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Photophysical Properties of MM Quadruply Bonded Complexes Supported by Carboxylate Ligands, MM = Mo_2, MoW, or W_2

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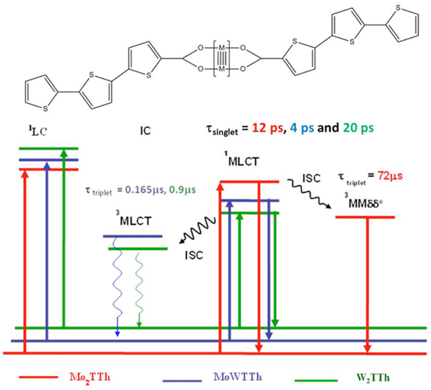
CONSPECTUS



While chemists have extensively studied the photophysical properties of d^6, d^8, and d^{10} transition metal complexes, their early transition metal counterparts have received less attention. Quadruply bonded complexes of molybdenum and tungsten supported by carboxylate ligands have intense metal-to-ligand charge transfer (MLCT) absorptions that arise from the electronic coupling of the metal–metal (MM) δ orbital with the CO_2 π-system. This coupling may in turn be linked to an extended π-conjugated organic functional group. The major interaction is akin to the so-called back-bonding in metal carbonyl complexes. By the appropriate selection of MM, its attendant ligands, and the organic group, this absorption can be tuned to span the visible and near IR range, from 400 to 1000 nm. Consequently, these complexes offer potential as photon harvesters for photovoltaic devices and photocatalysis.

In this Account, we describe recent studies of dinuclear M(II) containing complexes, where M = Mo or W, and show that there are both parallels and disparities to the monomeric transition metal complexes. These early transition metal complexes have relatively long lived excited state singlets when compared to other transition metal complexes. They also often show unusual dual emission (fluorescence and phosphorescence), with singlet (S_1) lifetimes that range from 1 to 20 ps, and triplet (T_1) lifetimes from 3 ns to 200 μs. The fluorescent S_1 states are typically ^{1}MLCT for both M = Mo and W. These extended singlet lifetimes are uncommon for mononuclear transition metal complexes, which typically have very short lived ^{1}MLCT states due to rapid femto-second intersystem crossing rates. However, the T_1 states differ. This phosphorescence is MLCT in nature when M = W, while this emission comes from the $\delta\delta^*$ state for M = Mo. Through time-resolved femtosecond infrared spectroscopy, we can detect the asymmetric stretch of the CO_2 ligand in both the singlet and triplet $\delta\delta^*$ states. Through these analytical methods, we can study how the charge distribution in the singlet and triplet excited states changes over time. In addition, we can detect delocalized or localized examples of MLCT states, which represent class III and I excited state mixed valence in the Robin and Day scheme.

Introduction

Complexes of d^6, d^8, and d^{10} transition metal centers have attracted considerable attention in the recent decades for their photophysical properties.[1] Among the earliest of this class were the $Ru(bpy)_3^{2+}$ salts and their related polypyridyl derivatives. These d^6 metal complexes show metal to ligand charge transfer, MLCT transitions in the region 400–600 nm with ε values on the order of $10-30 \times 10^3$ M^{-1} cm^{-1}. The ^{1}MLCT S_1 state is very short-lived, and intersystem crossing (ISC) gives rise to ^{3}MLCT states, T_1 with lifetimes that typically range from ~100 ns to 5 μs. Initial interest focused on the redox properties of their photoinduced excited states and in photocatalysis.[2] Subsequently, interest moved toward their applications as photon harvestors in dye sensitized photocells following the pioneering work of Graetzel and his co-workers.[3] Related mononuclear complexes of the d^8 (Pt(II), Pd(II), Au(III)) and d^{10} metals (Au(I), Ag(I), Zn(II)) have photoexcited states arising from ligand–ligand $\pi \rightarrow \pi^*$, ^{1}LLCT*, and intraligand charge transfer ^{1}ILCT with d orbital mixing. The major interest in these compounds has been in

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their luminescent properties which most commonly arise from the T_1 states due to fast ISC. Applications for these complexes arise as sensors and as light emitting diodes. Prime examples of the latter are found in Ir(III) complexes supported by aromatic cyclometalated ligands where the emission is both efficient and tunable to cover the visible spectrum. This area has been pioneered by Thompson and Forrest and their co-workers.[4] Platinum(II) containing complexes and oligomers have also been employed as photon harvestors in polymer based bulk-heterojunction photocells.[5] An excellent recent review by Yam and Wong describes these photophysical properties of luminescent d^6, d^8, and d^{10} complexes and emphasizes how excited state tuning can be brought about to avoid lower lying d-d excited states that facilitate fast radiationless relaxation.[1]

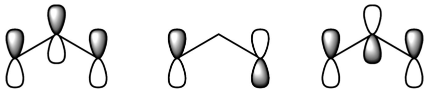
In contrast to the extensive photophysical studies involving d^6, d^8, and d^{10} complexes, the early transition metals have received relatively little attention. Here we describe recent studies of dinuclear M(II) containing complexes, where M = Mo or W, that show some interesting similarities and differences to the monomeric d^6, d^8, and d^{10} complexes mentioned above.

MM Quadruply Bonded Complexes

The discovery of the MM quadruple bond in the d^4-d^4, $Re_2Cl_8^{2-}$ anion heralded a new chapter in transition metal chemistry involving multiple bonds between metal ions.[6] The MM configuration $\sigma^2\pi^4\delta^2$ arises from the mutual overlap of the metal d_{z^2}, (d_{xz},d_{yz}) and d_{xy} orbitals with the metal-chloride bonds being formed from s, p_x, p_y, and d_{x2-y2} orbitals. Subsequently, many d^4-d^4 quadruply bonded complexes having 4-fold symmetry along the MM axis were discovered and much initial attention was devoted to the strength of the δ orbital and the assignment of the singlet $\delta \rightarrow \delta^*$ electronic transition which was generally observed as a relatively weak absorption in the region 450−700 nm.[7] The assignment and the nature of this electronic transition have been studied extensively, and Cotton and Nocera[8] stated that studies of the MM δ orbital had led to "The whole story of the two-electron bond with the δ orbital as a paradigm." However, it was Gray and co-workers[9,10] who first were attracted to the photophysical properties of quadruply bonded complexes and noted that for ions of the type $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ the excited state with electronic configuration $\sigma^2\pi^4\delta^1\delta^{*1}$ should have a staggered geometry as the occupation of the δ^* orbital would lead to a MM bond of order 3 and the lack of the δ bond would relax the preference for the D_{4h} eclipsed geometry. For complexes of the form $Mo_2Cl_4(PR_3)_4$ steric factors favor the eclipsed geometry due to the minimization of steric repulsion involving the bulky PR_3 ligands. These complexes were shown to exhibit fluorescence from the singlet $\delta\delta^*$ state with a negligible Stokes shift and vibronic features associated with ν(MoMo) of the ground state quadruple bond.[10]

Dimetal Carboxylate Complexes

$M_2(O_2CR)_4$. The dimetal tetracarboxylates of formula $M_2(O_2CR)_4$ have a central $M_2(O_2C)_4$ core with D_{4h} symmetry as a result of the four bridging carboxylates.[6] The d^4-d^4 interaction thus leads to the MM $\sigma^2\pi^4\delta^2$ configuration as in other complexes mentioned above but the presence of the CO_2 π-system perturbs this simple MM bonding picture. The carboxylate π orbitals are shown below. The bonding and nonbonding π orbitals, **I** and **II**, respectively, are filled and the C−O antibonding π^* orbital is empty. Both **I** and **III** have the correct symmetry to interact with the filled δ orbital and based on energy and overlap considerations, the most important interaction involves the CO_2 π^* orbital. The nonbonding orbital shown in **II** can interact with the δ^* orbital but only weakly because of the difference in energy and poor overlap.



For $M_2(O_2CR)_4$ compounds with D_{4h} symmetry, the δ orbital transforms as b_{2g} and the four CO_2 π^* orbitals as a_{2g}, e_u, and b_{2g}. The electronic transition from the δ orbital of b_{2g} symmetry to the CO_2 π^* orbital of e_u symmetry is therefore a fully allowed MLCT transition. The energy of the δ orbital lies roughly 0.5 eV higher in energy for related tungsten compounds when compared with their molybdenum homologues.[6] Thus, this ^{1}MLCT transition is notably red-shifted in $W_2(O_2CR)_4$ compounds, and for $M_2(O_2CR)_4$ compounds when the R groups can π-conjugate with the CO_2 π-system, the ^{1}MLCT occurs at lower energy in comparison to when R = alkyl. The MM δ^* orbital lies close in energy to the CO_2 π^* orbitals but only for $Mo_2(O_2CR)_4$ compounds, where R = H or alkyl, is the $^1(\delta \rightarrow \delta^*)$ transition observed. This is nicely seen in the spectra of the $M_2(O_2CR)_4$ complexes shown in Figure 1, where M = Mo or W and R= ^{t}Bu or Ph.[11] In all cases but for $Mo_2(O_2C^tBu)_4$, the intense ^{1}MLCT to the carboxylate ligands masks the weak $^1(\delta \rightarrow \delta^*)$ transition. Indeed, even for $Mo_2(O_2C^tBu)_4$, the $^1(\delta \rightarrow \delta^*)$ transition is dwarfed by the magnitude of the fully allowed M_2 δ to CO_2 π^* MLCT transition. For all the compounds under considera tion, the HOMO (highest occupied molecular orbital) is the M_2 δ orbital and, with the exception of various Mo_2-carboxylates the LUMO (lowest unoccupied molecular orbital) is a carboxylate π^*. This HOMO to LUMO electronic transition dominates the absoption spectra of these compounds.

With irradiation into the ^{1}MLCT bands of the carboxylate ligands, these complexes show weak solvent dependent fluorescence from the ^{1}MLCT states or in the case of $M_2(O_2CR)_4$ where R = alkyl from the $^1(\delta\delta^*)$ state. In addition, phosphorescence is commonly observed, and for molybdenum complexes this is almost invariably from the $^3(\delta\delta^*)$ state. This emission is solvent independent and shows vibrational structure due to ν(MoMo) $\sim$ 400 cm^{-1}. For tungsten containing complexes, emission from the $^3(\delta\delta^*)$ state is not normally observed as the ^{3}MLCT state lies lower in energy.

However, for the series of compounds MM(T^{i}PB)$_4$, where T^{i}PB is 2,4,6-triisopropylbenzoate and MM = Mo_2, MoW, and W_2, we see two important trends.[12] (1) The energy of the ^{1}MLCT follows the order $Mo_2 > MoW > W_2$. This reflects the relative energies of the MM δ orbital and follows what can be seen in their oxidation potentials as measured by electrochemical studies. (2) The energy of the emission from the T_1,$^3(\delta\delta^*)$ state is in the order $W_2 > MoW > Mo_2$. This is again a consequence of the rise in energy of the δ and δ^* orbitals with increasing tungsten content, and the energy of the $^1(\delta \rightarrow \delta^*)$ transition is relatively insensitive to the metal in the MM moiety. The absorption spectra and the emission from the ^{3}MM$\delta\delta^*$ states are shown in Figure 2.

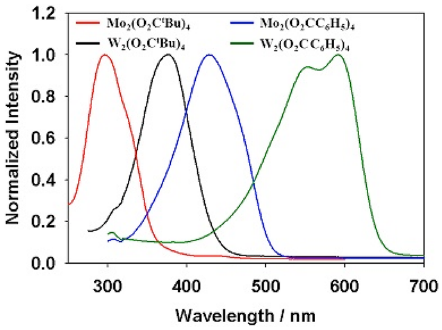


FIGURE 1. Electronic absorption spectra recorded in THF at room temperature for the titled compounds. (Reproduced with permission from ref 11. Copyright 2012 American Chemical Society.)

A series of dimolybdenum aryl carboxylates $Mo_2(O_2CAr)_4$, where Ar = phenyl, 1- and 2-naphthalene, 9-anthracene, and 1- and 2-pyrene, was prepared and shown to exhibit intense ^{1}MLCT absorptions ($\varepsilon \sim$ 50 000 M^{-1} cm^{-1}) in the visible region.[13,14] All of these complexes showed weak emission from the ^{1}MLCT state, and transient absorption spectroscopy indicated lifetimes on the order of 10 ps. Much longer lived triplet states, T_1, were observed with $\tau \sim 50\ \mu$s. Originally the triplet state was considered to be ^{3}MLCT, but further work on these and related complexes, vide infra, indicated that the lowest energy triplet state was ^{3}MoMo $\delta\delta^*$. The related tungsten complexes $W_2(O_2CAr)_4$, where Ar = Ph or 2-naphthyl, had T_1 states that were ^{3}MLCT with significantly shorter lifetimes, $\tau \sim$ 10–100 ns.

The compounds $M_2(O_2C^tBu)_4$ and $M_2(O_2CPh)_4$, where M = Mo or W, were also examined by femtosecond time-resolved infrared (fs-TRIR) spectroscopy in the region of $\nu_{as}(CO_2)$, namely, 1500–1600 cm^{-1} in tetrahydrofuran solution.[11] IR absorptions at 1549 cm^{-1} (M = Mo) and 1540 cm^{-1} $W_2(O^tBu)_6$) are assigned to the ^{3}MM$\delta\delta^*$ state. Removal of the electron from the δ^2 orbital reduces the magnitude of the back-bonding which in turn leads to a strengthening of the C–O π-bonding and an increase in the C–O stretching frequency. In relation to the $\nu_{as}(CO_2)$ of the ground state, which occurs as a bleach in the fs-TRIR spectrum, the shift to higher energy is 31 and 60 cm^{-1} for

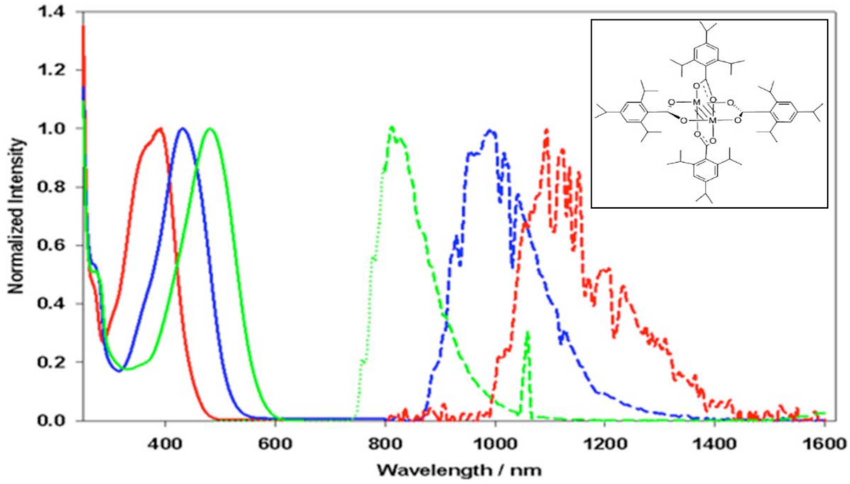


FIGURE 2. Absorption spectra (solid lines) and phosphorescence (broken lines) in THF solution, where MM = Mo_2 (red), MoW (blue), and W_2 (green). (Taken with permission from ref 12. Copyright 2009 American Chemical Society.)

TABLE 1. Selected Photophysical Properties of $M_2(O_2CR)_4$ Compounds

compd	λ_{max}/nm[a]	S_1, τ_1/ps[b]	T_1, τ_2/μs[c]	ref
$Mo_2(O_2CPh)_4$	430	12.9(3)	58(1)	11
$W_2(O2CPh)_4$	590	0.4(1)	0.06(1)[d]	11
$Mo_2(T^iPB)_4$	390	6.0(5)	43(4)	12
$MoW(T^iPB)_4$	430	0.45(2)	27(2)	12
$W_2(T^iPB)_4$	480	0.37(2)	1.6(1)	12
$Mo_2(O_2C\text{-}9\text{-anthracene})_4$	745	10(1)	76(1)	13, 14

[a] ^{1}MLCT absorption in THF (±5 nm). [b] ^{1}MLCT. [c] ^{3}MM$\delta\delta^{**}$. [d] ^{3}MLCT.

$Mo_2(O_2C^tBu)_4$ and $W_2(O_2C^tBu)_4$, respectively, and 28 cm^{-1} for $Mo_2(O_2CPh)_4$. The notably greater shift for M = W is most likely due to the enhanced degree of W_2 δ to CO_2 back-bonding. The spectra for $W_2(O_2CPh)_4$ are notably different and arise from the ^{3}MLCT state and not the ^{3}MM$\delta\delta^*$ state.

For $Mo_2(O_2CBu^t)_4$, the lowest energy singlet state is $^1\delta\delta^*$ (as can be seen in Figure 1) and this allowed us to examine $\nu_{as}(CO_2)$ by fs-TRIR spectroscopy.[11] This showed an initial absorption at 1520 cm^{-1} that decayed within 20 ps to give rise to the longer lived absorption at 1549 cm^{-1}. Although it is not intuitively obvious why the singlet and triplet states should have different values of $\nu_{as}(CO_2)$, since in both states an electron is removed from the δ orbital, it should be remembered that the two states have notably different energies and that the singlet has a different character from the triplet state. Whereas the $^3(\delta\delta^*)$ state is covalent, the $^1(\delta\delta^*$state) is primarily ionic.[7,8] However, another possibility is that in the singlet state the back-bonding involves all four CO_2 π^* orbitals, whereas in the triplet state it is localized. This matter needs further investigation.

Photophysical properties of some homoleptic compounds of formula $M_2(O_2CR)_4$ are summarized in Table 1.

$[(RCO_2)_3M_2]_2$ (μ-$O_2CR^1CO_2$) Compounds

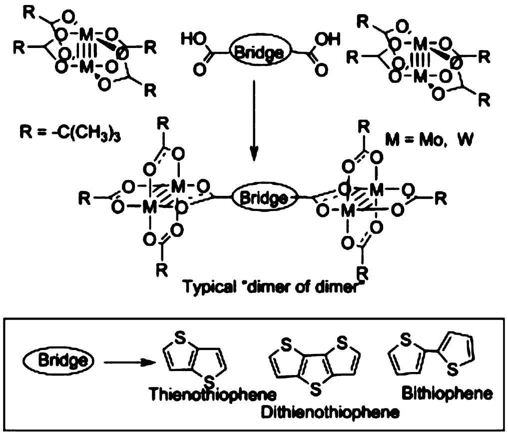
The reaction between the homoleptic compounds $M_2(O_2CR)_4$ and organic dicarboxylic acids (1 equivalent) in hydrocarbon solvents leads to the formation of the titled bridged tetranuclear complexes (R = Bu^t or T^iPB). When the bridge R^1 contains a conjugated π-system that is directly coupled to the carboxylate groups, the two dinuclear centers are electronically coupled by $M_2\delta$ to bridge π/π^* to $M_2\delta$ interactions. Complexes of this type, so-called "dimers of dimers" have been studied extensively in terms of the nature of their mixed valence states that are formed upon oxidation.[15] These compounds are intensely colored due to metal-to-bridge charge transfer and typically show strong thermochromism in solvents such as 2-methyltetrahydrofuran. The latter arises because the extent of metal-to-bridge bonding depends on the dihedral plane between the CO_2 and the bridging group.

TABLE 2. Selected Photophysical Properties of $[M_2(O_2CBu^t)_3]_2$(bridge) Compounds

compd					
M_2	bridge	λ_{max}/nm[a]	S_1, τ_1/ps[b]	T_1, τ_2/μs[c]	ref
Mo_2	O_2CCO_2	460	4.5(1)	36(1)	21
MoW	O_2CCO_2	580	1.8(1)	2.2(1)	21
W_2	O_2CCO_2	740	3.5(1)	0.08(1)[d]	21
Mo_2	TT	525	7.9(1)	69(2)	20
Mo_2	DTT	530	1.1(1)	60(2)	20
Mo_2	BTh	520	8.6(1)	72(2)	20
W_2	DTT	795	12(1)	2.8(1)d	20
W_2	BTh	790	14(1)	3.6(1)d	20

[a] MLCT absorption in THF (±5 nm). [b] ^{1}MLCT. [c] ^{3}MM$\delta\delta^*$. [d] ^{3}MLCT.

SCHEME 1. Synthesis of the Bridged Quadruply Bonded Complexes



This has been well documented for the bridging groups oxalate,[16,17] terephthalate,[18] and 2,5-thienyldicarboxylate.[19] Within these series of compounds, those with fused and nonfused 2,2′-linked thiophenes were examined by femotosecond and nanosecond transient absorption spectroscopy: $[(^tBuCO_2)_3M_2]_2(\mu$-bridge), where bridge = thienothiophene dicarboxylate, TT; dithienothiophene dicarboxylate, DTT, and bithiophene dicarboxylate, BTh.[20] These bridges are shown below in Scheme 1 along with their respective syntheses.

These compounds showed intense MLCT absorptions in the range 450−650 nm for M = Mo and from 600 to 850 nm for M = W in addition to the thienyl $\pi\pi^*$, ^{1}LLCT bands at 300−400 nm. The molybdenum compounds showed dual emission with a bridge independent triplet emission at ~1100−1200 nm with lifetimes ~ 70 μs. The related tungsten complexes showed fluorescence at lower energy than their molybdenum analogues but did not show phosphorescence, probably because the T_1 states were at sufficiently low energy that radiationless decay mechanisms are predominant.

Transient absorption spectroscopy, fs and ns, provided reliable estimates of the lifetimes of the S_1 and T_1 states, and these along with absorption data are summarized in Table 2.

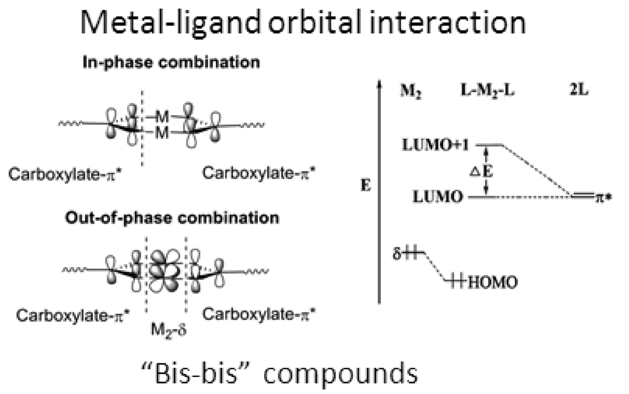


FIGURE 3. Simplified frontier MO diagram indicating the interaction of the M_2 δ orbital and the two *trans* π-acceptor ligands.

Of note here is that ^{1}LLCT excitation leads to ultrafast (<350 fs) $S_n \rightarrow S_1$ (^{1}MLCT) internal conversion which is followed by a relatively slow $S_1 \rightarrow T_1$ ISC (~10 ps). It is interesting to see that the lifetimes of the S_1 states are comparable for both the 4d and 5d elements with those of the 5d element being longer in certain instances. The T_1 lifetimes of the tungsten complexes were ~4 μs, notably shorter than the molybdenum analogues which probably reflects on the relative energy of T_1 states in accordance with the energy gap law. One final note is that the Stokes shifts of the bithienyl containing compounds were notably larger than those of the fused thienyl containing compounds. This probably arises from the difference in the dihedral angles of the two thienyl groups in the ground and excited state geometries. The preference for the planar geometry is notably favored in the excited state.

Oligomers: $[Mo_2(T^iPB)_2\ (O_2C{-}Th_n{-}CO_2)]x$

The reaction between $Mo_2(T^iPB)_4$ and 1 equiv of the 2,2′(2,5)-linked thienyldicarboxylic acids leads in toluene or tetrahydrofuran (THF) solutions to oligomers of the approximate formula noted above, where $n = 3$ or 5 and $x \sim 4{-}8$.[22] The species present in solution are in a dynamic equilibrium and have the predominant *trans* pattern of substitution. This is favored by the bulky steric demands of the T^iPB ligands, but there is no doubt some *cis* substitutions and end groups of T^iPB and O_2CTh_nCOOH are present. The degree of oligomerization $x \sim 4{-}8$ is estimated by vapor phase osmometry, but there are some shorter chains and molecular loops as seen by MALDI-TOF mass spectrometry. The species present in solution are soluble in THF and form thin films by spin-coating. The photophysical properties of the species in THF and in thin films are very similar and resemble those described above for the "dimers-of-dimers". The ^{1}MLCT absorptions of the thin films are broadened with respect to those obtained in THF solution, most probably because of the wide variety of dihedral angles along the thienyl chains. Both in solution and as thin films, dual emission is observed from the ^{1}MLCT and the T_1 state, ^{3}MoMo$\delta\delta^*$ at ~1100 nm. The lifetimes of the T_1 states in the thin films are ~200 μs, notably longer than those in solution.[23] This is possibly because in thin films triplet−triplet anihilation by diffusion is not possible. The thin films for $n = 5$, when fabricated in a device, showed electroluminescence from the S_1 state.[22]

trans-Disubstituted dicarboxylates: $M_2L_2(O_2CR)_2$

Compounds of this type having two *trans*-ligands, L, that are good π-acceptors allow a mixing of the M_2 δ and the CO_2 π^* orbitals of the out-of-phase combination. This leads to a splitting in energy of the in-phase and out-of-phase ligand π^* systems as shown schematically in Figure 3. The energy splitting of the two π^* systems, that are generally the LUMO and LUMO+1, is a relative measure of the electronic coupling of the ligands. Reduction to form *trans*-$M_2L_2(O_2CR)_2^-$ generates mixed valence ligands[24] that can be classified according to the Robin and Day scheme.[25] The class III ions, those where the charge is delocalized over both ligands, show low energy charge resonance transitions akin to those of class III mixed valence metal centered cations of the dimers of dimers.[26] In their neutral states, these complexes also show intense ^{1}MLCT transitions in the visible region of the spectrum arising from the promotion of an electron from the M_2 δ orbital to the in-phase π^* combination, typically the LUMO except for certain Mo_2-containing compounds where the $^1\delta\delta^*$ state is calculated to be lower in energy. However, even when the $^1\delta\delta^*$ state is the lowest state, the intense ^{1}MLCT absorption masks its observation.

These complexes typically show broad ^{1}MLCT transitions in THF at room temperature because of the Boltzmann thermal population of a variety of O_2C-ring−ring conformations. However, in 2-methyltetrahydrofuran, the compounds show marked thermochromism upon lowering the temperature as the planar geometry, which allows for maximum $L\pi^*{-}M_2\delta{-}L\pi^*$ bonding, becomes more prevalent. This is nicely seen in the spectra of *trans*-$M_2(T^iPB)_2(O_2C{-}CH{=}CH\text{-}2\text{-}C_4H_3S)_2$ compounds whose room temperature and ℓ.N_2 temperature spectra are compared in Figure 4.[27] In the solid-state the two vinylthienylcarboxylates form a plane that contains the two M_2 atoms, allowing for maximum $L\pi$-$M_2\delta$-$L\pi$ conjugation, while the aryl rings of the two T^iPB ligands

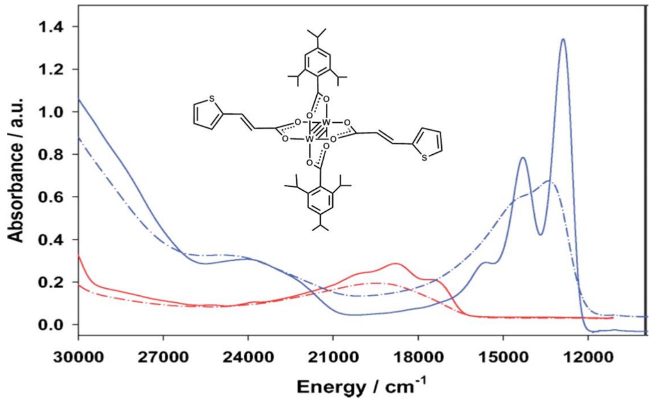


FIGURE 4. Absorption spectra for the vinylthienyl ligated complexes at room temperature in THF (dotted line) and at 77 K in 2-methyltetrahydrofuran (solid line) for M = Mo (red) and M = W (blue). (Taken from ref 27. Copyright 2011 Royal Society of Chemistry).

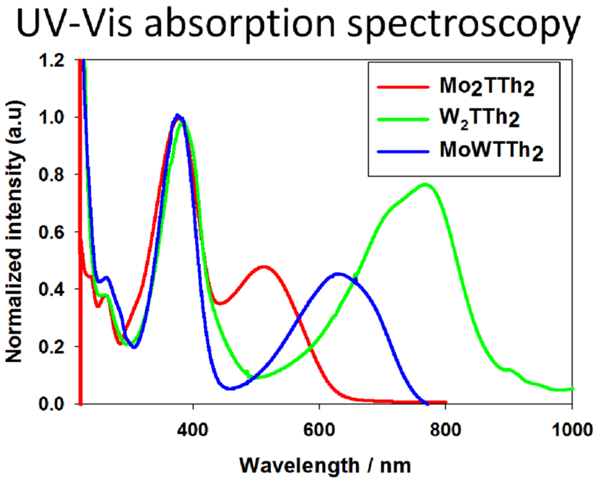


FIGURE 5. Room temperature absorption spectra in THF for the compounds *trans*-MM(T^{i}PB)$_2$(TTh)$_2$ where TTh is terthienyl carboxylate. (Taken with permission from ref 28. Copyright 2009 American Chemical Society.)

are twisted ~80° out of the plane of their CO_2 groups which minimizes their interaction with the M_2 δ orbital.

The influence of the energy of the MM δ orbital is nicely seen in the absorption spectra of the series *trans*-MM(T^{i}PB)$_2$(O$_2$CTTh)$_2$ that are shown in Figure 5.[28] The O_2CTTh ligand is shown in Figure 6. The ^{1}LLCT* transition of the terthienyl ligands occurs at ~400 nm for each compound and is not influenced by the nature of the MM moiety. The ^{1}MLCT transition, however, moves to lower energy with increasing W content in the MM moiety and is in all cases very broad and relatively featureless at room temperature. Upon cooling in 2-methyltetrahydrofuran, this absorption shifts to lower energy, sharpens, and shows vibronic features associated with $\nu(CO_2)$ akin to that seen in Figure 4.

Many of the compounds of the form *trans*-M$_2$(T^{i}PB)$_2$(O$_2$CR)$_2$ have been examined in solution by transient absorption spectra and steady state emission. In all cases, both the S_1 and T_1 states have been detected. The S_1 states are relatively short-lived with lifetimes ranging from 1 to 20 ps. These lifetimes tend to increase with M_2-R centroid distance and are not dissimilar for M = Mo and W despite the larger spin orbit coupling of the heavier 5d metal. The triplet lifetimes vary with MM content. For Mo$_2$-containing complexes, the T_1 state can be assigned as ^{3}MoMo$\delta\delta^*$ based on its uniform and solvent independent emission at ~1100 nm, with τ in the range 10–100 μs. The MoW- and W$_2$-containing compounds have notably shorter T_1 lifetimes, 10–100 ns, which are assigned to ^{3}MLCT states, many of which are not emissive.

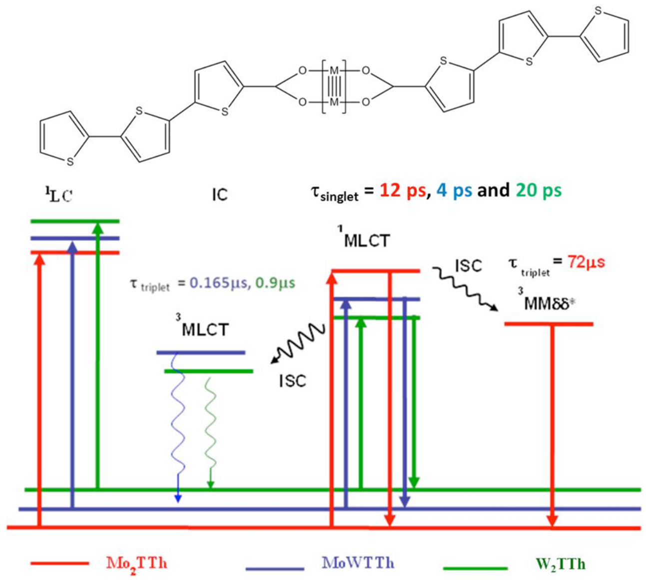


FIGURE 6. Generalized Jablonski diagram depicting the photophysical properties of the compounds *trans*-MM(T^{i}PB)$_2$(TTh)$_2$ where TTh is terthyenylcarboxylate.

Table 3 collects data for the photophysical properties of a number of compounds of this type, and for the *trans*-MM(T^{i}PB)$_2$(O$_2$CTTh)$_2$ compounds their spectroscopic and photophysical properties are summarized in the Jablonski diagram shown in Figure 6.

Time-Resolved Infrared Spectroscopy

The lifetimes of the singlet and triplet states are suitable for time-resolved infrared, TRIR, spectroscopic studies that can probe the detailed nature of the charge distribution in these photoexcited states. For example, for compounds of the type *trans*-M$_2$(T^{i}PB)$_2$L$_2$ photoexcitation removes an electron from the M_2 δ orbital and places it on the π-acceptor ligands L. The question that then arises is whether this is delocalized over both *trans*-ligands, L, or localized on one. These states represent the two limiting situations of excited state mixed valence.[32] In order to examine these possibilities, we prepared the compounds *trans*-$M_2(T^iPB)_2(O_2CC_6H_4\text{-}4\text{-}CN)_2$ and *trans*-$M_2(O_2CMe)_2[(Pr^iN)_2CC{\equiv}CPh)]_2$, where M = Mo and W.[33] In the latter compound, the amidinate ligands $(Pr^iN)_2CC{\equiv}CPh$ are the π-acceptors and are involved in the lower energy ^{1}MLCT transition and the C≡C unit provides a means to monitor the degree of charge delocalization. Similarly, the value of ν(C≡N) in the *para*-cyanobenzoate complexes provides an effective IR reporter group.

The FTIR spectra for the *para*-cyanobenzoates in the region of ν(C≡N) are shown in Figure 7. In both the Mo_2- and W_2-containing compounds, we see at short times an IR signal assignable to ν(C≡N) that is shifted to lower energy by ~60 cm^{-1}. This excited state absorption decays within picoseconds, consistent with the lifetime of the ^{1}MLCT state as determined by transient absorption spectroscopy for M = W. The triplet state for M = Mo has a lifetime of μs and emits at ~1100 nm consistent with the ^{3}MoMo$\delta\delta^*$ state. This state has no apparent new IR absorption assignable to ν(C≡N), whereas the long-lived triplet state for M = W shows ν(C≡N) at a value comparable to that of the ^{1}MLCT state. The magnitude of the shift in ν(C≡N) to lower energy is consistent with those calculated for the anions *trans*-$M_2(O_2CH)_2(O_2CC_6H_4CN)_2^-$ based on DFT calculations. This leads us to conclude that the MLCT states are fully delocalized over both *para*-cyanobenzoate ligands.

TABLE 3. Selected Photophysical Properties of *trans*-$M_2(T^iPB)_2L_2$ Compounds

compd					
M_2	L_2	λ_{max}/nm[a]	S_1, τ_1/ps[b]	T_1, τ_2/μs[c]	ref
Mo_2	$O_2CC_4H_3O$	420	5.3(1)	62(2)	29
W_2	$O_2CC_4H_3O$	460	2.5(3)	$3{-}10 \times 10^{-3d}$	29
Mo_2	$O_2CC_4H_3S$	430	4.1(1)	77(1)	29
W_2	$O_2CC_4H_3S$	520	0.59(1)	$3{-}10 \times 10^{-3d}$	29
Mo_2	$O_2CC_4H_3Se$	555	1.5(1)	67(1)	29
W_2	$O_2CC_4H_3Se$	635	0.9(1)	$3{-}10 \times 10^{-3d}$	29
Mo_2	O_2CTh_2	500	7(1)	83(1)	23
Mo_2	O_2CTh_3	450	12	72(1)	28
MoW	O_2CTh_3	620	4	0.17(1)[d]	28
W_2	O_2CTh_3	810	20	0.9(1)[d]	28
Mo_2	Azu[e]	675	7.6(1)	0.26(1)[d]	30
W_2	Azu[e]	900	4.5(1)	$3{-}10 \times 10^{-3d}$	30
Mo_2	OSCTh	630	1.99(6)	51	31
W_2	OSCTh	740	0.43(1)	$3{-}10 \times 10^{-3d}$	31

[a] ^{1}MLCT absorption in THF (±5 nm). [b] ^{1}MLCT. [c] ^{3}MM$\delta\delta^*$. [d] ^{3}MLCT. [e] Azu = 6-carboethoxy-2-carboxylateazulene.

The TRIR spectra for the amidinate complexes are shown in Figure 8. Again, for molybdenum, we see a short-lived infrared absorption assignable to ν(C≡C) shifted ~200 cm^{-1} to lower energy assignable to the S_1 state. On the nanosecond time scale, there is no detectible ν(C≡C) IR stretching vibration and the triplet state is assigned ^{3}MoMo$\delta\delta^*$. There is also a less intense short-lived IR band at higher energy shifted only ~40 cm^{-1} from the ground state IR band at ~2200 cm^{-1}. The shift in ν(C≡C) calculated for the anion *trans*-$Mo_2(O_2CH)_2[(NPr^i)_2CC{\equiv}CPh)]_2^-$ is 120 cm^{-1} which is much smaller than that observed for the intense ν(C≡C) of the ^{1}MLCT state. It is difficult to reconcile the appearance of two IR bands with a fully delocalized state. Our interpretation is that the photoexcited state has the negative charge principally localized on one of the $(NPr^i)_2CC{\equiv}CPh$ ligands with some smaller charge delocalization to the other. Moreover, the steady state emission

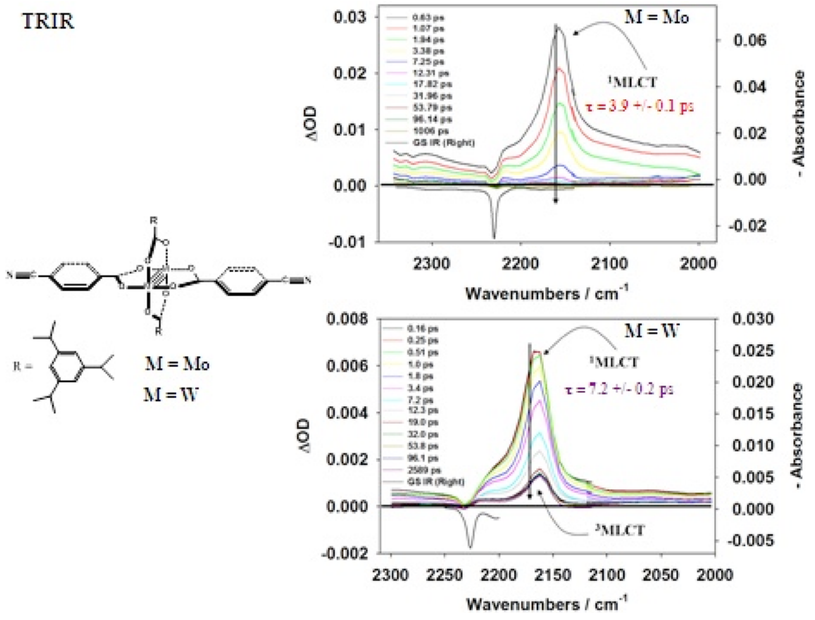


FIGURE 7. TRIR spectra in the C≡N stretching region of the compounds indicated. (Taken from ref 33. Copyright 2011 National Academy of Sciences, USA).

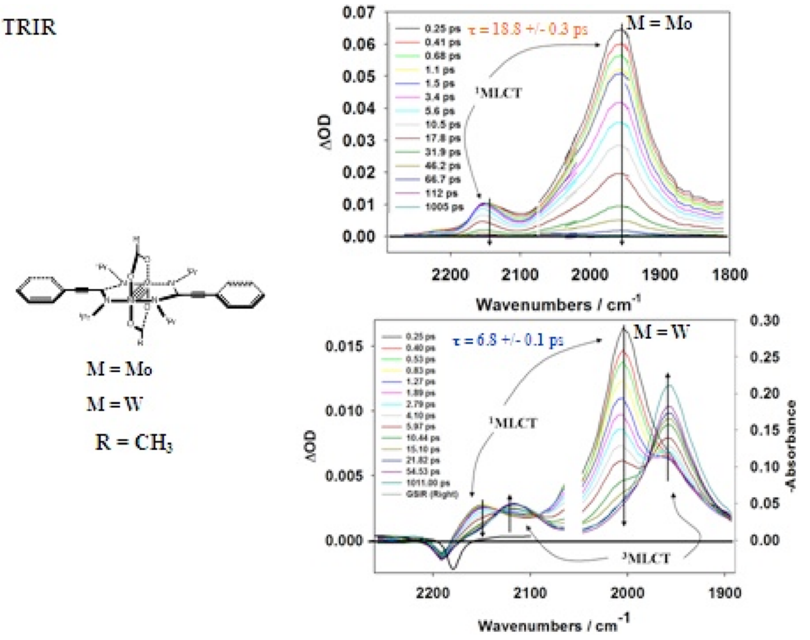


FIGURE 8. TRIR spectra for the compounds indicated in the region of the alkynyl stretching region. (Taken from ref 33. Copyright 2011 National Academy of Sciences, USA).

spectra from the S_1 state show a solvent dependence consistent with a polar excited state.

The initial short-lived TRIR absorptions for the related tungsten containing complexes are similar in showing a strong ν(C≡C) shifted ~200 cm^{-1} to lower energy and a lesser intense absorption shifted by ~40 cm^{-1}. However, as this decays new ν(C≡C) absorptions grow in for the longer lived ^{3}MLCT state and these are shifted to even lower energy. Again, we interpret this as being due to charge being principally localized on one of the ligands with a small charge spillover toward the other. However, there is a clear difference between the ^{1}MLCT and the ^{3}MLCT states with the latter having greater electron density on the C≡C π^* orbitals. This finding is consistent with the view that singlet excitons are more diffuse, more delocalized in contrast to their triplet counterparts which are more compact.

Why should the ^{1}MLCT state be delocalized for the *para*-cyanobenzoates and localized for the amidinates? The answer to this question would seem to lie in the energy of the HOMO−LUMO gap and the interchange of the linker, CO_2 versus $C(NR)_2$. The *para*-cyanobenzoates have notably lower ^{1}MLCT absorptions which are essentially solvent independent. The greater mixing of the M_2 δ and the out-of-phase Lπ^* combination favors delocalization in the excited state.

Another interesting pair of compounds is *trans*-$M_2(T^iPB)_2$-(O_2CC≡C-9-anthracene)$_2$.[34] These compounds (M = Mo and W) show ν(C≡C) ~ 2200 cm^{-1} and have broad and intense ^{1}MLCT transitions centered at 550 nm (M = Mo) and 800 nm (M = W). Upon photoexcitation into the ^{1}MLCT bands both compounds show new short-lived ν(C≡C) vibrations: 2110 (M = Mo) and 2150 cm^{-1} (M = W) with lifetimes of 10 and 18 ps, respectively, consistent with the lifetimes of the respective S_1 states determined by TA spectroscopy. The calculated shifts for ν(C≡C) upon reduction are ~100 cm^{-1} which leads us to conclude that for both compounds the S_1 ^{1}MLCT states have the negative charge delocalized over both ligands. The lifetimes of the T_1 states are 83 μs (M = Mo) and 3 ns (M = W), and in both states there is no evidence of ν(C≡C) in the TRIR spectrum. The molybdenum complex does show $\nu_{as}(CO_2)$ at 1540 cm^{-1} which together with the lifetime and emission at 1100 nm is consistent with the T_1 state being ^{3}MoMo$\delta\delta^*$. The T_1 state for the tungsten complex is undoubtedly ^{3}MLCT, and the absence of a detectible band assignable to ν(C≡C) is at first surprising. However, the TA spectrum of the T_1 state resembles that of an anthracene radical anion, and in the TRIR spectrum in the range 1200−1000 cm^{-1} we also have detected vibrational modes characteristic of the anthracenyl anion. We therefore conclude that for the tungsten complex the negative charge in the ^{3}MLCT state rests largely on an anthracene ligand.

Concluding Remarks

The quadruply bonded complexes of molybdenum and tungsten supported by carboxylate ligands show intense

^{1}MLCT absorptions that can be tuned to traverse the range 400−1000 nm by the appropriate selection of the metal and carboxylate. These complexes show relatively long-lived excited state singlets when compared to many transition metal complexes studied to date and are also unusual in often showing dual emission (fluorescence and phosphorescence). In some ways, they are complementary to the photophysical properties of *trans*-$PtL_2(alkynyl)_2$ complexes that have ^{1}LLCT absorptions with Pt 5d orbital mixing and similarly show dual emission from S_1 and T_1 states with lifetimes of nanosecond and microsecond spans, respectively. The lifetimes of the S_1 and T_1 states allow the use of fs- and ns-TRIR studies to probe the nature of the charge distribution in the singlet and triplet excited states and how this changes with time. This continues to be a topic of ongoing work as is their potential for photon harvesting for photovoltaic devices and photocatalysis.

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BIOGRAPHICAL INFORMATION

Malcolm Chisholm was born in Bombay to Scottish parents in 1945 and educated in England, B.Sc. 1963, Ph.D., 1960, London University. After postdoctoral studies at the University of Western Ontario and faculty appointments at Princeton and Indiana University, he moved to the Ohio State University in 2000 where he is Distinguished University Professor and Associate Director for the Institute of Materials Research. He has interests in Inorganic, Organometallic, and Materials Chemistry, is author of ~650 publications ,and is a member of the National Academies of Sciences (U.S.A., U.K., and Germany).

Terry L. Gustafson was born in 1953 in Brainerd, MN. He received his B.S. in chemistry and physics at Moorhead State University (MN) in 1975 and his Ph.D. in chemistry from Purdue University in 1979. He worked for nine years at Sohio Research and Development (later BP America Research and Development) before joining the faculty at The Ohio State University in 1989, where he is currently serves as Professor and the Director of the Center for Chemical and Biophysical Dynamics in the Department of Chemistry. He has been a Distinguished Visitor at the University of Auckland (2012) and a Visiting Professor in Japan (1994) and France (1999). His current research interests include the investigation of charge and energy transfer at interfaces and fundamental studies of excited state photophysics and photochemistry. He serves on the International Organizing Committee for the International Conference on Time-Resolved Vibrational Spectroscopy and on the Editorial Advisory Committee for the *Journal of Raman Spectroscopy*. He was presented with the *John T. Mount and Ruth Weimer Mount Award* in 2000 for outstanding service to The Ohio State University and its students. In 2001 he was presented with the *Honors Faculty Service Award* by the Colleges of the Arts and Sciences and the *Outstanding Teaching Award* by the Arts and Sciences Student Council.

Claudia Turro received her B.S.with Honors in 1987 from Michigan State University. She worked with Daniel G. Nocera and George E. Leroi at Michigan State University and received her Ph.D. in 1992. She was awarded a Jane Coffin Childs Memorial Fund for Medical Research Postdoctoral Fellowship to continue postodoctoral work at Columbia University with Nicholas J. Turro from 1993 to 1996. She has been a faculty member at The Ohio State University since 1996 and has been serving as Vice Chair for Graduate Studies since 2011. She received the Early CAREER Award by the National Science Foundation in 1998, the Arnold and Mabel Beckman Young Investigator Award in 1999, was named a 2010 Fellow of the American Chemical Society, and a 2011 Fellow of the American Association for the Advancement of Science. She was elected President of the Inter-American Photochemical Society (2012-2014) and Chair of the Bioinorganic Subdivision of the Division of Inorganic Chemistry of the American Chemical Society (2012-2015).

FOOTNOTES

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The authors declare no competing financial interest.

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