Long-Range Electronic Coupling of MM Quadruple Bonds (M = Mo or W) via a 2,3-Azulenedicarboxylate Bridge

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Introduction

Electron transfer (ET) is one of the most important phenomena in Chemistry, Biology and Physics. ET is the process of moving an electron from one location to another. There are a number of ways this can occur and a couple of them will be explained shortly.

Molecular photonics is an interesting area of chemistry that uses ET or superexchange. In Biology, ET is often a simple, yet critical processes. Life depends on ET in so many ways; Photosynthesis is an important well known processes. Iron-sulfur clusters work as ET carriers in different systems and are of interest to many research groups at MSU. In Physics, compounds responsible for ET are important to the study of bulk magnets and superconductors.

The study of ET was furthered in large part by Rudolph A. Marcus (born in Canada), a Professor at the California Institute of Technology. He won the 1992 Nobel Prize in Chemistry for his contributions to the theory of electron transfer reactions in chemical systems. Marcus Theory was based on his work in this field and states that for outer-sphere reactions:

1-Reactants diffuse together to form an outer-sphere complex in which both metal coordination spheres remain intact.
2-Bond distances around each metal change to become more “productlike”.
3-The solvent shell around the outer-sphere complex reorganizes.
4-The electron is transferred.
5-The products diffuse away; this step is generally fast.

In principle all outer sphere mechanism involves electron transfer from reductant to oxidant with the coordination shells or spheres of each staying intact. That is one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant. Such a mechanism is established when rapid electron transfer occurs between two substitution-inert complexes. However, for this paper, inner-sphere ET is of more importance. For inner-sphere ET one reactant (usually the oxidant) possess at least one ligand capable of binding simultaneously to two metal ions while the other reactant is substitutionally labile; i.e. one ligand must be replaced by the bridging ligand or a ligand that can be replaced by a bridging molecule. The following (from) shows an outer-sphere reaction and a inner-sphere reaction when one of the ligands of the outer-sphere reaction is replaced by a Cl that acts as a bridging ligand.
The inner-sphere transfer is much faster than the outer-sphere transfer due to the bridging ligand’s contribution.

Another part of the Marcus Theory, used for reaction rate constants, can be shown schematically (below). The curvature for products and reactants are assumed to be the same. In the diagram, $\lambda$ is the reorganization energy defined as the change in Gibbs energy if the reactant state ($D|A$) were to distort to the equilibrium configuration of the product state ($'D'|'A'$) without transfer of the electron. $\Delta G^*$ is the Gibbs energy of activation for forward ET and $\Delta G^0$ is the Gibbs energy between the equilibrium configurations of the product and reactant states.

From these diagrammatic interpretations, rate constants and reorganization energies can be calculated and worked with. Electronic coupling energy can also be determined by slightly modifying these diagrams.
Another important principle is the Franck-Condon principle that implies during the course of ET, the positions of the atoms remain unchanged; the transfer of the electron can be regarded as quasi-instantaneous with respect to nuclear motion. In the special case of a symmetric mixed valence compound containing metal centre M and its one-electron oxidation product M⁺ and bridged by ligand L, M - L - M⁺.

A classic ion used in the study of ET is the Creutz-Taube Ion. It was first obtained during efforts to create coordinatively defined and kinetically stable models for degenerate inner-sphere electron transfer. It has played a pivotal role in our understanding of electron delocalization in mixed valent systems. Taube (also Canadian) won the 1983 Nobel Prize in Chemistry for his work in this area. This ion contains two Ru centers each attached to 5 ammonias and bound to one another with a bridging ligand (usually pyrazine) \([(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5)^{5+}\] – see Figure 1.

![Figure 1 - Creutz-Taube ion](image)

It appears to be a delocalized species with an oxidation number of +2.5 for both metal centers. The reason many scientists have designed modified or new similar ions in this area of research, rather than sticking with the original Creutz-Taube ion, is due to the fact that the Creutz-Taube ion is much more complex than it needs to be. This is a result of the presence of three metal d-pi orbitals (dₓᵧ, dₓz, dᵧz) and spin-orbit coupling which give rise to several electronic transitions in the low energy region. This ion has been classified as class III, however, EPR has not yet been able to show delocalization on both Ru Centers.

These mixed-valence systems have been classified according to their M-L-M interaction. This method of classification is referred to as the Robin and Day classification. Here, mixed-valence systems are characterized as Class I, II or III depending on the strength of the electronic interaction between the two metal centers, ranging from essentially zero (Class I), to moderate (Class II), to very strong electronic coupling (Class III). The properties of Class I systems are basically those of the separate sites. In Class II, the interaction between the sites is sufficiently weak that these systems are valence trapped. In Class III systems the electron is delocalized and the system has its own unique properties. However the situation becomes much more complicated when the system shows borderline Class II/III behavior. The tungsten compound explored here shows similarities to complexes found on the Class II/III border. While the molybdenum complex is found to be Class II.

Superexchange, first introduced by McConnell in 1961, is the intermolecular charge transfer though a linking bridge. In this model, an electron is transferred between degenerate donor and acceptor orbitals, aided by the presence of high-lying empty bridge orbitals (figure 2 [1]). This differs from the “hopping” model in which the electron does not occupy any of the bridge orbitals during the transfer event (figure 2 [2]).
The rate of ET generally decays roughly exponentially with distance between donor and acceptor sites.\textsuperscript{11}

The complexes studied in this paper are $M_2$-Bridge-$M_2$ or $[(HCO_2)_3M_2]_2(\mu-O_2CC_{10}H_6CO_2)$ where $M = Mo$ or $W$ (Figure 3).

The reason for using Mo and W was to allow for comparison of the electronic factors on the mixed valence ions, since size and solvation factors should be almost identical for Mo and W.\textsuperscript{9} The different electronic factors between the Mo and the W is what gives rise to the Mo’s class II and the W’s Class III behavior.\textsuperscript{9} Because the distance between the $M_2$’s is nearly 14Å, this complex is categorized as a long range with respect to the ET.\textsuperscript{9}

**Methods and Techniques**

**Physical techniques**

EPR measurements were made at the Q-Band (34 GHz) frequencies using a Bruker Elexsys-500 Spectrometer with built in Bruker NMR gaussmeter and EIP digital
frequency counter to accurately measure the magnetic field and frequency of the microwaves. Temperature was varied from 4K to ambient with a helium cryostat. X-band EPR spectra were recorded using a Bruker ESP300 Electron Spin Resonance spectrometer.

![Figure 4](image)

UV-vis spectra of the bridge (Figure 4) were recorded along with the spectra of the Mo and W complexes (Figure 3 above). Quartz path lengths of 0.20, 1.00, or 10.00 mm were used. Background spectra of the solvents were subtracted.

NMR samples of the bridge were analyzed on a Bruker DRX-400 spectrometer. The $^1$H-NMR spectra of the two metal complexes were recorded on a 400 MHz Bruker DPX Avance spectrometer. Two-dimensional NMR techniques were employed to obtain unambiguous assignments of $^1$H and $^{13}$C NMR resonances.

Cyclic Voltammetry, which has the advantage that the product of the electron transfer reaction that occurred in the forward scan can be probed again in the reverse scan, was used along with differential pulse voltammetry on the two metal complexes. A Platinum wire auxiliary electrode and a pseudo-reference electrode consisting of a silver wire were used during the measurements.

Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) was performed on a Bruker Reflex III mass spectrometer operated in linear, positive ion mode with an N2 laser. Laser power was used at the threshold level required to generate signal. Accelerating voltage was set to 28 kV. Allotments of matrix and sample were thoroughly mixed together; 0.5 mL of this was spotted on the target plate and allowed to dry.

Electronic Absorption Spectra (EAS) were also gathered.

**Synthetic work**

All dimolybdenum or ditungsten ($[(^t$BuCO$_2$)$_3$M$_2$]$–$ where M=Mo or W) related reactions were done in a nitrogen-filled glovebox or by using standard Schlenk line techniques.

The bridging molecule was synthesized (with a 98% yield) using a method previously developed by another research group (Figure 5). The Diacid BridgeH$_2$ must be stored under moisture-free conditions, as it is extremely hygroscopic and strongly holds onto water.
To synthesis the complex studied (figure 3 above), the \([('BuCO_2)_3M_2]\) was mixed with the BridgeH\textsubscript{2} in a Schlenk tube (figure 6). Toluene was added and the suspension was stirred for 8 days (Figure 7). The precipitate was then dried giving a 68\%, and 54\% yield for the the Mo and W complexes respectively.

$$\begin{align*}
2M_2(O_2C' Bu)_4 + 2.6-(CO_2 H)_2 - C_{10}H_6 \quad &\xrightarrow{8 \text{ days}} \quad \text{toluene,} \\
\text{BridgeH}_2
\end{align*}$$

Electronic Structure Calculations

Electronic structure calculations on the complexes \([(HCO_2)_3M_2]_2(\mu-O_2C_{10}H_6CO_2)\) (M = Mo, W) were performed using density functional theory with the aid of the Gaussian03 suite of programs\textsuperscript{9}. Geometry optimizations were performed in C\textsubscript{2v} symmetry. The geometrically optimized ground state in the bridging azulene ring is planar with respect to the M\textsubscript{2} units, which maximizes M\textsubscript{2}-to-bridge \pi back-bonding. Hydrogen atom positions were initially determined by geometry and refined by a riding model\textsuperscript{9}. Non-hydrogen atoms were refined with anisotropic displacement parameters\textsuperscript{9}.

Results and Analysis

When the bridging molecule is dissolved in DMSO and aqueous KOH it gives a deep blue colour (yes, colour). The \textsuperscript{1}H NMR spectrum of the BridgeH\textsubscript{2} in anhydrous DMSO-\textsubscript{d}_6 features a somewhat broad signal at 13.32 ppm of the same intensity due to both acidic hydrogen atoms (seen in Figure 5). The expected resonances for the bridge protons in the aromatic region are present along with two singlet 'BuCO\textsubscript{2} resonances corresponding to the cis and trans ligands.
The molybdenum complex has an intense blue color, whereas its tungsten complex is pale green in the solid state and straw yellow in THF solutions. The electronic spectra of the two complexes are compared in Figure 9 below. In both cases, the lowest energy electronic transitions are assignable to metal-to-bridge charge transfer. The greater intensity and the lower energy of the tungsten absorption bands is due to the higher orbital energy of the $W_2$ orbitals, which are typically 0.5 eV above $Mo_2$ orbitals in related complexes. Another reason is the greater radial extension of the $W$ 5d orbitals (figure 8). The latter gives rise to enhanced $W_2$ $\pi$-to-bridge LUMO back-bonding. To a first-order approximation, the intensity of a MLCT band correlates with the degree of overlap and is inversely related to the orbital separation energy.

At 1140 nm (Red – W) there is a broad, much weaker transition, $\varepsilon \approx 8000 \text{ M}^{-1} \text{ cm}^{-1}$, band assignable to the spin-forbidden (spin-forbidden transitions are less intense than those of spin-allowed transitions) MLCT triplet transition which gains in intensity due to spin-orbit coupling with the heavy 5d metal. The intense MLCT band at 1140 nm ($\varepsilon = 85700 \text{ M}^{-1} \text{ cm}^{-1}$) is suggestive of a ground-state structure where the bridge and the $O_2C_1$ attached to the dimetal’s opposite side, are all in the same plane. The MLCT absorptions are at a higher energy in the solid state for both the Mo and W complexes, which reflects a poorer $M_2$ $\pi$-bridge overlap.

Electronic Absorption Spectra of the complexes’ cations (+1) The electronic absorption spectra of the radical cations MoComplex$^+$ and Wcomplex$^+$ is shown in Figures 10 and 11, respectively. The tungsten complex$^+$ shows an intense sharp band in the near-IR at 9260 cm$^{-1}$ (1080 nm) and a weaker narrow band centered at 3080 cm$^{-1}$ (3246 nm) in the infrared. The complete shape of this band is obscured by solvent absorption, but it is
clearly of the type seen for Class III compounds near the Class II/III border.\(^9\) This band is not seen for the neutral or 2+ W complexes. Based on the MO calculations on the model compounds, we can readily assign this band to originate from the HOMO-1 to HOMO transition and the higher energy band to the MLCT band\(^9\). Again, this conforms to the simple picture presented in Figure 9. No evidence of an LMCT is seen. In contrast, the spectrum of Mo Complex\(^+\) has a weak and broad low-energy band centered at 6250 cm\(^{-1}\) (1600 nm)\(^9\). This compound is best described as Class II in nature.

**Electronic Structure Calculations**

Gaussview plots of the LUMO, HOMO, HOMO-1, and HOMO-2 for the Metal complexes are shown in Figure 12.

For both M = Mo and W, the HOMO and HOMO-1 are M\(_2\) \& combinations and the LUMO is a bridge-centered \&* orbital as expected (figure 13)\(^9\). The HOMO-2 is a bridge \&-MO that is polarized toward the C\(_5\) ring (can been seen in figure A above), whereas, in the LUMO, the polarization is toward the C\(_7\) ring (can been seen in figure A above).

Similarly, the HOMO is an M\(_2\) \& combination having greater metal character associated with the M\(_2\) center (figure 13)\(^9\), which is adjacent to the C\(_5\) ring, M\(_2\)(A), and the HOMO-1 has more character from the M\(_2\) center adjacent to the C\(_7\) ring, M\(_2\)(B)\(^9\). The bridge-
centered filled orbital, the HOMO-2, is very close in energy to the Mo$_2$ manifold and, even for tungsten, is calculated to be only 0.5 eV below the HOMO-1 W$_4$ manifold$^9$.

**EPR Spectra of Mo complex$^+$ and W complex$^+$.**

The EPR spectra of the radical cations Mo complex$^+$ and W complex$^+$ were recorded at X-band and Q-band. The Q-band spectrum of the Mo complex$^+$ indicate that the radical cation is valence-trapped with the unpaired electron localized on one Mo$_2^{5+}$ center, presumably Mo$_2$(A) the center adjacent to the C$_5$ ring$^9$. The spectra of the W complex$^+$ are, however, much more interesting and is consistent with a metal based oxidation. The majority of tungsten nuclei have $I = 0$, but the $^{183}$W isotope has $I = \frac{1}{2}$ which occurs in 14.3% natural abundance. The W complex$^+$ was shown to be Class III with the single electron is delocalized over all four tungsten atoms.$^9$

**Electrochemical Studies**

Voltammograms of the two complexes are shown to the right (Figure 7). For the Mo complex (blue), the single-oxidized radical cation is more stable than the neutral and doubly oxidized compound.$^9$

For the Mo compound, the splitting of the 1st and 2nd oxidation waves shows the stability of the single-oxidized radical cation in relation to the neutral and doubly oxidized compound$^9$. In contrast, the tungsten complex (red) shows two oxidation waves that are suggestive of Class III characteristics.

**Conclusion**
The work done here has shown that the bridge (Figure 4) is an effective bridge when coupling 2 $M_2$ quadruply bonded centers. The coupling is greater for W than for Mo and is due to the greater radial extension of the W’s 5d orbitals (figure 8). This can be concluded from the more intense Metal-ligand charge transfer band in the lower energy electronic absorption spectra (figure 9). It was also shown that the W complex$^+$ cation has a fully delocalized electron whereas the Mo complex$^+$ cation shows one that is valence trapped (Class II).

The coupling of the two $M_2$ centers arises almost exclusively via electron transfer through the $\pi^*$ system of the bridge, via mixing of $M_2 \delta$ and bridge $\pi^*$ orbitals. Furthermore, there is essentially no CO$_2$ $\pi$ character to this orbital which further impedes any interaction with the $M_2 \delta^*$ orbitals, which in any event are energetically unfavorably disposed being notably higher in energy than the LUMO$^9$.

Although the charge was delocalized over the two W$_2$ it was polarized towards one of the centers. Based on the calculations and a consideration of the somewhat polar nature of the bridge the authors proposed that the charge had more W$_2$(A) character than W$_2$(B)$^9$.

Finally, these quadruply bonded $M_2$ complexes may be suitable for other similar studies in which electron coupling is investigated. It was also suggested that it might be possible to delocalize a charge well beyond the 14Å, preformed here, if a proper bridge was chosen to link two quadruply bonded $M_2$ complexes.

References:
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