PHOTOPHYSICS AND EXCITED STATE ELECTRONIC COMMUNICATION IN QUADRUPLY BONDED PADDLEWHEEL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

Dissertation

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By Brian Alberding
Graduate Program in Chemistry

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Dissertation Committee:
Malcolm H. Chisholm, Advisor
Terry L. Gustafson, Advisor
Claudia Turro
ABSTRACT

Molecule based electronics and devices are an increasingly popular area of research in chemistry. These molecular-based devices largely rely on the separation of charge from (solar cell, LED) or movement of charge through (wires) a molecular unit. Largely, it is desirable for these materials to be easily fabricated, absorb throughout the visible/NIR spectrum or emit certain wavelengths. Organic systems generally provide good fabrication properties while the incorporation of metals can provide more easily tunable physical properties. Metallo-organic paddlewheel compounds involving quadruple bonds have previously been made into soluble, linear polymers with tunable absorption and have been incorporated into an LED to show electroluminescence. In terms of device performance, it is important to know how well charge can be expected to flow through the material. In devices that rely upon photon absorption, charge transport ability is dependent on charge delocalization and rates of transport. As a first step in these regards a series of complexes which represent simple monomeric analogs to the individual repeating units of the polymer have been studied. They serve as model complexes to the polymeric and a better understanding of their fundamental properties should relate to better design of polymeric materials.

This dissertation uses both electronic and vibrational spectroscopies to characterize photoexcited states, determine their lifetimes, and evaluate the electronic delocalization within these states. Theoretical calculations also supported the results.
Four molecules constitute limiting cases across a wide set of properties and are the focus of this work. Chapters 2 describes the molecules $M_2(O_2CCH_3)_2(N^iPr)_2C\equiv C-C_6H_5]_2$ and 3 describes the molecules $M_2(O_2CT^iPB)_2(O_2C-C_6H_4C≡N)_2$ where $M = Mo$ or $W$, each focusing on results from electronic spectroscopy. In particular, assignments for the photophysical excited states were made as well as some elucidation of the electronic delocalization. Chapter 4 describes both ground state and time-resolved infrared (TRIR) experiments and directly compares the systems studied in chapters 2 and 3. The vibrational experiments confirm the excited state assignments and classify the electronic delocalization according to the Robin and Day Scheme.

In chapters 2 and 3, it was found by steady state absorption, emission, and DFT calculations that the $S_1$ state is $^1$MLCT for each compound whereas the $T_1$ state is a metal-centered $^3\delta\delta^*$ state for molybdenum and $^3$MLCT for tungsten. DFT calculations show the MLCT states involve the metal-$\delta$ HOMO and the $\pi^*$ LUMO from the amidinate or cyanobenzoate ligands. Transient absorption studies with femtosecond time resolution showed the photophysics proceeded directly from the $^1$MLCT state to the $T_1$ state on the 5 – 20 ps timescale while the return to the ground state was monitored with the nanosecond technique. $T_1$ states of $^3\delta\delta^*$ character were found to have lifetimes of $\sim 100$ ms. $^3$MLCT state lifetimes were less than 20 ns with the p-cyanobenzoic acid ligand but 1 $\mu$s for the amidinate ligand system due to its occurrence at higher energy. By solvent dependent studies of the absorption and emission spectroscopy, the molecules of chapter
2 were found to have symmetry broken MLCT states with the excited electron localized on an individual ligand. On the other hand, vibrational features observed in absorption and emission spectra collected at a low temperature were more telling in this regard for the molecules of chapter 3. In this case delocalized MLCT excited states were suggested.

In chapter 4 the excited state assignments determined above were confirmed. TRIR spectra showed strong bands associated with the ligand C≡C and C≡N stretching vibrations in the MLCT states and the disappearance of these bands upon conversion to the metal-centered \( \delta\delta^* \) states. In the weakly coupled systems of chapter 2, there were two bands associated with \( \nu(C≡C) \). One band was strong and shifted to significantly lower wavenumber compared to the ground state and the other was weak and shifted only slightly to lower wavenumber. This was consistent with a class II system on the Robin and Day scheme where the excited electron is associated mostly, but not entirely, with an individual ligand. On the other hand, in the systems of chapter 3, there is only a single band associated with \( \nu(CN) \) and this indicated a class III, delocalized system. Further measurements in the \( \nu_{as}(CO_2) \) region revealed an excited state IR absorption that could be attributed to the \( ^3\delta\delta^* \) state. Calculations of the vibrational spectra in the ground state and the singly reduced anions aided the interpretation of the data in terms of the Robin and Day classification.
DEDICATION

To my family: My parents Mr. Jon Alberding and Mrs. Cheryl Alberding; my brother and his wife, Mr. Nathan Alberding and Mrs. Jennifer Alberding and their daughter, my newborn niece, Ellison Alberding
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There are many people in my life who have helped arrive at the position that I have today. There are numerous professors, post-docs and fellow graduate students who have helped me along the way during my time in graduate school who shall be mentioned in due course. First and foremost, however, I would like to acknowledge those people in my life who have to begin with given me the opportunity to reach this point, both as a person and academically.

In this regard it is my parents to whom I am most thankful. They are the ones who taught me to always work hard and try my best. Most of all they both lead by example. They worked very hard to provide for me a nice home, a loving, caring environment to grow and learn, and the opportunity to go away to a good university. Their example is most definitely what encouraged me study hard and to try and do as well as I possibly could in college and as a result I was able to be accepted to graduate school. Secondly, I would also like to thank my brother. Over the last ten years I believe he and I have become closer friends and I always look forward to hanging out with him when I come back to visit home. Most of all, I truly feel as if my whole family is proud of me and that provides a real motivating factor to keep going.

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Lastly, I must thank those people who have been directly involved in helping me complete the work presented in this dissertation. When I first arrived in the Chisholm group Doug Brown trained me in the use of the schlenk line and in general synthetic techniques. After his departure, this was later taken up by Namrata Singh and these two people greatly helped me synthetically. Yao Liu, who was a post doc in Claudia Turro’s group collected the nanosecond transient absorption data of compounds 2a and 3a, while Carly Reed acquired this for 2b and 3b. The NIR emission experiment was also housed in the Turro lab and Yao Liu collected this data for compounds 2a and 2b. Carly also worked on the NIR emission experiment, acquiring this data for compound 3a. Furthermore, Yagnaseni Ghosh and Namrata Singh deserve acknowledgement for synthesizing many compounds that I had the opportunity to study in the spectroscopy lab. Their work allowed for the addition of my name on several papers and Yagna also synthesized compounds 2a and 2b. I must also acknowledge all of the other members of the Chisholm group, past and present, who have made my time in the lab enjoyable and memorable. My training in the Center for Chemical and Biophysical Dynamics (CCBD) is also noteworthy. Tomohisa Takaya, a post-doc for Prof. Gustafson, provided my initial training in broadband transient absorption and general usage of the LASER facility. Numerous other members including Chris Middleton, Joe Heinrich, and Nicole Dickson, provided general help and trained me with the use of OPAs. Kimm de la Harpe
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VITA

2001 – 2005.................................Bachelor’s of Science in Professional Chemistry
University of Evansville, Evansville, IN

2005 – 2009.................................................................Teaching Assistant
The Ohio State University

2009 – 2011.................................................................Research Assistant
The Ohio State University

Research Publications

1. Electron Delocalization in the $S_1$ and $T_1$ Metal-to-Ligand Charge Transfer States of $trans$-substituted Metal Quadruply Bonded Complexes

2. Photophysical Studies of $trans$-bis(phenylethynyl-diisopropylamidinato)-bis(acetato) Dimetal Complexes Involving MM Quadruple Bonds where $M$ = Mo or W

3. Concerning the Photophysical Properties of $Re_2^{4+}$ and $Re_2^{6+}$ Carboxylate Compounds
4. **Molecular, Electronic Structure and Spectroscopic Properties of MM Quadruply Bonded Units Supported by trans-6-carboethoxy-2-carboxylatoazulene Ligands**

5. **2-Thienylcarboxylato and 2-Thienylthiocarboxylato Ligands Bonded to MM Quadruple Bonds (M = Mo or W): A Comparison of Ground State, Spectroscopic and Photoexcited State Properties**

6. **Sexithiophenes Mediated by MM Quadruple Bonds: MM = Mo2, MoW, and W2**

7. **Quadruply Bonded Dimetal Units Supported by 2,4,6-Triisopropylbenzoates MM(TiPB)4 (MM = Mo2, MoW, and W2): Preparation and Photophysical Properties**

8. **[Bis(trispivalatodimolybdenum (II))-µ-bis(4’-carboxylato–2,2’:6’,2”-terpyridine) ruthenium (II)] (2+) tetrafluoroborate: Photophysical Studies.**

**FIELDS OF STUDY**

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LIST OF ABBREVIATIONS

(BBTA) Broadband transient absorption spectroscopy
(bpy) 2,2’-bipyridine
(CARS) Coherent anti-stokes Raman scattering spectroscopy
(CCD) Charge-coupled device
(DFG) Difference Frequency Generation
(DMABN) 4-(dimethylamino)-benzonitrile
(dpb) 4,4’-diphenyl-2,2’-bipyridine
(DPS) trans-4,4’-diphenylstilbene
(ESA) Excited State Absorption
(fs) Femtosecond
(FSRS) Femtosecond Stimulated Raman Scattering
(GVD) Group velocity Dispersion
(HITC) 1,1’,3,3,3’,3’-hexamethylindotricarbocyanine iodide
(HOMO) Highest Occupied Molecular Orbital
(ISC) Intersystem Crossing
(IVR) Intramolecular Vibrational Redistribution
(LMCT) Ligand-to-metal charge transfer
(LUMO) Lowest Unoccupied Molecular Orbital
(MCT) Mercury Cadmium Telluride, HgCdTe
(MeCN) Acetonitrile
(MLCT) Metal-to-Ligand Charge Transfer
(mW) Milliwatt
(NMR) Nuclear Magnetic Resonance
(ns) Nanosecond
(PES) Potential energy surface
(ps) Picosecond
(SOC) Spin-orbit Coupling
(SRA) Stimulated Raman amplification
(TA) Transient absorption spectroscopy
(TC-LIF) Two-color light induced fluorescence
(THF) Tetrahydrofuran
(TiPB) Triisopropylbenzene
(TRR) Time-resolved Raman scattering
(UV) Ultraviolet
(VC) Vibrational Cooling
(VR) Vibrational Relaxation
(XPM) Cross-phase modulation
(WLC) White light continuum
1.1 Photophysics

There are eight major disciplines that encompass the natural sciences (biology, chemistry, physics, astronomy, materials science, earth science, atmospheric science, and oceanography), whose primary goal is the development of laws to explain natural phenomena. Of these, chemistry and physics are involved with the study of discrete forms of matter in non-living systems. There are two more specialized forms of these two natural sciences that describe the interaction of matter with light.¹ Both describe the processes by which a molecule distributes excess energy obtained by the absorption of a photon of light. In photochemistry, these processes ultimately lead to the storage of at least some of the excess energy in the form of a stable chemical product whereas in photophysics the excess energy is transferred back to the surroundings and the molecule returns to its original state.

1.1.1 Photophysical processes between electronic states

In general, photophysical studies will attempt to summarize the results of their experiments in terms of a Jablonski diagram similar to that shown in Figure 1.1. The
horizontal lines represent the potential energy surfaces (PESs) of the various electronic states along with their superimposed vibrational levels within a molecule that can generally be reached by absorption of photons of UV/visible/NIR energy and the arrow represent the basic photophysical processes that occur thereafter to convert one state to another. In addition, the left panel represents processes that require only a single photon; the middle panel represents those processes that inherently require two photons, and the right panel represents processes that can occur within the electronic states. Also, in this case, the represented molecule is a closed shell, diamagnetic, so the excited states can have either multiplicity $S = 0$ (singlets) or $S = 1$ (triplets), but the general principles are true for other multiplicities. There are three categories within which to describe photophysical processes between these electronic states; radiative excitation, (a)-(b), luminescence (radiative de-excitation), (c)-(g), non-radiative de-excitation (h)-(l).

Radiative excitation refers to placing a molecule in a higher energy state by absorption of a photon. Excitation to any of the electronic states is possible; however a particular transition may only occur in a very small fraction of molecules depending on the nature of the transition. A transition between $S_0$ and $S_1$, $S_2$, etc., (a), is allowed by the spin selection rule but that between $S_0$ and $T_1$, etc., (b) is forbidden so the probability of its occurrence is small. Furthermore, a transition that is allowed by the spin rule may not be allowed by symmetry (Laporte Rule); transitions between electronic states must involve a change in angular momentum to counteract that gained from the incident photon such that the total angular momentum is conserved. This means transitions between states of the same inversion symmetry are forbidden by single photon absorptions. For atomic species, then, s-s, d-d, etc., transitions are forbidden but s-p
transitions are allowed and for molecular species g-g and u-u transitions are forbidden but g-u or u-g transitions are allowed.

States that are not formed through direct excitation of a single photon can still be formed by subsequent photophysical processes. If the two states are close enough in energy (see Figure A.1), their potential energy surfaces will overlap and they can interact through vibronic coupling. The vibronic coupling allows for tunneling between the potential energy surfaces and efficient transfer of energy from one state to another. Any energy difference between the initial and final states is lost as heat to the surroundings during this process. When non-radiative deactivation occurs, if the spin multiplicity of the two states is the same, it is known as internal conversion (IC), processes (i)–(l). If the spin changes during this process it is called intersystem crossing (isc), process (h).

On the other hand, if the energy separation between two states is large enough, vibronic coupling is less prevalent. In this situation, energy is lost by release of a photon with a frequency according to the energy separation between the two states. This is known as luminescence and can occur between states of the same spin, fluorescence (processes (c), (d), (f), (g)), or between states of different spin, phosphorescence (process (e)). It is important to note that the deactivation of any state can involve a mixture of non-radiative and radiative processes and the relative contribution of each defines the quantum yield for the process.

Usually luminescence will only occur from the lowest excited states $S_1$ or $T_1$ to $S_0$ because the higher excited states occur in a higher density of states (Kasha’s rule). In some cases the energy separation between an upper and lower excited state is large enough to see luminescence (processes (d), (f), (g)) and the classic example is azulene
where emission occurs from the $S_2$ state to $S_0$. This is also true in regard to isc. In $\pi$-conjugated organic compounds, spin-orbit coupling is small, $T_1$ is much lower in energy compared to $S_1$ ($\Delta_{ST} \sim 6000 \text{ cm}^{-1}$), and fluorescence is mostly observed even though a state of lower energy exists. As spin-orbit coupling increases by involvement of heavy elements, $S_1$ and $T_1$ become closer in energy, which allows observation of some phosphorescence. In some cases, spin orbit coupling can be so great that only phosphorescence is observed. If however $S_1$ and $T_1$ are too low in energy, they will be able to vibronically couple with $S_0$ and luminescence will be very weak compared to non-radiative processes (i.e. (i) and (k)).

![Figure 1.1](image)

Figure 1.1 Basic unimolecular photophysical processes. Left: Monophotonic. Middle: Biphotonic processes. Modified from reference. Right: Non-radiative relaxation processes within electronic states. Modified from reference.

All of the processes mentioned above and shown in the left of Figure 1.1 are initiated by or involve a single photon. The middle portion of Figure 1.1 shows some processes that are biphotonic in nature. First of all, excitation transitions can be initiated
by simultaneous absorption of two photons (two-photon absorption, TPA), process A, whose energy sum to the transition energy. Since two photons are absorbed in this case, conservation of angular momentum requires the transition is between states of the same inversion symmetry. Second, processes (B) and (C) follow monophotonic selection rules but are biphotonic in nature because they require initial absorption of a photon to generate an excited state. In other words, these processes represent electronic transitions in transient species generated by photoexcitation and are observed in pump-probe experiments, discussed in more detail below.

### 1.1.2 Photophysical processes within electronic excited states

Other processes can occur within the electronic states of molecules before undergoing conversion to another state and these include intramolecular vibrational redistribution (IVR)\(^5\), vibrational cooling (VC)\(^6\), and conformational changes\(^7\). IVR and VC are represented in the right panel of Figure 1.1 and occur as a result of an electronic state being populated with excess energy above its zero-point energy. Usually, the Franck-Condon transition that prepares the initial excited state is associated with a particular vibrational mode(s); the energy of excitation is deposited in particular modes in the excited state. These excited state modes can then spread the energy to lower frequency modes within the excited state and this process describes IVR. In addition, the initial excited state is often placed in an upper level in the manifold of vibrational quantum levels in accordance with the Franck-Condon principle; each vibrational mode is populated with \(\nu > 0\) and the molecule is said to be in a “hot” state. In this situation, the molecule undergoes intermolecular energy transfer to its surrounding solvent shell,
causing the temperature to increase. The first solvent shell then dissipates energy to the bulk solvent according to its thermal diffusivity parameter, reducing the local temperature of the solute molecule. As the temperature decreases, the molecule is allowed to proceed down its vibrational manifold to its equilibrium position in the excited state. It is this convoluted process that is described by the term VC.\textsuperscript{6} If there is a significant energy difference between electronic states, VC dynamics can also be observed following IC or isc events and not only in the initial photoexcited state.

Lastly, conformational changes can occur within excited states. These refer to any structural change that occurs in the molecule as a response to the new electron distribution resulting from photoexcitation. A common example is that a π-conjugated organic group will become more planar in the excited state.\textsuperscript{7} Within the framework of Figure 1.1, these types of changes would correspond to shifting of the electronic state position both in energy and along a general vibrational coordinate.

Usually, the processes mentioned in this section occur on very fast time-scales and ultrafast (femtosecond) time-resolved techniques are needed for their detection. They often occur convoluted with one another and are difficult to distinguish. In this thesis, multiple femtosecond (fs) time-resolved techniques are utilized. Descriptions of these techniques are given in a later section (1.2) which explains how each process can be indentified in these experiments.

1.2 Ultrafast (fs) pump-probe spectroscopy

Transient absorption (TA) spectroscopy is one method within a group of ultrafast experimental techniques that are described by the term pump-probe spectroscopy. These
methods utilize two ultra-short (< 100 fs) laser pulses. One pulse perturbs the sample (by generating an electronically excited state or a photochemical reaction product or intermediate) and then a second monitors the various photophysical processes that evolve with time thereafter. Of the techniques that use the pump-probe method, the transient absorption technique only measures the effect of the excited sample on the probe beam characteristics. In other techniques, such as time-resolved Raman scattering (TRR), coherent anti-stokes Raman spectroscopy (CARS), and two-color laser-induced fluorescence (TC-LIF) to name a few, the probe pulse is used to further perturb the sample and new effects (i.e. fluorescence or scattered light) are detected. For the work presented in this dissertation, TA spectroscopy utilizing both visible and IR probe light has been the centerpiece of the experimental results and so a more detailed description of this technique is given.

1.2.1 Basic principles of fsTA spectroscopy

General concepts for the femtosecond TA experiment are shown in the left in Figure 1.2. First, the pump and probe pulses are aligned spatially within the sample. The pump pulse generates an electronically excited state population whose absorbance spectrum is, ideally, different from the ground state. The absorbance of this new species is then determined by collecting the intensity of the probe light before and after the sample. Because the time-scale of the photo processes observed in the experiment is so short (on the order of fs to ps), typical electronic equipment cannot be used to obtain time resolved information. Instead, the absorbance as a function of time is obtained by use of a variable delay stage along either the pump or probe path. Essentially, the probe pulse
captures the state of the system at a particular point (takes a snapshot) during the dynamics that are initiated by photoexcitation. Various snapshots are taken by moving the delay stage and changing the relative pathlength difference (and therefore delay time) between the probe and pump pulses to the sample. This is represented in the right panel of Figure 1.2.

![Diagram of transient absorption experiment](image)

Figure 1.2 Left: General experimental scheme for transient absorption experiments. Reproduced from reference.⁸ Right: Representative transient absorption signal (solid line) measured as a function of delay time at a particular probe wavelength.

1.2.2 **General instrument components and specifications**

Commonly, the fundamental laser pulses used for producing the pump and probe in fsTA experiments are generated from the combined output of a mode-locked titanium sapphire (Ti:Sapphire) oscillator and regenerative amplifier. This equipment provides ~50 fs laser pulses with a 1 KHz repetition rate at 800 nm. Part of this output is sent to an optical parametric amplifier (OPA) which is used to produce the pump pulse and allows its wavelength to be tuned across the UV/visible/NIR region of the spectrum,⁹ resulting in
an increase of the laser pulse width to ~ 150 fs. The pump pulse is then directed through a chopper and shutter and focused onto the sample. The remaining part of the fundamental pulse is sent through another chopper, down the delay stage and then focused into a clear medium such as a CaF$_2$ plate, MgF$_2$, quartz, water, or ethylene glycol to generate the probe beam as a white light continuum (~ 400 – 1100 nm). The probe beam is then directed into the sample and spatially overlapped with the pump beam. A broad range of wavelengths within the white light continuum can either be detected simultaneously by a CCD array and polychromator to obtain the entire excited state absorption (ESA) spectrum (known as broadband transient absorption, BBTA) or single wavelengths can be isolated and detected by a photodiode coupled to a lock-in amplifier. The actual laser system and experimental setup for the BBTA experiments done in this work is shown in figure A.2 and originally described by Burdzinski, et. al.$^{11}$

1.2.3 Data acquisition and measured signal

Data acquisition for BBTA is accomplished by referencing the CCD detector to the probe chopper and is triggered by the arrival of the pump pulses. The probe chopper blocks 50% of the incoming probe pulses and operates at 25 Hz. Combined with the 1 kHz repetition rate, the TA experiment is repeated with 20 pulses during a 20 ms acquisition period and leaves the remaining 20 ms to reset the CCD for the next acquisition. A pump chopper that blocks 75% of the pump pulses operating at 12.5 Hz is synchronized to the probe chopper and allows for alternate acquisitions in the presence and absence of the pump. Multiple 20 ms acquisition periods are completed in both the presence ($I_{pumped}$) and absence ($I_{unpumped}$) of the pump and averaged at each delay time,
leading to improved signal-to-noise ratio. Figure 1.3 conceptually represents the data acquisition process.

![Diagram of pump and probe pulses](image)

Figure 1.3 Modulation of the pump and probe pulses by choppers and representation of 20 ms data acquisition periods with and without the pump beam. Blue = pump beam (20 pulses/20 ms). Red = probe beam (20 pulses/20 ms). Equation 1.1: Calculated ΔOD.

Since the pump pulse does not excite 100% of the ground state distribution, the measured signal after excitation from the pump beam is a mixture of the excited state population and remaining ground state species. Typically, transient absorption data are reported as a difference between the excited mixture (measured in the presence of the pump, \( I_{\text{pumped}} \)) and the ground state absorption (measured in the absence of the pump, \( I_{\text{unpumped}} \)). The measured signal is given in equation 1.1, shown at the bottom of Figure 1.3. There are three main components to the measured signal in the presence of the pump. One component is the absorption of the ground state molecules that were not
excited by the pump. Second is the ESA of those species that were excited by the pump. Third is stimulated emission, induced by the probe, from the excited molecules. Stimulated emission results in the conversion of pump photons into additional probe photons at the emission wavelength that were not present before the sample and therefore results in a negative contribution to $I_{\text{pumped}}$. Measurement of $I_{\text{unpumped}}$ and subtraction from the total absorbance leads to an overall negative value for the contribution of the ground state absorption towards the calculated $\Delta \text{OD}$. A typical transient absorption spectrum is shown in Figure 1.4 along with its various components. If the true ESA spectrum is necessary, the actual number of molecules excited by the pump must be determined and the ground state absorption and stimulated emission can be added back to the spectrum.\textsuperscript{12}

Figure 1.4 Components of a typical transient absorption spectrum. Excited state absorbance (blue), ground state absorbance (red), stimulated emission (green), and overall TA spectrum (black) at a particular delay time.
1.2.4 Unwanted signals, signal-to-noise improvement, and calculation of corrected ΔOD

Included in the experimental setup are several techniques that limit or remove unwanted signals and improve signal-to-noise ratio. These are taken into account when determining ΔOD. Signal-to-noise ratio is improved by using a reference probe beam to account for any fluctuations in the probe spectrum. Referring back to figure A.2, the probe beam is split by taking the reflections from the front and back surface of a CaF$_2$ plate and directing both towards the sample. They are usually separated by ~5 mm through the sample and detected simultaneously by a dual array CCD detector. Only one of the two probe beams is spatially overlapped with the pump and the other is used as the reference.

1.2.4.1 Background measurements: steady state emission and electronic noise

Figure 1.5 depicts how fluctuations in the probe beam, as well as electronic noise and steady state emission can be removed from the recorded signal. Steady state emission is an unwanted signal that adds to the overall signal just by the presence of the pump beam. This is not to be confused with stimulated emission which results from interaction of the probe beam with the excited molecules and represents an actual contribution to the TA signal. Electronic noise, on the other hand, is a random error that adds to the measured signal of the probe beam. Both signals can be measured and removed by subtraction under certain pump/probe on/off conditions that are applied by use of the shutters in the pump and probe paths. The steady state emission signal is obtained by data acquisition with the pump shutter open and the probe closed, panel 2) of
Figure 1.5, and the electronic noise signal is obtained with both the pump and probe shutters closed, panel 4). The steady state emission is subtracted from the total signal obtained during the pump on, probe on 20 ms acquisition, panel 1) (equivalent to the “pumped” situation of Figure 1.3), and the electronic noise is subtracted from the pump off, probe on 20 ms acquisition signal, panel 3) (equivalent to the “unpumped” situation of Figure 1.3). During all acquisitions, corresponding signals are measured for the reference beam and subtracted from the calculated absorbance. Using these reference and background signals, the overall ΔOD can be calculated according to equation 1.2, shown in the bottom of Figure 1.5, where the intensities represent the % transmittance through the sample.

\[ \Delta OD = \log\left[\frac{I_{ref,E}(v) - I_{ref,n}(v)}{I(v) - I_E(v)} \frac{I_{ref,p}(v) - I_{ref,n}(v)}{I_p(v) - I_n(v)}\right] \]  

(1.2)

Figure 1.5 Representations of the background and reference signals (top, panels 1 – 4) used in calculating the overall ΔOD, equation 1.2, bottom. The intensities shown represent the % transmittance through the sample. Modified from Reference.8
1.2.4.2 Group velocity dispersion

The refractive index of a condensed phase material can be modified by interaction with a light pulse and is dependent on both the intensity and frequency of the incident light. White light continuum (WLC) generation, used to produce the probe pulse, occurs due to the intensity dependence of the refractive index.$^{13}$ On the other hand, the frequency dependence of the refractive index causes the different frequency components of the white light pulse to travel at different velocities through condensed phase materials. This causes a temporal broadening of the WLC pulse and blue wavelengths are shifted to the leading edge and red wavelengths to the trailing edge of the pulse. This effect is known as the group velocity dispersion (GVD) and sometimes referred to as the chirp in the supercontinuum.

Already when the WLC pulse is generated some GVD has occurred. In addition, other optical components in the probe path, including the sample cuvette, can increase GVD based on their thickness. In regards to the TA experiment, GVD means that time-zero will change for different wavelengths and the shape of the BBTA spectrum will be time dependent at early delay times. The amount by which time-zero is shifted with wavelength can be measured directly and therefore corrected numerically after the experiment. Most commonly, it is done by measuring the optical Kerr effect in a pure solvent as a function of delay time$^{14}$ but it can similarly be done by measuring the two-color TPA in a pure solvent.$^{15}$
1.2.4.3 Polarization effects

Light with linear polarization is generally produced from the laser systems described above. On another note, a sample in solution consists of a random distribution of molecular orientations relative to the polarization direction. This means that only molecules with transition dipole moments oriented along the polarization direction of the pump light will be preferentially excited. In other words, the excited state distribution is initially isotropic with regards to the excited state transition dipole direction. Similarly, the probe beam is linearly polarized and when it interacts with the sample only those excited molecules with an excited state transition dipole moment oriented in the direction of probe pulse polarization will absorb photons. After excitation, the excited molecules are free to reorient. Reorientation will decrease the ability of the excited molecules to absorb probe photons and, therefore, these effects will contribute to the observed time-dependence of the TA signal.

The quantity that describes these reorientation effects is known as the anisotropy, r(t), and the time dependence is given by equation 1.3,\(^\text{16}\) where \(\theta\) is the angle between the pump and probe transition dipole moments and \(\tau_{\text{rot}}\) is the rotational diffusion time. This equation shows that the reorientation effects can be removed by manually setting the pump and probe polarization to the magic angle of 54.7° relative to one another.\(^\text{17}\) In the experimental setup shown in figure A.2, this is done by use of a \(\lambda/2\) waveplate placed in the probe path. First, the polarization of the pump beam is determined and then a polarizer is placed in the probe path set to 54.7° relative to the pump polarization and the intensity through the polarizer is minimized by rotating the waveplate. This reduces complication in the experimental results when only population dynamics are desired.
In many cases, however, information from anisotropic measurements can be useful. Polarization anisotropy transient absorption is the name of the pump-probe experiment that is concerned with these measurements. In order to measure the reorientation dynamics the quantity known as the depolarization ratio, equation 1.4, is measured and this is the quantity proportional to the reorientation decay.

\[
r(t) = \frac{\Delta OD_{\|}(t) - \Delta OD_{\perp}(t)}{\Delta OD_{\|}(t) + 2\Delta OD_{\perp}(t)}
\]  

(1.4)

Here, \( \Delta OD_{\|} \) and \( \Delta OD_{\perp} \) refer to that measured with the pump and probe beam set to parallel and perpendicular polarizations, respectively. In addition to reorientation dynamics, these experiments have made a significant contribution to the discussion on the extent of delocalization in the initially produced and relaxed metal-to-ligand charge transfer (MLCT) states of \( M(bpy)_3^{2+} \), where \( M = \text{Ru or Os} \) and \( \text{bpy} = 2,2'\text{-bpyridine} \). Specifically, the initial value of \( r(t) \) in equation 1.4 is obtained by experiment and can be used to calculate the angle between the pump and probe transition dipoles in the initially created excited state by equation 1.3. The angle between the ground state and excited state transition dipole moments changes based on whether the initial state is localized or delocalized over all three bpy ligands and therefore this angle indicates the extent of electron delocalization.

1.2.4.4 Other unwanted signals
Other unwanted signals such as stimulated Raman amplification (SRA), cross-phase modulation (XPM), and two-photon absorption (TPA) occur as a result of the solvent or the sample cuvette. These usually occur only very close to time-zero, when the pump and probe interact simultaneously and can mask the signal of the system being studied. In particular, XPM can cause oscillatory patterns around time zero which can be problematic for the interpretation of kinetic data.\textsuperscript{21,22} These effects can be minimized by choosing a solvent with low third order non-linear susceptibility, using cuvettes with thin windows, or any action that would minimize GVD. TPA effects can be reduced by paying close attention to the focus of the pump beam (spot size larger than the probe spot size) and the pump power (usually 1 – 2 mW) at the sample. If these erroneous signals cannot be avoided without acceptable loss of sample signal, they can be determined in a reference sample of pure solvent and subtracted from the sample data or the sample signal can be increased by preparing the sample with higher absorbance (higher solute concentration) at the excitation wavelength.\textsuperscript{22} One way to increase the sample absorbance is to increase the path length of the sample cell, but this will also increase the GVD effects. Path lengths of 1 – 2 mm are common for optical cells in TA experiments.\textsuperscript{23}

1.2.5 Effects of photophysical processes on BBTA spectra

Now that erroneous signals are identified, actual molecular properties that have an effect on BBTA spectra can be considered. The types of processes that are observed in a BBTA spectrum can be broken down into two categories. One type of process leads to the decay or formation of excited state species as evidenced by their measured absorption
bands. Take, for example, a system that undergoes intersystem crossing on the ps timescale. Excitation could place the system in the $S_1$ state and its initial absorption spectrum could be determined. As the delay times are increased, isc would lead to a decrease in the concentration of $S_1$ species and the formation of $T_1$ species. This process would be evidenced by the observed decrease in the $S_1$ absorption spectrum and observed increase in the $T_1$ absorption spectrum intensity. This, of course, assumes there is sufficient resolution of the two bands to monitor them independently. If there is overlap between the spectra of the two states, the situation becomes more complicated. Other basic processes of this type include internal conversion, fluorescence, and phosphorescence as described earlier. The other type includes those processes that have an effect on the shape and frequency of those TA features that belong to a particular excited state. Vibrational relaxation, VR, and conformational relaxation are the two main processes that can be observed by BBTA spectra in this way.

There are two main types of vibrational relaxation, IVR and VC. BBTA spectroscopy is not sensitive towards IVR whereas VR can be detected through dynamic effects on BBTA bands. Consider the manifold of $S_n$ potential energy surfaces (PES) shown in Figure 1.6, where the $S_1$ state has been populated in a highly excited vibronic level, $S_{1\nu_{n}}$, along the coordinate of a particular vibrational mode. Because of the large number of nodes associated with this level, Franck-Condon overlap will be greater for many more vibronic transitions between $S_1$-$S_n$ compared to the situation when $S_1$ has vibrationally relaxed. When some VC occurs, to say $S_{1\nu_{n-1}}$, the excited state transition on the red edge of the initial ESA band, $S_{1\nu_{n}}$ to $S_{2\nu_{0}}$, goes to higher energy. Similarly, as VC occurs, excited state transitions to the upper levels of $S_2$, i.e. $S_{2\nu_{n}}$, lose Franck-
Condon overlap and the intensity at the blue edge of the initial absorption band is reduced. Overall, the effect of VC is indicated by band narrowing in BBTA spectra. As a result of band narrowing, VC is often also indicated by a dependence of measured time-constants on the probe wavelength monitored at the edges of ESA bands.\textsuperscript{24}

For organic compounds, cooling to the lowest vibrational level in an excited state is normally faster than 1 ps\textsuperscript{25} although some exceptions exist. For example, in the dye HTIC, VC has been observed to depend on both the solvent and excitation wavelength, with lifetimes ranging from 1.7 – 7.1 ps.\textsuperscript{26} Furthermore, repopulation of the ground state from an excited state can occur to an upper vibrational level and subsequent relaxation takes place. This has been observed in azulene, with VC lifetimes ranging from ten’s to hundred’s of picoseconds depending again on the solvent medium.\textsuperscript{27-29} In transition metal complexes, the observation of excited state VC is more common, usually occurring after fast isc. The two most studied classes of compounds are those of Ru(II)\textsuperscript{30} and Cr(III)\textsuperscript{24} having pseudo-octahedral geometry and VC in the lowest triplet excited state occurs in several picoseconds or less. The rates of VC are connected to collisional deactivation processes with surrounding solvent molecules and can be described by Landau-Teller models.\textsuperscript{31}
Figure 1.6 General potential energy surface (PES) diagram for singlet states monitored by BBTA spectroscopy. Modified from reference.  

Also in regards to Figure 1.6, IVR would correspond to transferring energy among several PESs corresponding to different vibrational modes. Conceivably, the ESA bands observed in BBTA contain an envelope of all the vibronic transitions involved. The large bandwidth of ESA bands measured in BBTA largely masks any effects of IVR and a characteristic trend predicting the effects of IVR on BBTA spectra is unknown.

In some cases, the change in electron distribution associated with an electronic absorption also results in some structural rearrangement. In particular, the compound could undergo conformation changes to produce a more planar structure, which is common for compounds involving pi-conjugated organic units in their reduced or excited states. There are two ways that conformational relaxation (planarization) can be monitored in TA spectroscopy. First, conformational relaxation causes a time-dependent
shift in the BBTA spectra. Referring again to Figure 1.5, planarization in the excited state would modify the \( S_1 \) state PES. Depending on the nature of the \( S_{1}-S_n \) transition, the \( S_n \) PES may or may not be affected. For example, the \( S_1 \) energy could be stabilized relative to \( S_n \), or the displacement over the nuclear coordinate considered could change. Planarization would stabilize the \( S_1 \) state and/or shift the equilibrium bond distance by sharing the excited electron over more bonds through extended \( \pi \)-conjugation. Both effects would result in a time-dependent shift in the BBTA spectra. This time-dependent shift has been observed before in BBTA spectra of trans-4,4'-diphenylstilbene (DPS) and was attributed to planarization in the \( S_1 \) state.\(^{35}\) If there is only a small degree of shifting in the BBTA spectra, conformational relaxation can also be identified by a dependence of a measured decay rate on the viscosity of the solvent. More viscous solvent causes slower conformational dynamics. A recent paper reported this effect for a terpyridine compound with extended \( \pi \)-conjugation at the 4’ position where the conformational relaxation lifetime ranged from \( 20–100 \) ps upon changing the solvent from methanol to butanol.\(^7\) Conformational relaxation was also reported in Ru(dpB)_3\(^{2+}\), where dpB = diphenylbipyridine, with \( \sim 2 \) ps lifetime, although BBTA band shifting or solvent viscosity dependence was not reported.\(^{30}\)

1.2.6 Time-resolved infrared spectroscopy

Time-resolved infrared spectroscopy (TRIR) is another type of TA spectroscopy that has been used in this work. It is conceptually the same as the BBTA technique described above but instead uses a laser pulse from the mid-IR (\( \sim 4170 – 830 \text{ cm}^{-1} \)) as the probe beam. The fundamental laser pulse is generated in the same way as in the BBTA
Both experiments share the output from the mode-locked titanium sapphire oscillator but a separate regenerative amplifier is used. The output from the amplifier has similar specifications to the BBTA experiment and is split to be used with two separate OPAs. One OPA can be equipped with either a SFG or UV/vis harmonics box to generate the pump beam while the other OPA is equipped with a difference frequency generation (DFG) harmonics box to generate the probe beam, which is tunable across the mid-IR with 100 – 200 cm\(^{-1}\) bandwidth. The probe beam is directed through a shutter and then through a beam splitter to generate a reference beam. Both probe and reference beams are directed through the sample and the probe beam is overlapped with the pump. The general setup of the experiment is shown in figure A.3. The entire setup after the production of the IR pulse by DFG is housed in a Plexiglas box and purged with a steady flow of nitrogen gas to remove carbon dioxide and water vapor from the measurement.

Data acquisition is similar to that in the BBTA experiment. The probe beam is not chopped so it operates at a 1 kHz repetition rate. The pump beam does travel through a chopper operating at 500 Hz; hence there is one pump pulse for every two probe pulses allowing for pumped and unpumped conditions of the probe beam % transmittance to be measured. There is no measurement of background fluorescence or electronic noise for the system used in this work and, in the notation of Figure 1.4; the ΔOD is calculated according to equation 1.5.

\[
\Delta OD = \log\left(\frac{I_{ref}(v)}{I(v)} \cdot \frac{I_{ref,pr}(v)}{I_{pr}(v)}\right) \quad (1.5)
\]
This TRIR system has been previously described\textsuperscript{36} and is presented in detail in Chris T. Middleton’s dissertation.\textsuperscript{37}

1.2.7 Effects of photophysical processes on TRIR spectra

TRIR spectroscopy monitors excited state populations in the same manner as BBTA spectroscopy. As conversion occurs between different excited states, the measured signal changes in intensity. However, instead of being complicated by all vibronic contributions associated with excited state electronic transition, TRIR monitors only particular vibrational modes within an excited state.

TRIR is quite useful for the identification of excited state structures. For example, TRIR has been used to monitor structural rearrangements in the excited states of both organic\textsuperscript{38} and transition metal complexes\textsuperscript{39} and identify reaction intermediates\textsuperscript{40}. Furthermore, excited state vibrational frequencies are sensitive to both the extent of electron delocalization within excited states and the degree of charge separation. Mostly, these types of studies have involved the use of metal bound reporter ligands (CO or CN) whose stretching vibrations are sensitive to the degree of charge separation associated with MLCT transitions. When the MLCT transition occurs, a partial positive charge is left on the metal and this reduces the ability of the metal to donate electron density through back-bonding. As a result the CO or CN triple bond is strengthened and shifts to higher frequency. The closer the electron resides to the metal center, the weaker the effect and smaller the observed shift. This has been a major focus of research regarding the excited state properties of transition metal complexes.\textsuperscript{41}
If only metal bound reporter ligands are detected, it is more difficult to describe the extent to which the excited electron is shared across the ligand(s). When a vibration directly associated with a ligand being reduced (or oxidized) can be detected in the excited state it speaks directly to the part of the ligand that contains the excited electron (or hole). The magnitude that the excited state frequency is shifted from the ground state can also give some indication about the contribution each part of the ligand makes to the total space occupied by the excited electron. Several examples reporting the extent of delocalization across reduced ligands directly bound to reporter groups in the MLCT excited state exist.\textsuperscript{42,43} There also exists one case where reporter groups were not necessary.\textsuperscript{44} In this case, for instance, the absence of pyridine ring vibrations indicated that the excited electron in the MLCT state was localized only on a tetrazine ring.

In ultrafast TRIR spectra, vibrational relaxation can again play a role. VC is evidenced by a blue shift in the excited state IR frequency due to anharmonicity of the PES.\textsuperscript{45} In other words, as the system cools and proceeds down the progression of vibronic states, the spacing between adjacent vibrational levels increases. IVR, on the other hand, transfers energy from one vibrational mode to another and should cause growth of a new excited state frequency or additional decay components at the measured frequency. However, no reports of directly observing this process in TRIR spectra could be found. If observed, the lifetimes of these processes should occur within the lifetime of the monitored excited state. Therefore, correlation with the state lifetimes measured from another technique, BBTA for example, can help differentiate these processes.
1.3 Complexes involving metal-metal quadruple bonds

One general reason there has been significant interest in the photophysical properties of transition metal complexes is that they are able to absorb photons in the visible region of the electromagnetic spectrum. Technologically speaking, this feature is useful, for example, towards the development of photodynamic therapy agents\textsuperscript{46}, where photons of lower energy are better able to penetrate skin cells, and dye-sensitized solar cells\textsuperscript{47}, where a greater proportion of the solar spectrum could be used to convert photons into electrical energy. Many studies in this area have involved transition metals coordinated within a pseudo-octahedral environment. A class of compounds that has been significantly less explored in terms of their photophysical properties is those that involve metal-metal quadruple bonds. These types of compounds have lowest energy absorptions that can be readily tuned across the entire visible spectrum and into the NIR with large oscillator strengths and, because of this, there is potential towards technological applications.\textsuperscript{48,49} The strong absorption properties provide motivation for studying the photophysics of these compounds.

There are two basic structural motifs which can surround the quadruply bonded metal center as shown in Figure 1.8.\textsuperscript{50} In either case, each metal sits at the center of a square planar arrangement and each unit can take either a staggered or an eclipsed conformation relative to one another. In the case of only monodentate ligands, Figure 1.8 a), either conformation is possible. On the other hand, if ligands such as carboxylates or amidinates, which are able to bridge across the metal-metal axis, are used, as shown in Figure 1.8 b) and termed paddlewheel complexes, the eclipsed conformation is preferred. Additionally, each metal has an axial position that is available for coordination with
appropriate solvents, such as acetonitrile (MeCN) or tetrahydrofuran (THF), or within solid state environments depending on the amount of steric hindrance provided by the equatorial ligands.

![Figure 1.7](image)

Figure 1.7 Basic structures of quadruply bonded complexes showing both a) monodentate and b) bridging ligand arrangements in the equatorial positions L_eq (green). Potential axial coordination sites, L_ax (blue) are also shown. Reproduced from Reference.50

1.3.1 Electronic structure of general complexes

The first confirmed complex involving the quadruple bond was Re₂Cl₈²⁻ and adopted the structure suggested in Figure 1.7 a). For such a complex, the basic metal-based electronic structure is obtained by considering the d-orbital splitting for a square-planar complex and bringing the two metals together along the z-axis (perpendicular to the square plane). When this is done, there is appropriate symmetry to make a σ, two π, and a δ set of bonding and anti-bonding orbitals from the dₓ², dₓz and dᵧz, and dₓᵧ metal orbitals, respectively. For Re₂Cl₈²⁻, each Re atom is in the +3 oxidation state and therefore has a d⁴ electron configuration. Using these 8 electrons, the bonding orbitals can be filled to give a σ²π⁴δ² electron configuration and a bond order of 4. It can be seen in Figure 1.8 that maximum overlap of the dₓᵧ orbital is obtained when the ligands are in
the eclipsed arrangement and rotation of the square-planar units towards this conformation stabilizes the quadruply bonded structure where electrostatic repulsion between the ligands would otherwise favor the staggered arrangement. It should be noted that the totally eclipsed conformation is not always the most stable structure and other intramolecular interactions can play a role depending on the choice of ligands. Control of the conformational geometry around the MM axis was a major factor in the initial photophysical studies concerning these basic complexes.

![Figure 1.8 Orbital interactions providing the electronic structure for basic quadruply bonded complexes (left). Representative structures showing the eclipsed (top right) and staggered conformations (bottom right) and how the energy of the highest bonding orbital can be stabilized depending on the angle of rotation. Modified from reference.](image)

1.3.2 Photophysics and excited states of basic complexes of the type $[M_2^{n^+}X_8]^{m^-}$
Before undertaking questions concerning the photophysical processes in excited molecules, some understanding of the ground state electronic structure and observable absorbance transitions is warranted because it provides a framework for describing the possible excited states. Compounds having the $\sigma^2 \pi^4 \delta^2$ ground state electron configuration have absorption spectra that can be quite extensive and complicated. In general, they possess metal centered transitions (i.e. $M\delta - M\pi^*$, $M\pi - M\pi^*$, $M\delta - M\delta^*$) throughout the visible and higher energy LMCT (i.e. $L - M\delta^*$) transitions in the UV. Of these, the lowest energy transition is usually the $^1\delta\delta^*$ absorption. In (n-Bu$_4$N)$_2$Re$_2$Cl$_8$, the absorption spectrum consists of the $^1\delta\delta^*$ absorption at ~ 680 nm, a singlet $M\delta - M\pi^*$ type transition at 566 nm, and a singlet $M\delta - d_{x^2 - y^2}$ type transition at 478 nm. For the $^1\delta\delta^*$ transition the intensity is relatively weak ($\epsilon \sim 1530 / M^*cm$) although it is a fully allowed transition. Its weakness is attributed to the small $d_{xy}$ orbital overlap and the small transition dipole moment that results from the short MM bond (~ 2.23 Angstroms). The $M\delta - M\pi^*$ and $M\delta - d_{x^2 - y^2}$ transitions are dipole forbidden and therefore much weaker ($\epsilon < 100 / M^*cm$). Assignments of these transitions were made based primarily with single-crystal polarized electronic absorption spectra. For instance, the $^1\delta\delta^*$ transition occurs with $z$-polarized light (along the MM axis) and contains a progression corresponding to the excited state ReRe symmetric stretching frequency (248 cm$^{-1}$) which is reduced compared to the ground state value (272 cm$^{-1}$).

One of the first photophysical questions with these types of complexes concerned the location of the triplet $\delta\delta^*$ state. Excitation directly into the $^1\delta\delta^*$ absorbance band in (n-Bu$_4$N)$_2$Re$_2$Cl$_8$, (n-Bu$_4$N)$_2$Re$_2$Br$_8$, and K$_4$Mo$_2$Cl$_8$ led in each case to an emission band that is Stokes shifted such that the 0-0 vibronic peak does not overlap with that of the
absorbance band.\textsuperscript{55} It was postulated at that time that the observed emission could be from either the $^3\delta\delta^\ast$ state or a distorted $^1\delta\delta^\ast$ state. As stated earlier, the delta bond in these complexes stabilizes the eclipsed ligand conformation. When $\delta\delta^\ast$ excitation takes place, the delta bond is broken and repulsion of the ligands can cause rotation about the MM axis to the staggered conformation. In order to test this hypothesis, the emission spectra of Mo$_2$Cl$_4$(n-Bu$_3$P)$_4$ was measured because the bulky n-Bu$_3$P ligands inhibit rotation about the MM axis. For this complex, the emission spectrum had a smaller Stokes shift and became a mirror image of the absorption spectrum with overlap of the 0-0 bands, indicating the emission comes from the same state that absorbs.\textsuperscript{52} This result suggests these complexes do in fact emit from the $^1\delta\delta^\ast$ state, where in the absence of steric interactions distortions can occur that increases the Stokes shift, and that emission from $^3\delta\delta^\ast$ state does not occur.

Presumably, the $^3\delta\delta^\ast$ state in these complexes is non-emissive because it is low in energy and the singlet-triplet energy gap is large. One case where the location of the $^3\delta\delta^\ast$ in the monodentate complexes has been previously suggested reported the diffuse reflectance spectrum of (NH$_4$)$_4$Mo$_2$Cl$_8$. A band at $\sim$ 1600 nm was observed that exhibited a vibrational progression, again corresponding to the symmetric stretch of the molybdenum quadruple bond in the excited state.\textsuperscript{56} Since the $^1\delta\delta^\ast$ absorbance had already been identified at higher energy (522 nm), the band at 1600 nm was attributed to the direct absorption to the $^3\delta\delta^\ast$ state. The singlet-triplet energy gap is therefore greater than 8500 cm$^{-1}$, large enough that the coupling with the triplet state might be very small and the $^1\delta\delta^\ast$ state predominantly decays directly to the ground state.
One additional comment should be made about the complexes containing monodentate ligands concerning how the energetics of the metal-centered states is changed by different metals. For this consider $K_4Mo_2Cl_8$ and $(n-Bu_4N)_2Re_2Cl_8$. In $K_4Mo_2Cl_8$, the $^{1}\delta\delta^*$ absorption occurs at 522 nm$^{56}$ and is higher energy than that for $(n-Bu_4N)_2Re_2Cl_8$, which occurs at 680 nm.$^{54}$ Furthermore, the second lowest energy absorption in $K_4Mo_2Cl_8$, which is presumably the $M\delta-M\pi^*$ transition, also occurs at higher energy compared to $(n-Bu_4N)_2Re_2Cl_8$. The relative energies of these metal centered transitions reflect the strengths of the $\delta\delta$ bonding interactions and are indicated by the metal-metal bond lengths determined from the crystal structures. For $K_4Mo_2Cl_8$, the bond length is 2.139 Å,$^{57}$ shorter than the 2.222 Å$^{58}$ value for $(n-Bu_4N)_2Re_2Cl_8$. The longer bond length for the Re complex occurs because of greater core-core repulsions between the heavier elements and this reduces the overlap of the $\delta$ orbitals. In the Mo complex, the shorter bond length and better orbital overlap results in a greater energy separation between the $\delta$-HOMO and other metal based molecular orbitals, which increases the energy of the metal based transitions, such as the $\delta\delta^*$ transition, for example. These trends will be important in understanding the emissive properties of the paddlewheel complexes discussed later.

1.3.3 Paddlewheel complexes; geometric structure and synthesis

Work in the Chisholm group concerning the chemistry of quadruple bonds has focused mainly on compounds derived from the paddlewheel structural motif shown in Figure 1.7, b), where the metal is Mo or W and the bridging ligands are functionalized
carboxylates. These types of compounds can be further subdivided into four categories and their basic structures and synthesis can be seen in Figures 1.9 and 1.10.

In the first type of compound (i), all four of the carboxylate ligands are identical and are thus termed “homoleptic” compounds, Figure 1.9. For molybdenum, the homoleptic compound is obtained by refluxing Mo(CO)$_6$ with 2 equivalents of the desired carboxylic acid in a high boiling solvent.\textsuperscript{59} Tungsten compounds, on the other hand, utilize a method where WCl$_4$ is reduced with sodium amalgam and then reacted at 0°C in THF with 2 equivalents of the sodium carboxylate salt.\textsuperscript{60} Once obtained, these compounds readily undergo ligand exchange reactions and are used as starting materials for the other three types of compounds.

![Figure 1.9 Synthesis of homoleptic paddlewheel type compounds.](image)

Structures and the synthesis for the remaining three types of compounds are shown in Figure 1.10. In the second type of compound (ii), there are two sets of \textit{trans}-disposed ligands. These types of compounds are obtained by reaction of a homoleptic compound (i) containing a ligand that provides appropriate steric bulk, such
as triisopropylbenzoic acid (TIPB), with 2 equivalents of another carboxylic acid. For compounds of type (iii), two paddlewheel units are connected by a bridging ligand and these are obtained by reaction of a dicarboxylic acid and an appropriate homoleptic compound in a stoichiometric ratio of 1:2, respectively. Finally, in the last type (iv), polymers consisting of alternating quadruply bonds and organic units can be made by using equivalent stoichiometric amounts of the homoleptic compound and bridge.

Figure 1.10 Synthesis of paddlewheel structures i) homoleptic ii) trans-bis-bis and iii) dimer-of-dimers, where the uncoordinated ligands have protonated carboxylate groups and M = Mo or W. Modified from Reference.
1.3.4 Electronic structure and photophysical properties of homoleptic complexes

Recall $K_4M_2Cl_8$ where the lowest energy absorption occurs at 522 nm and is classified as $^1\delta\delta^*$. In the homoleptic paddlewheel compound $M_2(O_2C^\prime Bu)_4$, the lowest energy absorption occurs at $\sim 440$ nm (Figure 1.11, bottom right) and again was described as $^1\delta\delta^*$ by polarized absorption spectroscopy. The increase in energy of the $^1\delta\delta^*$ state can be explained by the nature of the molecular orbitals from the bridging carboxylate ligand.

Each carboxylate ligand forms a sigma bond with each metal through interaction of its oxygen lone pairs with the $d_{x^2-y^2}$ orbital, leaving the other $d$-orbitals to form the quadruple bond manifold. As shown in Figure 1.11, left panel, the carboxylate ligands also have three $\pi$-type orbitals, the fully-bonding, fully anti-bonding, and the non-bonding combination of $OCO$ $p_\gamma$-orbitals. In $D_{4h}$ symmetry, linear combinations of these ligand $\pi$ orbitals are formed and some of these have appropriate symmetry to interact with the $\delta$ and $\delta^*$ orbitals. The $\pi$ and $\pi^*$ orbitals both can interact with the $\delta$ orbital, while the non-bonding orbital interacts with the $\delta^*$. The $\delta^*$ orbital therefore goes to higher energy due to the interaction with the non-bonding $CO_2$ orbital and increases the $\delta\delta^*$ energy gap in paddlewheel type compounds.

As a direct result of this interaction, the $^3\delta\delta^*$ state increases in energy such that emission can occur. In fact, emission from the $^3\delta\delta^*$ state was first observed, at $\sim 800$ nm, in $Re_2Cl_2(L)_2$, where $L = N,N'$-di-(p-anisylformamidinate) and the Cl ligands are axially coordinated. Similar emission was observed later for the homoleptic $M_2(L)_4$ complexes, where $L = O_2C^\prime Bu$ (pivalate) or $T^\prime$PB (triisopropylbenzoate). For the $M_2(L)_4$ complexes where $L = T^\prime$PB, the $^3\delta\delta^*$ emission occurs at $\sim 1100$ nm for $M = Mo$ and $\sim 33$
815 nm for $M = W$. Since the $^3\delta\delta^*$ state is lower in energy for $M = Mo$, the intensity becomes much weaker, as indicated by the signal-to-noise in the emission spectra shown in the top right panel of Figure 1.11. The energy dependence on the identity of the metal arises from the fact that the delta orbitals increase in energy upon changing from Mo to W (below). In the complexes where $L = O_2C^tBu$, emission occurs at a similar energy for $M = W$ compared to $W_2(T^{i}PB)_4$, but was not observed for $M = Mo$.\textsuperscript{61}

Another important aspect of the electronic structure shown in Figure 1.10 is the presence of the low-lying $\pi^*$ orbital, which leads to MLCT type transitions in the absorption spectra. These transitions are fully allowed and have much greater intensity than the $^1\delta\delta^*$ absorbance due to good orbital overlap between the metal $\delta$ and ligand $\pi^*$ orbitals and greater transition dipole moment. Absorption spectra for $M_2(O_2C^tBu)_4$ are shown in the bottom right panel of Figure 1.11.\textsuperscript{60} For the Mo compound, the strong MLCT transition ($\varepsilon \sim 10,000 \text{ M}^{-1}\text{cm}^{-1}$) is seen at $\sim 300$ nm while the aformentioned $^1\delta\delta^*$ state is lower energy at $\sim 440$ nm. By changing from Mo$_2$ to the MoW and W$_2$ quadruple bonds, the metal centered delta bonding orbital is increased in energy relative to the ligand orbitals. As a result, the MLCT absorption goes to lower energy with that for W$_2(O_2C^tBu)_4$ occurring at 377 nm and masking the observation of the much weaker $^1\delta\delta^*$ transition. This trend is also indicated in the absorption spectra of the $M_2(T^{i}PB)_4$ complexes (Figure 1.11, top right) and in this case the $^1\delta\delta^*$ transition is completely masked in all cases because the $T^{i}PB \pi^*$ orbitals are at lower energy compared to $t^\primeBuCO_2^-$. The trend in the energy of the metal orbitals changes in this way due to the weaker delta bond interaction in W$_2$ compared to Mo$_2$ as represented by the longer bond lengths typical of the tungsten compounds.\textsuperscript{53} Assignment of the MLCT transitions based
on this trend was supported by electrochemistry and photoelectron spectroscopy where the first oxidation and ionization potentials were seen to decrease from Mo to W.\textsuperscript{60}

Figure 1.11 Left: MO diagram showing interactions of quadruple bond metal orbitals with $\pi$, $\pi^*$, and non-bonding bridging ligand orbitals (modified from Reference\textsuperscript{63}) Right, bottom: Absorption spectra of MM(O\textsubscript{2}C\textsuperscript{6}Bu\textsubscript{4}) (reproduced from Reference\textsuperscript{60}) Right, top: Absorption and emission spectra of MM(T\textsuperscript{1}PB)\textsubscript{4}, where M = Mo or W (modified from Reference\textsuperscript{61}).

The energy of the MLCT states is highly dependent on the nature of the ligand. Manipulation of the ligand by extended $\pi$-conjugation lowers the energy of the ligand based $\pi^*$ orbital and greatly influences the observed emissive properties. A study of a
series of homoleptic complexes employing various carboxylates of polyaromatic hydrocarbons was undertaken and their absorption and emission properties are shown in Figure 1.12. In these compounds the absorption spectrum consists of the MLCT absorption at lowest energy and a $\pi\pi^*$ absorption at higher energy. Excitation into the lowest energy absorption band now leads to $^1\text{MLCT}$ emission in all of these compounds. While, at that time, the NIR emission experiment was not accessible for the Chisholm group, detection of the lower energy triplet excited states in these complexes could only be done through nanosecond transient absorption (nsTA). Due to this, the triplet states were identified as $^3\text{MLCT}$ for all the complexes, although the identity of the metal and the ligand can be tuned to switch the nature of the lowest triplet state between $^3\delta\delta^*$ (for $M = \text{Mo}$) and $^3\text{MLCT}$ (for $M = \text{W}$). This achievement was more clearly shown from experiments involving bis-bis type compounds, which will be discussed later, but is evident through the lifetimes reported for these homoleptic complexes. In the W complexes, the triplet state lifetime is only $\sim 66$ ns whereas for Mo the lifetime is $\sim 60$ μs, on average. The longer lifetime in Mo is consistent with the $^3\delta\delta^*$ assignment because the transition between the $\delta$ and $\delta^*$ orbitals has smaller probability than the MLCT type transition.
### Table 1.12

<table>
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<th>M</th>
<th>(\lambda_{ex} (S_0)/\text{nm})</th>
<th>(\lambda_{em} (S_1)/\text{nm})</th>
<th>(\tau (T_1)/\mu\text{s})</th>
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<td>W</td>
<td>645</td>
<td>711</td>
<td>0.075</td>
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</table>

![Figure 1.12 Absorption and emission properties of homoleptic compounds. Top left: Table summarizing photophysical properties. Bottom left: Absorption and emission spectra \((\lambda_{ex} = 465 \text{ nm})\) of compound 4b. Right: Legend showing various compound structures. Reproduced from reference.][1]

The overall trends for the emissive properties of quadruply bonded compounds can be summarized as follows. Basic quadruply bonded compounds have only \(1\delta\delta^*\) emission because this is the \(S_1\) state and the \(3\delta\delta^*\) state is much lower in energy. When bridging ligands are used to support the quadruple bond, the \(3\delta\delta^*\) state becomes emissive because it increases in energy compared to the ground state. However, the \(1\delta\delta^*\) is not found to be emissive in any cases thus far. Also it is apparent that when the MLCT state is higher in energy than the \(1\delta\delta^*\), there is no fluorescence. Only when the MLCT state is reduced in energy such that it is lower than the \(1\delta\delta^*\) state does any fluorescence occur and it does so from the \(1\text{MLCT}\) state. This is evident from \(M_2(T^\text{TPB})_4\) compounds, where

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[1]: Figure 1.12 Absorption and emission properties of homoleptic compounds. Top left: Table summarizing photophysical properties. Bottom left: Absorption and emission spectra \((\lambda_{ex} = 465 \text{ nm})\) of compound 4b. Right: Legend showing various compound structures. Reproduced from reference.
the strong MLCT absorptions are found at the same energy the $^1\delta\delta^*$ absorption is expected to occur and only very weak fluorescence is observed, whereas in Mo$_2$(O$_2$CR)$_4$, where R = pyrene, fluorescence is readily observed.

One of the more confusing aspects concerning the emissive properties of the paddlewheel compounds is the loss of fluorescence and there is one example from the literature that may be able to offer an explanation. Consider again the basic complexes Mo$_2$Cl$_4$(PR$_3$)$_4$, where R = Me, Et, Pr, Bu. For R = Bu, a long-lived transient was observed through psTA and it was postulated that this species was due to a $^3\text{M}\pi$-$\text{M}\delta^*$ state that lies close in energy to the $^1\delta\delta^*$ state. Furthermore it was apparent that this $^3\text{M}\pi$-$\text{M}\delta^*$ state could be tuned such that in some cases it led to reduced $^1\delta\delta^*$ emission and in some cases it did not. In R = Me, for example, the quantum yield and lifetime is 0.26 and 140 ns, respectively, whereas those for R = Et, Pr, Bu is a factor of 10 smaller. This result was used to suggest that the long-lived state could not be the $^3\delta\delta^*$ state because the set of ligands used could not likely change the energy of the $^3\delta\delta^*$ state enough to have such a drastic effect. Instead, the nearby $^3\text{M}\pi$-$\text{M}\delta^*$ state in some cases falls lower in energy than the $S_1$ state, quenches the fluorescence and reduces the $S_1$ lifetime. In other cases, it falls higher in energy compared to $S_1$, so that decay pathway is unavailable and results in greater quantum yield and longer lifetime.

Moving now again to the carboxylate paddlewheel complexes, the $^3\text{M}\pi$-$\text{M}\delta^*$ state could also be present at lower energy than the $^1\delta\delta^*$ state. In Mo$_2$(O$_2$CtBu)$_4$, the $^1\text{MLCT}$ transition is clearly an $S_n$ state, from the absorbance spectrum, and according to Kasha’s rule should relax quickly to $S_1$, $^1\delta\delta^*$. There is no a priori reason to expect that this $^1\delta\delta^*$ state should not be fluorescent, considering that other homoleptic compounds have
\(^1\)MLCT fluorescence and the “basic” compounds have \(^1\)δδ* fluorescence. The \(^1\)δδ* state, then, could be strongly coupled to the lower energy \(^3\)Мπ-Мδ* state, which provides an alternate pathway to the T\(_1\) state and quenches the \(^1\)δδ* fluorescence. Since the \(^3\)δδ* state is higher in energy, the density of triplet states is higher in these types of complexes and the excited systems quickly find their way to the T\(_1\) \(^3\)δδ* state. Unfortunately, direct experimental detection of these states for Mo\(_2\)(O\(_2\)C\(^\text{tBu}\))\(_4\) has been difficult, but this pathway potentially accounts for the absence of fluorescence.

In Mo\(_2\)(T\(_i\)PB)\(_4\), all that can be said is the \(^1\)δδ* and \(^1\)MLCT states are close in energy. Some of the population generated from MLCT excitation could deactivate through the \(^1\)δδ* to \(^3\)Мπ-Мδ* pathway while the rest leads to weak fluorescence. Finally, when significantly extended π-conjugation is present, as is the case with complex 4b from Figure 1.12, the S\(_1\) state becomes the \(^1\)MLCT state and could be lower than the \(^3\)Мπ-Мδ* state. Now, the \(^3\)Мπ-Мδ* pathway is not accessible and coupling to the triplet manifold is weaker. As a result, fluorescence from the \(^1\)MLCT state is stronger and dual emission is observed.

1.3.5 Time-resolved studies on homoleptic paddlewheel compounds

There are two studies that have reported the fsTA of homoleptic paddlewheel compounds. The first report concerned Mo\(_2\)(O\(_2\)C-9-anth)\(_4\), complex 3 from Figure 1.12.\(^68\) Excitation into the MLCT absorbance band gave an initial spectrum that decayed in ~ 10 ps to give rise to a longer-lived spectrum. This spectrum included a stimulated emission band that occurred at the same wavelength as the \(^1\)MLCT fluorescence observed in Figure 1.10. Suggested by this result is that the initial spectrum describes the \(^1\)MLCT
state and the decay sets a benchmark for its lifetime in these types of complexes. Decay of the initial spectrum gave rise to a long-lived state similar to that observed by the nsTA referred to in Figure 1.10. Again, the long-lived state was initially reported as $^3\text{MLCT}$ but through related studies on bis-bis type compounds is more likely described by $^3\delta\delta^*$. 

The other study involving fsTA concerned the $\text{M}_2(\text{TPB})_4$ complexes, where $\text{M}_2 = \text{Mo}_2$, MoW, and W$_2$.$^{61}$ For each complex, this study revealed a short-lived excited state that decays directly to a second, longer-lived state. The fsTA study can detect the absorption spectra of both states but can only monitor the lifetime of the short-lived state because the triplet state lifetime is too long. By comparison with steady state electronic spectroscopy, the long-lived states were all assigned to $^3\delta\delta^*$ states while the short-lived states are $^1\text{MLCT}$. The lifetimes of the $^1\text{MLCT}$ states were found to follow the trend expected for increasing the spin-orbit coupling (SOC) across the series Mo$_2$, MoW, and W$_2$, varying from 6 ps, to ~ 0.5 ps, and to ~ 0.4 ps, respectively.$^{61}$

### 1.3.6 Photophysical studies of *trans*-bis-bis compounds: motivations and properties

Motivation for studying the photophysics of these types of compounds has stemmed from an earlier finding that an LED fabricated using a related polymeric material showed electroluminescence.$^{69}$ Generally, it is important to have a clear understanding of the time-scales and pathways by which the excited polymer will dissipate excess energy when deciding the potential for optoelectronic device incorporation. The *trans*-bis-bis compounds nicely compare to and serve as models for the discrete polymeric units but additionally they have greater solubility and are therefore easier to study. In particular, the Chisholm group has recently set out to confirm the
nature and determine the lifetimes of the lowest energy singlet and triplet excited states (as MLCT or $\delta\delta^*$) and much of the initial work has focused on these details. Also, the Chisholm group is interested in electronic delocalization within these excited states. This property should be related to charge mobility in the polymers and for this reason has been a major focus for the work presented in this thesis.

Photophysical properties of trans-substituted bis-bis compounds can be tuned in a qualitatively similar fashion to those for homoleptic compounds. The energies of the MLCT states are readily tuned by both the metal and by $\pi$-conjugation in the ligand and the $\delta\delta^*$ states are highly dependent on the metal. Most of the preliminary studies have involved compounds with a set of triisopropylbenzoate ligands which provide steric bulk and favor the trans-arrangement with another set of functionalized ligands. In these cases it was found the photophysics following MLCT excitation to the functionalized ligands involved two excited states by the fsTA experiment. For all compounds studied the short-lived state is $^1$MLCT and can have lifetimes ranging from < 1 ps to ~ 20 ps. The triplet state, however, was found to vary depending on the metal. For Mo, $T_1$ is the $^3\delta\delta^*$ and the lifetime is on the μsec time-scale whereas for W, $T_1$ is the $^3$MLCT state. By nsTA, the transient spectra match that for the long-lived transient in fsTA and the $T_1$ lifetimes were measured. In some cases for W complexes, the lifetimes of the long-lived states observed in fsTA were too short to be measured by nsTA (~ 10 ns time resolution), so those could only be estimated to be < 10 ns. In other cases for W complexes the lifetimes could be measured and were on the 10 – 250 ns timescale. On the other hand, the Mo compounds were found to be three orders of magnitude longer, 10 – 100 μs. The long lifetimes on the ns or greater time-scales reflected the triplet state.
assignment for transition metal complexes and the even longer lifetimes for Mo complexes reflected the $^3\delta\delta^*$ assignment. Due to the small dipole moment change associated with the transition between the $^3\delta\delta^*$ and ground state, the transition probability is smaller compared with that for an MLCT state and results in a longer lifetime.

The assignments of the $S_1$ and $T_1$ states were also supported by DFT calculations as well as solvent dependent steady state absorbance and emission experiments. In the case of the Mo complexes, dual emission is observed and the two states responsible for each emission are associated with the short and long-lived states. The lower energy emission was found to be solvent independent and this property is a signature of the $^3\delta\delta^*$ state due to the small dipole moment associated with its transition to the ground state.

Identification of the $S_1$ and $T_1$ states as MLCT or $\delta\delta^*$ leads to further questioning. For the work in this thesis, evaluation of the electron distribution and electronic coupling within these excited states, particularly the MLCT states, is a goal. In order to do this, some extra theoretical framework within which to evaluate these properties is needed.

1.3.7 Basic electron transfer and electronic coupling: Marcus-Hush theory

The electron distribution of quadruply bonded complexes is studied in accordance with intramolecular electron transfer theory, which describes how strongly states derived from particular groups within a molecule are coupled together.\textsuperscript{2,72} In general, this theory is developed considering a model molecule, DBA, where the electron donor (D) and acceptor (A) are connected by a bridging group (B). The molecule is known as a mixed-valence molecule when D and A have different and interchangeable oxidation states, $D'B\leftrightarrow DBA^-$. If a state from the isolated donor group, D, has appropriate energy and
symmetry/orbital overlap with a state from the isolated acceptor, A, the two groups can interact to give a set of states (adiabatic states) described by in-phase and out-of-phase combinations of the isolated groups. The strength of the interaction is called the electronic coupling, $H_{DA}$ and the purpose of the bridge is either simply to bring D and A into close enough proximity to directly interact or to provide an orbital interaction that facilitates electronic coupling.

A potential energy surface representation can be used to visualize easily the electronic coupling. Shown in Figure 1.13 for a symmetrical system where D = A, the PESs represent both the change in energy associated with the movement of atoms along a particular vibrational mode and reorientational movement of the surrounding medium as an electron is transferred from D to A under the harmonic oscillator approximation. The dashed lines represent the PES for the diabatic states in the absence of electronic coupling between states D and A. As the interaction increases, the diabatic states begin to mix, resulting in an in-phase (lower) and out-of-phase (upper) combinations of the two surfaces.

In these mixed-valence systems, there exists two ways to transfer the electron from D to A. First, the mixing of the states results in an activation barrier, $\Delta G^*$ that can be overcome thermally and there is an Arrhenius (transition state theory) expression to describe the electron transfer rate ($k_{el}$), equation 1.6 where $R$ is the ideal gas constant, $T$ is the temperature, $A$ is a pre-exponential factor, and $\Delta G^*$ is the activation energy.$^{73}$ The activation energy is calculated by equation 1.7 and depends on $H_{DA}$ and the reorganization energy, $\lambda$, the energy difference between the upper and lower surfaces at the donor equilibrium configuration, $Q_D$. There are two contributions to $\lambda$, an outer-
sphere contribution, $\lambda_o$, which takes into account free energy changes associated with solvent reorientation, and an inner-sphere contribution, $\lambda_i$, which takes into account free energy changes associated with vibrational and conformational changes within the molecule, equation 1.8.

$$k_{et} = A \exp[-\frac{\Delta G^*}{RT}] \quad (1.6)$$

$$\Delta G^* = \frac{(\lambda - 2H_{DA})^2}{4\lambda} \quad (1.7)$$

$$\lambda = \lambda_o + \lambda_i \quad (1.8)$$

Second, electron transfer can be induced by absorption of a photon of energy equal to $\lambda$. In this case, the transition state configuration is favorably achieved along the upper surface after excitation and ET can occur upon relaxation back to the lower surface. This absorption feature is termed the intervalence charge transfer (IVCT) band.

Figure 1.13 Potential energy surface representation of electronic coupling in a symmetrical system. $Q$ = Reaction coordinate. $Q_D$ and $Q_A$ = Donor and acceptor equilibrium configuration, respectively. $\Delta G^*$ = Activation Energy. $H_{DA}$ = Electronic coupling. $\lambda$ = Reorganization energy.
Robin and Day developed a classification system within which allows molecules to be categorized according to the degree of electronic coupling, Figure 1.14. Measurement of the IVCT band by absorption spectroscopy is particularly useful for providing experimental support for a class assignment. In Class I, $H_{DA} = 0$, the molecule maintains the properties of separate groups, and the IVCT band is very weak. In Class II, $H_{DA}$ increases and the PESs mix together to create an upper surface and a lower surface with a double minimum that still possesses properties of the individual sites. The IVCT band gains intensity and its $\nu_{\text{max}} = \lambda$. A symmetrical, Gaussian, shaped IVCT band is a strong indication of Class II behavior. Upon further increase of $H_{DA}$ a special case is observed that has been termed the Class II/III border. In this case, the lower surface is a single minimum well and $\nu_{\text{max}} = \lambda = 2H_{DA}$. An asymmetrical IVCT band is observed because as the PESs move apart the low frequency side of the band is shifted to higher energy, as indicated by the vertical arrows in panels II and II/III of Figure 1.14. Generally, it is more difficult to differentiate between behavior in the Class II/III regime and the fully delocalized class III. In Class III, the electron is fully delocalized across both groups and the PESs are analogous to those in a $\pi\pi^*$ transition. The IVCT band in this class loses CT character and is referred to as a charge resonance band (CRB). This loss of CT character also leads to a transition that is solvent independent and this is one way to differentiate Class III.
1.3.8 Electronic structure and excited state electron communication in *trans*-bis-bis compounds

Consider the MO energy diagram shown on the left of Figure 1.15. On the left we have the orbital splitting for the typical $M_2$ paddlewheel compound and on the right is shown a degenerate set of filled $\pi$ and unfilled $\pi^*$ orbitals corresponding to each of the *trans*-disposed ligands, 2 L. The individual $\pi^*$ orbitals on each ligand can interact with one another to form in-phase (bonding) and out-of-phase (non-bonding) combinations. In the metal complex, the out-of-phase combination has appropriate symmetry to interact with the $M \delta$ orbital through back-bonding. As a result, the ligand out-of-phase combination is destabilized and gains some metal character while the metal-based delta orbital is stabilized and gains some ligand character. The in-phase ligand combination, on the other hand, has no metal character. A similar interaction occurs for the filled $\pi$ orbitals, but the energy separation is larger and therefore it is less important. The orbital representation of this is shown on the right of Figure 1.15. The bottom picture is
representative of the HOMO and is out-of-phase with respect to the ligands but bonding with respect to the interaction with the metal. The top picture has mostly ligand character and is also out-of-phase with respect to the ligands but anti-bonding with respect to the metal. The middle picture is ligand based in-phase with respect to the ligands and non-bonding with respect to the metal. Within the PES representation, the in-phase combination is an orbital that contributes to the excited state described by the lower mixed-valence surface. The out-of-phase combination is an orbital that contributes to the excited state described by the upper mixed-valence surface.

Figure 1.15 MO energy diagram for \textit{trans}-bis-bis compounds. Left: Ground state configuration where the vertical arrows show the lowest energy allowed transitions. The IVCT band becomes allowed after MLCT photoexcitation. Right: Orbital diagram showing the back-bonding interaction responsible for providing electronic coupling between the \textit{trans}-disposed ligands.
It is this back-bonding interaction that gives rise to the coupling between the ligands in these MM paddlewheel complexes. In the absence of back-bonding, the L-\(\pi^*\) orbitals remain isolated and isoenergetic (Class I). By the choice of ligands or metals, the relative energy of the M-\(\delta\) or L-\(\pi^*\) orbitals can be shifted and therefore the extent of back-bonding (coupling) tuned, causing energy separation of the in-phase and out-of phase combinations (and therefore excited states involving these orbitals) leading to Class II or Class III properties. In Class II, the molecular orbital described by the in-phase combination of L-\(\pi^*\) orbitals has a greater contribution, X, from one of the ligands than the other. In other words the orbital is a linear combination of D and A orbitals such that the wavefunction is described by \(\Psi = X\psi_D + (1-X)\psi_A\), where \(X > 0.5\). In this situation there are two resonance forms of the lower PES where the electron occupies a majority of either the D or A states and oscillates between the two at \(k_e\) within this excited state. In class III, the wavefunction is equally shared across both D and A (\(\Psi = X\psi_D + (1-X)\psi_A\), where \(X = 0.5\)) and there is no longer an electron transfer reaction in the excited state.

One of the goals of this thesis is to classify the \textit{trans}-bis-bis compounds under the Robin and Day Classification Scheme. By utilizing ligands containing IR-active functional groups, TRIR becomes an attractive method. In this method, the mixed valence state is generated by photoexcitation of the MLCT transition and we are interested in the delocalization of the photoexcited electron within the MLCT excited state. If the molecule is Class III, the electron will distribute evenly across both ligands and the shift in vibrational frequency expected by populating the L \(\pi^*\) orbital will be equivalent across both D and A. On the other hand, if the molecule is Class II, the
electron is not equally shared and the vibrational frequencies associated with the localized D and A states will be different. Additionally, TRIR spectroscopy has the added feature of providing more definitive proof and confirmation of our earlier assignments of the δδ* and MLCT states as the δδ* states have Raman active MM stretches and are largely silent in TRIR spectroscopy in the IR-active group frequency region.

1.3.9 Electronic structure and excited state electron communication in dimer-of-dimers type compounds

In dimer-of-dimers the concern is how two metal centers interact with one another across a bridging π-conjugated ligand. The orbital interactions responsible for the electronic coupling in dimer-of-dimers are shown in the MO diagram of Figure 1.16. Consider the delta bonding orbital on each metal center, which are degenerate in the absence of coupling. These orbitals can combine to form in-phase and out-of-phase combinations. In this case the in-phase combination has appropriate symmetry to interact with the un-filled L-π* orbital on the bridge. Additionally, the out-of-phase combination also has appropriate symmetry to interact with the bridge but it is the unoccupied L-π* orbital. As a result, the M-δ based orbitals are coupled and split in energy with the in-phase combination being lower.

In these compounds the mixed valence state is generated by removal of an electron from the HOMO and this can be accomplished by oxidation, which is a topic of a previous study, or photoexcitation of the MLCT transition, which is a concern for this thesis. Now, of interest is the delocalization of the electron remaining in the M-δ orbital or equivalently the delocalization of the hole left by the photoexcited electron. In
particular, the delocalization can be monitored in these compounds by FSRS. This technique is appealing because the MM stretches are Raman active and should be sensitive to the electronic occupation across each metal center. Similar to the fsTRIR technique used for the trans-bis-bis compounds, if the electron is on one metal center (class I or II), the MM stretching frequencies will be different whereas if the electron is delocalized over both metal centers (Class III) the MM stretching frequencies will be equivalent.

Figure 1.16 MO energy diagram for dimer-of-dimers. Left: Ground state configuration where the vertical arrows show allowed transitions. The IVCT band becomes allowed after MLCT photoexcitation. Right: Orbital diagram showing the backbonding interactions responsible for providing electronic coupling between the trans-disposed ligands. Modified from reference.76
One report from the Chisholm group on the photophysical properties of dimer-of-dimers type complexes of Mo and W involved various thiophene containing bridging carboxylates, whose representative structures are shown in Figure 1.17. Similar experiments to those for the \textit{trans}-bis-bis complexes were utilized to evaluate the photophysics of these complexes. Here again, dual emission was observed as well as a short lived and long-lived excited state by fsTA and nsTA suggesting the involvement of two excited states in the photophysics. The short-lived state was assigned as the $S_1$ \textit{1MLCT} state, although due to mixing of the M $\delta$ with the filled L $\pi$ orbital there is some $\pi\pi^*$ character. The lifetimes of the \textit{1MLCT} states for both Mo and W complexes were found to be $\sim 8 - 14$ ps. For the triplet states, there was again a difference seen between complexes involving Mo \textit{versus} W. When W is the metal, the lifetimes are $\sim 2.8 - 4.0$ $\mu$s which is markedly longer than the $\textit{3MLCT}$ states of the analogous \textit{trans}-bis-bis compounds utilizing carboxylate ligands. Due to the greater ligand character in the filled $\delta$-based orbital and the greater $\pi\pi^*$ character of the MLCT state, the spin-orbit coupling is weaker and the lifetimes are longer in dimer-of-dimers complexes. When Mo is the metal, the lifetimes are on the order of $60 - 70$ $\mu$s, which is similar to the $\delta\delta^*$ state lifetimes in the \textit{trans}-bis-bis complexes.
1.4 **Statement of Purpose**

The goal of this thesis has been to determine the extent of electronic coupling or electron delocalization within the photoexcited states of complexes that consist of molybdenum and tungsten quadruple bonds and \( \pi \)-conjugated ligands. These complexes serve as models for analogous polymeric materials derived from similar monomeric units. It is believed that the electron delocalization in the model complexes relates directly to the expected electron transport properties of the polymers and eventual incorporation of the polymers into optoelectronic devices is the long term goal. Two types of complexes have been studied: One, those involving two \( \pi \)-conjugated ligands in a trans-arrangement bridged by the metal center (trans-bis-bis) and, two, those with two metal centers and a \( \pi \)-conjugated bridge (dimer-of-dimers). Experiments have focused on femtosecond time-resolved pump-probe techniques and these have been supported by other spectroscopic and theoretical methods.
Chapter 1 first introduces the topic of photophysics and deals with various types of these processes can occur within molecules. The second part deals with the basic principles of the pump-probe experiments that have been undertaken and how these photophysical properties can be observed. In the third part, previous work done on quadruply bonded compounds that relates to their electronic structure and photophysical properties is given. In addition, this part outlines the factors that motivate the study of electronic coupling/delocalization within these compounds.

Chapter 2 discusses the basic photophysical properties of trans-substituted bis-bis compounds that exclusively employ carboxylate linker groups. In particular, attention is given to the compounds with molecular formula \( \text{trans-}M_2(T\text{PB})_4(O_2C\text{PhC}=\text{N})_2 \) where \( M = \text{Mo or W} \). The nature of the singlet and triplet excited states is described and a determination of their emissive properties and lifetimes is made. Also, the effects of changing both the nature of the ligand and also the metal on the photophysical properties is described. For these compounds, the typical heavy atom effect on the lifetimes of the singlet states is not followed and this is acknowledged.

Chapter 3 discusses the basic photophysical properties of two variations of the \( \text{trans-} \)substituted compounds whose molecular formulas are \( \text{trans-}M_2(O_2\text{CMe})_2[C(\text{PrN})_2\text{C}=\text{C-Ph}]_2 \), where \( M = \text{Mo or W} \) and the ligands are connected to the quadruple bond via an amidinate linker. The nature of the singlet and triplet excited states is described and a determination of their emissive properties and lifetimes is made. Also, the effects of changing both the nature of the ligand and also the metal on the photophysical properties is described. Furthermore, the extent of electronic coupling within the \( ^1\text{MLCT} \) state is elucidated from electronic spectroscopy.
Chapter 4 deals with determining the extent of electron delocalization within the MLCT excited states of \textit{trans}-bis-bis compounds using time-resolved infrared spectroscopy. The focus is placed on the compounds discussed in chapter 2 and 3, monitoring in probe region of the $\nu$(C≡N) and $\nu$(C≡C) vibrational modes. The spectral results are evaluated in terms of the Robin-Day classification system and are supported by DFT calculations. A summary of TRIR spectroscopy results that has been done for other compounds is also given as well as results monitoring in other characteristic group frequency regions of the infrared spectrum. The results of this chapter also confirm earlier photophysical assignments of excited states as MLCT or $\delta\delta^*$ in nature. Probing in the 1500 – 1600 cm$^{-1}$ carboxylate region of the spectrum was particularly useful for identifying the $^3\delta\delta^*$ state.
CHAPTER 2

PHOTOPHYSICAL STUDIES OF *TRANS*-SUBSTITUTED DIMETAL PADDLEWHEEL COMPOUNDS OF MM QUADRUPLE BONDS (WHERE M = MO OR W) INVOLVING 4-CYANOBNZOATE AND 2,4,6-TRISOPROPYLBNZOATE LIGANDS

2.1 Introduction

One of the major motivating factors for photophysical studies is the potential incorporation of molecular systems to opto-electronic devices, such as dye-sensitized (DSSCs) or polymer (PSC) solar cells, light emitting diodes, or as molecular wires. In these devices, the function of the molecular system is generally to provide light absorbing or emitting properties as well as electron or hole mobility. However, there are two major aspects of the molecular properties that determine how effectively this function can be completed. One is that the molecular system must possess an electronic structure that is conducive to electron donation and acceptance relative to the electrode band structure. In this fashion, for example, absorbed energy from sunlight can be converted into an electric potential by donation of an excited electron from the LUMO of the molecular material towards the anode and acceptance of an electron into the HOMO from the cathode in the device. In addition, the excited states formed following
absorption must give up the excited electron on a faster time-scale than other elementary photophysical processes. Electron-hole recombination via IC or emission would lead to reduction in photocurrent, for instance. Alternatively, internal conversion (IC) to another excited state with electron density localized on a particular part of the molecule could lead to a reduction in photocurrent as well. Knowledge of the excited state lifetimes and electron distribution as well as the basic ground state electronic structure is therefore important and photophysical studies can reveal this information.

In PSCs, such as the bulk heterojunction cell, a blend of electron donating and electron accepting polymers is used to both absorb light and transport the photogenerated electron pair towards the electrodes. The addition of electron withdrawing groups has been done in several situations to tune these properties in favor of enhanced performance in polymeric devices. In particular, addition of cyano groups to the backbone of several polymers used in opto-electronic devices, such as derivatives of polyphenylenevinylene (PPV)\(^\text{82,83}\) and polythienylenevinylene (PTV)\(^\text{82}\), has resulted in a lower valence band energy, lower band gap, and greater electron delocalization.\(^\text{84}\) The lower valence band energy allows for more stable electrode materials to be used without sacrificing device performance and also makes the polymer more strongly electron accepting.\(^\text{85}\) Additionally, the lower band gap also results in red-shifted absorbance and a better match with the solar spectrum, which therefore gives increased device efficiency.

Another way of improving the overlap with the solar spectrum is to use metallo-organic polymers. In these cases, metal-ligand interactions allow for more easily tunable electronic and photophysical properties\(^\text{86}\) while maintaining the physical advantages of
organic polymeric materials, such as ease of processing and fabrication, flexability, and light weight.\textsuperscript{87}

For the purposes of studying fundamental photophysical processes, Ru(bpy)\textsubscript{3}\textsuperscript{2+} and its derivatives have been extremely valuable and serve as prototypical examples. They have long lived triplet states that are MLCT in character and have been used to construct DSSCs with good efficiency.\textsuperscript{88} A major issue with the photophysics of these types of complexes concerned the delocalization of the excited electron across multiply bpy ligands. It has now become widely accepted that the excited electron is localized on an individual bpy ligand and this feature is useful for DSSCs where the concentration of the excited electron at the ligand directly bound to the TiO\textsubscript{2} surface should allow for better injection. In terms of PSCs, on the other hand, the incorporation of Ru(bpy)\textsubscript{3}\textsuperscript{2+} subunits into polymeric structures has been problematic due to the stereoisomerism caused by the bpy ligands. An achiral alternative is the terpyridine (tpy) ligand, which allows for oligomeric structures to be grown in a linear fashion by using appropriate bridging ligands.\textsuperscript{89} Photophysically, on the other hand, complexes of this type can also be problematic because of a low lying metal-centered (MC), d-d, state that quenches the luminescence and reduces the lifetime of the \textsuperscript{3}MLCT state. When incorporated into polymeric devices, the MC states can possibly act as traps and reduce photocurrents. However, the addition of electron withdrawing cyano groups on the tpy ligand has resolved this problem by reducing the energy of the \textsuperscript{3}MLCT state relative to the MC state.\textsuperscript{90}

Similar to the Ru(tpy)\textsubscript{2}\textsuperscript{2+} complex, compounds involving quadruple bonds can be grown into linear polymers using appropriately bulky spectator ligands, L\textsubscript{1}, that enforce
trans-geometry about the metal center, see scheme 1 (Left). These polymers have been incorporated into an LED device and showed MLCT electroluminescence.\textsuperscript{69} It is therefore desirable to determine the types of excited states involved in the photophysical relaxation pathways and the electron distribution within these states. The polymers, however, are in most cases insoluble and difficult with which to work. For that reason model compounds are used. Trans-bis-bis compounds, scheme 1 (middle), are used to study electron delocalization across the ligands through the metal center and dimer-of-dimers, scheme 1 (right), are used to study hole delocalization across the metal centers through the ligands. It is expected that greater delocalization in these model systems will relate to the enhanced photoconductive properties of the polymers.

**Scheme 2.1**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Trans-bis-bis</th>
<th>Dimer-of-dimers</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
</tbody>
</table>

To some extent the photophysical properties have already been identified for model compounds of the type shown in scheme 1. For the work presented in this chapter,
the concern is *trans*-bis-bis compounds. In these systems, the $S_1$ states live long enough

to be observable and are MLCT in nature while the $T_1$ states are $\delta-\delta^*$ for Mo and MLCT

for W.\textsuperscript{48,70} Only in cases where the $\pi$-accepting ligands are extremely low energy, as is

the case for Mo$_2$(azu)$_2$, where azu = 6-carboethoxy-2-azulene carboxylate,\textsuperscript{49} are the $T_1$

states of Mo compounds MLCT in nature. Conversely, only when the $\pi$-accepting

ligands are extremely high in energy is $T_1 \delta-\delta^*$ for W, as is the case for W$_2$(T$i$PB)$_4$, where

T$i$PB = 2,4,6-triisopropylbenzoic acid.\textsuperscript{61} This chapter will focus on *trans*-bis-bis

compounds of molybdenum (2a) and tungsten (2b) involving cyanobenzoate ligands, as

shown in scheme 1 (bottom), and how their electronic spectroscopy leads to the excited

state assignments. Arrangement of the ligands in the *trans*-configuration is shown by the

crystal structure, Figure 2.1, and is similar for both the Mo and W analogs. The cyano

group is IR active, occurring in a well isolated part of the infrared spectrum and in this

case its stretching frequency serves as a vibrational signal for the electron delocalization,

a.k.a. the electronic coupling between the ligands, in the MLCT excited states. It is the

vibrational studies that will reveal more direct information regarding the electronic

delocalization and photoconductivity and is the concern of chapter 4.
2.2 Experimental Section

2.2.1 General Considerations

All solutions were prepared inside a glove box in a nitrogen atmosphere and solvents were dried, distilled, and degassed prior to use.

2.2.2 Synthesis of [Mo₂(O₆CPh-4-C≡N)₂(T₄PB)] (2a)

Mo₂(T₄PB)₄ (0.3 g, 0.25 mmol) was dissolved in dry toluene and then added to the 4-cyanobenzoic acid (0.0673g, 0.46 mmol). The suspension was stirred at room temperature for 3 days, at the end of which a wine-red precipitate had formed. This was centrifuged and washed with toluene (2 x 10 ml) before being dried in vacuo to give 0.2g (82% yield) of a red solid. Recrystallized from THF. Microanalysis found: C 58.85, H 5.63, C₈₈H₅₄Mo₂N₂O₆ requires: C, 58.90; H, 5.56. NMR (THF-d₈): ¹H (400 MHz) 8.48
(d, 4H, $J_{HH} = 9$Hz), 7.98 (d, 4H, $J_{HH} = 9$Hz), 7.02 (s, 4H), 2.99 (m, 4H), 2.88 (m, 2H),
1.23 (d, 12H, $J_{HH} = 7$Hz), 1.02 (d, 24H, $J_{HH} = 7$Hz) ppm. MALDI-TOF: Calculated
monoisotopic MW for C$_{48}$H$_{54}$Mo$_2$N$_2$O$_8$: 978.83. Found: 981.3 (M$^+$).

2.2.3 Synthesis of [W$_2$(O$_2$CPh-4-C≡N)$_2$(T$i$PB)$_2$] (2b)

W$_2$(T$i$PB)$_4$ (0.41 g, 0.3 mmol) was dissolved in dry toluene and then added to the
4-cyanobenzoic acid (0.08g, 0.54 mmol). The suspension was stirred at room temperature
for 3 days, at the end of which a blue precipitate had formed. This was centrifuged and
washed with toluene (2 × 10 ml) before being dried in vacuo to give 355 mg (75% yield)
of a blue solid. Recrystallized from THF. Microanalysis found: C 49.85, H 4.67
C$_{48}$H$_{54}$W$_2$N$_2$O$_8$ requires: C, 49.93; H, 4.71. NMR (MeCN-d$_3$): $^1$H (400 MHz) 8.12 (d,
2H, $J_{HH} = 9$Hz), 7.84 (d, 2H, $J_{HH} = 9$Hz), 7.09 (s, 4H), 2.91 (m, 3H), 1.24 (d, 12H, $J_{HH} =
7$Hz), 1.22 (d, 24H, $J_{HH} = 7$Hz) ppm. MALDI-TOF: Calculated monoisotopic MW for
C$_{58}$H$_{62}$Mo$_2$N$_2$O$_{12}$: 1154.63. Found: 1154.4 (M$^+$).

2.2.4 Electronic Structure Calculations

Density Functional Theory was used in the Gaussian03 (2a and 2b): Revision
4.02) suite of programs to optimize the gas-phase geometry of the model complexes,
trans-M$_2$(O$_2$CH)$_2$[O$_2$CPh-4-CN]$_2$ (where M = Mo (2a) or W (2b)) in D$_{2h}$ symmetry. The
B3LYP functional was used along with the 6-31+G* basis set for for C, H, N, and O,
while the SDD energy consistent pseudopotential was used for Mo and W. Optimization
was confirmed to be a minimum on the potential energy surface by frequency analysis
and orbital analysis (isosurface value = 0.02) was completed using GaussView. The
Guassian 03 program suite was also used to simulate the ground state absorption spectra using Time-Dependent Density Functional Theory (TD-DFT).

2.2.5 Photophysical Measurements

All solutions were prepared and sealed in the glove box in a nitrogen atmosphere. The room temperature absorption and luminescence spectra were acquired in a 1 x 1 cm quartz cuvette equipped with a Kontes stopcock sealed with a Teflon tap. The low temperature absorption spectra were acquired in a liquid IR cell with CaF$_2$ windows separated by a 1 mm Teflon spacer. Low temperature emission was carried out in J. Young NMR tubes using an optical dewar sample holder. Absorption spectra at both room and low temperature were obtained using a Perkin-Elmer Lambda 900 spectrometer. The low temperature absorbance data were acquired with the liquid IR cell housed in a Specac Variable Temperature Cryostat. The steady-state visible luminescence spectra between 290 – 840 nm were acquired on a SPEX Fluoromax-2 spectrofluorimeter. Low temperature emission measurements at 77 K were obtained as a glass in 2-methyltetrahydrofuran and the room temperature data were taken using THF as the solvent. All samples were excited within the MLCT absorbance band.

Steady-state NIR-luminescence spectra were acquired on a home-built instrument with a germanium detector. A RG830 long-pass filter was placed between the sample and detector. Room temperature spectra were obtained in the quartz cuvette. Low-temperature spectra were obtained at 77 K as a glass in 2-methyltetrahydrofuran in J-Young NMR tubes. The samples were excited at 532 nm for 2a (with all solvents) and at 658 nm for 2b.
Nanosecond transient absorption spectra were measured using 1 x 1 cm quartz cuvettes. The instrument is home-built and pumped by a frequency doubled (532 nm) or tripled (355 nm) Spectra-Physics GCR-150 Nd:YAG laser (fwhm ~ 8 ns, ~ 5 mJ per pulse). The signal is collected by a photomultiplier tube (Hamamatsu R928) and processed by a Tektronics 400 MHz oscilloscope (TDS 380). For 2a and 2b, the excitation wavelength was 532 nm.

Femtosecond transient absorption experiments were carried out using laser and detection systems that have been previously described. The samples were excited at 514 nm for 2a and 675 nm for 2b (with excitation power ~ 1 – 2 μJ at the sample) by the output of an optical parametric amplifier (OPA) equipped with a sum frequency generation (SFG) or second harmonic generation (SHG) attachment, respectively. A notch filter at 514 nm was placed between the sample and the detector in the experiment for 2a. During the measurements the samples were kept in constant motion by manual movement of an XYZ stage in the vertical and horizontal directions. To ensure that no photodecomposition occurred during data collection, absorption spectra were recorded before and after the TA measurements. The measurements were repeated multiple times at each of the pump-probe delay positions to confirm data reproducibility throughout the experiment, and the resulting spectra were corrected for the chirp in the white-light continuum. Kinetics were fit in general to a sum of exponential decay terms of the form \( S(t) = \sum_i A_i \exp(-t/\tau_i) \), with amplitudes \( A_i \), lifetime, \( \tau \), and offset, \( C \), using Microcal Origin 6.0. Error bars for the lifetime are reported as the standard error of the fit. In these experiments, the sample cuvette was again quartz and equipped with a Kontes stopcock but had a 1 mm path length.
2.3 Results and Discussion

2.3.1 DFT Calculations

Electronic structure calculations were carried out on compounds 2a and 2b using density functional theory (DFT) methods and the optimizations were verified to be a minimum on the ground state PES by vibrational frequency analysis. In this case, the compounds were simplified to save computation time by replacing the large T\textsuperscript{i}PB ligands with a hydrogen atom to make formate ligands. The optimized structure has D\textsubscript{2h} symmetry and a nearly planar dihedral angle between the cyanobenzoate ligand \( \pi \)-system and the MM quadruple bond, which agrees with the experimental crystal structure.\textsuperscript{91} Furthermore, the crystal structure shows a nearly 90° dihedral angle between the spectator T\textsuperscript{i}PB ligand and the MM quadruple bond. Such a large dihedral angle disrupts interaction of the T\textsuperscript{i}PB ligand with the metal center and justifies the substitution of hydrogen in the calculated structure.

A molecular orbital (MO) diagram for compounds 2a and 2b is shown in Figure 2.2. For both compounds the orbital picture for the HOMO shows the electron density is composed mostly of the dimetal based \( \delta \)-bonding orbital with some contribution from the cyanobenzoate ligand \( \pi \) system. Each compound also has a set of ligand-based \( \pi^* \) orbitals, the LUMO and LUMO + 2 for 2a and the LUMO and LUMO + 1 for 2b, which are the in-phase and out-of-phase combinations, respectively, resulting from the interaction of the individual ligand \( \pi^* \) orbitals. In the out-of-phase combination there is appropriate symmetry to interact with the HOMO and as a consequence this orbital has some contribution from the M-\( \delta \). Consequently, this backbonding interaction
stabilizes the HOMO and destabilizes the out-of-phase combination, causing a splitting of the two ligand based orbitals. Another low-lying orbital in each compound has a majority of its character from the anti-bonding δ* orbital, which is LUMO + 1 for 2a and LUMO + 2 for 2b. As the Gaussview plots show, this orbital has some contribution from the CO₂ non-bonding (n.b.) orbital of the ligand. This results from interaction between the δ* and occupied n.b. orbital, which tends to push the δ* MO to higher energy.⁶³

Figure 2.2 Ground state frontier orbital energy diagram calculated by DFT for compounds 2a (left, red) and 2b (middle, purple) with selected Gaussview orbitals (right). L represents an orbital based primarily on the p-cyanobenzoate ligands and M either on Mo or W. ΔE₁ represents the energy difference between the HOMO and the in-phase L-π* combination while ΔE₂ represents that between the in- and out-of-phase L-π* combinations.

A comparison of the MO energies for molybdenum and tungsten can be made and this relies heavily on the strength of the δδ bonding interaction in each case. For W, the
lanthanide contraction causes a much denser core shell of electrons and this leads to
greater repulsion between the metal atoms.\textsuperscript{95} As a result, longer bond lengths are
observed for W compounds compared to the Mo analogs, which has been shown
experimentally by X-ray crystal structure data.\textsuperscript{96-99} Due to the small overlap that is
inherent to the $\delta$-bonding interaction, the longer bond length can significantly reduce its
strength. The weaker interaction provides W compounds less stabilization and causes
the HOMO to be comparatively higher in energy than with Mo systems and this is
indicated by the calculations for compound 2a and 2b. This trend in the calculated
HOMO energy has also been observed in related quadruply bonded compounds as well as
experimentally by electrochemistry and photoelectron spectroscopy.\textsuperscript{49,100} A secondary
result of the higher energy HOMO is that there is better energy overlap with the L-$\pi^*$
out-of-phase combination and increased backbonding. This is indicated by the splitting
between the in-phase and out-of-phase combinations, which was found to increase from
0.27 eV to 0.39 eV upon changing the metal center from Mo to W. Similarly, the
strength of the MM-$\delta$ bonding interaction also affects the energy of the $\delta^*$ orbital. For
W, the weaker interaction causes the energy of the $\delta^*$ orbital to decrease. An
experimental indication of this has been demonstrated by the compounds of the type
$[\text{M}_2\text{X}_4(\text{PR}_2\text{R}’)_4]$, where $\text{X} =$ halide ion, $\text{R} =$ CH$_3$, and $\text{R'} =$ C$_6$H$_5$, where the $\delta\delta^*$ transition
occurs at lower energy for W compared to the Mo analogs.\textsuperscript{101} When bridging ligands
such as carboxylates are used, however, the lower energy of the $\delta^*$ orbital allows for
greater interaction with the filled CO$_2$ n.b. orbital and so there is greater destabilization
from this interaction in W compounds and the $\delta^*$ orbital is actually higher energy compared to Mo systems.

These lowest energy orbitals provide a framework for the excited states expected to be involved in photophysical relaxation pathways. From time-dependent density functional theory (TD-DFT) calculations the possible singlet excited states were calculated as shown in Table 2.1. As expected from the MO diagram, the lowest energy transition with good oscillator strength, $f$, of compound 2b ($M = W$), is completely the HOMO to LUMO transition. The contributions to each orbital clearly show this is an MLCT transition. At higher energy is another MLCT transition between the HOMO and an orbital composed of the in-phase combination of the formate L-$\pi^*$ (LUMO + 4).

There are two other low energy transitions of note that are symmetry allowed although they have negligible oscillator strength. One is the transition between the HOMO and the out-of-phase cyanobenzoate L-$\pi^*$ combination (LUMO + 1) and this is forbidden due to the Laporte selection rule. The other is a mixture of transitions but is composed mainly of the HOMO to M-$\delta^*$ (LUMO + 2), i.e. the $\delta\delta^*$ transition, which is fully allowed but weak due to small orbital overlap and transition dipole moment. These weak transitions will not absorb efficiently but they, or their triplet analogs, could be populated in photophysical relaxation pathways. In the Mo compound, 2a, these same singlet states are observed but since the $\delta^*$ orbital falls close in energy to the L-$\pi^*$ orbitals, the $\delta\delta^*$ transition is actually calculated as the lowest energy transition. The two lowest transitions with significant oscillatory strength are again the MLCT transitions mentioned above.
Table 2.1 Calculated transitions by TD-DFT for compounds 2a and 2b

<table>
<thead>
<tr>
<th>Compound 2a (M = Mo)</th>
<th>Description</th>
<th>Coeff. (Norm)(^a)</th>
<th>Energy / eV</th>
<th>f</th>
<th>Sym.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOMO – (LUMO +1)</td>
<td>(M(\delta)) – (M(\delta^*))</td>
<td>0.634 (0.839)</td>
<td>2.414</td>
<td>0.000</td>
<td>B(_{2u})</td>
</tr>
<tr>
<td>(HOMO – 1) – (LUMO + 4)</td>
<td>[(M(\pi)) – (M(\pi^*))](_{xz})</td>
<td>-0.198 (0.0815)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HOMO – 2) – (LUMO + 3)</td>
<td>[(M(\pi)) – (M(\pi^*))](_{yz})</td>
<td>-0.196 (0.0798)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOMO – LUMO</td>
<td>[M(\delta)] – [L(\pi^*) (#)]</td>
<td>0.675 (1.000)</td>
<td>2.594</td>
<td>0.633</td>
<td>B(_{2u})</td>
</tr>
<tr>
<td>HOMO – (LUMO + 2)</td>
<td>[M(\delta)] – [L(\pi^*) (###)]</td>
<td>0.671 (1.000)</td>
<td>2.916</td>
<td>0.000</td>
<td>A(_g)</td>
</tr>
<tr>
<td>HOMO – (LUMO + 8)</td>
<td>[M(\delta)] – [L’(\pi^*)(#)]</td>
<td>0.678 (1.000)</td>
<td>4.10</td>
<td>0.110</td>
<td>B(_{1u})</td>
</tr>
<tr>
<td>Compound 2b (M = W)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOMO – LUMO</td>
<td>[M(\delta)] – [L(\pi^*) (#)]</td>
<td>0.647 (1.000)</td>
<td>2.229</td>
<td>0.827</td>
<td>B(_{3u})</td>
</tr>
<tr>
<td>HOMO – (LUMO + 1)</td>
<td>[M(\delta)] – [L(\pi^*) (###)]</td>
<td>0.653 (1.000)</td>
<td>2.630</td>
<td>0.000</td>
<td>A(_g)</td>
</tr>
<tr>
<td>HOMO – (LUMO + 2)</td>
<td>(M(\delta)) – (M(\delta^*))</td>
<td>0.641 (0.838)</td>
<td>2.688</td>
<td>0.000</td>
<td>B(_{2u})</td>
</tr>
<tr>
<td>(HOMO – 1) – (LUMO + 6)</td>
<td>[(M(\pi)) – (M(\pi^*))](_{xz})</td>
<td>-0.200 (0.0818)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(HOMO – 2) – (LUMO + 5)</td>
<td>[(M(\pi)) – (M(\pi^*))](_{yz})</td>
<td>-0.198 (0.0799)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HOMO – (LUMO + 4)</td>
<td>[M(\delta)] – [L’(\pi^*)(#)]</td>
<td>0.662 (1.000)</td>
<td>3.651</td>
<td>0.147</td>
<td>B(_{1u})</td>
</tr>
</tbody>
</table>

\(^a\)Coefficients normalized according to: \(\sum_{n=0}^{2} N(a_n^2) = 1\)

(##): In-phase combination, (###): Out-of-phase combination
L = Cyanobenzoate ligand, L’ = Formate Ligand
f = Oscillator Strength, Sym = Symmetry of Excited State
2.3.2 Absorbance Spectroscopy

The calculations, above, support the assignment of the bands observed in the absorbance spectra, shown in red for compound 2a and purple for compound 2b in Figure 2.3 at room temperature. Each spectrum has two notable transitions of high intensity. In 2a, these transitions occur at \( \lambda_{\text{max}} \approx 330 \text{ nm} \) and 504 nm with molar absorptivities, \( \varepsilon \), on the order of 6,500 M\(^{-1}\)cm\(^{-1}\) and 12,500 M\(^{-1}\)cm\(^{-1}\), respectively, and in 2b at 395 nm and 715 nm with \( \varepsilon \) on the order of 10,000 M\(^{-1}\)cm\(^{-1}\) and 35,000 M\(^{-1}\)cm\(^{-1}\). The large molar absorptivities are consistent with those for a fully allowed charge transfer transitions\(^{102}\). Further support of this is that the corresponding bands shift to lower energy upon changing from Mo to W, which is consistent with the MO diagram picture that shows the metal-based HOMO is higher energy in 2b but the L-\( \pi^* \) (in-phase) is approximately the same energy. Therefore, these two bands are associated with the calculated \(^1\)MLCT transitions by TD-DFT, where the lowest energy band is to the cyanobenzoate ligand and the higher energy band to the triisopropylbenzoate ligand. Although calculated to be very weak, \( \delta\delta^* \) transitions are observable in related compounds of the type M\(_2\)(O\(_2\)CR)\(_4\), where R = i-Bu and M = Mo or W, with \( \varepsilon \approx 100 \text{ M}^{-1}\text{cm}^{-1} \).\(^{60}\) The breadth and large intensity of the \(^1\)MLCT transitions likely masks the observation of the \( \delta\delta^* \) transitions in these compounds. Of further note, there are intense ligand based \( \pi-\pi^* \) transitions (not shown or calculated) at higher energy in the ultraviolet.
Figure 2.3 Electronic absorption spectra of compounds 2a (M = Mo, red) and 2b (M = W, purple) at room temperature in THF.

The photophysical experiments described in the later sections were done by using an excitation source tuned within the lowest energy MLCT transition associated with the cyanobenzoate ligand. Interpretation of these experiments is made much less complicated if the excitation occurs directly to only a single state rather than a mixture of states. For 2a, it is possible the $\delta\delta^*$ transition occurs in the same region as the $^1$MLCT transition near 500 nm. However, since the intensity of the $\delta\delta^*$ transition is expected to be similar to that for related compounds ($\sim 100 \text{ M}^{-1}\text{cm}^{-1}$), the intensity of the overall band suggests that if excitation did coincide with this state it would only represent $\sim 1 - 2$ % of the excited population. In 2b, the $\delta\delta^*$ state was calculated to be significantly higher energy than the cyanobenzoate MLCT and so it is not expected to interfere.
Another observation from the absorbance spectra is the band for compound 2b clearly contains a high energy shoulder at ~ 650 nm and that for 2a a low energy shoulder at ~ 545 nm. Without any further information, these could be mistaken for separate electronic transitions. In order to verify, the absorption spectra were collected at liquid nitrogen temperature as a glass in 2-methyltetrahydrofuran (2-MeTHF) and these spectra can be seen as the solid lines in Figure 2.4. Apparent from the structure of these compounds is that there is possible rotation about the C-C single bond that connects the carboxylate group to the phenyl ring in the cyanobenzoate ligand. This rotation will affect the energy of the MLCT transition and causes the band to broaden at room temperature. At low temperature, the molecules favor their lowest energy planar structure, the bands sharpen such that additional features are observed in the 1MLCT bands, and \( \lambda_{\text{max}} \) shifts to lower energy. In 2a, the low energy shoulder becomes resolved at 550 nm, the main peak occurs at 514 nm, and a high energy shoulder occurs at ~ 475 nm. In 2b, the main peak is bathochromically shifted to 739 nm, the higher energy shoulder becomes resolved at 670 nm, and an even higher energy feature is observed at ~ 606 nm. The average spacing between adjacent features is 1370 cm\(^{-1}\) for 2a and 1386 cm\(^{-1}\) for 2b. Although this spacing is not identical to a known Raman active vibration it can be associated with a combination of ligand based vibrations that are each coupled to the electronic transition because vibrations involving the metals occur at much lower frequency. Similar vibrational features are observed in the \( \delta\delta^* \) transition of quadruply bonded compounds, but the spacing is only on the order of 300 – 400 cm\(^{-1}\).\(^{103,104}\) In related bridged species, \( \text{M}_4(\text{O}_2\text{C}^\dagger\text{Bu})_6[\mu-\text{C}_2\text{O}_4] \), vibrational features have also been
observed and those for multiple vibrations resolved. Furthermore, that the spacing is similar in both compounds suggests the vibration is ligand based and further supports the assignment as a MLCT transition. Taken together, the lowest energy bands and their associated features originate mostly from a single transition that is MLCT in nature.

2.3.3 Emission Spectroscopy

Upon irradiation into the \(^1\)MLCT bands, various states could be populated during photophysical relaxation and steady state emission spectroscopy can reveal which of those states decay radiatively. For each compound, there is an emission band that is broad and featureless at room temperature and occurs at slightly lower energy than the absorption band (see Figure B1). In Figure 2.4, the emission spectra at low temperature are shown as bold lines and have been normalized to the corresponding low temperature absorption spectra. It can be seen that the vibrational features have a similar mirror-image pattern to those in the absorption spectra. For example, in \(2a\) there are two clearly resolved peaks and a shoulder that leads to the tail to lower energy (in the emission spectrum). In \(2b\), the lower energy part of the emission band is cut-off by the edge of the detector but the first two vibrational peaks are clearly resolved. The similarity in breadth and shape between the absorbance and emission spectra is indicative of the emission occurring from the same state that absorbs. In other words, the emission shown in Figure 2.4 occurs from the \(^1\)MLCT state. Although this is the lowest energy singlet state, lower energy triplet states could also be present. Also of note is that the relative intensities of the vibrational peaks change from the absorption to the emission spectra and this point will be addressed in the following section.
Figure 2.4 Absorbance (solid line) and emission spectra (bold line) of compounds 2a (red) and 2b (purple) recorded at room temperature (dashed line) and 77 K in 2-methyltetrahydrofuran as a transparent glass.

In order to check for lower energy emissive states emission spectra were also collected in the NIR region, shown in Figure 2.5, after \(^1\)MLCT excitation. Starting with compound 2a, shown in the left panel, an emission band is observed with \(\lambda_{\text{max}} \sim 1080\) nm. This band can immediately be assigned as occurring from the triplet manifold of states for the following reasons. The lowest energy singlet states have already been identified as being either \(^1\)MLCT or \(^1\)\(\delta\delta^*\) and occur at similar energies by calculation. The emission from the \(^1\)MLCT state has also already been identified so this leaves the \(^1\)\(\delta\delta^*\) state as a possibility. However, the Stokes shift for this state would then be \(\sim 8800\) cm\(^{-1}\), which is likely too large for singlet emission. Upon cooling to 77 K, vibrational features in this band are resolved with an average spacing of 364 cm\(^{-1}\). This value is on
the same order as that found for related compounds, such as Mo₂(T²PB)₂[L₂], where L = [2-(CO₂)-TTh] = (2,2':5',2''-terthiophene)-5-carboxylate. The energy of the emission also occurs at nearly the same energy as observed in the series where L = [2-(CO₂)-(Th)_n] and n = 1, 2, or 3, which implies small dependence of this low energy emission on the ligand system. In these related systems where the metal is Mo, the low energy emission was assigned as arising from the \(^3\delta\delta^*\) state and the emission in Figure 2.5 is also consistent with that assignment.

Figure 2.5 Emission spectra of compounds 2a (left) and 2b (right) recorded in the NIR at room temperature and at 77 K in THF and 2-methyltetrahydrofuran, respectively.

For compound 2b, some emission is also observed in the NIR. However, recall that the maximum of the \(^1\text{MLCT}\) emission occurs at ~ 780 nm. In the NIR experiment, the detector rapidly loses response at wavelengths shorter than 800 nm and so the emission observed is attributed to the tail of the \(^1\text{MLCT}\) state. Therefore for 2b no lower
energy emissive states are observed. There could still be, on the other hand, lower energy states that emit outside of the detection range of Figure 2.5 or decay non-radiatively. There are few examples of related compounds whose \( ^3 \)MLCT states are high enough energy to show emission. One such example is found in \( W_2(TiPB)_2[2-(CO_2)-(Th)]_2 \), where \( 2-(CO_2)-(Th) = Thiophene-2-carboxylate \). This compound shows two emission bands, one in the visible and another in the NIR at \( \sim 1100 \) nm, that were assigned as \( ^1 \)MLCT and \( ^3 \)MLCT, respectively. The emission of the \( ^1 \)MLCT state for \( 2b \) is \( \sim 1730 \) cm\(^{-1} \) lower than that for \( W_2(TiPB)_2[2-(CO_2)-(Th)]_2 \). Based on the relative energies of the ligand \( \pi \) systems, the emission of the \( ^3 \)MLCT state for \( 2b \) could then be expected to be approximately the same amount of energy less than that for \( W_2(TiPB)_2[2-(CO_2)-(Th)]_2 \) as is the \( ^1 \)MLCT state energy. Therefore, the energy of the \( ^3 \)MLCT emission for \( 2b \) is estimated to occur at \( \sim 1330 \) nm. This is within the detection range of the NIR experiment so if a lower energy \( T_1 \) state does exist, it must decay non-radiatively. In that situation, transient absorption spectroscopy can still be used to detect the presence of a lower energy state.

2.3.4 Electronic Coupling by Absorbance and Emission Spectroscopy

One interesting feature about the MLCT states of these compounds is they represent a symmetrical mixed-valence species. Recall from chapter 1 that mixed-valence species contain two equivalent and interchangeable redox active sites and, according to the Robin-and-Day scheme, there are different degrees to which these two sites can interact (couple) with each other. In compounds \( 2a \) and \( 2b \), this situation is represented by the cyanobenzoate ligands and can be generated by placing an electron
into the cyanobenzoate-π* orbital by photoexcitation of the MLCT transition. Figure 2.6 gives the PES representation considering both the ground state and the MLCT excited state. \( S_0 \) is represented by a single potential well because the ground state is symmetrical. The left side of Figure 2.6 represents a weakly coupled system and so the \( S_1 \), MLCT, state has a double potential well. Each well within this PES represents one of the resonance forms where the excited electron occupies one of the ligand sites or the other and as the system evolves along this surface the electron changes sites. The potential minima are symmetrically displaced from the ground state minima because the change in nuclear configuration associated with placing the electron on one site or another should be identical. As the coupling is increased, as depicted by the right side of Figure 2.6, the redox sites become mixed to a greater extent and the potential minima move closer together. With this picture in mind the intensity pattern of the vibrational features observed in the absorbance and emission spectra at low temperature can be understood.

For a very strongly coupled system, the electron is equally shared between the two ligand sites, the excited molecule is symmetrical, and the \( S_0 \) and \( S_1 \) states have their potential minima at the same nuclear configuration. Therefore, in this situation, the 0-0 transition observed in the absorbance and emission spectra should be the most intense. As the coupling is progressively decreased, the redox sites become localized, breaking the symmetry, and the offset of the \( S_0 \) and \( S_1 \) PESs increases. As a result the 0-1 (absorbance) or 1-0 (emission) vibronic peaks gain intensity at the expense of the 0-0 transition. This will be shown for compounds \( 2a \) and \( 2b \) by referring again to Figure 2.4.

In comparing the low temperature absorbance spectra of \( 2a \) and \( 2b \), it can be seen that the lowest energy vibronic peak has the largest intensity in \( 2b \) whereas in \( 2a \) it is the
second lowest energy peak that has the greater intensity. This implies that the coupling between the virtual MLCT states, those states that are directly excited by photon absorption, when the system is in the ground state is qualitatively weaker in the molybdenum analog, 2a, than in the tungsten analog, 2b. A similar argument can be made for the low temperature emission spectra. In 2b, the highest energy, 0-0, transition is by far the most intense. In 2a, the highest energy peak now also has become the most intense but relative to the second vibronic peak it is much less dominant, which indicates that in the MLCT excited state the coupling between the individual states is somewhat weaker for 2a than for 2b.

The intensity pattern for each compound observed in the absorption spectrum compared to the intensity pattern in the emission spectrum also underlines an important point. Once the excited state has been formed, the strength of the orbital interaction between the ligands can be different compared to in the ground state because there is now a positive charge on the metal and a negative charge on one or both of the ligands. Looking at both the absorption and emission spectra at low temperature for 2a, it can be clearly seen that the 0-1 transition is most intense in the absorption and the 0-0 transition is most intense in the emission spectra. For 2b, the 0-0 transition is most intense in both, but in the emission spectra the relative intensity of the 0-0 to the 0-1 is larger. In each case, it can therefore be concluded that the electronic coupling between the ligands is appreciably greater in the S₁ MLCT state relative to that in the S₀ ground state.
Figure 2.6 Potential energy surfaces of the ground state, $S_0$, and the mixed valence excited states, $S_1$ and $S_2$, for weakly coupled (left) and strongly coupled (right) systems. $S_1$ represents the excited state where one electron occupies the HOMO and the other occupies the in-phase L-\(\pi^*\) combination while $S_2$ represents the state where the excited electron occupies the out-of-phase L-\(\pi^*\) combination.

2.3.5 Nanosecond Transient Absorption Spectroscopy

Nanosecond transient absorption can reveal information on timescales ranging from 10’s of nanoseconds to microseconds. Usually excited state dynamics are completed within this time window so this experiment can reveal information concerning the lowest energy excited state. The spectra for compound 2a are shown in Figure 2.7 at a time coincident with the excitation laser pulse (blue) and again at 50 \(\mu\)s (red). There are two bands with negative intensity at \(\sim 510\) nm and 330 nm and these correspond to the ground state bleach of the two MLCT absorptions. There is also a very weak positive band at \(\sim 350\) nm. Following the dynamics within the ground state bleach at 510 nm yields the kinetic trace shown as the inset and the bleach completely recovers with a
lifetime of 93 μs. Complete recovery of the ground state bleach implies that the experiment monitors the conversion of the lowest energy excited state back to the ground state. At this stage, the excited state responsible for the spectrum shown in Figure 2.5 is therefore associated with the lowest energy emission, the \(^3\delta\delta^*\) state. This point will become clearer after femtosecond transient absorption experiments, below, have been presented. The assignment is also supported by results from similar compounds whose lowest energy triplet states have been assigned as \(^3\delta\delta^*\) and all have similar lifetimes on the order of 100 μs.\(^71\)

Nanosecond transient absorption experiments were also carried out for compound 2b, however they did not yield as clear results. In many of the compounds of this type that have been studied previously, the nature of the triplet state changes to \(^3\)MLCT and the lifetime is significantly reduced to 100’s of nanoseconds or less.\(^48,70\) In this case, a spectrum was able to be obtained at ~ 17 ns after the laser pulse containing negative signal at ~ 750 nm and 420 nm and a weak positive signal between 400 - 600 nm, shown in Figure B2. These signals, however, occur within the pulse width of the excitation source and so the lifetime is considered to be less than ~ 20 ns.
Figure 2.7 Nanosecond transient absorption spectra of compound 2a in THF at room temperature after excitation at 532 nm. Inset: representative kinetics collected at 510 nm.

2.3.6 Femtosecond Transient Absorption Spectroscopy

Transient absorption experiments on faster timescales were also conducted, which in this case covered between 100’s of femtoseconds to 3 nanoseconds. Again the compounds were excited into the $1\text{MLCT}$ bands and the absorption spectra monitored thereafter and these spectra are shown for compound 2a in the left panel of Figure 2.8. Initially, the spectrum at 0.5 ps consists of positive features at 375 nm, 430 nm, and 560 nm, and negative features above 600 nm, which corresponds to the emission band from the $1\text{MLCT}$ state, and between 450 nm and 550 nm, which corresponds to the ground state bleach. These initial bands decay to directly give rise to the long-lived spectrum shown at 2000 ps. A better representation of the long-lived state is shown in Figure B3 by plotting spectra obtained only after a 20 ps delay. This spectrum still contains the ground state bleach but the other features (the positive bands and the stimulated emission
band) have decayed to leave only a very weak absorption at ~ 370 nm. By comparison with Figure 2.7, it can be seen that the nanosecond transient absorption spectrum is in good agreement with this spectrum. The combined transient absorption experiments imply that two excited states are involved with the excited state dynamics between 0.5 ps after excitation and ground state recovery. Therefore these two excited states are associated with the two emissive states, the higher energy $^1\text{MLCT}$ and lowest energy $^3\text{δδ*}$ states.

Kinetic traces for 2a showing the femtosecond dynamics are shown in the right panel of Figure 2.8. The kinetic trace measured in the high energy absorption band at 435 nm is compared with the one collected in the stimulated emission band at 655 nm. At 435 nm, the decay is single exponential with a lifetime of 3.38 ps. Since this decay is single exponential, the decay of the excited state responsible for the high energy absorption band can be assigned to this absorption band and lifetime. When monitoring in the stimulated emission band at 655 nm, which can only arise from the $^1\text{MLCT}$ state that is responsible for that emission, the kinetics can be fit reasonably well to a single exponential ($R^2 = 0.993$) but noticeably better results are obtained when using a dual exponential fit ($R^2 = 0.998$). In this case the lifetimes are 0.78 ps and 3.73 ps. That the lifetime of 3.73 ps measured at 655 nm in the stimulated emission band is so similar to that measured at 435 nm of 3.38 ps is significant and indicates the two lifetimes monitor the same process. Therefore, the initial spectrum at 0.5 ps can be identified with the $^1\text{MLCT}$ state, which is the state of initial absorption, and the ~ 3.5 ps process with the observed decay rate of this state by both fluorescence and intersystem crossing to the $^1\text{T}_1$ $\text{δδ*}$ state. The shorter lifetime, 0.78 ps, can be associated with processes that occur
within the $^1$MLCT state, for example solvent or vibrational relaxation. Further experiments would be needed to assign unequivocally this process.

Figure 2.8 Femtosecond transient absorption spectra (left) of compound 2a following excitation at 514 nm at room temperature in THF. Representative kinetic traces (right).

The kinetic trace at 560 nm reveals different decay components. There is a $\sim 6$ ps decay associated with the decay of the ESA band here and also a $\sim 200$ ps decay component associated with further dynamics, shown in Figure B4. It is possible that there is some small contribution to the triplet state spectrum at this wavelength. In that case, the 200 ps component could be associated with relaxation of a hot triplet state, which gets formed with approximately 8000 cm$^{-1}$ of excess energy according to the emission spectra. The 6 ps component could still be associated with the singlet state lifetime. At this wavelength, the observed lifetime becomes longer due to overlap with the ground state bleach dynamics. Since the molecule is fluorescent, decay of the $S_1$ absorption must be accompanied by recovery of the bleach and at this wavelength these two processes overlap. These two processes also each monitor the $S_1 - S_0$ conversion, so
they should have similar lifetimes, which would make the observed lifetime appear longer. For this reason the decay at 435 nm is considered to be a better representation of the $S_1$ state lifetime.

Femtosecond transient absorption spectra and associated kinetic traces for compound 2b are shown in Figure 2.9. Initially, at 0.3 ps, the spectrum consists of a broad positive band between ~ 400 nm and 600 nm with negative contributions at 400 nm and greater than 600 nm. The negative contributions can be easily ascribed to the two MLCT transitions of the ground state. In addition, the initial spectrum contains apparent peaks at 475 nm, 530 nm, 570 nm, and 630 nm. Decay of the initial spectrum occurs over the course of approximately 30 ps to gives rise to a spectrum that is longer-lived. At 30 ps, the spectrum has become narrowed on the red edge, covering a range from 400 nm to 560 nm, and has better resolved features that then occur at 460 nm, which is more intense, and 515 nm. After this point, this spectrum evolves further such that the spectrum at 3000 ps still contains two peaks but the one at higher energy has shifted to 450 nm and has about the same intensity as the peak at 515 nm. Also of note is that during the times between 30 and 3000 ps, the bleach at wavelengths greater than 600 nm recovers concomitantly with the decay of the positive band and in accordance with this there is an isosbestic point at 555 nm. The dynamics and spectral features associated with this longer decay component are more easily recognized by plotting only the spectra that cover this time range and this is shown in Figure B5.

Analysis of the kinetic trace obtained at 550 nm reveals three components to the decay at that wavelength having lifetimes of 0.51 ps, 6.2 ps, and ~ 925 ps. The long component can be associated with the spectral dynamics occurring after 30 ps and the
presence of the isosbestic point between the excited state absorption and ground state bleach implies this process reforms the ground state. The lifetime on the order of 100’s of picoseconds to nanoseconds is too long to be associated with the S1 1MLCT state and so this process and corresponding spectral features are assigned as belonging to the partial decay of the T1 state. Consistent with the earlier result from nanosecond transient absorption, the lifetime of this T1 state is shorter than 20 ns but longer than the 3 nanoseconds represented in the femtosecond transient absorption experiment as the long-lived spectrum does not completely decay. Since the lifetime is in the nanosecond regime, it also suggests that the T1 state can be assigned as the 3MLCT state. Prime examples for comparison are found with W2(TiPB)4 and W2(TiPB)2[2-(CO2)-(Th)]2. In W2(TiPB)4, the T1 state was assigned as 3δδ* and has a lifetime of ~ 1 μs, much longer than observed for 2b.61 Conversely, in W2(TiPB)2[2-(CO2)-(Th)]2, partial decay of the T1 state was also observed in femtosecond transient absorption experiments on the order of 1 ns and the T1 state for this compound was assigned as 3MLCT.70

Figure 2.9 Femtosecond transient absorption spectra of compound 2b (left) following excitation at 675 nm at room temperature in THF. Kinetic trace (right) at 550 nm.
There are two possibilities for the assignment of the remaining components to the decay at 550 nm. One possibility is that the initial excitation to the $^1$MLCT state undergoes ultrafast intersystem crossing in 0.51 ps. This would imply that after the decay of 0.51 ps, the spectrum belongs to the T$_1$, $^3$MLCT state and the spectral changes associated with the 6.2 ps component that occur thereafter take place within this electronic state. Processes such as vibrational cooling or conformation relaxation, for example, could be consistent with the spectral changes that occur during this time period.\textsuperscript{24,35} In chapter 4, however, vibrational spectroscopy reveals a decay of the excited state C≡N stretching wavenumber with a similar lifetime, but this band does not undergo any significant dynamic shift in wavenumber, which is not consistent with the first assignment.\textsuperscript{106} Also, because the singlet state is emissive, it suggests the S$_1$ lifetime would not be so fast. The other possibility, then, is that the 0.52 ps component is associated with some ultrafast relaxation within the $^1$MLCT state and the 6.2 ps component is ascribed to intersystem crossing to the T$_1$, $^1$MLCT state. Although the band at 0.3 ps occurs in the same wavelength range as that at 20 ps and 3000 ps, the shapes and features within each spectrum are, in fact, quite different. For example, the longer-lived spectra clearly contain only two features whereas the initial spectrum contains four. That the shape of the initial spectra compared to the long-lived spectra is so different suggests that those spectra come from different electronic excited states. The TA experiments of compound \textbf{2b} also suggest two excited states are involved in the relaxation dynamics and they are assigned as the singlet and triplet MLCT states.
2.4 Conclusions

The assignments for the excited states involved in relaxation from the initially formed excited state back to the ground state can be summarized as follows and depicted by use of a Jablonski diagram, Figure 2.10. The combined TA experiments suggest that in each compound there are two electronic excited states involved in the photophysical relaxation. The first state is the initially excited $^1\text{MLCT}$. Decay of this state is observed to occur on the picosecond time scale by both fluorescence back to the ground state and intersystem crossing directly to the $T_1$ state. For 2a, the $T_1$ state is $^3\delta\delta^{*}$ and this results in a long $T_1$ lifetime, vibrational features in the lowest energy emission band, and a weak UV absorption in the TA experiments. On the other hand, for 2b, the $T_1$ state is MLCT, which leads to a much shorter $T_1$ lifetime and a broad excited state absorption in the visible. The use of cyanobenzoate ligands lowers the energy of the MLCT states enough such that both 2a and 2b have $S_1$ as MLCT but only for 2b is this true for $T_1$. However, for 2b, the $T_1$ state is lowered such that it becomes non-emissive. The lifetimes of the $S_1$ $^1\text{MLCT}$ states were also found to be $\sim 3.5$ ps for 2a and $\sim 6.2$ ps for 2b. While the picosecond lifetimes on the order of 10 ps are common for related quadruply bonded compounds$^{68}$ it is usually expected that addition of a heavier element causes the singlet state lifetime to decrease. Although it is unusual that the heavy-atom effect is not followed, it is not totally unprecedented in transition metal complexes.$^{107,108}$ A table of the observed photophysical properties is also shown in appendix B. A further point is that the MLCT states are mixed-valence in nature and the low temperature absorption and
emission spectra are particularly revealing towards this point for the $S_1$ states. Vibrational spectroscopy will further support this finding and is presented in chapter 4.

Figure 2.10 Jablonski diagram summarizing assigned photophysical properties.

2.5 Supporting Information

The following have been included in Appendix B as supporting information: Low temperature absorption and emission for both 2a and 2b (Figure B1), nanosecond transient absorption for compound 2b (Figure B2), femtosecond transient absorption of compound 2a between 20 ps and 2000 ps (Figure B3), kinetic trace collected at 565 nm for the femtosecond transient absorption of compound 2a (Figure B4), femtosecond transient absorption of compound 2b between 30 ps and 3000 ps (Figure B5), Summary of photophysical properties of both 2a and 2b (Table B1).
CHAPTER 3

PHOTOPHYSICAL STUDIES OF TRANS-BIS(PHENYLETHYNYL-DIISOPROPYLAMIDINATO)-BIS(ACETATO) DIMETAL COMPOUNDS

INVOLVING MM QUADRUPLE BONDS WHERE M = MO OR W

3.1 Introduction

The incorporation of MM quadruply bonded units into organic extended π-systems has been a topic of interest for some time. The long term goal has been towards the development of opto-electronic devices where the quadruply bonded compounds serve as the photon harvesting or emitting material. At this point, the polymers or oligomers have already been shown to undergo electroluminescence and have potential applications in light harvesting materials for photovoltaics based on easily tunable MLCT absorptions spanning the visible to the NIR region of the electromagnetic spectrum.\textsuperscript{69,109} However, to optimize device performance fully, a complete understanding of the processes by which these types of molecules dissipate excess energy obtained upon formation of their excited states is warranted.

Discrete molecular species such as the title complexes provide model systems for the higher order oligomers and afford the opportunity for detailed spectroscopic studies due to greater solubility and more facile manipulation. The molecular structure of the tungsten complex 3b, which was previously determined by a single crystal X-ray study,
is shown in Figure 3.1 and is similar to the Mo analogue, 3a. One important feature of this paddlewheel MM quadruply bonded molecule is the \textit{trans}-arrangement of the two amidinate ligands and the essentially co-planar arrangement of the extended \(\pi\)-system. In this situation, the \(M_2\) \(\delta\) orbital interacts with the out-of-phase \(\pi^*\) orbital combination of the phenylethynylamidinate ligand. This interaction facilitates electronic coupling between the ligands and provides intensity to MLCT type transitions. Previous studies of similar compounds possessing carboxylate groups have already been done that show these similar interactions. These title compounds, however, have unique photophysical properties that result from the utilization of the particular amidinate functional group and exploring this modification relative to the carboxylate compounds is a topic of this chapter.

Figure 3.1 ORTEP diagram of compound 3b drawn with 50% probability displacement ellipsoids with hydrogen atoms omitted. The starred (*) atoms are related to the corresponding unstarred atom by the crystallographic inversion center. There is a 9.0° dihedral angle between the phenyl ring and its amidinate group. Reproduced from reference.\textsuperscript{110}
Within the context of transition metal photophysics, photoexcitation commonly produces initial excited states that undergo ultrafast intersystem crossing (isc). The most commonly studied systems have been those of d⁶, diamagnetic, ruthenium and osmium involving polypyridyl ligands, where isc from ¹MLCT to ³MLCT occurs in less than 100 fs. Furthermore, paramagnetic complexes such as Cr(acac)₃ and some polypyridyl complexes of Fe(II) have also been found to have isc times of less than 100 fs. Although the presence of closely lying Tₙ states of different orbital type can be important for isc times (El Sayed’s Rules), it is, in general, also apparent that systems where the organic ligand ring π-system is directly bound to the metal center have stronger coupling to the metal center and faster isc times. When the ligand π-system is extended away from the metal center, as has been shown for square planar platinum complexes of the type trans-Pt[(C≡CPh)ₙ][PBU₃]₂ (where (C≡CPh)ₙ = phenylacetylide oligomers and PBU₃ = tributylphosphine), the isc time was shown to increase from 70 fs to 2.1 ps as n goes from 1 to 3. In all of the above mentioned complexes, observation of photophysical processes has been limited to the spin crossover states and those occurring within the initial excited state have remained absent due to these ultrafast isc times.

In particular, many of the photophysical studies on Ru(bpy)₃²⁺, Os(bpy)₃²⁺ (where bpy = 2,2’-bipyridine) and derivatives thereof have been concerned with the extent of electron delocalization within the initially formed MLCT excited state. While localization onto a single ligand is widely accepted for the longest lived triplet state when using polar solvents, the nature of the state that exists approximately 1 ps after initial excitation has been extensively debated but suggested to be at least partly if not completely delocalized. Homoleptic complexes involving a
quadruple bond between molybdenum or tungsten atoms supported by bridging carboxylate ligands have been shown to possess $S_1$ states that can be classified as MLCT having much longer lifetimes on the order of 10 ps. In this chapter, the photophysics of the trans-substituted complexes possessing similar geometry involving phenylethynylamidinate ligands is explored. Given the long lifetimes of the $^1$MLCT states in these types of complexes, this study also affords the opportunity to monitor photophysical processes occurring within the $^1$MLCT state, including localization dynamics as well as the extent of electronic coupling between the ligands.

3.2 Experimental Section

3.2.1 General Considerations

The complexes 3a and 3b were obtained according to previously reported procedures. Solutions were prepared inside a glove box in a nitrogen atmosphere. All solvents were dried, distilled, and degassed prior to use.

3.2.2 Electronic Structure Calculations

Density Functional Theory was used in the Gaussian03 (Mo: Revision c.0292 W: Revision D.01123) suite of programs to optimize the gas-phase geometry of the model complexes, trans-$M_2(O_2CH)_{2}[(NMe)_2CCCPh]_2$ (where $M = Mo$ or $W$) in $D_{2h}$ symmetry. The B3LYP functional was used along with the 6-31+G* basis set for C, H, N, and O, while the SDD energy consistent pseudopotential was used for Mo and W. Optimization was confirmed to be a minimum on the potential energy surface by frequency analysis.
and orbital analysis (isosurface value = 0.02) was completed using GaussView. The Guassian 03 program suite was also used to simulate the ground state absorption spectra using Time-Dependent Density Functional Theory (TD-DFT).

### 3.2.3 Photophysical Measurements

All solutions were prepared and sealed in the glove box in a nitrogen atmosphere. The room temperature absorption and luminescence spectra were acquired in a 1 x 1 cm quartz cuvette equipped with a Kontes stopcock sealed with a Teflon tap. The low temperature absorption spectra were acquired in a liquid IR cell with CaF$_2$ windows separated by a 1 mm Teflon spacer. Low temperature emission was carried out in J. Young NMR tubes using an optical dewar sample holder. Absorption spectra at both room and low temperature were obtained using a Perkin-Elmer Lambda 900 spectrometer. The low temperature data were acquired with the liquid IR cell housed in a Specac Variable Temperature Cryostat. The steady-state visible luminescence spectra between 290 – 840 nm were acquired on a SPEX Fluoromax-2 spectrofluorimeter. Low temperature measurements at 77 K were obtained as a glass in 2-methyltetrahydrofuran and the room temperature data were taken using THF as the solvent.

Steady-state NIR-luminescence spectra were acquired on a home-built instrument with a germanium detector. The samples were excited at 532 nm for 3a in all solvents. A RG830 long-pass filter was placed between the sample and detector. Low-temperature spectra were obtained at 77 K as a glass in 2-methyltetrahydrofuran.

Nanosecond Transient Absorption (nsTA) spectra were measured using the 1 x 1 cm quartz cuvettes. The instrument is home-built and pumped by a frequency doubled
(532 nm) or tripled (355 nm) Spectra-Physics GCR-150 Nd:YAG laser (fwhm ~ 8 ns, ~ 5 mJ per pulse). The signal is collected by a photomultiplier tube (Hamamatsu R928) and processed by a Tektronics 400 MHz oscilloscope (TDS 380). For both 3a and 3b, the excitation wavelength was 532 nm.

Femtosecond Transient Absorption (fsTA) experiments were carried out using laser and detection systems that have been previously described. The samples were excited at 514 nm for 3a and 600 nm for 3b (with excitation power ~ 1 – 2 μJ at the sample) by the output of an optical parametric amplifier (OPA) equipped with a sum frequency generation (SFG) or second harmonic generation (SHG), respectively, attachment. Notch filters at 514 nm and 600 nm were placed between the samples and the detector in the respective experiments. The notch filter at 600 nm also had a small section at ~ 400 nm with low transmittance. During the measurements the samples were kept in constant motion by manual movement of an XYZ stage in the vertical and horizontal directions. To ensure that no photodecomposition occurred during data collection, absorption spectra were recorded before and after the TA measurements. The measurements were repeated four times at each of the pump-probe delay positions to confirm data reproducibility throughout the experiment, and the resulting spectra were corrected for the chirp in the white-light continuum.

Kinetic traces for complex 3a were also monitored using single probe wavelengths. In these cases, the white-light continuum was generated from a water cell having a 1 cm path length and the probe wavelengths were isolated by 10 nm bandwidth interference filters placed between the sample and detector. The detector was a joule meter (mlectron) and the signals were acquired by a lock-in amplifier referenced to an
optical chopper in the pump pulse path. The kinetics were fit in general to a sum of exponential decay and/or exponential rise to a maximum terms of the form \( S(t) = \sum_i A_i \exp(-t/\tau_i) + \sum_j B_j [1 - \exp(-t/\tau_j)] + C \), with amplitudes \( A_i \) and \( B_j \), lifetime, \( \tau \), and offset, \( C \), using Origin 6.0. Error bars for the lifetime are reported as the standard error of the fit. In these experiments, the sample cuvette was again quartz and equipped with a Kontes stopcock but had a 1 mm path length.

3.3 Results and Discussion

3.3.1 Theoretical Calculations by DFT and TD-DFT Methods

A frontier molecular orbital diagram is shown in Figure 3.2 for the lowest energy ground state structure of model compounds of 3a and 3b. In this case the methyl group of the acetate ligand has been replaced by hydrogen and the isopropyl groups on the amidinate ligand have been replaced by methyl groups and these substitutions save computational resources. The geometries were optimized and confirmed as a minimum on the ground state potential energy surface by frequency analysis using DFT methods. The diagram shows the energies of some important orbitals along with the corresponding orbital pictures for compound 3a, which are qualitatively similar to those for compound 3b. In both compounds, the HOMO is the \( \delta \) bonding orbital with some ligand \( \pi^* \) character and the LUMO and LUMO + 1 are the in-phase and out-of-phase combinations of the ligand \( \pi^* \) orbitals, respectively. The out-of-phase combination has appropriate symmetry to interact with the \( \delta \) orbital and therefore the LUMO + 1 shows \( \delta \) bonding character and the LUMO contains no contribution from the \( \delta \) orbital. The observation of these orbital contributions is an indication of the backbonding interaction which gives
rise to the electronic coupling between the ligands. Lying at higher energy is the \( \delta^* \) orbital, which shows contribution from the non-bonding orbitals of the amidinate \( \text{CN}_2 \) and carboxylate \( \text{CO}_2 \) groups. Also at higher energy is shown the energy level for the in-phase combination belonging to the formate ligands.

Comparison of the orbital energies of the compounds shows that the \( \delta \) HOMO is significantly higher in energy for \( 3a \) than for \( 3b \). This is consistent with the idea that the \( \delta \) bonding interaction is weaker in the W containing compound and is supported by the crystal structure data that shows the W bond length is longer.\(^{110}\) As a result of this higher energy HOMO, the backbonding interaction between the \( \delta \) orbital and the out-of-phase combination is stronger in \( 3b \). The energy separation between the in-and-out of phase combinations is indicative of the strength of this interaction since the LUMO has no metal orbital character. For \( 3b \), this separation as determined by the calculations is 0.493 eV whereas for \( 3a \) it is slightly less at 0.457 eV, suggesting slightly greater coupling between the ligands in \( 3b \).
In an attempt to predict possible electronic transitions and gain a more quantitative interpretation of their character, time-dependent DFT calculations on the model complexes were carried out. The calculated energies (eV) of the singlet excited state transitions of these model complexes in the gas phase are given in Table 3.1 and Table 3.2 along with both their oscillator strengths and their orbital origin. The main point to emerge from the calculations is that the lowest energy bands are indeed virtually 100% M$_2$ δ to amidinate π* and can be assigned as the S$_1$ MLCT absorption. The observed tungsten absorption is somewhat red-shifted in relation to the calculated value$^{124}$ as has been seen before for related complexes$^{77,125,126}$ and presumably reflects the greater degree of spin-orbit coupling with the 5d element. Furthermore, solvent effects are likely to shift the electronic transition energy relative to the gas phase value that was calculated. The transition of primarily δδ* character, labeled as transition 2 for both 3a and 3b in tables 1 and 2 respectively, is also fully allowed but has essentially zero
calculated oscillator strength, presumably due to the small change in dipole moment associated with this transition. Due to the interaction of the $\delta^*$ orbital with the non-bonding combination of CN$_2$ and CO$_2$ group orbitals and low energy of the amidinate ligand $\pi^*$ orbitals, the $\delta^*$ orbital occurs at higher energy than the MLCT absorption for both compounds. Transition 3 for both compounds is characterized by a MLCT to the formate ligands and occurs at lower energy for 3b because the HOMO is at higher energy compared to 3a. At higher energy for 3b is a transition that has primarily phenylethynylamidinate ligand $\pi\pi^*$ character, labeled as transition 4. In 3a, a similar transition occurs and this is labeled transition 5. Furthermore, another transition, 4, occurs in 3a between the non-bonding p-orbitals on the amidinate CN$_2$ group and the metal $\delta^*$ orbital, which classifies it as a LMCT transition. The energies of the calculated transitions were plotted alongside the absorption spectra, Figure 3.3, and are in good agreement with the observed spectrum.
Table 3.1 Some calculated transitions for compound 3a

<table>
<thead>
<tr>
<th></th>
<th>Orbitals</th>
<th>Description</th>
<th>Coeff. (Norm)(^a)</th>
<th>Energy / eV</th>
<th>f</th>
<th>Sym</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HOMO - LUMO</td>
<td>Mδ – L(\pi)^*(#)</td>
<td>0.663 (1.000)</td>
<td>2.426</td>
<td>0.933</td>
<td>B(_{3u})</td>
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<tr>
<td>2</td>
<td>(HOMO – 5) – (LUMO + 4)</td>
<td>M(\pi) – M(\pi)^*(xz)</td>
<td>-0.171 (0.060)</td>
<td>2.674</td>
<td>0.000</td>
<td>B(_{2u})</td>
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<td></td>
<td>(HOMO – 3) – (LUMO + 5)</td>
<td>M(\pi) – M(\pi)^*(yz)</td>
<td>-0.193 (0.077)</td>
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<tr>
<td></td>
<td>HOMO – (LUMO + 2)</td>
<td>Mδ – Mδ*</td>
<td>0.646 (0.863)</td>
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<tr>
<td>3</td>
<td>HOMO – (LUMO + 9)</td>
<td>Mδ – L’(\pi)^*(#)</td>
<td>0.681 (1.000)</td>
<td>3.930</td>
<td>0.094</td>
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<tr>
<td>4</td>
<td>(HOMO – 1) – (LUMO + 2)</td>
<td>L(\pi)(#) – Mδ*</td>
<td>0.617 (0.824)</td>
<td>4.075</td>
<td>0.513</td>
<td>B(_{3u})</td>
</tr>
<tr>
<td></td>
<td>HOMO – (LUMO + 11)</td>
<td>Mδ – L(\pi)^*(#)</td>
<td>0.285 (0.176)</td>
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<td>5</td>
<td>(HOMO – 7) – (LUMO)</td>
<td>[L(\pi)(##) + Mδ] – L(\pi)*(#)</td>
<td>0.313 (0.210)</td>
<td>4.352</td>
<td>0.593</td>
<td>B(_{3u})</td>
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<td></td>
<td>(HOMO – 6) – (LUMO + 1)</td>
<td>L(\pi)(#) – [L(\pi)^*(##) + Mδ]</td>
<td>-0.193 (0.080)</td>
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<td>(HOMO – 1) – (LUMO + 2)</td>
<td>L(\pi)(#) – Mδ*</td>
<td>-0.158 (0.053)</td>
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<td></td>
<td>HOMO – (LUMO + 11)</td>
<td>Mδ – L(\pi)^*(#)</td>
<td>0.554 (0.657)</td>
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\(^a\)Coefficients normalized according to: \(\sum_{n=0}^{2} N(a_n^2) = 1\)

(#) In-phase combination, (##): Out-of-phase combination
L = Phenylethynylamidinate Ligand, L’ = Formate Ligand
f = Oscillator Strength, Sym = Symmetry of Excited State
### Table 3.2 Some calculated transitions for compound 3b

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<th>Orbitals</th>
<th>Description</th>
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<th>Energy / eV</th>
<th>f</th>
<th>Sym</th>
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<tbody>
<tr>
<td>1</td>
<td>HOMO – LUMO</td>
<td>Mδ – Lπ*(#)</td>
<td>0.641 (1.000)</td>
<td>2.191</td>
<td>1.115</td>
<td>B$_{3u}$</td>
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<tr>
<td>2</td>
<td>HOMO – (LUMO + 3)</td>
<td>Mδ – [Mδ* + Lπ*(##)]</td>
<td>-0.277 (0.156)</td>
<td>3.425</td>
<td>0.002</td>
<td>B$_{2u}$</td>
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<td></td>
<td>HOMO – (LUMO + 5)</td>
<td>Mδ – [Lπ*(##) + Mδ*]</td>
<td>0.645 (0.844)</td>
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</tr>
<tr>
<td>3</td>
<td>HOMO – (LUMO + 8)</td>
<td>Mδ – L’π*(#)</td>
<td>0.688 (1.000)</td>
<td>3.528</td>
<td>0.121</td>
<td>B$_{1u}$</td>
</tr>
<tr>
<td>4</td>
<td>(HOMO – 7) – LUMO</td>
<td>[Lπ(##) + Mδ] − Lπ*(#)</td>
<td>0.569 (0.723)</td>
<td>4.494</td>
<td>0.981</td>
<td>B$_{3u}$</td>
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<td>(HOMO – 2) – (LUMO + 3)</td>
<td>Lπ(#) − [Mδ* + Lπ*(##)]</td>
<td>-0.229 (0.117)</td>
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<tr>
<td></td>
<td>(HOMO – 2) – (LUMO + 5)</td>
<td>Lπ(#) − [Lπ*(##) + Mδ*]</td>
<td>-0.101 (0.023)</td>
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<tr>
<td></td>
<td>HOMO – (LUMO + 18)</td>
<td>Mδ − L’(##)</td>
<td>-0.248 (0.137)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Coefficients normalized according to: \[ \sum_{n=0}^{2} N(a_n^2) = 1 \]

(#): In-phase combination, (##): Out-of-phase combination

L = Phenylethynylamidinate Ligand, L’ = Formate Ligand

f = Oscillator Strength, Sym = Symmetry of Excited State
3.3.2 Electronic Absorption Spectra

The electronic absorption spectra for the two complexes recorded in THF at room temperature are shown in Figure 3.3. The low energy intense absorption bands in the visible region correspond to the calculated transition from the $M_2 \delta$ orbital to the phenylethynyl amidinate ligand in-phase combination $L-\pi^*$ orbital, namely the LUMO. As can be seen from the frontier MO diagram of Figure 3.2 and the calculated oscillator strength, the absorption is fully allowed by symmetry and can be described as a charge transfer transition. This is also in agreement with the large determined molar absorptivities of $\sim 22000 / \text{M}^{-1} \text{cm}^{-1}$ for 3a and $\sim 45000 / \text{M}^{-1} \text{cm}^{-1}$ for 3b. The MLCT transition occurs at lower energy for the tungsten complex because of the $W_2 \delta$ orbital occurs at higher energy while the $L-\pi^*$ (in-phase combination) is approximately the same for both compounds. At higher energy, other electronic transitions of note are present. For 3b, the strong transition at 270 nm is associated with calculated transition 4, which is primarily $\pi\pi^*$ in character and the weaker transition at 350 nm is associated with transition 3, which is the MLCT transition involving the carboxylate $\pi^*$. The higher energy portion of the spectrum for 3a is somewhat more complicated. There are two intense peaks observed in the 250 – 350 nm range and these can be associated with the calculated transitions 4 and 5 with large oscillator strength that are $\pi\pi^*$, 260 nm, and LMCT, 290 nm, transitions. In 3b, this second high intensity peak, the LMCT transition, is presumably not observed because the higher energy of the $M-\delta^*$ orbital pushes it to much higher energy. The weak transition in 3a that would be associated with the carboxylate $\pi^*$ MLCT transition is also not observed. It should occur at even higher
energy compared to 3a and therefore is presumably overwhelmed by the more intense LMCT and/or ππ* transitions. These states provide a framework for excited states expected in the photophysical experiments, below, especially the lowest energy MLCT and δδ* states.

![Electronic absorption spectra](image)

Figure 3.3 Electronic absorption spectra at room temperature in THF and calculated TD-DFT transitions for compound 3a (orange) and compound 3b (blue). f = calculated oscillator strength.

### 3.3.3 Steady State Emission

The steady state emission spectra for complexes 3a and 3b in THF at room temperature are shown in Figure 3.4, along with their absorption spectra. Both complexes show dual emission which can be assigned to fluorescence and phosphorescence. Notably, the energy separation from the S\textsubscript{1} and T\textsubscript{1} states is lower for the tungsten complex, 3b, than for 3a. We have also examined the absorption and emission properties of these complexes at low temperature. As shown in Figure C2 of
appendix C, the high energy emission for both complexes is the mirror image of the absorption and has a small Stokes shift clearly supporting the view that this emission occurs from the $S_1$ MLCT state. The lowest energy emission band for the molybdenum complex 3a shows vibronic features but with a spacing of $\sim 400 \text{ cm}^{-1}$ at low temperature, as shown in Figure C3, which has been seen before in Mo$_2$-carboxylates.\cite{48,61,70} This progression suggests that $T_1$ for 3a is the MM$\delta\delta^*$ state. For 3b, the lowest energy emission from $T_1$ is different and can be assigned as the $^3$MLCT state, which will be further supported below.

While $^3\delta\delta^*$ emission from the Mo$_2$-carboxylates occurs at $\sim 1100 \text{ nm}$, complex 3a emits at significantly higher energy and shorter wavelength, with $\lambda_{\text{max}} \sim 860 \text{ nm}$. Emission from the $^3\delta\delta^*$ state of quadruply bonded complexes was first observed in Re$_2$Cl$_2$(L)$_4$ (where L = N,N'-p-anisoleformamidinate).\cite{64} In this complex, radiative decay is enhanced due to a larger energy gap between the $^1\delta^2$ and $^3\delta\delta^*$ states relative to that for complexes of the type [M$_2$X$_8$]$^n$ (where X = Cl$^-$, PR$_3$, M = Mo$^{2+}$, Re$^{3+}$, for example), which have emissive $^1\delta\delta^*$ states and non-radiative $^3\delta\delta^*$ states.\cite{52,55} For $\pi$-conjugated bridging ligands such as formamidinates or carboxylates, there exists an occupied, non-bonding p-orbital combination that has appropriate symmetry to interact with the metal $\delta^*$ orbital, resulting in higher energy $^1\delta\delta^*$ and $^3\delta\delta^*$ excited states and allowing radiative decay to occur from the latter. This interaction has been previously shown to be greater for Mo$_2$-formamidinates by photoelectron spectroscopy\cite{63} and explains the energy of the $^3\delta\delta^*$ emission of complex 3a compared to the related Mo$_2$-carboxylates.
3.3.4 Solvent Dependence of Absorption and Emission Spectra

We have examined the solvent dependence of both the absorption and emission spectra of 3a and 3b in CH$_3$CN, CH$_2$Cl$_2$, THF, benzene, and hexanes. The solvent dependence for the emission is shown in Figure 3.5.

First we note that the emission spectra of both bands from complex 3b show significant solvent dependence and this is consistent with emission from MLCT states, S$_1$ and T$_1$. For complex 3a, only the emission from S$_1$ shows a solvent dependence, consistent with the assignment of S$_1$ an MLCT state. The lack of solvent dependence for the triplet emission in complex 3a is consistent with a $3\delta\delta^*$, metal-centered state.
Figure 3.5 Solvent dependence of luminescence at room temperature in THF for a) compound 3a excited at 490 nm ($\lambda_{\text{obs}} = 500 – 800$ nm) and excited at 532 nm ($\lambda_{\text{obs}} = 800 – 1100$ nm) and b) compound 3b excited at 600 nm ($\lambda_{\text{obs}} = 620 – 840$ nm).

In contrast to the solvent dependence seen for the $S_1$ emissive states of 3a and 3b, neither complex exhibits a significant solvent dependence in their absorption, as shown in Figure 3.6. Note, for example, that the absorption maximum for complex 3b is the same for hexane, benzene, dichloromethane, and THF despite their differing dielectric constants and donor ability. The one solvent that does differ is acetonitrile which yields a blue shift for both 3a and 3b. Given the sterically demanding diisopropylamidinate ligands, we suggest that of all these solvents only CH$_3$CN can reasonably axially coordinate to the metal atoms along the M-M axis. This type of axial ligation is common in M$_2$-paddlewheel complexes$^{65,105}$ of molybdenum and tungsten and can also be observed upon crystallization from coordinating solvents.$^{61,69,71,127}$ It is then perhaps this small ground-state stabilization in CH$_3$CN that results in the blue shift relative to the other solvents.
It is unusual for a MLCT band to show no dependence on solvent dielectric constant\textsuperscript{128} and this suggests that the electronic transition does not involve a change in dipole moment. At the same time we see that emission from the $S_1$ state does show a solvent dependence (Figure 3.5). This leads us to suggest that the initial photon absorption occurs to a delocalized state and that this rapidly relaxes to a polar state. In other words, the photoexcited $S_1$ state can be viewed as a mixed valence state: $L_{a-}M_2-L_{b-}^{-1e}$ $\leftrightarrow$ $^{-1e}L_{a-}M_2-L_{b-}$, where $L =$ the phenylethynylamidinate ligand. A representation of the potential energy surface of the $S_0$ and $S_1$ states can be seen in Figure 3.7. Similarly, the solvent dependence of the phosphorescence for the tungsten complex, II, suggests that the triplet emission is from an excited state described by an electron localized most on a single amidinate ligand. Furthermore, Ru(bpy)$_3^{2+}$, which has also been suggested to possess a delocalized initial excited state (as stated above) also shows a very small solvent dependence on its MLCT absorption band, occurring at 449 nm in methanol and 454 nm in octanol and pyridine.\textsuperscript{129}

Figure 3.6 Solvent dependence of absorption spectra at room temperature in THF for a) compound 3a b) compound 3b.
Figure 3.7 Potential energy surface (PES) representation of the ground state and mixed-valence excited state along the electron transfer reaction coordinate, where $S_1 = \text{in-phase } L\pi^* \text{ combination}, S_2 = \text{out-of-phase } L\pi^* \text{ combination}, \Delta G^* = \text{activation energy}, H_{el} = \text{electronic coupling between ligands}, \lambda = \text{reorganization energy}, \lambda_{ex} = \text{MLCT excitation wavelength}, Q = 0 \text{ refers to the ground state potential minimum and } Q_R \text{ and } Q_P \text{ refer to the minimum of the reactant and product potential surfaces, respectively.}

3.3.5 **Low Temperature Absorbance and Emission Spectra**

Collecting the absorbance and emission spectra at low temperature can also reveal information about the electronic coupling between the ligands. In Figure 3.8 is shown a comparison of the room temperature absorbance spectra with that at low temperature. In general, it is observed that upon cooling, the spectra sharpen to reveal vibrational structure and shift to lower energy. Both molecules can have rotation of the phenyl groups relative to the plane containing the MM quadruple bond. The shift to lower energy results from a greater proportion of rotamers obtaining a planar conformation as thermal energy decreases. In conjunction with the DFT calculations, above, the energy of
the optimized geometry was compared to the energy of the structure where one phenyl ring was rotated at a $90^\circ$ dihedral angle relative to the plane containing the MM quadruple bond. The difference between these two conformations was 1.82 kcal/mol for 3a and 2.01 kcal/mol for 3b and this represents an estimate for the rotational barrier of the individual phenyl rings. At room temperature there is sufficient thermal energy to produce a wide range of dihedral angles among the ground state distribution. Those molecules with a large dihedral angle contribute to the higher energy portion of the absorbance spectrum and as a result are shifted to lower frequency upon cooling the temperature. Also, the calculated values for the rotational barrier are representative of the extent of backbonding, and therefore electronic coupling, in the ground state compounds. When the ground state structure is more planar, there is greater interaction between the metal HOMO and the $\pi$-system and greater stabilization through backbonding. Conformational changes associated with the overlap of the $\pi$-system must overcome this stabilization energy. Similar calculations have been done on analogous compounds involving only carboxylate ligands and the rotational barrier was found to be on the order of $\sim 10$ kcal/mol.\textsuperscript{130} The larger value is consistent with the idea that the $\pi^*$ orbitals of the carboxylate ligands lie at lower energy and therefore undergo a stronger backbonding interaction with the M-$\delta$ orbital.
Figure 3.8 Absorbance (solid line) and emission spectra (bold line) of compound 3a (orange) and 3b (blue) recorded at room temperature (dashed line) and 77 K (solid lines) in 2-methyltetrahydrofuran as a transparent glass.

Another way the presence of electronic coupling between the ligands can be indicated is by the observation of vibronic features at low temperature in the absorption and emission spectra. As described in chapter 2, the offset of the ground state and mixed-valence excited state PESs depends on the electronic coupling and this affects the appearance of the vibrational features in the MLCT transitions. For example, in a weakly coupled system as depicted in Figure 3.7, excitation would occur with greatest overlap to vibronic levels with higher quantum number. The vibrational spacing would be smaller and therefore vibronic peaks would be less resolved in the absorbance spectrum. At low temperature in both compounds 3a and 3b, the absorption bands are asymmetric and contain a shoulder at high energy. This is notably contrasted with the cyanobenzoate
compounds of chapter 2, which have multiple clearly resolved vibrational features at low temperature. On the other hand, in agreement with the cyanobenzoate compounds, the emission spectra at low temperature are observed to become more resolved and the relative intensity of the $\lambda_{\text{max}}$ peak increases. According to the model set forth by the Robin and Day scheme, this observation indicates an increase in the magnitude of electronic coupling upon excitation to the $^1\text{MLCT}$ state. Furthermore, since the relative intensity of the $\lambda_{\text{max}}$ peak for $3b$ is larger compared to $3a$, it indicates slightly greater coupling when the tungsten is used for the metal.

3.3.6 Nanosecond Transient Absorption Spectroscopy

A comparison of the nsTA spectra of complexes $3a$ and $3b$ in THF is shown in Figure 3.9. For both complexes, the spectra consist of the bleach corresponding to the ground state $^1\text{MLCT}$ absorption and positive transient absorption bands. These positive bands are notably different and this suggests they arise from different types of excited states. For complex $3b$, the ligand is reduced in the excited state and for complex $3a$, the excitation remains centered on the metal. Our assignment of the T$_1$ states as MM$\delta\delta^*$ for M = Mo and $^3\text{MLCT}$ for M = W is consistent with this result. Also it should be noted that platinum complexes involving phenylacetylide ligands have been shown to possess $^3\text{MLCT}$ states having a broad absorption between 400 nm and 750 nm with $\lambda_{\text{max}} \sim 600$ nm.$^{117,131}$ Such a band is clearly not present for the T$_1$ state of $3a$, consistent with the assignment of the $^3\text{MoMo}\delta\delta^*$ state. For complex $3b$, the bleach at 600 nm is coincident with the positive absorption features observed in the MLCT TA spectrum of the platinum
complex and the TA absorption seen at ~ 670 nm could well arise from the edge of the reduced ligand based absorption.

Figure 3.9 Nanosecond transient absorption at room temperature in THF for a) compound 3a and b) compound 3b both with λ_ex = 532 nm. Inset: Selected kinetic traces.

Kinetic traces are shown as insets to Figure 3.9 a) and b) and show the complete recovery of the excited state absorption and ground state bleach with identical lifetime. This suggests the experiment does monitor the conversion of the lowest energy excited state, T_1, to the ground state, S_0. The lifetimes of the T_1 states differ for the two complexes with τ = 100 μs for 3a and τ = 4.8 μs for 3b. It is likely that the shorter lifetime of 3b compared to 1 is due to greater spin orbit coupling between the T_1 and S_0 states with the heavier metal. Also, 3b has a longer T_1 lifetime than those reported for other tungsten paddlewheel complexes, where lifetimes ranging from less than 10 ns to 260 ns have been observed. In 3b, the T_1 state is at higher energy such that it becomes emissive and has a longer lifetime in accordance with the energy gap law.
3.3.7 Femtosecond Transient Absorption Spectroscopy

The fsTA spectra of complexes 3a and 3b are shown in Figure 3.10. Initially, for both complexes, we observe the ground state bleach, an excited state absorption at higher energy, and a negative band due to stimulated emission. Decay of the initial spectra results in transient spectra at longer times that are comparable to those measured in the nsTA experiments, such that the spectral traces follow the conversion of the $S_1$ to the respective $T_1$ state. The early time TA spectra for both 3a and 3b show a strong absorption at $\sim 400$ nm. This absorption is better represented for 3b because of its red-shifted ground state MLCT bleach signal. In both instances, this feature arises from the reduced ligands in the $S_1$ state.

The absorption and stimulated emission decay with similar lifetimes, $\tau = 19.2 (3)$ ps for 3a and $\tau = 5.6 (10)$ ps for 3b. The presence of the stimulated emission band and its
concurrent decay with the excited state absorption bands identifies these states in compounds 3a and 3b as the $^1$MLCT state. The shorter lifetime of the tungsten complex in its $S_1$ state most likely reflects the greater spin-orbit coupling of the 5d element. These bands decayed to give rise to an overall spectrum that was similar to that in the nanosecond transient absorption experiment. The combined experiments indicate therefore that two excited states are involved in the photophysical relaxation following MLCT excitation and those states can be associated with the $^1$MLCT for both compounds and the $^3\delta\delta^*$ for 3a and the $^3$MLCT for 3b.

A more detailed kinetic analysis of the fsTA spectra of complex 1 reveals dual-exponential decay and a faster process with $\tau = 2.2$ ps. It is suggested that this fast process corresponds to the relaxation of the initially formed delocalized state to the localized state as represented in Figure 3.7. This conversion likely involves solvent reorganization and torsional relaxation of the aryl rings toward co-planarity, where quinoidal geometry is expected for the reduced ligand in the excited state. For 3b, we do not detect the shorter component of the decay in the singlet state probably because of its shorter lifetime. However, we do detect a longer component of $\sim 37$ ps which possibly corresponds to thermal equilibration within the triplet state since it is formed with $\sim 3000$ cm$^{-1}$ of excess energy as suggested by Figure 3.4.

Further kinetic analyses show that the dynamics of complex 3a monitored within the bleach at 450 nm involve a third component that is not present in the positive absorption features. Shown in Figure C4, the kinetic trace at long delay times reveals partial recovery of the ground state bleach with lifetime of 170 ps. A similar decay component is also observed for complex 3b when monitoring the bleach at 540 nm (data
not shown) with a shorter lifetime of ∼ 40 ps. Since these lifetimes are much longer than the respective singlet state lifetimes and much shorter than the triplet state lifetimes, we suggest that the most stable ground state is not produced directly from the $^1\text{MLCT}$ emission but a non-equilibrated ground state that must then undergo further relaxation is formed instead. A possible assignment for the ground state recovery components is conformation dynamics associated with rotation of the ligand phenyl group relative to the plane containing the quadruple bond. The relaxed singlet state is likely planar with a quinoid structure, which has been shown to occur previously for reduced ligands$^{32}$ and MLCT excited states$^{33,34}$. On the other hand, the low temperature absorbance spectra (Figure C1) further suggest that a distribution of rotamers could be present in the ground state at room temperature as the absorption band is observed to sharpen and shift to lower energy. Therefore, it is possible that decay of the $^1\text{MLCT}$ state directly forms the planar ground state conformation and then subsequently reforms the rotameric distribution at room temperature. Conformational and vibrational relaxation processes have been previously identified and are distinguishable by transient Raman experiments.$^{133}$ Complexes 3a and 3b possess strong Raman vibrations associated with the metal-metal and acetylene group stretches and these experiments should be well suited to address these points in the future.

3.4 Concluding Remarks

Based upon the above experiments, a Jablonski diagram can be constructed comparing the photophysical properties of the molybdenum (3a) and tungsten (3b) complexes and this is shown in Figure 3.11. Characteristic properties are also tabulated
in Table C1. In reference to Figure 3.7, excitation of the lowest energy absorption band occurs to the mixed valence $^1\text{MLCT}$ excited state. The electron in this initial excited state can be described as being delocalized over both amidinate ligands and therefore excitation places the system above the activation barrier within the mixed valence state. Excitation directly to the upper mixed valence surface, $S_2$, is forbidden by the parity selection rule. Subsequently, the excited electron relaxes by solvent induced localization into an individual potential well within this state and by planarization of the ligand structure. According to the fsTA experiments, these relaxation processes must occur convoluted within 2.2 ps, as no other decay processes are observed within the lifetime of the $^1\text{MLCT}$ state. The excited state distribution then bifurcates decaying by both emission to a non-equilibrated ground state and intersystem crossing to the lowest energy triplet state. Completion of the excited state dynamics finally occurs by the emission of another photon from the triplet state.
Figure 3.11 Jablonski diagram summarizing observed photophysical processes for 3a (left, orange) and 3b (right, blue). $^1\text{MLCT}$* indicates delocalized mixed-valence state. GS* indicates non-equilibrated ground state.

The compounds 3a and 3b have fascinating photophysical properties and are unusual in showing dual emission. For transition metal complexes, the $S_1$ states have remarkably long lifetimes which perhaps results from the extent of charge delocalization away from the metal center in the $^1\text{MLCT}$ state. It is also interesting to find that for molybdenum the $T_1$ state can be described as the metal-centered $^3\text{MoMoδδ}$* state while for tungsten it is a $^3\text{MLCT}$ state at higher energy. The solvent dependence of the absorption and emission spectra leads us to suggest that the $S_1$ states can be represented as mixed-valence states and that the initial photoexcitation generates a state in which the electron is delocalized over both phenylethynylamidinate ligands. This Franck-Condon state then relaxes to a solvent stabilized excited state where the electron is localized on a single phenylethynylamidinate ligand from which fluorescence and ISC occurs.

In regards to the strength of the electronic coupling, the solvent dependence experiments of the emission spectra compared to the absorbance spectra give the clearest
indication that the ligands in the MLCT states are only weakly coupled in compounds 3a and 3b. Other experiments such as the low temperature absorption spectra, through the appearance of vibrational features, and the calculated values of the rotational barriers also speak to the extent of electronic coupling. However, for 3a and 3b these points are less clear than for the cyanobenzoate compounds of chapter 2. Vibrational spectroscopy speaks directly to the electron distribution that occurs within the excited states possessed by these compounds. These experiments should provide a much clearer picture of the electronic coupling in these systems that have been the topic of chapters 2 and 3 and this will be shown in chapter 4 by time-resolved infrared spectroscopy.

3.5 Supporting information

The following items have been included as supporting Figures in appendix C: Low temperature absorption (Figure C1) and emission (Figure C2) of compounds 3a and 3b, low temperature emission of compound 3a (Figure C3), and complete kinetic trace from fsTA monitored at 450 nm for compound 3a (Figure C4). This information is available in appendix C.
CHAPTER 4

ELECTRON DELOCALIZATION IN THE S₁ AND T₁ METAL-TO-LIGAND CHARGE TRANSFER STATES OF TRANS-SUBSTITUTED METAL QUADRUPLY BONDED COMPOUNDS

4.1 Introduction

Conjugated organic polymers have been intensely studied over the past two decades because of their fascinating optoelectronic properties. Aside from the sheer scientific curiosity that they aroused, it soon was recognized that a plastic electronics industry was possible and a good deal of this expectation has already been realized. Conjugated organic polymers find commercial applications as field-effect transistors¹³⁴, light emitting diodes¹³⁵ and photovoltaic devices.¹³⁶,¹³⁷ As an extension of this field there is considerable interest in incorporating metal ions into conjugated organic systems and numerous reports are to be found in the literature concerning the role of metal ions in tailoring the opto-electronic properties of the organic conjugated systems. For example, the attachment of π-conjugated ligands to Ir(III) has allowed the luminescence to cover the entire region of the visible spectrum¹³⁸,¹³⁹ and the incorporation of Pt(II) into conjugated ethynylthiophenes has led to a significant enhancement of the efficiency of a
bulk heterojunction photocell. Furthermore it is generally thought that electronic delocalization through oligomeric units leads to enhanced charge carrier properties through the overall material.

Knowledge of electronic structure is vital to the understanding of these properties and the ability to manipulate electronic structure by selection of metal-organic components holds the promise of custom design. The MM quadruply bonded unit (MM = Mo₂, MoW, or W₂) has many attractive features due to the tunability of the energy of the M₂-δ orbital by selection of the metal and its attendant ligands and due to M₂-δ to organic π-conjugation. In this chapter, it is shown how this can influence the charge dynamics and delocalization of singlet and triplet photoexcited states which may be delocalized or localized (valence trapped) MLCT states or MM δδ* states. In order to achieve this the trans-substituted compounds M₂(TⁱPB)₂(O₂CC₆H₄-4-CN)₂, where TⁱPB = 2,4,6-triisopropylbenzoate and M = Mo (2a) or W (2b), and M₂(O₂CMe)₂((PrN)₂CC≡CC₆H₅)₂, where M = Mo (3a) or W (3b), whose solid state structures are shown in Figure 4.1 were prepared. Here, the bulky TⁱPB and amidinate ligands favor the trans-substitution and allow the extended conjugation of the two trans-ligands via Lπ-M₂δ-Lπ conjugation. Evidence of this is seen in the molecular structures found in the solid-state that reveal the near co-planarity of the aryl groups of the p-cyanobenzoate and amidinate ligands in 2a and 3b, respectively.
The ground state geometry and symmetry of these discrete compounds presents a situation where added charge could reside on either of two interchangeable redox active ligand sites. This situation is, by definition, described by the term mixed valency. In the case of compounds 2a, 3a, and their tungsten analogs 2b and 3b, an electron can be added to the ligand sites by photoexcitation of the MLCT transition and they therefore can be further classified as excited state mixed valence (ESMV) compounds. Depending on how strongly the ligand sites interact with one another, the excited electron can be completely localized (valence trapped) on one ligand, completely delocalized over both ligands, or only partially delocalized.

These various classifications of the mixed valence states can be visualized by the potential energy surfaces (PES) shown in Figure 4.2. When the ligands are non-interacting, there are two degenerate PESs in the MLCT, S1 state. This is known as Class I under the Robin and Day scheme. When the mixed valence state is an excited
state the positioning of the PESs relative to the ground state surface must be considered and this is most easily rationalized for the Class I situation. The offset between the ground and excited state surfaces occurs because the electron distribution has changed in the excited state. Regardless of which ligand receives the photoexcited electron, the shift in nuclear coordinate should be the same and so the individual potential wells must be symmetrically displaced from the ground state. As the electronic coupling, $H_{ab}$, begins to increase, the ligand-based states interact to give a lower, in-phase ($S_1$), and upper, out-of-phase ($S_2$), combinations of the states, i.e. $\Psi_{\text{lower}} = C_a \Psi_a + C_b \Psi_b$ and $\Psi_{\text{upper}} = C_a \Psi_a - C_b \Psi_b$.\textsuperscript{73} When the coupling is small, two distinct ligand-based states remain and the lower PES is a double well. An electron in this state can be said to be localized on a single ligand and is known as Class II, shown in Figure 4.2. An excited state transition can occur within this mixed valence state that overcomes the barrier between the two surfaces and transfers the electron between the ligand sites, analogous to the intervalence charge transfer (IVCT) band of ground state mixed valence compounds.\textsuperscript{144} As the strength of the coupling increases further, the two states have greater mixing and the electron can begin to become delocalized over both ligands. As a result, the PESs move closer together and the potential energy barrier between the two sites decreases. Eventually, a point is reached where there is no longer a barrier and the electron is nearly equally shared, i.e. $C_a \sim C_b$ and the transition loses charge transfer character. This occurs at the class II/III border and is shown in the right panel of Figure 4.2. When the electron finally becomes completely delocalized, class III, $C_a = C_b$ and the transition between $S_1$
and $S_2$ becomes like that for a $\pi-\pi^*$ transition, for example. In this case the IVCT transition becomes known as a charge resonance band.\textsuperscript{76}

![Figure 4.2](image.png)

Figure 4.2 Potential energy surface representation of the mixed valence excited states for a symmetrical system under the Robin and Day system. $S_1$ represents the state where an excited electron occupies the in-phase $L-\pi^*$ and $S_2$ the state where an excited electron occupies the out-of-phase $L-\pi^*$ combination. Left: Class I; weakly coupled localized. Right: Class III strongly coupled, delocalized. Middle: Class II-II/III; $0 < a < 1$.

The electronic coupling of the states involving the two organic $\pi$-systems arises from the interaction of the $M_2-\delta$ orbital with the carboxylate, $CO_2$, or amidinate, $NCN$, $\pi$ orbitals shown in A and B of Scheme 1, below. The orbital interactions shown in A involve the in-and-out-of-phase combinations of the LUMO of the $CO_2$ or $NCN$ moiety. The out-of-phase combination has a symmetry match with the $M_2-\delta$ orbital and is a metal-to-ligand backbonding interaction. On the other hand, the interactions in B involve the filled orbitals of the carboxylate or amidinate ligands and based on orbital energetics it is the former interaction, A, that is more important. Given that $O$ is more
electronegative than N, the LUMO of the carboxylates is lower in energy relative to the amidinate LUMO and thus the mixing with the \( M_2-\delta \) orbital and the coupling between the \textit{trans}-ligands is greater in the \( p \)-cyanocarboxylates. Also, since the \( M_2-\delta \) orbital in closely related compounds is roughly 0.5 eV higher in energy for \( M_2 = W_2 \) relative to \( Mo_2 \), the interactions in the tungsten complexes are greater.

Scheme 4.1

Time-resolved infrared spectroscopy (TRIR) is a technique with the ability to probe directly electronic delocalization. In transition metal complexes, carbonyl ligands, for example, are shifted to higher frequency upon photoexcitation and removal of an electron from the metal center to which they are bound. The magnitude of this shift can be used to gauge the extent of charge separation away from the metal center in the
excited state.\textsuperscript{145} Vibrational modes directly involved with the ligand reduction can also be observed but results of this situation are less frequent.\textsuperscript{146-148} Delocalization across multiple molecular subunits in mixed-valence systems can also be probed by these IR-reporter groups. This has mostly been done in systems where two metal centers, with bound carbonyl groups for example, are bridged by an organic $\pi$ system. In that case, the concern is the delocalization through the bridge of the positive charge that remains on the metal center upon MLCT excitation and this is monitored by the CO stretching frequencies on each metal center.\textsuperscript{149,150} On the other hand, the complexes of type 2 and 3 represent mixed valence systems where the communication of the electron across the ligands in the excited state can be investigated. This situation has been observed before in octahedral metal complexes by electronic spectroscopy.\textsuperscript{151} This chapter describes how TRIR can be used to probe excited state electronic communication in compounds 2a, 2b, 3a, and 3b and verifies the excited state assignments proposed in the previous chapters 2 and 3.

4.2 Experimental Section

4.2.1 TRIR measurements

The laser system utilizes a Ti:Sapphire oscillator and regenerative amplifier combination operating at 1 kHz that has been described in detail previously.\textsuperscript{93} The fundamental laser beam is split to pump either an SFG or UV/vis OPA to produce pump pulses tunable throughout the visible spectrum and a DFG OPA to produce mid-IR pulses (2 to 10 μm). The IR beam is split into a probe and a reference beam by a Ge beamsplitter. Each are focused onto the sample cell where only the probe is overlapped.
with the pump beam. After the sample, the probe and reference beams are directed to a
grating spectrometer (Triax 320) and spectrally dispersed onto separate HgCdTe array
(32 elements) detectors cooled by liquid nitrogen. The pump and probe pulses are
synchronized by passing the pump pulse through a chopper operating at 500 Hz, allowing
for measurement of the probe signal under pump on/off conditions. Corresponding
absorbance signal from the reference beam is subtracted to obtain the overall signal. The
TRIR setup has been described previously.\textsuperscript{152}

Samples were sealed in a Perkin Elmer rectangular semi-demountable cell with a
0.1 mm Teflon spacer between a 4 mm thick CaF\textsubscript{2} back window and 2 mm thick CaF\textsubscript{2}
front window in a glove box. THF was the solvent and the concentration was such that
the absorbance was \( \sim 1.0 - 2.0 \) at the MLCT \( \lambda_{\text{max}} \). During measurements, the static
sample cell was periodically translated manually using an XYZ stage. Absorption
spectra were obtained before and after measurements to ensure that no photo-
decomposition had occurred.

4.2.2 Steady-state Infrared Measurements

Ground state infrared spectra were obtained with a Perkin Elmer Spectrum GX.
Samples were sealed in a Perkin Elmer rectangular semi-demountable cell with a 0.1 mm
Teflon spacer between a 4 mm thick CaF\textsubscript{2} back window and 2 mm thick CaF\textsubscript{2} front
window. THF was the solvent and the concentration was such that the absorbance was \( \sim 1.0 - 2.0 \) at the MLCT \( \lambda_{\text{max}} \). The spectra were baseline corrected and smoothed with the
instrument software and then the background THF spectrum was subtracted.
4.2.3 DFT Calculations

Electronic structure calculations leading to Figure 4.3 were completed as in chapters 2 and 3 for compounds 2a and 2b and 3a and 3b, respectively. The vibrational analyses from these calculations were used to generate tables D1 and D2. Calculations for the doublet state of the reduced anion of each compound were also completed in a similar fashion.

4.3 Results and Discussion

4.3.1 Electronic Structure Calculations

Qualitative bonding descriptions (as outlined in Scheme 1, above) can gain more quantitative insight by the application of electronic structure calculations, employing density functional theory with the aid of commercial programs. In our calculations we have used model compounds that substitute formate ligands for the bulky TiPB groups in 2a and 2b (Mo and W) and that substitute methyl groups for iPr in 3a and 3b (Mo and W). This saves in computational time and even though the substitution of H for 2,4,6-iPr3C6H2 may seem severe, the orientation of these aryl groups removes the C6 aryl ring from π-conjugation with the attendant carboxylate, see Figure 4.1. Similarly in 3a and 3b, the employment of the acetate spectator ligand ensures maximum conjugation of the two amidinate ligands.

The frontier MO energy diagram for the model compounds M2(O2CH)2(O2CC6H4-4-C≡N)2 and M2(O2CMe)2(H3CN)2CC≡CC6H5)2 are shown in Figure 4.3 and the HOMO is shown along with the unoccupied L-π* based orbitals as Gaussview plots. The HOMO is the M2-δ with some ligand admixture whereas the in-
phase and out-of-phase combinations of the L-\(\pi^*\) orbitals are the LUMO and LUMO + 2 for \(2a\) and LUMO and LUMO + 1 for \(2b\), respectively. In \(2a\), the \(\delta^*\) orbital is low enough in energy to fall between the in- and out-of-phase L\(\pi^*\) combinations. As anticipated, for the tungsten complexes, the M\(_2\) \(\delta\) orbital is higher in energy and the energy splitting between the L-\(\pi^*\) combinations is also larger.\(^{49}\) The magnitude of the energy splitting between the in-and-out-of-phase L-\(\pi^*\) orbitals is in part a measure of the electronic coupling between the two \(trans\)-ligands.

![Figure 4.3](image.png)

Figure 4.3 Ground state molecular orbital (MO) energy diagrams calculated by DFT with selected orbitals shown for compound \(2a\) and \(2b\) (left) and \(3a\) and \(3b\) (right).

The calculations for the model compounds \(3a\) and \(3b\) are qualitatively similar: the HOMO is the M\(_2\)-\(\delta\) orbital and in both cases the LUMO and LUMO + 1 are the in-phase and out-of-phase L-\(\pi^*\) combinations, respectively. The orbital energies reflect the notion that the amidinate ligand orbitals occur at higher energy compared to the
carboxylate ligands. As a result, the M₂-δ* orbitals are at higher energy due to greater interaction with the NCN non-bonding type orbital and the M₂-δ orbitals are also at higher energy due to weaker interaction with the L-π* out-of-phase combination (A, Scheme 1) and better interaction with the L-π out-of-phase combination (B, Scheme 1).

The relative orbital energies calculated for the two types of systems do lead to the expectation that the amidinate compounds (3a and 3b) should be more weakly coupled due to the weaker M₂-δ interaction with the L-π* out-of-phase combination. The extent of the electronic coupling is related to the electron delocalization and therefore time resolved infrared spectroscopy is a useful technique for this purpose. This is shown experimentally for the photoexcited MLCT states in each of the compounds below.

4.3.2 Absorbance Spectroscopy

All of the compounds are strongly colored due to metal-to-ligand charge transfer (MLCT) and their electronic absorption spectra are shown in Figure 4.4. Though allowed by symmetry, the 1δδ* MM transition is weak due to the relatively poor overlap of the metal d orbitals. In each case, the lowest energy transition is characterized as MLCT. Although the planar D₂h structure of these molecules is the ground state structure, thermal energy leads to a Boltzmann distribution of conformers/rotamers in which the aryl groups of the ligand deviate from coplanarity with the carboxylate CO₂ or amidinate NCN moieties. The room temperature solution spectra represent the combined absorptions of an ensemble of molecules which together with vibronic features arising from the displacement of the ground and excited state potential energy surfaces leads to the broadening of these MLCT bands. Upon cooling to 77K in a 2-methyltetrahydrofuran
glass, these bands sharpen with the peak shifting to lower frequency and the vibronic features becoming better resolved. At higher energy to these MLCT bands associated with the conjugated ligands, we also observe weaker MLCT bands involving the CO$_2$ moieties of the TPB (in 2b) and acetate ligands (in 3b). The TRIR results below were all conducted using excitation wavelengths within these lowest energy MLCT bands.

![Figure 4.4](image)

Figure 4.4 Electronic absorption spectra showing the molar absorptivity (ε) of 2a (red) 2b (purple), 3a (green), 3b (blue) at room temperature in THF.

### 4.3.3 Summary of Photophysical Properties from Electronic Spectroscopy

All of the compounds are emissive and compounds 2a, 3a, and 3b each emit from both the S$_1$ and T$_1$ states. In compound 2b, the T$_1$ – S$_0$ energy gap is estimated to be small and this favors non-radiative decay. Interestingly, the S$_1$ states of both 3a and 3b
show a solvent dependent emission whereas the MLCT absorptions do not. Furthermore, the phosphorescence of the tungsten complex (3b) shows a solvent dependence but the phosphorescence from the molybdenum compound (3a) does not. The more limited range of solubilities of compounds 2a and 2b made solvent dependent studies less clear. However for 3a, the interpretation of the solvent dependence is that the initial absorption occurs without a significant change in dipole moment whereas that change associated with the emission from the S\(_1\) states is significant. Since the ground state molecules are symmetrical (D\(_{2h}\)) and have a center of inversion, the Franck-Condon absorption conserves the symmetry and places the excited electron delocalized over both ligands. Further relaxation of the Franck-Condon S\(_1\) states in polar solvents leads to the localization of the excited electron mostly on an individual ligand, increasing the dipole moment of the S\(_1\) state and causing the emission solvent polarity dependence.

Similarly, T\(_1\) emission for 3b is solvent dependent but emission from T\(_1\) for 3a is not. At low temperature, the emissive T\(_1\) state for 3a shows vibronic features assignable to the MoMo stretching frequency with \(\nu\) (MoMo) \(\sim\) 400 cm\(^{-1}\). The vibronic spacing together with the lack of solvent dependence in the T\(_1\) state emission for 3a is consistent with the assignment of this state as the \(^3\)MoMo\(\delta\delta^*\) state. Furthermore we should note that the lowest energy emission for 3b also shows solvent dependence and suggests an assignment of \(^3\)MLCT for the T\(_1\) state of this complex. Again, our evaluation of the electron delocalization within the MLCT excited states is further substantiated by the fsTRIR spectroscopy experiments, below, which also confirm our assignments of the S\(_1\) and T\(_1\) states as MLCT or \(\delta\delta^*\).
The compounds have been previously analyzed by fs and ns transient absorption spectroscopy (fsTA and nsTA), and in all cases both the S\textsubscript{1} and T\textsubscript{1} states were detected. The lifetimes for the S\textsubscript{1} MLCT states measured for these types of quadruply bonded compounds is generally on the order of 10 ps\textsuperscript{48,68,71} and the compounds under investigation here range from \(\sim 3 - 20\) ps. On the other hand, the lifetimes of the T\textsubscript{1} states generally range from 0.010 – 100 \(\mu\)s depending largely upon the metal and give an indication of their nature as \(^3\)MLCT or \(^3\)\(\delta\delta^*\).\textsuperscript{48,61,65,70} For carboxylate complexes, if the T\textsubscript{1} state is \(^3\)MLCT, the lifetime is on the order of hundreds of nanoseconds or less. In the case of \(2b\), the T\textsubscript{1} state is detected in the fsTA as a long-lived transient but the lifetime is shorter (\(\tau < 10\) ns) than the time resolution of the nsTA experiment. On the other hand, if the T\textsubscript{1} state is \(^3\)\(\delta\delta^*\), the lifetimes are longer, lasting for \(\sim 100\) \(\mu\)s. In amidinate complexes, the lifetimes are observed to increase as a result of the ligand based orbitals originating at higher energy compared to the carboxylate ligands. In \(3b\), the T\textsubscript{1} state has \(\tau = 4.6\) \(\mu\)s and in \(3a\) it is \(\sim 105\) \(\mu\)s. In general we find that T\textsubscript{1} for Mo complexes is \(^3\)\(\delta\delta^*\) and the lifetimes are several orders of magnitude longer than T\textsubscript{1} for W complexes which are \(^3\)MLCT. Based upon the absorption, emission, and transient absorption results we can formulate a Jablonski diagram describing the general photophysics of the four compounds, and this is shown in Figure 4.5.
Figure 4.5 Jablonski diagram showing excited states in compounds 2a (Red), 2b (purple), 3a (green) and 3b (blue) observed after MLCT photoexcitation.

4.3.4 DFT Calculations: Vibrational Analysis

In addition to ensuring a minimum energy structure is obtained in the DFT calculations, the vibrational analysis can provide a framework of vibrational modes that might be expected to appear in the ground state infrared spectra and help support which modes are being observed in the time-resolved infrared experiment. Table D1 (2a and 2b) and Table D2 (3a and 3b) list several vibrations observed in the vibrational analysis with significant IR intensity that occur in the mid-IR region that is accessible by the TRIR experiment. All of the modes listed derive IR intensity from the symmetry of the molecules in question. Due to the trans-geometry of the ligands, each mode has a contribution from each symmetry related ligand and there is a combination with g-symmetry, which is Raman active, and a combination with u-symmetry that is IR active.
Although these vibrations are IR active, the associated change in dipole moment is small due to the large size of the molecules and the experimental intensities, below, can be quite weak compared to the solvent background.

Most important is the vibration involving the C≡N group for compounds 2a and 2b and the vibration involving the C≡C group for 3a and 3b. These calculated vibrations occur in the 2300 cm\(^{-1}\) region for each compound and are well isolated from any other vibrations. This makes the identification of these vibrations in both the ground state and excited state infrared spectra unmistakable. Also these vibrations highlight a problem with the DFT calculations where the predicted wavenumbers differ by ~ 100 cm\(^{-1}\) from the experimentally observed values. Other vibrations in the mid-IR involve the symmetric and asymmetric CO\(_2\) stretches of the formate and p-cyanobenzoate ligands in 2a and 2b, those of the CN\(_2\) and CO\(_2\) of the phenylethynylamidinate and formate ligands, respectively, in 3a and 3b. The asymmetric stretches are higher frequency than their symmetric counterparts and the CN\(_2\) stretches occur at lower wavenumber compared to the CO\(_2\) ligands. Of these, the highest frequency vibration is the asymmetric stretch involving the CO\(_2\) group of the formate ligands and it is predicted to occur in the 1550 cm\(^{-1}\) region. There are also two modes involving the symmetric and asymmetric C=C stretch of the phenyl ring in each compound. These occur at similar frequency with the symmetric stretch at slightly larger wavenumber in the 1650 cm\(^{-1}\) region. A complicating matter is the presence of CH vibrations associated with the formate, p-cyanobenzoate, and phenylethynylamidinate ligands. These vibrations do not accurately represent the experimental molecules due to the simplifications made to accommodate computational
limitations and this will make any identification of their presence in the ground state infrared spectrum more difficult.

4.3.5 Steady State Infrared Spectroscopy

The infrared spectrum for each compound is shown in Figure 4.6. The most easily identifiable peaks in the infrared spectra are those of the C≡C and C≡N stretching modes. The C≡N stretches occur at 2230 cm\(^{-1}\) and 2226 cm\(^{-1}\) for 2a and 2b, respectively. For 3a and 3b, the C≡C stretching modes occur in a similar region at 2195 cm\(^{-1}\) and 2180 cm\(^{-1}\), respectively, although for 3a the intensity is much weaker. These peaks are particularly useful for probing the electronic delocalization on the cyanobenzoate and phenylethynylamidinate ligands in the MLCT states and their location in a naturally isolated part of the infrared spectrum is appealing. For 3b, there is also a second peak that occurs at 2215 cm\(^{-1}\). There are two possibilities for the occurrence of this peak. The first is simply that there is a small amount of free ligand impurity in the sample. If this is the case, it should not have caused complications for the following reason. The free ligand should not absorb in the same wavelength region as the MLCT transition, which is much lower in energy. This was confirmed by collecting excitation spectra of the \(^1\)MLCT fluorescence for each of the compounds and this result is shown for compound 3a in the right panel of Figure D1. Good agreement is found between the absorption and excitation spectra indicating the absorption band purely gives rise to the fluorescence. Since MLCT excitation is used, the presence of free ligand should not interfere with the fluorescence or other time-resolved measurements. The other possibility is that the shoulder at higher wavenumber represents a symmetry broken situation. Conformational
rotamers present at room temperature could provide this situation since the rotations of the phenyl ring on each ligand occur independently. At a particular instant the dihedral angle of the phenyl ring on each ligand would not be equivalent and so different CC stretching frequencies would be expected. A similar pattern is also observed in the vibrations occurring at 1596 cm$^{-1}$ and 1493 cm$^{-1}$. Further experiments would be required to confirm this possibility.

Figure 4.6 Steady state infrared spectra for compounds 2a (red), 2b (purple), 3a (green), and 3b (blue) collected in THF at room temperature. The THF background spectrum has been subtracted.
The remainder of the infrared spectra is more complicated but still important because the vibrations involving the CO$_2$ or CN$_2$ modes could be representative of the $\delta\delta^*$ states due to the interactions of the non-bonding oxygen p-orbitals with the $\delta^*$ orbital and the $\pi^*$ with the $\delta$ orbital. The peaks in this region of the spectrum have been assigned as listed in Table D3. Peaks corresponding to the C=C symmetric and asymmetric stretches of the phenyl ring occur at ~1600 cm$^{-1}$ and 1560 cm$^{-1}$, respectively. This is the characteristic frequency region for these vibrations and can be confirmed by comparison of the IR spectrum for 4-cyanobenzoic acid and phenylacetylene.\textsuperscript{153} In 2a and 2b, similar vibrations could occur for the 2,4,6-triisopropylbenzoate ligand and they are possibly coincident with those for 4-cyanobenzoic acid in the metal compound. Most important is the assignment of the asymmetric CO$_2$ stretch of the acetate group in 3a and 3b and the T\textsuperscript{i}PB ligand in 2a and 2b. Previous work concerning the vibrational spectra of dimolybdenum and ditungsten quadruple bonds has mostly concerned the lower frequency region of the spectrum where the M-M and M-L vibrations occur. One compound whose IR spectrum has been well analyzed is Mo$_2$(O$_2$CCH$_3$)$_4$.\textsuperscript{154} The asymmetric stretch of the CO$_2$ group was assigned as a strong transition that occurs at 1500 cm$^{-1}$ and in each of the compounds the strongest band near this value can be assigned as such with reasonable confidence. Also, of the set of four CO$_2$ and/or CN$_2$ stretching modes in each molecule, the calculations predict the asymmetric stretch of acetate or T\textsuperscript{i}PB ligand to occur at the highest frequency. The assignment of the three remaining CO$_2$/CN$_2$ stretching modes is less confident. They were assigned in the same frequency order as predicted by the calculations. Those vibrations for the tungsten
compounds were chosen at slightly lower frequency than the molybdenum analogs because slightly greater backbonding is expected with the higher energy HOMO for tungsten. It should also be noted that it is common to observe overtone vibrations associated with aromatic groups in the region of 1600 – 2000 cm$^{-1}$ that are weak but could nonetheless contribute to the overall spectra.

One other issue is the presence of the strong band at ~ 1720 cm$^{-1}$ in 2a and 2b. For 2a, this band at 1720 cm$^{-1}$ shifts to 1700 cm$^{-1}$ and 1702 cm$^{-1}$ when the sample is prepared as a Nujol mol or as a KBr pellet, respectively. The intensity of this band relative to $\nu$(C≡N), for example, also depends on the sample medium being the weakest in KBr. It is possible for these compounds there is some amount of 4-cyanobenzoic acid impurity and this peak can be associated with the free COOH stretch, which occurs at ~ 1700 cm$^{-1}$ in the free acid.$^{153}$ However, the NMR of the sample was also collected and did not contain any indication of the free acid peak at 13.6 ppm, shown in Figure D2. The possibility that this band is actually associated with the samples also cannot be ruled out. It could be a combination band but the low frequency part of the spectrum was not collected due to poor solvent subtraction and so a reasonable assignment could not be found. As mentioned above, emission excitation experiments were carried out on both 2a and 2b to confirm the purity of the MLCT absorbance band and good agreement between the absorption and excitation spectra was obtained, Figure D3, so the presence of free ligand should not interfere with the time-resolved measurements that have been done.
4.3.6 Femtosecond Time-Resolved Infrared Spectroscopy: Cyano Group Region

Particularly convenient for studying the nature of these types of photoexcited states is the presence of the IR active C≡N and C≡C functional groups within the ligands. As a consequence, the compounds have also been subjected to femtosecond time-resolved, visible pump, IR probe (fsTRIR) spectroscopy.

The $p$-cyanobenzoates, 2a and 2b, show $\nu$(C≡N) ~ 2230 cm$^{-1}$ in the ground state and upon excitation a single new band occurs that is shifted to lower energy by ~ 60 – 70 cm$^{-1}$, as shown in the TRIR spectra below, Figure 4.7. In the case of 2a (Mo), this band decays completely with a lifetime of ~ 3.9 ps, similar to the $^1$MLCT state lifetime determined by fsTA, and no new transient band is observed thereafter. In the case of 2b, however, this band decays with a lifetime of 7.2 ps (again similar to the $^1$MLCT lifetime by fsTA) to give rise to a long lived transient that is present after 1000 ps at nearly the same frequency. This result is a clear indication that for 2b (W) both the $S_1$ and $T_1$ states are MLCT and further suggests that the charge distribution in both the singlet and triplet states is similar. The spectroscopic features of the ligands in MLCT excited states commonly resemble those of the reduced ligand. For this reason, we have completed DFT calculations on the model anions to predict the change in the C≡N stretching frequency upon reduction of the ligand. The expectation is that, since the anion calculations were done at the optimized ground state geometry with $D_{2h}$ symmetry, the calculated shift predicts the experimental shift in the situation that the photoexcited electron is delocalized over both ligands (Class III). For both compounds 2a and 2b, the calculated shift is ~ 65 cm$^{-1}$. Since the experimental values are similar, it implies that the
$^1$MLCT excited states for both complexes as well as the $^3$MLCT excited state for 2b are delocalized or Class III mixed-valence (MV) ions on the Robin and Day scheme. The results are also consistent with the expectation that in a fully delocalized excited state both of the $trans$-ligands are equivalent and both should have identical stretching frequencies. A summary of the TRIR experimental and DFT calculated C≡N frequencies are shown in Table 4.1 and representative kinetic traces for the fsTRIR spectra are shown in Figure D4.
Figure 4.7 Femtosecond TRIR spectra for 2a (top) and 2b (bottom) in THF at room temperature.

Relatively few examples occur in the literature of excited state infrared spectra for molecules involving cyano groups. One example that does exist is 4-(dimethylamino)benzonitrile (DMABN). It is generally agreed that, in polar solvents, the lowest excited state of DMABN is described by the transfer of an electron from the amino group to benzonitrile and there is a 90 degree dihedral angle between these groups, which has been named the twisted-intramolecular charge transfer state (TICT) state.¹⁵⁵ There are two
reports of TRIR in the C≡N stretching frequency region of the TICT state for this molecule.\textsuperscript{156,157} In THF, the observed shift is 102 cm\textsuperscript{-1} to lower frequency, significantly larger than what is observed for 2a and 2b. This further supports the view that the excited electron is delocalized across two cyanobenzoate ligands in 2a and 2b whereas in DMABN the electron can occupy only one benzonitrile unit.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ground State</th>
<th>Excited State</th>
<th>Shift</th>
<th>Neutral</th>
<th>Anion</th>
<th>Shift</th>
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</thead>
<tbody>
<tr>
<td>2a (*MLCT)</td>
<td>2230</td>
<td>2157</td>
<td>73</td>
<td>2345</td>
<td>2278</td>
<td>67</td>
</tr>
<tr>
<td>2b (*MLCT)</td>
<td>2225</td>
<td>2164</td>
<td>61</td>
<td>2343</td>
<td>2279</td>
<td>64</td>
</tr>
<tr>
<td>2b (**MLCT)</td>
<td>2225</td>
<td>2162</td>
<td>63</td>
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</tr>
</tbody>
</table>

### 4.3.7 Femtosecond Time-Resolved Infrared Spectroscopy: Ethynyl Group Region

The vibrational spectroscopic features associated with the compounds 3a and 3b are even more fascinating. In the ground state these compounds show weak IR bands close to 2200 cm\textsuperscript{-1} associated with \( \nu(C≡C) \). Upon photoexcitation, the S\textsubscript{1} states of these compounds have two distinct transient bands that have both been shifted to lower frequency compared to the ground state, see Figure 4.8. One band has weaker intensity at \( \sim 2150 \text{ cm}^{-1} \) and the other, with much stronger intensity, occurs at much lower frequency between 1950 and 2000 cm\textsuperscript{-1}. Similar to the \( p \)-cyanobenzoates, these initial transient bands decay with lifetimes 18.8 ps and 6.8 ps (Figure D5) for 3a and 3b, respectively, in agreement with the \( ^1 \text{MLCT} \) lifetimes determined by fsTA. For 3a, the transient decays completely and no new transient band is observed thereafter. On the other hand, the
decay of the initial transients at 2150 cm\(^{-1}\) and 2005 cm\(^{-1}\) for \(\text{3b}\) is accompanied by the formation of a new set of transient bands at 2115 cm\(^{-1}\) and 1950 cm\(^{-1}\) that are long-lived and persistent. The presence of these persistent transient bands in \(\text{3b}\) clearly indicates that the \(T_1\) state is \(^3\)MLCT and the absence of these bands in \(\text{3a}\) implies the \(T_1\) state can be assigned to \(^3\)MoMo\(\delta\)\(\delta^*\).

Figure 4.8 TRIR spectra of compounds \(\text{3a}\) (top) and \(\text{3b}\) (bottom) in THF at room temperature.
Another interesting feature of the TRIR spectra for 3b is that the transient bands associated with ν(C≡C) in the $^3$MLCT state are shifted to even lower frequency than those for the corresponding $^1$MLCT state. This suggests that in the T$_1$ state the negative charge is more localized on the C≡C triple bond relative to the S$_1$ state. It is also consistent with the general view that singlet states are more diffuse than triplet states, which are lower in energy and more tightly bound.

In order to evaluate the electronic coupling within the Robin and Day scheme for the compounds of type 3a, a set of calculations on the model anions were again completed. These calculations predict a shift for ν(C≡C) of ~ 130 cm$^{-1}$ to lower frequency in the reduced anion. This shift is notably larger than what was calculated for the $p$-cyanobenzoates. In Figure D6 of the supporting information, the MO picture for the LUMO, as determined from DFT, shows that the electron density has a much greater contribution from the C≡C anti-bonding orbital in 3b than that contribution from the C≡N anti-bonding orbital in 2b. Therefore, the observed shifts are larger for the ligands with C≡C moieties compared to the C≡N moiety. As stated above, the MO calculations pertain to the delocalized model or MV ion of Class III. The observed TRIR shift of the major peak in the compounds 3a and 3b is notably greater than the calculated value, which together with the solvent dependent emission implicates a polarized MLCT state where one ligand has been mostly reduced by the photoexcited electron with only a small "spill over" to the other ligand. In other words, the amidinate complexes 3a and 3b exist as only partially delocalized mixed valence Class II ions in both their relaxed $^1$MLCT and $^3$MLCT states. The observation of two distinct transient peaks in the TRIR spectra is an...
experimental signature of this situation. Also, recall the earlier statement that the Franck-Condon absorption is to a delocalized state. Since the initial spectra after excitation contain two peaks, it appears that the charge localization process that places the excited electron mostly on one ligand occurs more rapidly than can be detected and within the lifetime of the \(^1\)MLCT states.

The specific C≡C stretching frequencies determined for compounds \(3a\) and \(3b\) are collected in Table 4.2 along with the calculated frequencies for the model compounds and their corresponding anions. There it can be seen that \(\Delta v_2\) for the \(^1\)MLCT state of \(3a\) is notably larger than that for \(3b\), which may be an indication of the more C≡C triple bond localized nature of the charge in the \(^1\)MLCT state for the molybdenum compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental (TRIR)</th>
<th>Calculated (DFT)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ground State</td>
<td>Excited State</td>
</tr>
<tr>
<td>(3a) ((^1)MLCT)</td>
<td>2200*</td>
<td>2155</td>
</tr>
<tr>
<td>(3b) ((^1)MLCT)</td>
<td>2180</td>
<td>2152</td>
</tr>
<tr>
<td>(3b) ((^3)MLCT)</td>
<td>2180</td>
<td>2116</td>
</tr>
</tbody>
</table>

*Value obtained from Raman spectrum due to weak IR intensity.

There have been several reports of excited state infrared spectra for square-planar transition metal complexes of platinum involving phenylacetylide ligands that monitor the C≡C triple bond stretching frequency.\(^{158-161}\) The most notable comparison is that for the complex trans-Pt[(CCPh\(_2\)](PBu\(_3\))\(_2\) in its \(^3\)MLCT state.\(^{158}\) This molecule has a HOMO which is composed of ligand \(\pi\) orbitals with some admixture of Pt 5d\(_{xy}\) and the
LUMO is totally ligand $\pi^*$. Photoexcitation is thus a mixture of $\pi\pi^*$ and MLCT and this yields a triplet state that has a transient IR band assignable to $\nu(C\equiv C)$ that is shifted ~ 360 cm$^{-1}$ to lower wavenumber and another that is shifted to higher wavenumber ~ 10 cm$^{-1}$ relative to the ground state $\nu(C\equiv C)$ value. This is consistent with a localized triplet state arising from $\pi\pi^* +$ MLCT where one phenylacetylide is in the photoexcited state and the other feels the positive charge on the platinum which lessens the Pt 5d to ligand $\pi^*$ backbonding. It is thus evident that the higher energy $\text{M}_2\delta$ orbitals and the smaller HOMO-LUMO gap for these MM quadruply bonded complexes allows greater coupling of the two ligand $\pi^*$ systems.

4.3.8 Femtosecond Time-Resolved Infrared Spectroscopy: Carboxylate Region of Molybdenum Compounds

Up to this point the MLCT state have been easily identified by directly monitoring vibrational modes specifically associated with the ligands involved in that state. It would be appealing, however, if a direct observation of the $^3\delta\delta^*$ state could be made by the TRIR method. For this reason, TRIR spectra for compounds 2a and 3a were also collected in the mid-IR region near the characteristic carboxylate and phenyl ring stretch frequency regions, 1500 – 1700 cm$^{-1}$. Several vibrational modes could be active in the excited state in this region of the IR spectrum, and they must be differentiated in order to understand the TRIR signal that results from occupation of the $^3\delta\delta^*$ state. Reasonable possibilities for each compound include the asymmetric CO$_2$ stretch associated with T$_{\text{PB}}$ or acetate ligands and both the symmetric and asymmetric C=C stretches of the phenyl rings on the 4-cyanobenzoate ligand (2a and 2b) or phenylethynylamidinate ligand (3a and 3b). In addition, similar C=C stretches could also
be present for the T^IPB ligand in 2a and 2b however no significant change is expected in these modes upon generation of the excited state due to the orientation of the phenyl ring relative to the metal-metal bond.

The results are shown for compounds 2a and 3a in Figure 4.9 and in this section these two molecules are shown together because the T_1 state is considered to be ^3\delta\delta^* for both. In the left panel, compound 2a initially contains two instances of excited state IR absorption, a clear band with peak frequency at 1635 cm\(^{-1}\) and a broad flat band with a peak at 1517 cm\(^{-1}\). These bands decay with lifetimes of 4.3 ps and 4.1 ps, respectively, as shown in the left panel of Figure D7. The lifetimes are similar to those measured in the C≡N stretch region (and also those measured by femtosecond TA) and so they can be associated with the \(^1\)MLCT state. Due to this, the ESA bands must be associated with vibrations that would be active in this state.

There are several possibilities for the identity of the initial bands and these include the C=C stretches either of the 4-cyanobenzoate or the T^IPB ligands, the T^IPB CO\(_2\) asymmetric stretch, or possibly phenyl ring overtone vibrations. For the initial band at 1635 cm\(^{-1}\), the C=C stretches associated with 4-cyanobenzoate can be ruled out because these bands would be expected to shift to lower energy in the excited state and this ESA band occurs at comparatively higher energy. The same stretches associated with the T^IPB ligands could be expected to shift to higher frequency due to decreased backbonding with the metal in the excited state; however, the orientation of the T^IPB phenyl ring due to steric hindrance likely limits this interaction, i.e. there may not be any change in these vibrations upon generating the excited state. Overtones associated with
the phenyl ring vibrations is a possibility because the shift of the ESA band to lower frequency is appropriate, however the inherent weakness of these bands and inability to observe them in the ground state makes this assignment unlikely. This leaves the TiPB CO$_2$ asymmetric stretch as the best possibility and it has shifted to higher wavenumber in the $^1$MLCT excited state because an electron has been removed from the HOMO which has CO$_2$ $\pi^*$ character. The shift to higher wavenumber for this mode can be understood by the electron configuration of the MLCT excited state. Removal of an electron from the HOMO decreases the $\pi^*$ character of the CO$_2$ groups bound to the metal and results in less backbonding, analogous to what has been well reported for metal-carbonyl type complexes.\textsuperscript{162} Based on the above considerations, the ESA band at 1517 cm$^{-1}$ can be reasonably thought as the C=C phenyl ring vibrations, the symmetric and/or the asymmetric modes, of the 4-cyanobenzoic acid ligand, which have been shifted to lower frequency in the $^1$MLCT state.

Most noteworthy is that the initial spectra between 1570 – 1470 cm$^{-1}$ decay to give rise to a long-lived spectrum consisting of the ground state bleach at 1508 cm$^{-1}$ and an ESA at 1535 cm$^{-1}$. This is better represented in the right panel of Figure D7. The bleach can easily be associated with the asymmetric stretch of the TiPB CO$_2$ group due to good correlation with the ground state peak wavenumber value. Shifted to higher wavenumbers by $\sim$ 27 cm$^{-1}$ is the ESA band and this is assigned as the excited state counterpart of the asymmetric TiPB CO$_2$ stretch in the $^3\delta\delta^*$ state. Within this state the electron configuration consists of removing an electron from an orbital containing CO$_2$ $\pi^*$ character, the HOMO, and placing it in one possessing CO$_2$ non-bonding character,
the δ* orbital. Removal of the π* contribution strengthens the CO₂ π bonding and leads to the expectation that the vibration shifts to higher frequency, which is consistent with the observed spectrum. However, the shift is much smaller than in the ¹MLCT state, perhaps because the electron resides much farther away from the metal in that situation. At this point it is realized that this peak occurring at ~ 1540 cm⁻¹ could be a defining quality of the δδ* state, which could not be directly observed by monitoring vibrations pertaining to the 4-cyanobenzoate ligand.

Figure 4.9 TRIR spectra of the molybdenum containing compounds 2a (left) and 3a (right) collected in the carboxylate group wavenumber range in THF at room temperature.

In the right panel of Figure 4.9 is shown the TRIR spectra for compound 3a detecting in the 1500 – 1600 cm⁻¹ region of the IR spectrum. The initial spectrum consists of a major peak at 1555 cm⁻¹ and a much weaker shoulder at 1585 cm⁻¹. The initial spectrum decays to reveal one that is long-lived which contains an ESA band at 1540 cm⁻¹ and a very weak bleach feature at ~ 1520 cm⁻¹, which is coincident with the ground state asymmetric CO₂ stretch of the acetate ligand. Kinetic traces in Figure D8
show the decay of the initial spectrum has a lifetime of 18.8 ps, which is consistent with the $^1$MLCT lifetime suggested previously for this compound.

It is believed this set of peaks at 1555 cm$^{-1}$ and 1585 cm$^{-1}$ is most likely derived from the symmetric C=C phenyl ring vibration given its larger inherent intensity. It should also be noted that this band resembles that measured from 2200 – 1850 cm$^{-1}$ in that there is one very intense peak shifted to lower wavenumber and another much smaller peak that is shifted much less but still to lower wavenumber. Similar to the analysis in the ethynyl group region, this pattern could arise from localization of the excited electron mostly onto a single phenylethynylamidinate ligand. A small amount of the excited electron is, in fact, shared with the second ligand, however. The experiment indicates this conclusion because the smaller peak is still shifted to lower wavenumber compared to the ground state value.

The long-lived peak in 3a is more easily seen in the right panel of Figure D8. For the assignment of the long-lived peak, the supplementary experiments described previously indicate it must be associated with the $^3\delta\delta^*$ state. It it is also noteworthy that it occurs at similar frequency and has similar band shape to the $^1$PB asymmetric CO$_2$ peak in compound 2a, suggesting they each arise from similar environments. Further experiments have been done on related compounds M$_2$(L)$_4$, where M = Mo or W and L = trimethylacetate or benzoate. They each show a long-lived spectra similar to that shown for compounds 2a and 3a, consistent with the $^3\delta\delta^*$ state. The detailed photophysics and infrared dynamics of these compounds, however, is the topic of a separate study.
4.4 Conclusions

The nature of the photoexcited states in compounds 2a, 3a, and their tungsten analogs can be correlated with the electronic structures of the molecules in their ground states. First, the lower energy of the Mo$_2$ δ and δ* orbitals leads to the T$_1$ states being $^3$MMδδ* and this can be expected to be generally the case unless the ligand π* orbital is very low in energy and the $^1$MLCT absorption falls in the near infrared (NIR). Conversely, the higher energy of the W$_2$ δ and δ* will lead to T$_1$ being $^3$MLCT unless the energy of the ligand π* orbital is notably high in energy and the $^1$MLCT absorption is in the high energy region of the UV/visible spectrum. Second, the coupling of the two trans-ligands is dependent primarily on the energy separations between the M$_2$-δ and the ligand based LUMO π* orbital. The smaller the energy gap the greater the coupling and this can lead to fully delocalized S$_1$ and T$_1$ MLCT states. As the coupling of the two ligands via the M$_2$-δ decreases, the photoexcited state can take on mixed valence Class II characteristics. The initial photoexcitation may be to a delocalized, Class III state which rapidly relaxes to the charge localized Class II MV state. This is seen for the amidinate compounds and their ground state and photoexcited state potential energy surfaces can be represented by Figure 4.2, above. Third, the extent of charge delocalization in the singlet and triplet MLCT states is in general expected to be different with the higher energy S$_1$ state being more diffuse than the lower energy T$_1$ state. This was very nicely revealed in the TRIR spectra of 3b.

It is particularly appealing that these four molecules have revealed these limiting cases as summarized in Table 4.3. Furthermore, based on considerations of orbital
energies involving the M₂-δ and the ligand π* we anticipate these findings will be applicable to the photoexcited states of conjugated polymers incorporating MM quadruple bonds.⁷¹

### Table 4.3 Summary of photophysical assignments and Robin and Day Classification

<table>
<thead>
<tr>
<th>Compound (M)</th>
<th>State</th>
<th>Assignment</th>
<th>TRIR τ / ps</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a (Mo)</td>
<td>S₁</td>
<td>¹MLCT</td>
<td>3.9 +/- 0.1</td>
<td>Class III</td>
</tr>
<tr>
<td></td>
<td>T₁</td>
<td>³δδ*</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>2b (W)</td>
<td>S₁</td>
<td>¹MLCT</td>
<td>6.5 +/- 0.1</td>
<td>Class III</td>
</tr>
<tr>
<td></td>
<td>T₁</td>
<td>³MLCT</td>
<td>N.A.</td>
<td>Class III</td>
</tr>
<tr>
<td>3a (Mo)</td>
<td>S₁</td>
<td>¹MLCT</td>
<td>20.1 +/- 0.4</td>
<td>Class II</td>
</tr>
<tr>
<td></td>
<td>T₁</td>
<td>³δδ*</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>3b (W)</td>
<td>S₁</td>
<td>¹MLCT</td>
<td>7.1 +/- 0.3</td>
<td>Class II</td>
</tr>
<tr>
<td></td>
<td>T₁</td>
<td>³MLCT</td>
<td>N.A.</td>
<td>Class II</td>
</tr>
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</table>

In addition, the nature of the excited states involved in photophysical relaxation can be definitively assigned according to the observation of particular vibrational modes. Most clearly, the C≡C and C≡N stretching modes shifted to lower frequency are indicative of the MLCT states that involve those ligands. Furthermore, the removal of electron density away from the metal center has an effect on the other spectator acetate or TiPB ligands through backbonding. This was seen for 2a where the asymmetric CO₂ stretch was shifted to higher frequency. For identification of the δδ* states the modes associated with the MM bridging CO₂ or CN₂ are useful due to the interaction between these groups non-bonding combination with the δ* orbital. The CO₂ asymmetric stretch associated with the spectator ligand is most useful because it naturally occurs at the
highest frequency. In the $^3\delta\delta^*$ excited state, it is shifted to even higher frequency due to removal of an electron from the $\delta$ HOMO but its shift is smaller compared to in the MLCT state because the charge resides closer to the metal. The peak at $\sim 1540$ cm$^{-1}$ is the first indication of observing the $^3\delta\delta^*$ state by TRIR spectroscopy and provides motivation for the study of some related yet more structurally simple quadruply bonded compounds.

4.5 Supporting Information

The following have been provided in appendix D of the supporting information. Selected vibrational frequencies for compounds $2a$ and $2b$ and $3a$ and $3b$ are summarized in Tables D1 and D2, respectively. Emission excitation spectra for compounds $3a$ and $3b$ are shown in Figure D1 and for $2a$ and $2b$ in Figure D2. Table D3 summarizes vibrational frequencies observed in the ground state infrared spectra and their assignments for each compound. Kinetic traces for the TRIR spectra collected in the C≡N and C≡C region are shown in Figures D3 and D4. Figure D6 shows gaussview molecular orbital plots for the LUMO of $2b$ and $3b$. Figure D7 and D8 show kinetic traces and long-lived spectra for compounds $2a$ and $3a$, respectively.
Figure A.1 Potential energy surface representation of vibrational mixing between electronic states. Reproduced from reference.²
Figure A.2 Experimental setup and laser system for femtosecond broadband transient absorption spectroscopy.

Figure A.3 Experimental setup and laser system for femtosecond TRIR spectroscopy.
Figure B.1 Absorbance (solid line) and emission (bold line) spectra of compounds 2a (red) and 2b (purple) in THF at room temperature.
Figure B.2 Nanosecond transient absorption spectra of compound 2b in THF at room temperature after excitation at 532 nm.
Figure B.3 Femtosecond transient absorption spectra for 2a obtained at long delay times after the decay of the initial state, revealing a better representation of the absorption at 375 nm.

Figure B.4 Kinetic traces monitored at 565 nm taken from transient absorption spectra of compound 2a shown in figure 2.7. Delay times less than 50 ps (left) and the full kinetic trace (right).
Femtosecond transient absorption spectra for 2b obtained at long delay times after the decay of the initial state, revealing a better representation of the isosbestic point at 550 nm.

Table B.1 Summary of photophysical properties for compounds 2a and 2b

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{abs}}$ / nm</th>
<th>$\varepsilon$ / M$^{-1}$*cm$^{-1}$</th>
<th>$\lambda_{\text{em}}$ / nm (S$_1$)</th>
<th>$\lambda_{\text{em}}$ / nm (T$_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>549, 512, 475(sh)</td>
<td>1.25 X 10$^4$</td>
<td>597, 637, 701(sh)</td>
<td>1014, 1050, 1093</td>
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<tr>
<td>2b</td>
<td>738, 668, 609</td>
<td>3.82 X 10$^4$</td>
<td>774, 838</td>
<td>N.A.</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau$ / ps (S$_1$)</th>
<th>Assignment, S$_1$</th>
<th>$\tau$ / $\mu$s (T$_1$)</th>
<th>Assignment, T$_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
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<td>$^{1}\text{MLCT}$</td>
<td>~93</td>
<td>$^{3}\delta\delta*$</td>
</tr>
<tr>
<td>2b</td>
<td>6.2 +/- 0.2</td>
<td>$^{1}\text{MLCT}$</td>
<td>~1 X 10$^{-3}$</td>
<td>$^{3}\text{MLCT}$</td>
</tr>
</tbody>
</table>

$^a$Peak values obtained from low temperature spectrum

$^b$Value at $\lambda_{\text{max}}$ of room temperature spectrum
APPENDIX C

Supplementary Information for Chapter 3

<table>
<thead>
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<th>Wavelength / nm</th>
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<td>400</td>
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<tr>
<td>450</td>
<td>0.1</td>
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<td>600</td>
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</tr>
<tr>
<td>650</td>
<td>0.5</td>
</tr>
<tr>
<td>700</td>
<td>0.6</td>
</tr>
</tbody>
</table>

3a Room Temperature
3a 98 K
3b Room Temperature
3b 100 K

Figure C.1 Absorbance spectra of Compounds 3a (orange) and 3b (blue) at room temperature (dashes) and low temperature (solid).
Figure C.2 Low temperature absorbance and emission spectra of complexes 3a ($\lambda_{ex} = 490$ nm) and 3b ($\lambda_{ex} = 600$ nm) in 2-MeTHF.
Figure C.3 Emission spectra for complex 3a at room temperature in THF and low temperature (77K) in 2-methyltetrahydrofuran with $\lambda_{\text{ex}} = 490$ nm.

$\Delta \nu \sim 383$ cm$^{-1}$
Figure C.4 Kinetic trace for compound 3a from the femtosecond transient absorption measurements shown in Figure 3.9 monitored at 450 nm showing further decay in the ground state bleach at long delay times.

Table C.1 Summary of photophysical properties for compounds 3a and 3b

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^\text{a}\lambda_{\text{abs}}$ / nm</th>
<th>$^\text{b}\varepsilon$ / M$^{-1}$cm$^{-1}$</th>
<th>$^\text{a}\lambda_{\text{em}}$ / nm (S$_1$)</th>
<th>$^\text{a}\lambda_{\text{em}}$ / nm (T$_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>497, 465 (sh)</td>
<td>24,550</td>
<td>530, 560 (sh)</td>
<td>796, 821</td>
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<tr>
<td>3b</td>
<td>607, 558 (sh)</td>
<td>48,800</td>
<td>642, 680</td>
<td>789</td>
</tr>
<tr>
<td>Compound</td>
<td>$\tau$ / ps (S$_1$)</td>
<td>Assignment (S$_1$)</td>
<td>$\tau$ / $\mu$s (T$_1$)</td>
<td>Assignment (T$_1$)</td>
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<tr>
<td>3a</td>
<td>19.2 +/- 0.3</td>
<td>$^1$MLCT</td>
<td>105 +/- 2</td>
<td>$^3\delta\delta^*$</td>
</tr>
<tr>
<td>3b</td>
<td>5.6 +/- 1.0</td>
<td>$^1$MLCT</td>
<td>4.6 +/- 0.1</td>
<td>$^3$MLCT</td>
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</tbody>
</table>

$^\text{a}$Peak values obtained from low temperature spectrum

$^\text{b}$Value at $\lambda_{\text{max}}$ of room temperature spectrum
## APPENDIX D

Supplementary Information for Chapter 4

### Table D.1 Calculated vibrational frequencies for 2a and 2b

<table>
<thead>
<tr>
<th>Group</th>
<th>Vibration</th>
<th>Compound</th>
<th>Freq / cm(^{-1})</th>
<th>IR Intensity</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡N</td>
<td>Stretch</td>
<td>2a</td>
<td>2345</td>
<td>97.3</td>
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<tr>
<td></td>
<td></td>
<td>2b</td>
<td>2343</td>
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<tr>
<td>Benzene C=C</td>
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<td></td>
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<tr>
<td></td>
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<td>1552</td>
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<td>Benzene CH</td>
<td>Rock</td>
<td>2a</td>
<td>1552</td>
<td>0.6</td>
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<tr>
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<td>CO(_2)</td>
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<td>Formate CH</td>
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<td></td>
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<td>1328</td>
<td>43.8</td>
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</table>

Asym = asymmetric; Sym = symmetric
CO\(_2^-'\): formate ligand; CO\(_2\): p-cyanobenzoate ligand
Table D.2 Calculated vibrations for compounds 3a and 3b

<table>
<thead>
<tr>
<th>Group</th>
<th>Vibration</th>
<th>Compound</th>
<th>Freq / cm(^{-1})</th>
<th>IR Intensity</th>
<th>Symmetry</th>
</tr>
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<tbody>
<tr>
<td>C≡C</td>
<td>Stretch</td>
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<td>Benzene</td>
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<td>79.6</td>
<td>B(_{3u})</td>
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Asym = asymmetric; Sym = symmetric

CO\(_2\): formate ligand; CO\(_2\): phenylethynylaminidinate ligand
Figure D.1 Absorption (black), emission (blue), and excitation (red or green) spectra for compounds 3a (left) and 3b (right) collecting the emission within the $^1$MLCT fluorescence (680em, red) and the $^3$MLCT phosphorescence (815em, green).

Figure D.2 NMR spectrum for compound 2a in THF-d8 at room temperature.
Figure D.3 Absorption (black), emission (blue), and excitation (red) spectra for compound 2a (left) and 2b (right) in THF at room temperature.
Table D.3 IR peak positions and assignments

<table>
<thead>
<tr>
<th>Compound 2a</th>
<th>Compound 2b</th>
<th>Compound 3a</th>
<th>Compound 3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freq / cm(^{-1})</td>
<td>Assignment</td>
<td>Freq / cm(^{-1})</td>
<td>Assignment</td>
</tr>
<tr>
<td>2230(s)</td>
<td>C≡N stretch</td>
<td>2226(s)</td>
<td>C≡N stretch</td>
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<tr>
<td>1604(s)</td>
<td>C≡C Sym(^{a})</td>
<td>1594(vs)</td>
<td>C≡C Sym(^{a})</td>
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<tr>
<td>1573(s)</td>
<td>C≡C Asym(^{a})</td>
<td>1547(w)</td>
<td>C≡C Asym(^{a})</td>
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<tr>
<td>1508(vs)</td>
<td>CO(_2)' Asym(^{b})</td>
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<td>1409(vs)</td>
<td>CO(_2)' Sym(^{c})</td>
<td>1396(s)</td>
<td>CO(_2)' Sym(^{c})</td>
</tr>
</tbody>
</table>

\(^{a}\)Phenyl Ring localized vibrations associated with either ligand; \(^{b}\)Carboxylate group associated with TiPB ligands
\(^{c}\)Carboxylate group associated with 4-cyanobenzoic acid ligands
Figure D.4 Kinetic traces from TRIR shown in figure 4.7 for 2a (left) and 2b (right).

Figure D.5 Representative kinetic traces from TRIR shown in Figure 4.8 for 3a (top) and 3b (bottom).
Figure D.6 Molecular orbitals for the LUMO of 2b and 3b determined from DFT calculations and displayed with an isosurface value of 0.06.

Figure D.7 Kinetic traces (left) from TRIR spectra shown in figure 4.9 for 2a and a better representation of the long-lived state (right).

Figure D.8 Kinetic traces (left) from TRIR spectra shown in figure 4.9 for 3a and a better representation of the long-lived state (right).
Bibliography


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(130) Unpublished work.


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