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ELECTRONIC ABSORPTION SPECTRA OF M_2L_6 COMPOUNDS CONTAINING METAL–METAL TRIPLE BONDS OF $\sigma^2\pi^4$ CONFIGURATION

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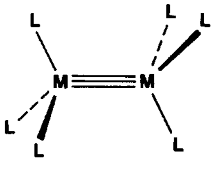
Abstract—The electronic absorption spectra of compounds containing metal–metal triple bonds of $\sigma^2\pi^4$ valence electronic configuration are presented and discussed. The lowest-energy transition of M_2L_6 compounds (M = Mo or W, L = CH_2Bu^t or OBu^t) is expected to be the dipole-allowed $\pi \rightarrow \pi^*$ ($e_u \rightarrow e_g$) transition. This appears to be the case for $M_2(CH_2Bu^t)_6$ and $M_2(OBu^t)_6$ compounds, in which the lowest energy absorption bands occur between 26,000 and 28,000 cm^{-1} ($\varepsilon = 1.1 \times 10^3$–$1.8 \times 10^3$ M^{-1} cm^{-1}). For $M_2(NMe_2)_6$ compounds, the lowest energy absorption is not the $\pi \rightarrow \pi^*$ transition but is assigned instead to a LMCT transition originating from nitrogen lone-pair orbitals, $N_{1p} \rightarrow \pi^*$, observed at 30,800 cm^{-1} ($\varepsilon = 1.4 \times 10^4$–$1.9 \times 10^4$ M^{-1} cm^{-1}). The $\pi \rightarrow \pi^*$ transition is not observed in these compounds, but is presumably masked by the more intense LMCT. These assignments are derived from Xα-SW calculations performed and described by other authors (Bursten *et al.*, *J. Am. Chem. Soc.* 1980, **102**, 4579).

The rapid growth in the synthetic and structural chemistry of dinuclear transition-metal complexes containing strong metal–metal bonds has provided a wealth of information concerning the nature of metal–metal bonding interactions. The study of strong metal–metal bonding interactions initially focused on the family of quadruple bonds of valence configuration $\sigma^2\pi^4\delta^2$ where the combination of sophisticated calculations, electronic absorption, emission, and photoelectron spectroscopic studies have provided a fairly detailed understanding of this class of multiple bond.[1] More recently, active research programs involving the study of metal–metal triple bonds have developed in several major research groups. Again, sophisticated molecular-orbital calculations coupled with photoelectron spectroscopy have demonstrated that triple bonds between metal atoms may contain a variety of valence electronic structures ranging from $\sigma^2\pi^4$ or $\sigma^2\pi^4\delta^2\delta^{*2}$ to the recently discovered $\pi^4\delta^2$ configuration.[2] Although the latter two configurations have been the subject of much recent attention, we note that there has been no study of the electronic absorption spectra of a homologous series of the $\sigma^2\pi^4$ triple bonds. We report here a comparison of the electronic absorption spectra of M_2L_6 compounds (M = Mo or W; L = CH_2Bu^t, NMe_2 or OBu^t) which have the $\sigma^2\pi^4$ valence M–M electronic configuration, and offer a tentative assignment for the lowest-energy transitions.

RESULTS AND DISCUSSIONS

The $\sigma^2\pi^4$ M≡M *bond*

The simplest of complexes containing the $\sigma^2\pi^4$ M≡M bonding configuration are the unbridged, "ethane-like" d^3–d^3 dinuclear compounds of molybdenum and tungsten of formula M_2L_6 (L = R,[3] NR_2,[3] OR[3] or SAr[4]) depicted in **I**. The qualitative view that the valence electronic structure is composed of one σ- and two π-components has been



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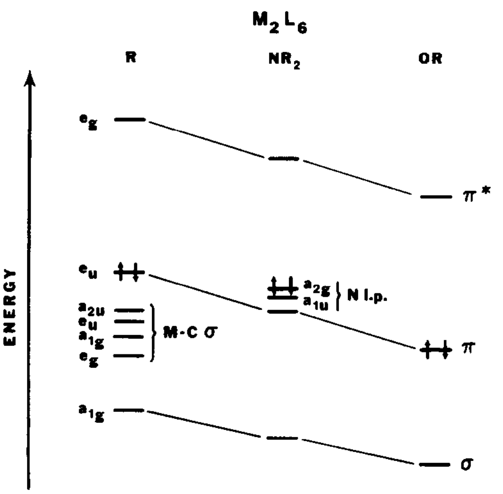

Fig. 1. Qualitative valence energy level diagram for $Mo_2(OR)_6$, $Mo_2(NR)_2)_6$ and $Mo_2(R)_6$ adapted from Reference 2(b).

confirmed by photoelectron spectroscopy[2,5] and a variety of molecular-orbital calculations employing the Xα-SW,[2(a),(b)] Hartree–Fock–Slater,[6] Hartree–Fock,[7] generalized molecular orbital,[8] and extended Hückel[9] methods. The Xα-SW calculations have been performed on $Mo_2(OH)_6$, $Mo_2(NH_2)_6$, $Mo_2(NMe_2)_6$ and $Mo_2(CH_3)_6$, and the projected Xα formalism applied to determine accurate orbital populations and atomic charges for these systems.[2(b)] The latter calculations were shown to be in favorable agreement with the results of photoelectron spectroscopy, and these results are summarized in the form of a qualitative energy level diagram shown in Fig. 1. The lowest unoccupied molecular orbital (LUMO) in each compound was calculated to be a Mo–Mo π^*-orbital of e_g-symmetry in the D_{3d} point group.[2(b)] The highest occupied molecular orbital (HOMO) was calculated to be a Mo–Mo π-bonding orbital of e_u-symmetry for L = CH_3 and OH, yet for L = NH_2 and NMe_2 the calculated HOMO was predicted to be a nitrogen lone-pair orbital of either a_{2g}- or a_{1u}-symmetry. These calculations have found support from photoelectron spectroscopic studies.[2(b),5] For L = OR, there is a clear separation in energy between the $\sigma^2\pi^4$ M≡M bonding orbitals and the orbitals of the M–L σ-bonds, and this shows up very nicely in the He(I) and He(II) photoelectron spectra of these compounds. For L = R, extensive mixing is observed between M–M and M–L bonding orbitals which complicates the simple description of the valence electronic structure as $\sigma^2\pi^4$.

Electronic absorption spectra of M_2L_6 *compounds*

A summary of electronic absorption data and tentative band assignments for a representative series of M_2L_6 compounds (M = Mo or W; L = CH_2Bu^t, NMe_2 or OBu^t) are given in Table 1. A series of electronic absorption spectra comparing homologous Mo and W compounds for L = CH_2Bu^t, NMe_2 and OBu^t are shown in Figs 2–4. For each ligand set, the lowest-energy transition occurs in the UV and tails into the visible region of the spectrum, accounting for the characteristic yellow to red colors of the M_2L_6 compounds.

The ground state of the M_2L_6 systems is $^1A_{1g}$, and symmetry-allowed transitions are to excited states of A_{2u}- and E_u-symmetry in the D_{3d} point group. Thus the M≡M $\pi \rightarrow \pi^*$ ($e_u \rightarrow e_g$) transition is orbitally-allowed and expected to be the lowest-energy transition for compounds where L = CH_2Bu^t or OBu^t. For these compounds, the lowest-energy transitions are observed as relatively weak ($\varepsilon = 1200\text{–}1700\,M^{-1}\,cm^{-1}$) bands centered between 25,000–27,000 cm^{-1}. These absorptions are tentatively assigned to the dipole-allowed $\pi \rightarrow \pi^*$ ($^1A_{1g} \rightarrow {}^1E_u$) transitions in these molecules. The relatively weak intensity of these transitions presumably arises from a mixing of M–M π and δ character in the π- and π^*-orbitals under D_{3d}-symmetry. The PXα results indicate that this δ–π mixing in the occupied π-orbitals is only appreciable in magnitude for L = alkyl.[2(b)] Fenske–Hall calculations performed in our laboratory yield the same result, but, more important, they reveal that the magnitude of δ–π mixing in the π^*-orbitals is severe,[10] and we feel that this will have important consequences to the intensity of the $\pi \rightarrow \pi^*$ transition in these compounds. Absorption intensity is expected to increase as the square of the overlap between ground and excited states, and in this regard we note that the intrinsically weak, yet fully-allowed $\delta \rightarrow \delta^*$ transition in quadruply bonded dimers has been rationalized by use of the weak coupling model.[11] A shoulder on the $\pi \rightarrow \pi^*$ transition is observed for $W_2(OBu^t)_6$ but not for $W_2(CH_2Bu^t)_6$ and we propose that this arises from the dipole-allowed, spin-forbidden triplet component $^3(\pi \rightarrow \pi^*)$ of the $\pi \rightarrow \pi^*$ transition. For heavy atoms such as tungsten, the effects of spin–orbit coupling become significant and can contribute to the intensity of forbidden transitions.[12] A slight mixing of triplet character into the ground state, or a mixing of singlet character into the triplet state, will contribute to the intensity of singlet–triplet transitions. The lack of a $^3(\pi \rightarrow \pi^*)$ component for $W_2(CH_2Bu^t)_6$ may be the result of the increased mixing of M–M and M–C bonding orbitals, resulting in a

Table 1. Electronic absorption data for M_2L_6 compounds (M = Mo or W; L = CH_2Bu^t, NMe_2 or OBu^t)[a]

Compound		λ (nm)	λ (cm^{-1})	ε ($M^{-1}cm^{-1}$)	Tentative assignment[b]
$Mo_2(CH_2Bu^t)_6$		368	2.72×10^4	1.7×10^3	$\pi \rightarrow \pi^*$
		303	3.30×10^4	1.2×10^4	$\sigma_{MC} \rightarrow \pi^*$
		263	3.80×10^4	1.9×10^4	NA
		230	4.35×10^4	2.2×10^4	NA
$W_2(CH_2Bu^t)_6$		387	2.58×10^4	1.8×10^3	$\pi \rightarrow \pi^*$
	sh	269	3.72×10^4	6.4×10^3	NA
		232	4.31×10^4	1.9×10^4	NA
$Mo_2(NMe_2)_6$		325	3.08×10^4	1.9×10^4	$N_{lp} \rightarrow \pi^*$
	sh	265	3.77×10^4	2.7×10^4	NA
		240	4.17×10^4	3.7×10^4	NA
$W_2(NMe_2)_6$	sh	360	2.78×10^4	1.0×10^3	$\pi \rightarrow \pi^*$
		282	3.55×10^4	1.7×10^4	$N_{lp} \rightarrow \pi^*$
	sh	235	4.26×10^4	3.0×10^4	NA
$Mo_2(OBu^t)_6$		392	2.55×10^4	1.4×10^3	$\pi \rightarrow \pi^*$
	sh	285	3.50×10^4	6.4×10^3	NA
$W_2(OBu^t)_6$	sh	460	2.17×10^4	6.0×10^2	$^3(\pi \rightarrow \pi^*)$
		378	2.65×10^4	1.6×10^3	$\pi \rightarrow \pi^*$
	sh	250	4.00×10^4	3.9×10^3	NA

[a] Spectra recorded in THF solution using matched 1.0-cm quartz cells.
[b] π and π* denote the M–M character of predominantly metal-based orbitals. σ_{MC} and N_{lp} denote M–C σ and N lone-pair orbitals, respectively. NA = not assigned.

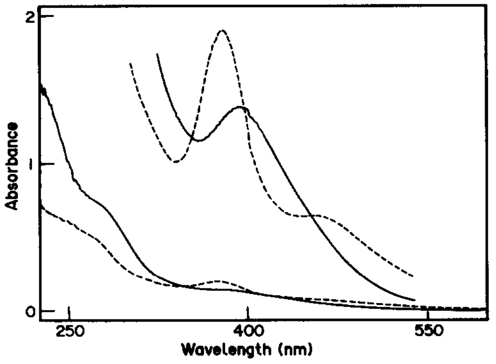

Fig. 2. Comparison of the electronic absorption spectra of $Mo_2(OBu^t)_6$ (solid line) and $W_2(OBu^t)_6$ (dashed line) in THF solutions, at 1.0×10^{-3} and 1.0×10^{-4} M.

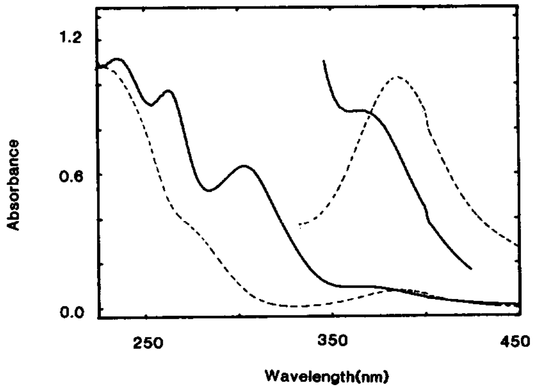

Fig. 3. Comparison of the electronic absorption spectra of $Mo_2(CH_2Bu^t)_6$ (solid line) and $W_2(CH_2Bu^t)_6$ (dashed line) in THF solutions, at 5.7×10^{-4} and 5.7×10^{-5} M.

lower percent metal character in the M–M π-orbitals compared to those of $W_2(OBu^t)_6$.[2(b)]

By contrast, for $M_2(NMe_2)_6$ compounds the lowest-energy transition is expected to be a ligand-to-metal charge transfer transition (LMCT) arising from a nitrogen lone-pair excitation to the M≡M π*-orbital ($^1A_{1g} \rightarrow {}^1E_u$) ($a_{1u} \rightarrow e_g$) which is in good agreement with the observed absorption energy (30,800 cm^{-1}), and intensity [$\varepsilon = 1.4 \times 10^4$ M^{-1} cm^{-1} (M = Mo) and intensity [$\varepsilon = 1.4 \times 10^4 M^{-1} cm^{-1}$; M = Mo]. Interestingly enough, the LMCT in $W_2(NMe_2)_6$ is found at higher energy ($3.55 \times 10^4 cm^{-1}$) than the corresponding transition in $Mo_2(NMe_2)_6$. This shift uncovers a shoulder at *ca.* 360 nm ($2.78 \times 10^4 cm^{-1}$, $\varepsilon = 1.0 \times 10^3 cm^{-1} M^{-1}$) which is most likely the $\pi \rightarrow \pi^*$ transition. Presumably in $Mo_2(NMe_2)_6$ the $\pi \rightarrow \pi^*$ transition is masked by or hidden beneath the LMCT.

When comparing the spectra of $M_2(CH_2Bu^t)_6$

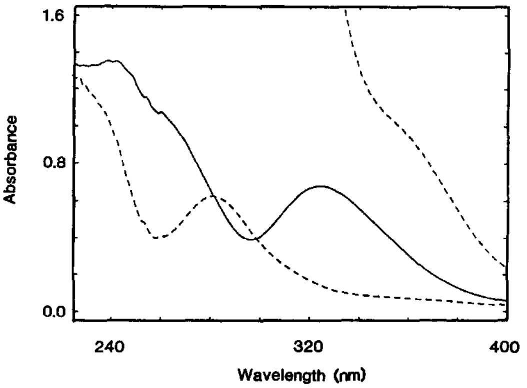

Fig. 4. Comparison of the electronic absorption spectra of $Mo_2(NMe_2)_6$ (solid line) and $W_2(NMe_2)_6$ (dashed line) in THF solutions, at 3.5×10^{-5} M.

compounds, transitions are observed for the molybdenum compound which are not observed for the tungsten counterpart. The origin of these absorption features, which occur at higher energy than the $\pi \rightarrow \pi^*$ transitions are admittedly much more speculative. However, the Xα-SW calculations and photoelectron spectroscopic studies indicate that M–C σ-bonding orbitals of a_{2u}- and e_u-symmetry are located energetically just below the M≡M π-bonding orbitals.[2(b)] Transitions from these M–C σ bonding orbitals into the empty M≡M π^*-orbitals are dipole-allowed under D_{3d}-symmetry. Furthermore, from photoelectron spectroscopy it is known that the metal–metal bonding orbitals for tungsten compounds lie higher in energy than those of molybdenum counterparts, yet the metal–carbon orbitals remain at about the same energy.[13] We summarize the effect of changing the metal from molybdenum to tungsten in the form of a qualitative energy level diagram in Fig. 5. Orbitals with large amounts of metal character will be raised in energy for tungsten relative to molybdenum, whereas orbitals with large amounts of carbon character will be relatively unaffected. Thus, while the π to π^* separation remains relatively unchanged, the separation of M–C σ- and M≡M π^*-orbitals is greatly changed. We feel that this diagram qualitatively accounts for the observation of M–C $\sigma \rightarrow$ M≡M π^* transitions at lower energy for molybdenum relative to tungsten.

Concluding remarks

We have presented a summary of the electronic absorption spectra for the prototypical compounds containing metal–metal triple bonds of valence M–M configuration $\sigma^2\pi^4$, namely the M_2L_6 compounds of molybdenum and tungsten. For, M = Mo, W; L = CH_2Bu^t OBu^t and L = NMe_2; M = W the lowest-energy absorptions can reasonably be assigned to the $\pi \rightarrow \pi^*$ transition whereas for M = Mo; L = NMe_2 the lowest-energy absorption is most likely LMCT. The overall understanding of these metal–metal triple bonds from both a theoretical and experimental basis seems quite satisfactory. Calculations using the Xα-SW method have proved useful in the interpretation of both the electronic absorption spectra and the photoelectron spectra. It should be recognized that the valence molecular orbital description of $\sigma^2\pi^4$ is only an approximation, and that this description is dependent on the ligands L, and that the degree of M–M and M–L mixing increases in the order OBu^t to NMe_2 to CH_2Bu^t.

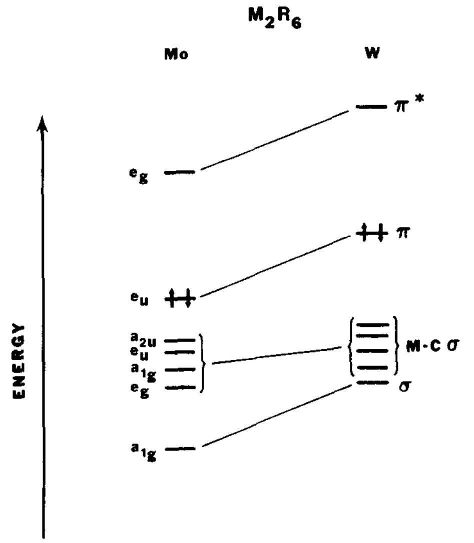

Fig. 5. Qualitative valence energy level diagram describing the differences between $Mo_2(R)_6$ and $W_2(R)_6$.

EXPERIMENTAL

Compounds were prepared using standard Schlenk and glove-box techniques as described elsewhere* and were purified by either sublimation

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* $Mo_2(CH_2Bu^t)_6$ was prepared from $MoCl_3$ and $LiCH_2Bu^t$: K. J. Ahmed, Ph.D. thesis, Indiana University. $W_2(CH_2Bu^t)_6$ was prepared from $NaW_2Cl_7(THF)_5$ and $LiCH_2Bu^t$: M. H. Chisholm *et al.*, results to be published. $Mo_2(NMe_2)_6$: M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shrive and B. R. Stults, *J. Am. Chem. Soc.* 1976, **98**, 4469. $W_2(NMe_2)_6$ was prepared from $NaW_2Cl_7(THF)_5$: M. H. Chisholm *et al.*, results to be published. $Mo_2(OBu^t)_6$: M. H. Chisholm, F. A. Cotton, C. A. Murillo and W. W. Reichert, *Inorg. Chem.* 1977, **16**, 1801. $W_2(OBu^t)_6$: M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine, D. A. Haitko, D. Little and P. E. Fanwick, *Inorg. Chem.* 1978, **18**, 2266.

($L = CH_2Bu^t$ and NMe_2) or recrystallized from hexane ($L = OBu^t$). Prior to examination of the electronic absorption measurements, compound purity was checked by ^1H NMR spectroscopy. Spectral-grade THF was distilled from sodium benzophenone and stored over 3-Å sieves and under nitrogen. Electronic absorption spectra were recorded in THF solution on a Hewlett–Packard 8450A spectrophotometer using matched 1.0-cm quartz cells. As a check on reproducibility, spectra were recorded at various concentrations which allow the estimate of accuracy for ε ($M^{-1}cm^{-1}$) listed in Table 1.

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