Mixed valence complexes involving MM quadruple bonds \((M=\text{Mo or W})\)

BY MALCOLM H. CHISHOLM*

The Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA

The MM quadruple bond of configuration MM \(\sigma^2\pi^4\delta^2\) is redox active and in many ways ideally suited for studies of mixed valency when two or more such centres are linked by a bridging ligand. In this account, the mechanism of electronic coupling is examined for complexes of the type \([L_3M_2\text{bridge}M_2L_3]^{0/+}\) where L, a pivalate; bridge, a dicarboxylate or related ligand and M, Mo or W. The represented examples allow us to probe electronic factors close to the class II/III border and readily distinguish between electron and hole transfer in the superexchange mechanism. The potential for mixed valence organic radical anions mediated by the M2 centre is also raised and one specific example of class III behaviour is described.

Keywords: molybdenum; tungsten; quadruple bonds; carboxylate ligands

1. Introduction

The year 2004 marked the fortieth anniversary of the discovery of the MM quadruple bond in the \(\text{Re}_2\text{Cl}_8^2-\) anion (Cotton et al. 1964). Since that time, the chemistry of complexes containing MM multiple bonds has formed an important chapter in modern coordination chemistry (Cotton et al. 2005). In 1989, we set out to prepare polymers incorporating MM quadruple bonds as exemplified by the schematic shown in I where \(\sim\sim\sim\) represents a bridging ligand (Cayton & Chisholm 1989; Cayton et al. 1991a), and this project continues to be a focal point of my group.

\[
\begin{array}{c}
\sim\sim\sim[M_2] \sim\sim\sim[M_2] \sim\sim\sim \\
\text{n}
\end{array}
\]

In order to ascertain the influence of both the M2 unit and the organic bridging ligand, studies of model compounds such as dimers of dimers, II, or dinuclear complexes with ‘arms or wings’, III, have proved most useful in anticipating the properties of I (Chisholm 2007).

\[
\begin{array}{c}
[M_2] \sim\sim\sim[M_2] \\
\sim\sim\sim[M_2] \sim\sim\sim
\end{array}
\]

II

III

*chisholm@chemistry.ohio-state.edu

One contribution of 15 to a Discussion Meeting Issue ‘Mixed valency’.
The electronic coupling of the organic moiety and the dinuclear unit arises from the frontier orbital interactions of the $\text{M}_2\sigma^2\pi^4\delta^2$ orbitals and the $\pi$-system of the organic moiety represented by $\text{M}_2\sigma^2\pi^4\delta^2$. The electronic coupling occurs in the ground states of these molecules as well as in their photoexcited states and their oxidized or reduced forms. The latter represent the II and III mixed valence states and form the topic of this article.

The $\text{MM}$ quadruple bond of electronic configuration $\text{M}_2\sigma^2\pi^4\delta^2$ is in many ways ideal for studying mixed valence. For example, in the chemistry of molybdenum and tungsten, oxidation of the quadruple bond leads to an $\text{M}_2\sigma^2\pi^4\delta^1$ unit of electronic configuration $\text{MM}\sigma^2\pi^4\delta^1$ which is a mixed valence ion of class III characteristics on the Robin & Day (1967) Scheme. These ions have well-defined structural and spectroscopic features that are readily distinguished from their $\text{MM}$ quadruply bonded counterparts. Owing to the lanthanide contraction, molybdenum and tungsten are of almost identical size. Also they have very similar metal-ligand bond strengths and solvation energies. Each metal exists in a variety of naturally occurring isotopes, the majority of which have no nuclear spin, $I=0$, but some do: $^{95/97}\text{Mo}, I=5/2$ with approximately 25% combined natural abundances and almost identical magnetic moments and $^{183}\text{W}, I=1/2$, 14.5% natural abundance. The electron paramagnetic resonance (EPR) spectra of the $\text{M}_2(\text{O}_2\text{CBu}^\prime)_4\pi^+$ ions, $\text{M}=$ Mo and W and $\text{MoW}(\text{O}_2\text{CBu}^\prime)_4\pi^+$ are shown in figure 1 and are illustrative of

Figure 1. (a) Solution electron paramagnetic resonance (EPR) spectra of (i) $\text{Mo}_2(\text{O}_2\text{CBu}^\prime)_4\pi^+$ and (ii) $\text{W}_2(\text{O}_2\text{CBu}^\prime)_4\pi^+$ in dichloromethane at 210 K and (b, (i)) $\text{MoW}(\text{O}_2\text{CBu}^\prime)_4\pi^+$ in THF at 225 K. Adapted with permission from Chisholm et al. (2005a).

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the power of EPR spectroscopy in aiding in the study of mixed valence complexes derived from II and III (Chisholm et al. 2005a). First, in each instance there is a central resonance for the isotropic spectrum that is well differentiated from those of organic radicals: $g \sim 1.9$ for $M = \text{Mo}$; $g \sim 1.8$ for $M = \text{W}$. This is flanked by a hyperfine spectrum with $A_0 \sim 28$ G for $M = ^{95/97}\text{Mo}$ and $A_0 = 51$ G for $M = ^{183}\text{W}$. For the $\text{MoW(O}_2\text{CBu}^\dagger\text{)}_5^+$ ion, the hyperfine coupling to $^{95/97}\text{Mo}$, $A_0 = 44$ G and to $^{183}\text{W}$, $A_0 = 31$ G. With respect to the homonuclear ions $\text{Mo}_2^{5+}$ and $\text{W}_2^{5+}$, the changes in $A_0$ values reflect the polarization of the MoW$\delta$ orbital. The unpaired electron is roughly 70% Mo $d_{xy}$ and 30% W $5d_{xy}$ in character indicating the polarization of the MoW$\delta$ orbital towards the more electronegative Mo atom.

2. Dimers of dimers

The typical preparation of complexes of type II has involved the reaction of a dicarboxylic acid or equivalent with a $M_2(O_2CR)_4$ compound as exemplified by reaction (2.1) (Cayton et al. 1991b).

$$2\frac{M_2(O_2CBu^\dagger)_4 + \text{HOOC–X–COOH}}{25^\circ\text{C}} \xrightarrow{\text{toluene}} [(\text{Bu}^\dagger\text{CO}_2)_3\text{M}_2]_2 \xrightarrow{(\mu–O_2C–X–CO}_2 + 2\text{Bu}^\dagger\text{COOH}. \quad (2.1)$$

An alternative procedure that has proved useful for molybdenum is the salt metathesis reaction shown for equation (2.2) (Cayton et al. 1991a).

$$2\frac{[\text{Mo}_2(O_2CBu^\dagger)_3(\text{CH}_3\text{CN})_2]^{\dagger}\text{BF}_4}{25^\circ\text{C}} \xrightarrow{\text{CH}_2\text{Cl}_2} [(\text{Bu}^\dagger\text{CO}_2)_3\text{Mo}_2]\text{ bridgel} + 2[\text{Q}^{\dagger}\text{BF}_4]. \quad (2.2)$$

A characteristic feature of the dimers of dimers of type II is that they show intense low-energy electronic bands in the visible or near IR region of their electronic absorption spectra. For dicarboxylate-linked compounds, the electronic coupling of the two dinuclear centres arises from in- and out-of-phase combinations of $M_2\delta$ orbitals interacting with the $\pi$ orbitals of the CO$_2$ units. The CO$_2$ units thus act as alligator clips in, both physically (covalently) and electronically, coupling the $M_2$ centres as shown in IV and V below for oxalate.

Of these two orbital interactions, IV is the most important from both energy and overlap considerations, and this interaction is notably greater for tungsten than molybdenum. Consequently, in related complexes the degree of electronic coupling is always greater for tungsten.
The simplest of dicarboxylate-bridged compounds involve the oxalate ligand and much attention has been given to the study of these complexes in their neutral and oxidized forms. The oxidized radical cations all show spectroscopic features characteristic of class III behaviour both on the EPR and the optical time scale. For the Mo$^{4+}$-containing complex, $A_0 \approx 14$ G and for W$^{4+}$, $A_0 \approx 27$ G (Chisholm et al. 2002). The near IR/IR optical spectra for the oxalate M$^{5+}$ ions are shown in figure 2 (Chisholm et al. 2005a).

All of these ions can be classified as fully delocalized; on the Robin and Day Scheme, they are class III and the magnitude of the coupling $H_{AB} \approx 1/2 \nu_{\text{max}}$. The shape of these charge resonance bands changes greatly as one approaches the class II/III border and is entirely consistent with theoretical predictions (Demadis et al. 2001; Brunschwig et al. 2002). For a fully delocalized ion, the low-energy electronic transition involves promotion of an electron from the stabilized M$^{d}$ combination to the destabilized M$^{\delta}$ one (figure 3). At higher energy there is a metal-to-liquid charge transfer (MLCT) transition. For dicarboxylate-bridged compounds, the ligand-to-metal charge transfer (LMCT) transition is not observed in the vis-NIR since the CO$_2$ $\pi$-filled combination is at much lower energy (Chisholm & Patmore 2007).

As the bridge is extended in distance, the degree of electronic coupling is diminished and terephthalate-bridged complexes with M$_2$ to M$_2$ distances approximately $11 \text{ Å}$ show mixed valence characteristics of class II for M=Mo and class III for M=W (Bursten et al. 2002; Chisholm et al. 2005b). This is readily apparent from the EPR data and the electronic spectral data. For M=Mo, the complexes show $A_0 \approx 27$ G, typical of a Mo$^{5+}$ ion but for M=W, $A_0 = 27$ G, roughly one-half the value of that for W$^{5+}$. The near IR spectra for a related pair of ions are shown in figure 4. The sharp/narrow low-energy band, $\nu_{\text{max}} \approx 3200 \text{ cm}^{-1}$ for the tungsten complex, is typical of a charge

Figure 2. NIR electronic absorption spectra of [(‘BuCO$_2$)$_3$M$_2$]$_2$(μ-O$_2$CCO$_2$)$_2$PF$_6$ [M$_2$=Mo$_2$ (red), MoW (purple) and W$_2$ (blue)] recorded in THF solutions at room temperature. The spectral feature at $4400 \text{ cm}^{-1}$ relates to absorption in a sample cell. Reproduced with permission from Chisholm et al. (2005a).
resonance band while for M = Mo, the broad band at higher energy is readily classified as an intervalence charge transfer (IVCT) transition based on Hush theory (Hush 1967, 1985).

Correlations of the degrees of electronic coupling based on electrochemical measurements, optical spectroscopy and EPR spectroscopy are given in table 1 for a small selected group of bridged compounds.

A number of points are noteworthy from an inspection of the data in table 1. (i) The magnitude of the electronic coupling as determined by electrochemical methods (Richardson & Taube 1981) correlates well with that determined by optical spectroscopy. (ii) The $K_c$ values relating the relative stability of the monocation to the neutral and doubly oxidized species span the range from the statistical value of 4 to more than $10^{12}$ and even relatively modest values of approximately $10^3$ and $10^4$ correlate with class III behaviour. (iii) Dicarboxylates such as 1,8-anthracenedicarboxylate which align the metal

Figure 3. Qualitative MO diagram showing the formation of a strongly coupled $[\text{M}_2\text{-bridge-M}_2]^+$ species from $\{\text{M}_2(\text{O}_2\text{C}^{\text{tBu}})_3\}$ and $\{\text{O}_2\text{C–X–CO}_2\}$ fragments. Salient electronic transitions have been highlighted. Reproduced with permission from Chisholm & Patmore (2007).
atoms in close proximity, as shown in VI, do not yield strongly coupled systems, which is a clear indication that the electronic coupling involves $M_2\delta$-bridge $\pi$ interactions: $K_c \sim 4$ for $M = Mo$ and 280 for $M = W$ (Cayton et al. 1991b).

The data for the 2,6-azulenedicarboxylate-bridged compounds warrant special comment since this is a polar bridge (Barybin et al. 2005). Azulene itself has a dipole moment of approximately 1 Debye as a result of the contribution of the resonance form that places a negative charge on the five-membered ring and a positive charge on the seven. The electrochemical and spectroscopic data for the tungsten-containing radical cationic complex indicate class III behaviour and the EPR spectrum reveals an isotropic signal, $g \sim 1.80$ with two hyperfine coupling constants to $^{183}W$, $A_0 \sim 20$ and 40 G. Electronic structure calculations on the model compound $[(\text{HCO}_2)_3\text{W}_2]_2(\mu-2,5$-dihydroxyterephthalate) indicate that the HOMO and HOMO-1 are indeed $W_2\delta$ combinations: the HOMO is largely centred on the $W_2$ unit closest to the

Figure 4. NIR electronic absorption spectra of $[(\text{tBuCO}_2)_3\text{M}_2]_2(\mu-2,5$-dihydroxyterephthalate)$^+PF_6^- [M = Mo (grey) and W (black)]$ recorded in THF at room temperature. The gap between 2610 and 3280 cm$^{-1}$ for $[(\text{BuCO}_2)_3\text{W}_2]_2(\mu-2,5$-dihydroxyterephthalate)$^+PF_6^-$ corresponds to a THF solvent absorption. Reproduced with permission from Chisholm et al. (2005b).
five-membered ring of the azulene and the HOMO-1 is centred on the other W$_2$
unit. This is, of course consistent with expectations of the polar nature of the
bridge and the EPR data indicate that the single-electron wave function is
similarly polarized roughly 2 : 1 in favour of the W$_2$$^\delta$ orbital adjacent to the
five-membered ring of the azulenedicarboxylate bridge (Barybin et al. 2005).

Table 1. Comparison of data for selected bridged MM quadruply bonded complexes and their
mixed valence ions.

<table>
<thead>
<tr>
<th>bridge (2-)</th>
<th>metal</th>
<th>$^1$MLCT (nm)</th>
<th>$K_c$</th>
<th>$H_{AB}$ (cm$^{-1}$)</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>O CO O O O</td>
<td>Mo</td>
<td>460</td>
<td>$5.4\times10^4$</td>
<td>2000</td>
<td>Cayton &amp; Chisholm (1989); Bursten et al. (2002); Chisholm et al. (2005a)</td>
</tr>
<tr>
<td>O CO O O</td>
<td>W</td>
<td>800</td>
<td>$1.3\times10^{12}$</td>
<td>2980</td>
<td>Cayton &amp; Chisholm (1989); Bursten et al. (2002); Chisholm et al. (2005a)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>Mo</td>
<td>550</td>
<td>$\sim4$</td>
<td>$\sim400$</td>
<td>Chisholm et al. (2005b)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>W</td>
<td>727</td>
<td>$5.1\times10^2$</td>
<td>1500</td>
<td>Chisholm et al. (2005b)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>Mo</td>
<td>490</td>
<td>13</td>
<td>—</td>
<td>Bursten et al. (2002)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>W</td>
<td>900</td>
<td>$6.6\times10^4$</td>
<td>1500</td>
<td>Bursten et al. (2002)</td>
</tr>
<tr>
<td>O S C O O</td>
<td>Mo</td>
<td>645</td>
<td>$1.3\times10^3$</td>
<td>—</td>
<td>Chisholm &amp; Patmore (2006)</td>
</tr>
<tr>
<td>O S C O O</td>
<td>W</td>
<td>777</td>
<td>$5.7\times10^8$</td>
<td>2160</td>
<td>Chisholm &amp; Patmore (2006)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>Mo</td>
<td>700</td>
<td>78</td>
<td>380</td>
<td>Barybin et al. (2005)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>W</td>
<td>1140</td>
<td>$8.2\times10^7$</td>
<td>1540</td>
<td>Barybin et al. (2005)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>Mo</td>
<td>450</td>
<td>$1.7\times10^7$</td>
<td>—</td>
<td>Cayton et al. (1993)</td>
</tr>
<tr>
<td>O C C O O</td>
<td>W</td>
<td>704</td>
<td>$4.5\times10^10$</td>
<td>1900</td>
<td>Chisholm et al. (2004)</td>
</tr>
</tbody>
</table>

3. The mechanism of electronic coupling

The coupling in dicarboxylate-bridged compounds arises from the frontier orbital
interactions shown in IV and V and, as noted earlier, the orbital interaction with the CO$_2$ $\pi^*$ orbital is more important due to energy considerations. In reviewing
the data given in table 1, we also see that the coupling is always greater for tungsten than molybdenum for a common bridge. This can also be traced to
orbital energetics and overlap considerations. Indeed, for a given $M_2$ to $M_2$ distance, the magnitude of the coupling in these mixed valence ions correlates closely with the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap and the energy of the MLCT transition of the neutral and oxidized radical cations (figure 3). In the superexchange mechanism this is equivalent to electron transfer via the bridge (McConnell 1961). Hole transfer is not observed even when, as is the case for the azulenedicarboxylate or 9,10-anthracenedicarboxylate, the bridge-filled $\pi$ orbital of highest energy lies close to that of the $M_2\delta$. Indeed, for the Mo$_4$-containing complexes these bridge $\pi$ orbitals lie less than 1 eV below the $M_4\delta$ combinations. This energy separation is notably smaller than the HOMO–LUMO gap. The lack of hole transfer can be traced to the CO$_2$ groups which act as gates.

If an oxygen atom of the carboxylate is replaced by a nitrogen atom as in the 2,7-dioxynaphthyridine (Cayton et al. 1991b) and 3,6-dioxypyradazine bridges, shown in VII and VIII, respectively, the electronic coupling is greatly enhanced for molybdenum (Chisholm et al. 2004).

Here, the higher energy filled $N\pi$ orbital mixes more with the $M_2\delta$ (see V) and it may well be that hole transfer as well as electron transfer both contribute significantly to the coupling. For tungsten, however, it is still clear that electron transfer is the dominant path as even the 3,6-dioxypyradazine bridge, which brings the inner W atoms to within a distance of 3.5 Å, is not as strongly coupled as the oxalate-bridged complex where the $W_2$ centres are separated by approximately 6 Å. See data in the table 1.

Also as shown in table 1, the replacement of one carboxylate oxygen by a sulphur with the formation of the thiocarboxylate group greatly enhances the coupling (Chisholm & Patmore 2006). The C–S $\pi$-bond is notably weaker than the C–O $\pi$-bond and the C–S $\pi^*$ orbital lower in energy. Again the MLCT of the bridge is lower in energy for the thiocarboxylate-bridged compounds indicating a facile electron transfer process in the superexchange mechanism. However, the sulphur 3p orbital is also notably higher in energy than the oxygen 2p orbital which facilitates $M_2\delta$-Sp mixing and thus again hole transfer may also complement electron transfer in these systems.

4. Mixed valence ligands

Dinuclear complexes having two unsaturated ligands extended as arms or wings may show strong coupling of the ligands as a result of $M_2\delta$ to ligand $\pi$-conjugation. Employing the carboxylate linker to the dimetal centre, we find that one of the ligand combinations has a symmetry match with the $M_2\delta$ orbital.
as shown in IX below.

The filled $M_2\delta$ orbital back bonds to the out-of-phase ligand $\pi^*$ combination. This stabilizes the $M_2\delta$ orbital and splits the energies of the two ligand $\pi^*$ combinations with the one that interacts with the $M_2\delta$ being raised in energy.

An example of this type of complex is shown in figure 5 (Barybin et al. 2007). The bulky 2,4,6-triisopropyl benzoate ligands occupy trans-positions and the aryl ring is twisted roughly 90° to relieve steric congestion. This removes CO$_2$-aryl $\pi$ conjugation. On the other hand, the two 6-carboethoxy-2-carboxylato azulene ligands are ideally set up to employ extended conjugation via the $M_2\delta$ orbital as described in IX.

Electronic structure calculations on the model compound where formate substitutes for the triisopropylbenzoate ligands indicate that the HOMO is the $W_2\delta$ orbital at approximately $-5.2$ eV stabilized by back bonding to the azulene carboxylate ligand. The LUMO is the in-phase combination of the azulene carboxylate $\pi^*$ orbital and the LUMO+1 is the out-of-phase combination. The latter is the $M_2$ ligand antibonding counterpart of the HOMO. The calculated splitting of the LUMO and LUMO+1 is approximately $0.5$ eV and this is a measure of the degree of electronic communication of the two azulenecarboxylates via the $W_2\delta$ orbital (Barybin et al. 2007).

This compound undergoes a single electron reduction in its reaction with cobaltacene and in 2-methyltetrahydrofuran at 223 K, the EPR spectrum consists of a single relatively sharp signal, $g=2.0$ with no evidence of hyperfine coupling. This is in marked contrast to the oxidized species described before which show $g \sim 1.8$ and hyperfine coupling to $^{183}$W (Barybin et al. 2007).

The complementary nature of the $W_4$ azulenedicarboxylate-bridged cation of type II$^+$ and the $W_2$ bisazulene carboxylate anion of type III$^-$ is seen in their electronic absorption spectra shown in figure 6. Both species show an intense absorption in the NIR at approximately 1100 nm due to MLCT and at much lower energy a charge resonance band in the IR at approximately 3000 cm$^{-1}$. In the case of the $W_4$-containing cation, this is due to an electronic transition between the singly occupied HOMO and the HOMO-1, the two $W_2\delta$ combinations, (figure 3) whereas for the $W_2$ (bisazulene carboxylate)-containing anion it is an electronic transition between the azulene-based singly occupied LUMO and the LUMO+1.
5. Concluding remarks

The MM quadruply bonded systems described herein, along with those prepared independently by Cotton, Murillo and their coworkers with attendant formamidinate ligands, (Cotton et al. 2003, 2006) have proved exemplary species for the studies

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of mixed valence complexes. Unlike mononuclear d⁵–d⁶ mixed valence complexes typified by the Creutz–Taube ion (Creutz & Taube 1969) their spectroscopic features are not complicated by low-energy absorptions due to d–d configuration interactions. Thus, the assignment of the IVCT or charge resonance band is straightforward. As has been briefly outlined here, the systems lend themselves to the study of intervalence near the class II/III border and the mechanisms of electronic coupling. Modern electronic structure calculations employing density functional theory with commercial programs such as those provided by GAUSSIAN v.03 provide an excellent basis for the more quantitative interpretation of various aspects of bonding and spectroscopy, much of which has been omitted from discussion in this article for the sake of brevity but can be found in the literature cited herein. Finally, it should be noted that the present article has been restricted to an understanding of the ground state properties of the neutral and mixed valence species. Much of our current work is now aimed at studying the charge distribution in ¹MLCT and ³MLCT photoexcited states. These too can be viewed as mixed valence species and the lifetimes of ¹MLCT (approx. 10 ps) and ³MLCT (approx. 70 μs) endear these species to detailed time-resolved vibrational studies from which the sites of oxidation and reduction can be determined (Burdzinski et al. 2006).

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