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Review

Charge distribution in metal to ligand charge transfer states of quadruply bonded metal complexes

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Contents

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ABSTRACT

The application of fs time resolved infrared, TRIR spectroscopy to complexes of the form M_2L_4, $M_2L_3L^1$ and $M_2L_2L_2{}^1$ where M = Mo or W and L or L^1 = a carboxylate or amidinate has allowed the nature of ^{1}MLCT S_1 states to be probed with respect to the location of charge on the ligands. The ^{3}MLCT states, which are formed by intersystem crossing, have similarly been probed in a few instances where M = W but for M = Mo the T_1 states are typically ^{3}MoMoδδ*. Examples of localized, valence trapped and delocalized ligand excited states have been found with the latter being favored by strong ligand–ligand coupling via the M_2δ orbital.

1. Introduction

The advent of pump-probe spectroscopy employing ultra-fast laser techniques has allowed the study of molecules in their photoexcited states within the time span close to the initial absorption of a photon, femtoseconds, to the time of ultimate relaxation. Organometallic and coordination compounds have been the topics of considerable interest because they commonly have metal-to-ligand charge transfer transitions that lead to charge separation: the metal is oxidized and the ligand is reduced. This leads to the interesting situation that the photoexcited state of the molecule is both a better oxidizing agent and better reducing agent compared to the ground state molecule. These charge separated states are of particular interest in the areas of photocatalysis and photovoltaics. Perhaps more generally stated, they may be useful in the harvesting of light for chemical and physical transformations. There are now a number of excellent reviews that forms on the application of ultra-fast spectroscopic studies involving both transient absorption and infrared, as applied to metal to ligand charge transfer, MLCT, states [1–3].

1.1. MM quadruple bonds

Most of the early photophysical studies of quadruply bonded metal complexes focused on the δ to δ* electronic transition [4,5]. This typically is a rather weak transition and can be masked by more intense metal to ligand charge transfer absorptions in dimetal carboxylates. Indeed, only for $Mo_2(O_2CR)_4$ compounds, where R = alkyl, is the $^1(\delta \rightarrow \delta^*)$ transition detectible with $\varepsilon \sim 100\,M^{-1}\,cm^{-1}$. A qualitative frontier molecular orbital energy level diagram for such a carboxylate is given in Fig. 1. The carboxylate π* ligand based orbitals lie just above the δ* orbital for R = alkyl but when the R is an organic unsaturated group such as aryl, thienyl or vinyl, then the ligand π* orbitals are lowered in energy and the $^1(\delta \rightarrow \delta^*)$ transition is not seen [6].

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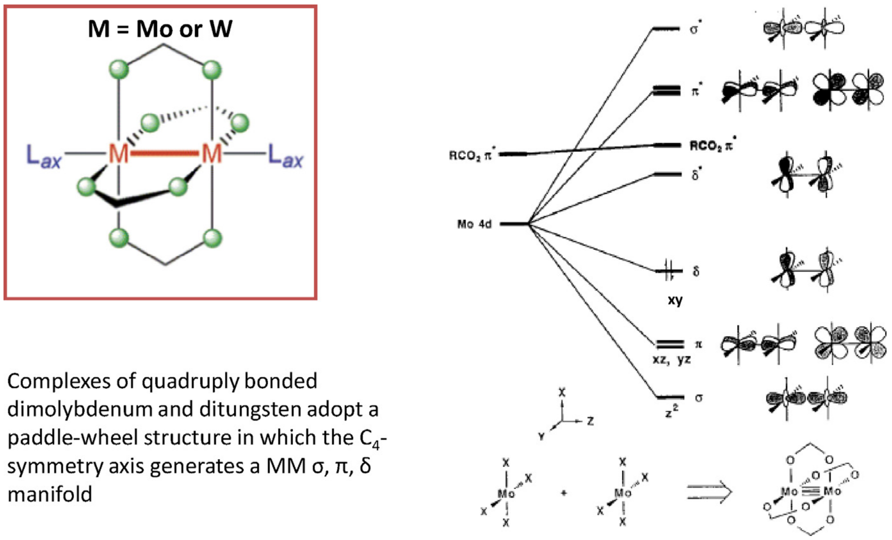

Complexes of quadruply bonded dimolybdenum and ditungsten adopt a paddle-wheel structure in which the C_4-symmetry axis generates a MM σ, π, δ manifold

Fig. 1. Frontier molecular orbital diagram for a MM quadruply bonded carboxylate.

The W_2 δ orbital lies roughly 0.5 eV higher in energy than its Mo_2 counterpart in otherwise related complexes and for ditungsten carboxylates the $^1(\delta\rightarrow\delta^*)$ is masked by the $M_2\delta$ to $CO_2\pi^*$ transition even when R = alkyl [7].

For the homoleptic compounds, $M_2(O_2CR)_4$, the carboxylate π^* orbitals transform as b_{2g}, a_{1g} and e_u in the symmetry point group D_4h. Thus the M_2 δ orbital which also transforms as b_{2g} is involved in back-bonding to the carboxylate π^* orbital of its symmetry match.

In the case of amidinate ligands $RNCR^1NR$, where R = alkyl or aryl and R^1 = H, alkyl or aryl, the lesser electronegative NR group relative to oxygen raises the energy of the $M_2\delta$ and δ^* orbitals, but the energy of the $^1(\delta\rightarrow\delta^*)$ transition remains similar to that of the carboxylates. The ^{1}MLCT transition can be lowered in energy when R^1 is a conjugated organic group. However, because of steric congestion involving R and R^1 the conjugation to R^1 is limited unless an alkynyl group is introduced as in $RNC(C{\equiv}CR^1)NR$ [8].

Many of the fundamentals of the photophysical properties of carboxylates bound to M_2 quadruply bonded species were the subject of a recent account and will not be extensively covered in this article which focuses on the application of time resolved infrared spectroscopy, TRIR, toward the determination of charge localization in the photo-excited state [6]. It is sufficient here to note the following:

1. The ^{1}MLCT states are relatively long-lived with $\tau \sim 1$–20 ps. These are notably longer than those in the majority of 2nd and 3rd row d^6 metal complexes, such as $Ru(bpy)_3{}^{2+}$, which undergo intersystem crossing within femtoseconds.
2. The dimolybdenum tetracarboxylates show $^3MoMo\delta\delta^*$ emission at ~1100 nm. The introduction of amidinate ligands moves this emission to higher energy and shorter wavelength ~850 nm. Similarly the ditungsten tetracarboxylates have $^3MM\delta\delta^*$ states that are at higher energy which allows the T_1 states commonly to be ^{3}MLCT.
3. The lifetimes of the T_1 states are typically 10–100 μs for $^3MoMo\delta\delta^*$ and ~10 ns for ^{3}MLCT. For a $^3WW\delta\delta^*$ state the lifetime is also in μs and thus it is relatively easy to distinguish between $^3MM\delta\delta^*$ and ^{3}MLCT states.

2. *Trans*-$M_2(T^iPB)_2(O_2CR)_2$ compounds

The reaction between $M_2(T^iPB)_4$, where T^iPB is the 2,4,6-triisopropylbenzoate ligand, and two equivalents of a conjugated carboxylic acids, RCOOH, leads to compounds of the form *trans*-$M_2(T^iPB)_2(O_2CR)_2$. In these compounds the bulky aryl groups of the T^iPB ligands are twisted out of conjugation with respect to their carboxylates and thus do not interact effectively with the $M_2\delta$ orbitals. In contrast the trans-RCO_2 ligands are coupled electronically by their interaction with the $M_2\delta$ orbital. The molecular structures of several of these complexes determined by single crystal X-ray crystallography reveal this extensive $L\pi$–$M_2\delta$–$L\pi$ conjugation in the ground state and variable temperature electronic absorption spectra recorded in the low melting and glassy frozen solvent 2-methyltetrahydrofuran bear this out [9]. The variable temperature absorption spectra reflect a Boltzmann distribution of molecules having a thermal-population of O_2C-R dihedral angles, Φ, that upon lowering the temperature favor $\Phi \sim$ O. Thus the room temperature spectra, which are broad, sharpen upon cooling and show resolved vibronic features at low temperatures. This matter has been discussed elsewhere and will not be the topic of further review here. It is, however, worthy of note that Zink and Yoo in 1983 examined the $Mo_2\delta$ to $CO_2\pi^*$ transition in $Mo_2(O_2CCF_3)_4$ and based on a detailed analysis of the $Mo_2\delta$ to $CO_2\pi^*$ transition and its vibrational features concluded that in the ^{1}MLCT photo-excited state the Mo–Mo distance was larger by ~0.04Å relative to the ground state [10]. The formal MM bond order in the MLCT state is 3.5 and with our present structural knowledge of MM triple and quadruple bond distances differing by 0.08 Å, [7] Zink's conclusion based on the analysis of vibrational progressions seems all the more remarkable. Zink also noted that the CO_2 vibrations in the excited state ^{1}MLCT were also significantly perturbed but at that time he was not capable of commenting further. We shall return to the matter of homoleptic carboxylates shortly in this article. The matter of the *trans*-$M_2(T^iPB)_2(O_2CR)_2$ is more simple in as much as the question of charge location in the ^{1}MLCT S_1 state concerns whether only one of the O_2CR ligands or both enjoy receiving the photo-excited electron. To make this matter more readily addressable we have employed RCO_2 ligands where the R group contains a C≡X triple bond (X = N, O or CR). Here the C≡X vibration falls in the region 2200–2000 cm^{-1} and is relatively well separated from other C—C and C—H vibrations. For example, the organometallic carboxylate ligands where R = $(C_6H_5)Cr(CO)_3$ [11] or $(bpy)Re(CO)_3Cl$ [12] both show ν(CO) of the carbonyl ligands moved to lower energy, lower wavenumber in their photo-excited state by an amount comparable to $\Delta\nu(C{\equiv}O)$ predicted by density functional theory for the anions $[trans\text{-}Mo_2(T^iPB)_2(O_2CR)]^-$. This leads us to conclude that the photo-excited states ^{1}MLCT are