Francisco, 2014

AWARDS AND HONORS

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Penn State Department of Chemistry Travel Award	2014, 2015