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Spectral Studies of Octamethyldimetalates of Molybdenum(II), Rhenium(III), and Chromium(II). The Assignment of the $\delta \rightarrow \delta^*$ Transition[1]

Sir:

Two recent theoretical studies[2,3] of the quadruply bonded octachlorodimetalates $Mo_2Cl_8^{4-}$ and $Re_2Cl_8^{2-}$ have suggested that the lowest energy visible absorption band for each complex (~1.88 and ~1.42 μm^{-1}, respectively) be assigned as the electric dipole allowed $b_{2g}\delta \rightarrow b_{1u}\delta^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) transition. The δ and δ^* orbitals are symmetry determined as $\delta = [d_{xy}(1) + d_{xy}(2)]/2^{1/2}$ and $\delta^* = [d_{xy}(1) - d_{xy}(2)]/2^{1/2}$ and are the highest filled and lowest unoccupied molecular orbitals. The polarized crystal spectrum[4,5] of $[(C_4H_9)_4N]_2Re_2Cl_8$ has confirmed this assignment for the rhenium(III) dimer. Entirely complementary results come from the resonance Raman experiments[6] on this compound and its bromo analogue. Corroborating evidence for a similar assignment of the 1.88-μm^{-1} band in salts of the dimolybdenum ion rests on the observation[7] of resonance Raman effects when these complexes are irradiated with 514.5 Ar^+ laser excitation, a wavelength close to the absorption maxima.

Although primarily metal d in character, the δ and δ^* orbitals interact with halide $p\pi$ orbitals of identical symmetry. Group theoretical considerations, based on D_{4h} molecular symmetry, establish the existence of b_{2g} and b_{1u} ligand π orbitals, and SCF-XαSW calculations of ground state valence energy levels reveal that these interactions may be considerable. Norman and Kolari[2] calculate for $Mo_2Cl_8^{4-}$ that $b_{2g}\delta$ and $b_{1u}\delta^*$ are 11 and 7% halide in character. For $Re_2Cl_8^{2-}$ these values increase to 21 and 18%, respectively, and may be even higher.[3] The higher formal oxidation state of rhenium may in part account for this behavior. It is clear that a discussion of $\delta \rightarrow \delta^*$ transitions in these two dimers must recognize the influence of metal-halide π bonding.

One way to alleviate the effect of this M-L π bonding on the orbitals is to study closely related complexes where this bonding is reduced due to the intrinsic properties of the ligand. We report here some observations on the electronic spectra of the octamethyldimetalates of chromium(II), molybdenum(II), and rhenium(III), the first isoelectronic series which encompasses all three transition metal series. Inasmuch as the methyl ligand meets the requirement specified above, these complexes afford an excellent opportunity to study the $\delta \rightarrow \delta^*$ transition as a function of the metal atoms without complications due to varying degrees of metal-ligand π interaction. In the methyl dimers, $M_2(CH_3)_8{}^{n-}$, the δ orbitals become essentially 100% metal in character. Thus the $\delta \rightarrow \delta^*$ transition should reflect the extent of metal-metal overlap,[8] although (as discussed below) an increase in metal-metal δ overlap does not necessarily imply observable M-M bond shortening.

Table I. ^1H and $^{13}C\{^1H\}$ NMR Parameters for $M-CH_3$[a]

Complex	δ^1H	$\delta^{13}C$
$[Li(Et_2O)]_4Cr_2(CH_3)_8$	−0.47	+9.60
$[Li(Et_2O)]_4Mo_2(CH_3)_8$	−0.30	+4.71
$[Li(Et_2O)]_2Re_2(CH_3)_8$	+0.71	—
$[Li(THF)]_2Re_2(CH_3)_8$	—	+16.06

[a] All complexes were run as solutions in benzene-d_6. Proton and carbon-13 chemical shifts were adjusted to the Me_4Si scale using the known chemical shifts for deuteriobenzene (+7.24 and +128 ppm, respectively). Proton NMR were run on a Varian Associates A60-A spectrometer; Fourier transform carbon-13 NMR were run on a Varian Associates XL-15FT spectrometer operating at 25.16 MHz.

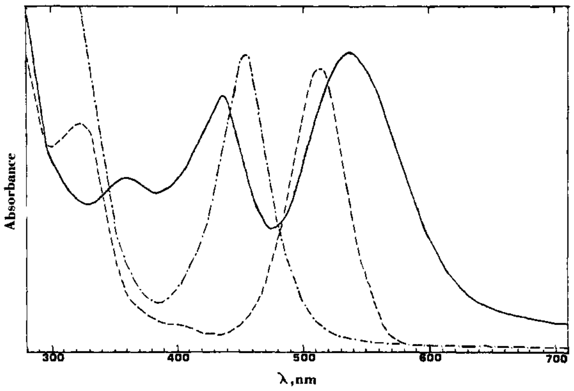

Figure 1. Electronic spectra of $Re_2(CH_3)_8{}^{2-}$ (—), $Mo_2(CH_3)_8{}^{4-}$ (- - ·), and $Cr_2(CH_3)_8{}^{4-}$ (· · -) in diethyl ether. Band maxima are presented in Table II. The ordinate is not drawn to scale (see note *c* in Table II).

The chromium[9] and molybdenum[10] complexes were prepared by literature methods and characterized by NMR (Table I) and/or metal analysis. The rhenium complex was prepared from $Re_2(CH_3COO)_4Cl_2$ and methyl lithium in diethyl ether at 0 °C. Metal analysis and NMR are consistent with the formulation $[Li(Et_2O)]_2Re_2(CH_3)_8$. All three complexes are exceedingly sensitive to air and moisture. The crystal structures of the group 6 complexes have been reported.[10,11] The molecular units possess structural and magnetic properties consistent with their formulation as quadruply bonded complexes. While pursuing these studies, we became aware of the independent preparation of the methyl rhenium dimer by two other groups.[12] A structural characterization consistent with δ-bond formation has been presented.

For UV-visible spectrophotometry an all-glass greaseless apparatus was constructed so that reactions between metal precursors and methyllithium could be performed in situ and filtered and the spectra of complexes recorded without the necessity of solution transfers.[14] The spectra are presented in Figure 1 and band positions are listed in Table II. No other band maxima were observed between the wavelengths of 230 and 2000 nm. All spectra were reproduced at least three times.

The spectrum of $Mo_2(CH_3)_8{}^{4-}$ emphasizes a point made earlier. It is qualitatively very similar to that of $Mo_2Cl_8{}^{4-}$.[7] There is a slight blue shift of the $\delta \rightarrow \delta^*$ transition from ~1.88 to 1.95 μm^{-1} which we attribute to an increase in metal-metal δ overlap concomitant with removal of 7-11% ligand character in the δ orbitals. That this small increase in overlap does not result in any observable decrease in bond length is evident from

Table II. Band Positions in μm^{-1} for $M_2(CH_3)_8^{n-}$ Complexes[a,b]

Complex	Energy	Assignment
$[Li(Et_2O)]_4Cr_2(CH_3)_8$	2.20[c]	$\delta \rightarrow \delta^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$)
$[Li(Et_2O)]_4Mo_2(CH_3)_8$	1.95[c]	$\delta \rightarrow \delta^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$)
	2.50	
	3.08	
$[Li(Et_2O)]_2Re_2(CH_3)_8$	1.86[c]	$\delta \rightarrow \delta^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$)
	2.29	
	2.76	

[a] Electronic spectra were recorded using a Cary 14 spectrometer. [b] All spectra in this table were obtained from diethyl ether solutions of the complexes in 1-cm cells. Diethyl ether was used as a reference. [c] Because of the difficulty of accurately measuring extinction coefficients on these extremely air-sensitive complexes, only upper limits of ϵ have been obtained for $\delta \rightarrow \delta^*$. These are: chromium ~700 M^{-1} cm^{-1}; molybdenum and rhenium ~1500 M^{-1} cm^{-1}.

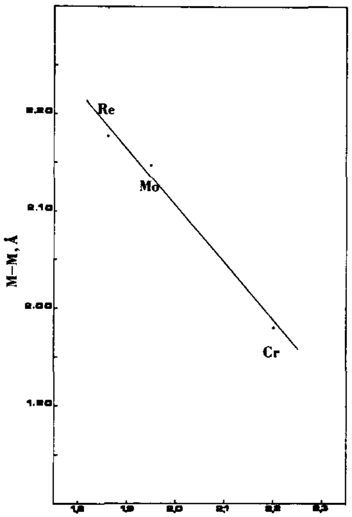

Figure 2. Plot of metal–metal bond distance (Å) vs. energy (μm^{-1}) of the $\delta \rightarrow \delta^*$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) transition for the octamethyldimetalates of chromium(II), molybdenum(II), and rhenium(III).

the structural data on $[Li(THF)]_4Mo_2(CH_3)_8$[10] and $(NH_4)_4Mo_2Cl_8 \cdot NH_4Cl \cdot H_2O$.[15] The M–M bond lengths for these complexes are 2.148 (2) and 2.150 (5) Å, respectively. Furthermore, when benzene solutions of $Mo_2(CH_3)_8^{4-}$ are irradiated with 488.0 or 514.5 nm Ar^+ laser excitation, an intense Raman band is observed at 336 ± 1 cm^{-1} which we assign as the ν_1 (MoMo)a_{1g} stretching frequency. This band is to be compared with the similarly assigned band[7] found in the ammonium salt of $mo_2Cl_8^{4-}$ at 338 cm^{-1}.

As noted in Table II, two other regions of absorption are apparent in the solution spectrum of $Mo_2(CH_3)_8^{4-}$. Since both of these bands are weaker than $\delta \rightarrow \delta^*$, it is unlikely that they are dipole allowed transitions. However, a complete assignment of the spectra of $Mo_2(CH_3)_8^{n-}$ species must await further work.

For $Re_2(CH_3)_8^{2-}$ we assign the lowest energy band at 1.86 μm^{-1} as $\delta \rightarrow \delta^*$. This band is responsible for the red-purple color of the complex. The position of this transition represents a blue shift of >4000 cm^{-1} relative to the lowest energy band in $Re_2Cl_8^{2-}$. Such a significant shift in energy must reflect a large increase in δ overlap. This shift is consistent with the greater M–L π interaction calculated for $Re_2Cl_8^{2-}$ although it is much larger than expected. The structures of $[(C_4H_9)_4N]_2Re_2Cl_8$[5] and $[Li(Et_2O)]_2Re_2(CH_3)_8$[12] indicate significant M–M bond differences, however. In the latter complex the metal-metal bond distance (2.178 (1) Å) is almost 0.05 Å shorter than its chloro analogue (2.224 (1) Å), indicating an increase in *both* M–M π and δ bonding. Two other bands of lower intensity than $\delta \rightarrow \delta^*$ were uncovered in the spectrum of $Re_2(CH_3)_8^{2-}$ (Table II) and are presumably dipole forbidden.[16]

In the spectrum of octamethyldichromate(II) ion, only one band was observed in the visible region of the spectrum at 2.20 μm^{-1}. It is responsible for the golden yellow color of the compound. It is logical to assign this band to $\delta \rightarrow \delta^*$ inasmuch as the M–M separation is only 1.980 (5) Å,[11] one of the shortest metal-to-metal bonds known. Such a close approach of metal atoms apparently results in favorable δ overlap, even exceeding that found in the molybdenum analogue.

In Figure 2 we have plotted M–M bond length vs. the position of the $\delta \rightarrow \delta^*$ transition. This plot suggests a reasonable correlation. As the metal–metal separation decreases, the overlap of metal orbitals presumably increases, resulting in the shift of $\delta \rightarrow \delta^*$. The spectrum[13] of the recently discovered $W_2(CH_3)_8^{4-}$ anion strengthens this correlation. Raman spectral measurements of the methyl dimers are in progress.

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(16) It is puzzling that the band near 2.29 μm^{-1} in the $Re_2(CH_3)_8^{2-}$ is only a factor of two less intense than the band at 1.95 μm^{-1}. We examined the possibility that oxidation was involved but have consistently reproduced the spectrum presented. Introduction of oxygen produces no new band in this region but causes bands to develop near 300 and 600 nm. Recrystallization produced no change in the character of the spectrum. Further spectroscopic studies clearly are desirable; however, the extreme air sensitivity of these materials makes such work exceedingly difficult.

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Crystallographic Proof of the Stability of a Quadruple Bond between Tungsten Atoms

Sir:

Since the recognition that a quadruple bond exists in the $Re_2Cl_8^{2-}$ ion,[1,2] such bonds have been found in other dirhenium(III) species,[2,3-6] in many dimolybdenum(II) compounds,[2,7-12] including the anions $M_2(CH_3)_8^{n-}$ for Cr,[2,13]