

for the observed electronic transitions of V_2 , Cr_2 , Nb_2 , and Mo_2 , we find that the bond dissociation energies of the second-row diatomic molecules are consistently higher than those of their first-row congeners (Table II), analogous to the trend found for first- and second-row transition metal cluster compounds.²⁴

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Registry No. Nb_2 , 12596-70-2; Mo_2 , 12596-54-2; Nb, 7440-03-1; Mo, 7439-98-7; V_2 , 12597-60-3; Cr_2 , 12184-82-6.

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- Using 4880-Å excitation, preliminary matrix Raman studies of Mo_2 in argon show an intense band at 315 cm^{-1} which we tentatively assign to the fundamental Mo-Mo stretching mode. The frequency of this mode would support the idea of a very high bond order of Mo_2 . Dye laser studies are under way to check on the possible interference of resonance Raman and/or fluorescence effects as originally suggested by M. Moskovits (personal communication).
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- In view of Norman's²⁰ recent SCF-X α -SW molecular orbital calculations on Mo_2 , a closed-shell configuration for Nb_2 ($1\sigma_g^2 1\pi_u^4 2\sigma_g^2 1\delta_g^2$) and Mo_2 ($1\sigma_g^2 1\pi_u^4 2\sigma_g^2 1\delta_g^4$) would appear to be a reasonable assignment.
- Although our minimum energy geometry (metal-metal bond length) for dimolybdenum is in close agreement with that derived from SCF-X α -SW calculations,²⁰ it should be pointed out that less correspondence exists between the respective assignments of the actual electronic spectrum.²⁰ The main reason for this is that the splitting of the 4d band at the equilibrium Mo-Mo distance calculated by SCF-X α -SW procedures is about 5 times as large as that derived from extended-Hückel molecular orbital techniques.²⁰

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Electronic Structure of $\text{Mo}_2(\text{O}_2\text{CH})_4$, Mo_2^{4+} , and Mo_2

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SCF-X α -SW calculations on $\text{Mo}_2(\text{O}_2\text{CH})_4$ are used to discuss the metal-metal and metal-ligand bonding in molybdenum(II) carboxylates and interactions between the two. Comparisons are made with similar calculations on HCO_2^- , Mo_2^{4+} , and Mo_2 , and previous work on $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Re}_2\text{Cl}_8^{2-}$. The ordering of the metal-metal orbitals for the carboxylates appears to be the same as for the chloro anions, but the metal-ligand bonding is more covalent, the Mo-Mo bond is stronger, and interactions between the Mo-O π and Mo-Mo bonds are greater in the former. Possible structural implications of these interactions are explored. Mo_2 is found to have a sextuple metal-metal bond, due to the stabilization, relative to Mo_2^{4+} and $\text{Mo}_2(\text{O}_2\text{CH})_4$, of a 5s-orbital σ -bonding combination which becomes the HOMO. The possibility of such an orbital being occupied in very covalent D_{4h} complexes is discussed. The calculations are in excellent agreement with the UV photoelectron spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$; the observed peaks at 7.7, 9.5, 11.6, and 12.7 eV are assigned mainly to ionization of Mo-Mo δ , Mo-Mo π , Mo-O, and Mo-Mo σ orbitals, respectively. The 80-K electronic spectrum of $\text{Mo}_2(\text{O}_2\text{CH})_4$ shows peaks at 22.9, 30.8, 33.5, and 4.44 μm^{-1} , with oscillator strengths of 0.0008, 0.03, 0.19, and 0.02, respectively. These are tentatively assigned to forbidden $\delta \rightarrow \pi^*$, allowed $\delta \rightarrow \delta^*$, allowed $\delta \rightarrow \text{C-O } \pi^*$, and allowed $\pi \rightarrow \pi^*$ transitions, respectively.

Recently, the nature of the quadruple metal-metal bonds in $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Re}_2\text{Cl}_8^{2-}$ has been defined in detail using SCF-X α -SW calculations.^{3,4a} A consistent assignment for the electronic spectra of these ions has also been achieved by combining the X α -SW predictions with polarization data from spectra of single crystals.³⁻⁵ For theoretical studies of strong metal-metal bonding, the chloro anions have the advantage of simple structure. However, they are known only for Mo, Re, and Tc.⁶ By far the largest class of compounds of this general structural type (D_{4h} symmetry) is the dinuclear carboxylates, $\text{M}_2(\text{O}_2\text{CR})_4\text{L}_2$, which are well characterized for $\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{Re}, \text{Ru}, \text{Co}, \text{Rh},$ and Cu and a variety of axial ligands L .⁷ The occurrence of the same basic structure for so many metals makes these compounds ideal for a theoretical comparison of metal-metal bonding as a function of d^n configuration. We have begun such an investigation with

SCF-X α -SW calculations on molybdenum(II) formate, $\text{Mo}_2(\text{O}_2\text{CH})_4$. This paper reports the results of these calculations and a proposed assignment for the electronic spectrum of the compound. A preliminary account of the calculations, done with sphere radii ca. 5% smaller than those used here, has appeared.⁸ We also present some interesting theoretical results on the species Mo_2^{4+} and Mo_2 .

Computational and Experimental Section

Initial Parameters for $\text{Mo}_2(\text{O}_2\text{CH})_4$. The SCF-X α -SW method has been thoroughly reviewed.⁹ The bond parameters Mo-Mo = 2.09 Å, Mo-O = 2.11 Å, C-O = 1.29 Å, and angle Mo-Mo-O = 92° were taken from the x-ray structure of $\text{Mo}_2(\text{O}_2\text{CH})_4$;¹⁰ the C-H distance used was 1.08 Å. Coordinates to the nearest 0.00001 bohr were derived from these parameters using the relation 1 bohr = 0.529177 Å and the assumption of D_{4h} symmetry. The coordinate system is shown by

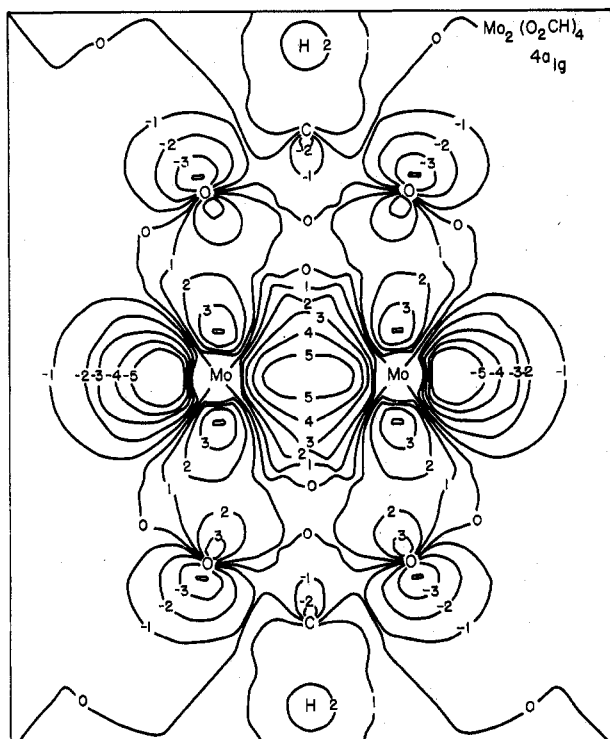


Figure 2. Contour map of the wave function for the $4a_{1g}$ level of $\text{Mo}_2(\text{O}_2\text{CH})_4$. This and all subsequent maps are in the xz plane; interior contours close to the atomic centers are always omitted for clarity. The contour values are $0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5 = 0, \pm 0.02, \pm 0.05, \pm 0.09, \pm 0.13, \pm 0.17$, respectively.

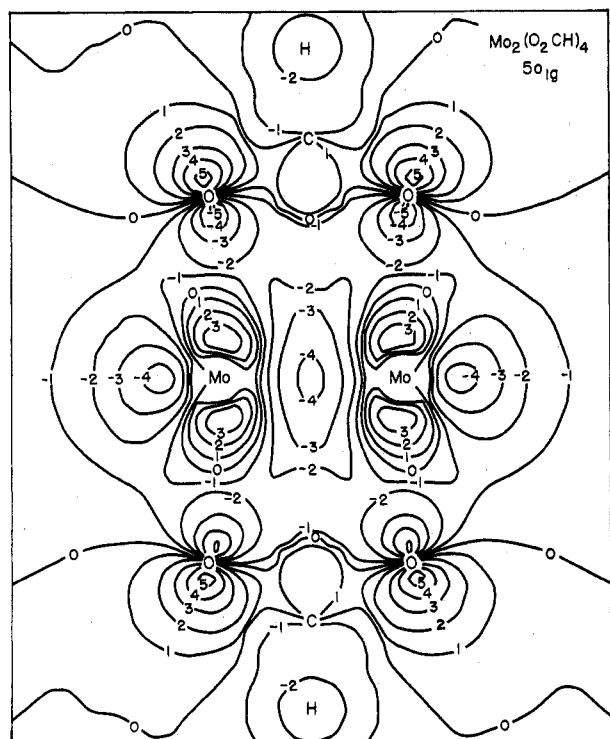


Figure 3. Contour map of the wave function for the $5a_{1g}$ level of $\text{Mo}_2(\text{O}_2\text{CH})_4$, with the same contour values as Figure 2.

of electrons within the Mo, O, C, H, intersphere, and outer regions are 41.03, 7.97, 5.20, 0.95, 5.43, and 0.14, respectively.

Discussion

Bonding in $\text{Mo}_2(\text{O}_2\text{CH})_4$. The basic features of the bonding are clear from Figure 1. Eight of the 16 C–O π and O 2p lone-pair orbitals of the four formate ions pick up 9–48% metal

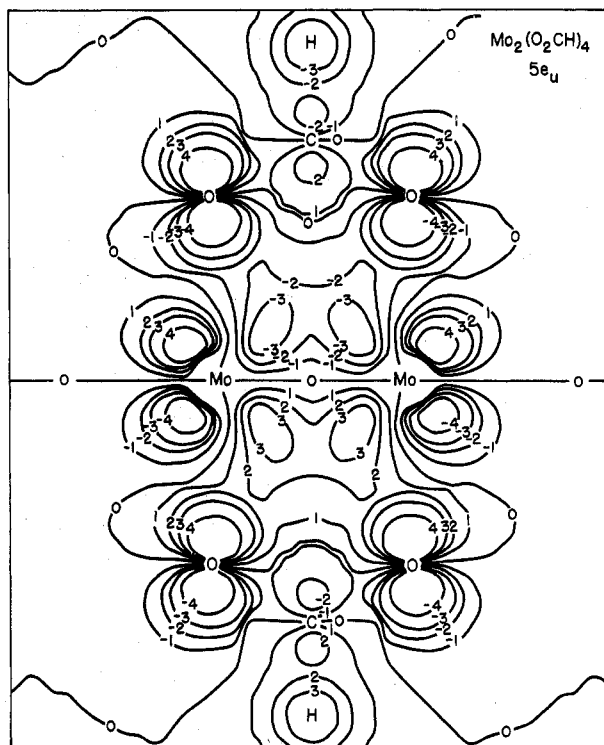


Figure 4. Contour map of the wave function for the $5e_u$ level of $\text{Mo}_2(\text{O}_2\text{CH})_4$. The contour values are $0, \pm 1, \pm 2, \pm 3, \pm 4 = 0, \pm 0.04, \pm 0.07, \pm 0.092, \pm 0.135$.

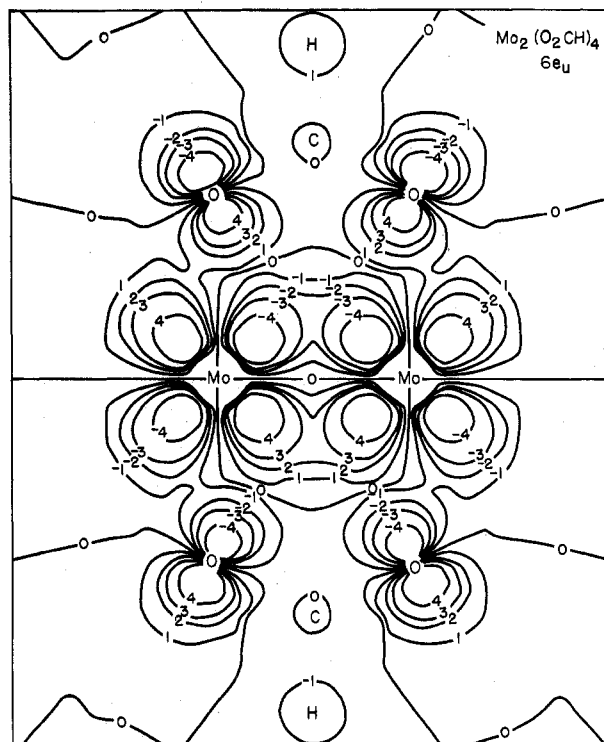


Figure 5. Contour map of the wave function for the $6e_u$ level of $\text{Mo}_2(\text{O}_2\text{CH})_4$, with the same contour values as Figure 4.

character and thus approximately represent the eight Mo–O bonds in the complex. Interaction with the formate ions greatly decreases the effective positive charge on the Mo_2^{4+} unit, thereby expanding its orbitals and increasing the effectiveness of metal–metal bonding. This is reflected in a marked decrease in Mo–Mo distance (2.09 Å for $\text{Mo}_2(\text{O}_2\text{CH})_4$, 2.9 Å calculated for Mo_2^{4+}) and a dramatically increased splitting of the

Table I. Upper Valence Energy Levels (hartrees),^a Charge Distribution,^b and Ionization Energies (eV) for Mo₂(O₂CH)₄

Level	Energy	% charge ^b				Mo sph har ^c	Type	Calcd IE ^d	Exptl IE ^e
		2 Mo	8 O	4 C	4 H				
2a _{2g}	-0.0187		36	64			C-O π*		
5a _{2u}	-0.0203	94	6	0		d _{z²} , p _z	Mo-Mo σ*		
7e _u	-0.0293	0	28	71	0		} C-O π*		
3b _{2g}	-0.0389	8	55	37					
4b _{2u}	-0.0441	77	22	1		d _{x²-y²}	} Mo-O σ*		
5b _{1g}	-0.0448	69	29	0	2	d _{x²-y²}			
5e _g	-0.0941	96	3	1		d _{xz,yz}	Mo-Mo π*		
2b _{1u}	-0.1435	86	14			d _{xy}	Mo-Mo δ*		
2b _{2g} ^f	-0.1990	89	3	8		d _{xy}	Mo-Mo δ	8.00	7.7
6e _u	-0.2714	65	32	1	2	d _{xz,yz}	Mo-Mo π, Mo-O π	9.68	9.5
4e _g	-0.2940	2	98	0			} O lone pair	(10.2)	} 10.1 sh
1a _{1u}	-0.2965		100					10.23	
5e _u	-0.3062	38	48	5	9	d _{xz,yz} , p _{x,y}	Mo-O π, Mo-Mo π	(10.6)	} 11.0 sh
5a _{1g}	-0.3105	48	42	3	7	d _{z²} , s	Mo-O π, Mo-Mo σ	(10.9)	
3e _g	-0.3115	1	99	0			O lone pair	(10.7)	} 11.6
3a _{2u}	-0.3244	10	89	1		d _{z²} , s	Mo-O σ	(11.0)	
3b _{2u}	-0.3349	16	82	2		d _{x²-y²}	Mo-O π	11.29	} 12.0 sh
1b _{1u}	-0.3447	14	86			d _{xy}	Mo-O σ	(11.6)	
4b _{1g}	-0.3616	28	55	6	11	d _{x²-y²}	Mo-Mo σ, Mo-O σ	(12.0)	} 12.7
4a _{1g}	-0.3863	75	19	2	4	d _{z²}	Mo-Mo σ, Mo-O σ	13.06	
1a _{2g}	-0.3874		78	23			} C-O π	(12.7)	} 14.9
4e _u	-0.4017	1	78	22	0			Mo-OC π	
1b _{2g}	-0.4287	9	73	18		d _{xy}		(13.7)	} 16.1
3b _{1g}	-0.5179	0	45	33	22		} Co-O σ, C-H	(16.2)	
2e _g	-0.5182	3	75	22					(16.3)
3a _{1g}	-0.5213	0	43	33	23			(16.2)	} 16.7
3e _u	-0.5241	2	43	32	22			(16.3)	
2a _{2u}	-0.5392	6	72	22				(16.9)	
2b _{2u}	-0.5399	9	70	21				(16.9)	

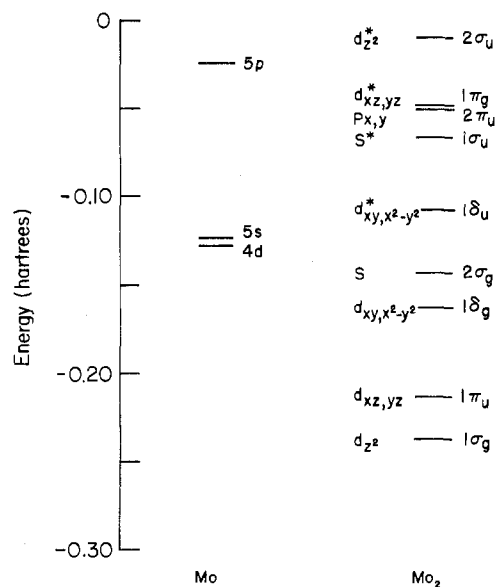
^a All levels between -0.600 and -0.025 hartree except for diffuse Rydberg-state orbitals. These occur at -0.0855 (4a_{2u}), -0.0744 (6a_{1g}), and -0.0259 (7a_{1g}). Only 3-18% of their charge is located within the atomic spheres. ^b Relative amounts of charge within the two molybdenum, eight oxygen, etc. spheres. The occupied and unoccupied levels have 74-100% and 37-93% of their charge within the atomic spheres, respectively. ^c Spherical harmonic basis functions contributing more than 10% of the molybdenum charge for the Mo-Mo and Mo-O levels, listed in order of decreasing importance. The largest non-d contribution is in the 5a_{1g} level, which is 43% s within the Mo spheres. ^d Values in parentheses are estimates only, representing eigenvalues found in explicit transition-state calculations of other levels. Examination of shifts between the different explicit calculations indicates that the estimates should be accurate to within 0.1 eV. ^e From ref 16. Shoulders on main peaks are indicated by sh; the ones at 10.1 and 12.0 eV, while evident in the published spectrum in ref 16, were not explicitly mentioned by the authors. The value 7.7 eV for the 2b_{2g} level was given in their table as 7.5 eV, although the peak is clearly at 7.7 eV in the published spectrum. ^f The highest occupied level.

Table II. Calculated and Experimental Electronic Spectra of Mo₂(O₂CH)₄^a

Transition	Excited state	Type ^b	Spectra, μm ⁻¹	
			Calcd ^c	Exptl ^d
2b _{2g} → 5e _g	¹ E _g	δ → π*	2.56	2.29 (f = 0.0008)
2b _{2g} → 2b _{1u}	¹ A _{2u}	δ → δ*	1.47	3.08 (f = 0.03)
4e _g → 2b _{1u}	¹ E _u	O → δ*	3.71	
3e _g → 2b _{1u}	¹ E _u	O → δ*	4.09	
2b _{2g} → 7e _u	¹ E _u	δ → C-O π*	4.19	3.35 (f = 0.19)
6e _u → 5e _g	¹ A _{2u}	π → π*	4.14 ^e	4.44 (f = 0.02)

^a Band positions were obtained from the calculated values using the relation 1 hartree = 21.947 46 μm⁻¹. ^b π, π*, δ, and δ* denote the Mo-Mo character of mainly metal orbitals. O denotes an oxygen lone-pair orbital. ^c All spin- and dipole-allowed transitions below ca. 4.8 μm⁻¹ and the only spin-allowed, dipole-forbidden transition (2b_{2g} → 5e_g) which should not be obscured by allowed bands. ^d Gaussian-resolved maxima at 80 K in a 4:1 ethanol-methanol glass, with oscillator strengths at room temperature given in parentheses. See text for basis of assignment to particular transitions. ^e Actually a prediction of the average transition energy to the four singlet states arising from the 6e_u³5e_g¹ configuration. Only the transition to the ¹A_{2u} state is dipole allowed and thus likely to be observed.

Mo-Mo bonding and antibonding orbitals. The interaction does not change the basic σ < π < δ < δ* < π* < σ* ordering of these orbitals, except for a lifting of the degeneracy of the 1δ_g and 1δ_u pair; the d_{x²-y²} ± d_{x²-y²} components, which point directly at the formate oxygen atoms, are greatly raised in energy, pick up 20-30% oxygen character, and are better considered as Mo-O σ* than as a second pair of Mo-Mo δ

**Figure 6.** Valence energy levels for Mo and Mo₂ (with Mo-Mo = 4.0 bohrs). Mo has a 4d⁵ 5s¹ configuration, while Mo₂ is closed shell with 2σ_g as the highest occupied orbital. The main character of the Mo₂ orbitals is indicated; see Figure 1 for explanation of symbols.

and δ* orbitals. Essentially unperturbed C-O π* levels appear at the top of the diagram. The highest occupied orbital is 2b_{2g}, the Mo-Mo δ-bonding component, giving a Mo-Mo bond order of 4 as expected.^{3,7}

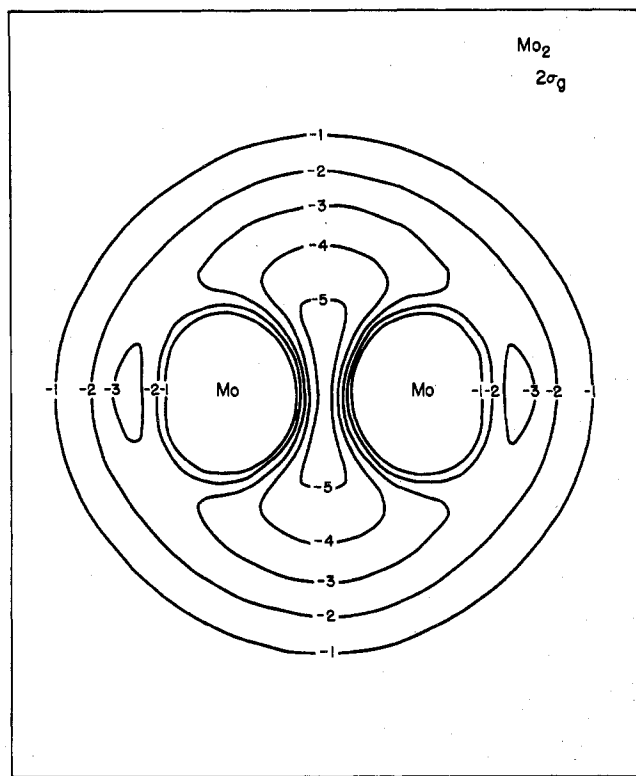


Figure 7. Contour map of the wave function for the $2\sigma_g$ level of Mo_2 . The contour values are 0, -1, -2, -3, -4, -5 = 0, -0.02, -0.03, -0.04, -0.05, -0.06.

The energy level diagram for $\text{Mo}_2(\text{O}_2\text{CH})_4$ is completely analogous to that for $\text{Mo}_2\text{Cl}_8^{4-}$ in the occupation and ordering of the metal-metal bonding and antibonding orbitals. The splitting between each bonding and antibonding pair is greater for $\text{Mo}_2(\text{O}_2\text{CH})_4$, reflecting the stronger bond (2.09 Å in $\text{Mo}_2(\text{O}_2\text{CH})_4$, 2.14 Å in $\text{Mo}_2\text{Cl}_8^{4-}$ —a considerable difference in this range of bond order). The only other qualitative changes in level positions from the $\text{Mo}_2\text{Cl}_8^{4-}$ diagram are a marked stabilization of the Mo-Mo π^* ($5e_g$) orbital relative to the other metal-metal orbitals and appearance of four additional unoccupied orbitals of C-O π^* character. As discussed below, these two changes, though not important for ground-state bonding, have a significant effect on the electronic spectrum.

Examination of orbital character and wave function contour maps shows that the metal-ligand bonding is more covalent¹⁸ and confirms that the Mo-Mo overlap is greater in $\text{Mo}_2(\text{O}_2\text{CH})_4$ than in $\text{Mo}_2\text{Cl}_8^{4-}$. The former is probably the main reason for the latter, since a smaller effective positive charge on the metal atoms means that their orbitals will be less contracted and hence overlap more effectively with each other. This is the most straightforward of a number of interesting interactions between the metal-metal and metal-ligand bonds revealed by the calculations; we discuss the others for the remainder of this section.

Although the $4a_{1g}$ and $6e_u$ orbitals are best classified as Mo-Mo bonding, and the $5a_{1g}$ and $5e_u$ orbitals, as Mo-O bonding, Figures 2-5 and Table I show that each has considerable character of both types. This complex situation is a result of strong interactions between the Mo-Mo bond and the Mo-O π bonds, much stronger than analogous interactions in $\text{Mo}_2\text{Cl}_8^{4-}$. Mo-O π bonding may be classified as interior or exterior, i.e., on the same side of the Mo-O direction as the metal-metal bond or on the opposite side, respectively. The former will tend to "steer" charge into, and the latter out of, the metal-metal region, thus strengthening and weakening the

metal-metal bond, respectively. In the e_u levels (Figures 4 and 5), the majority of the Mo-Mo π bonding is found in the upper level, as for $\text{Mo}_2\text{Cl}_8^{4-}$ (see Figure 3 of ref 3), but it is slightly weakened there by the presence of some exterior Mo-O π bonding and significantly enhanced in the lower e_u level by fairly strong interior bonding. Interior and exterior Mo-O π bonding of about equal strength occurs in the upper a_{1g} level (Figure 3); the overall effect is to delocalize the charge distribution to the extent that it becomes somewhat incompatible with the strongly localized character of the Mo-Mo σ bond, and most of this character escapes into the lower a_{1g} level (Figure 2), where the Mo-O bonding is σ . This contrasts with $\text{Mo}_2\text{Cl}_8^{4-}$, where nearly all of the Mo-Mo σ bonding is in the upper a_{1g} level; what weak interactions with the Mo-Cl bond are present there are interior, thus reinforcing the Mo-Mo character (see Figure 2 of ref 3).

The contour maps, especially Figure 4, illustrate an important effect of the metal-metal bond on the ligand system which is entirely general for D_{4h} systems of this type, independent of which ligands or metals are present. Consider the electronic interaction between ligand donor atoms that face each other across the metal-metal axis. So long as a net metal-metal bond is present, there will be more orbitals in which this sort of interaction is attractive than orbitals in which it is repulsive. This comes about simply because any orbital whose symmetry is bonding rather than antibonding for metal-metal interaction will necessarily also be bonding for interactions between such ligands. All other things being equal, nonbridged D_{4h} dimers, such as $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Cr}_2(\text{CH}_3)_8^{4-}$, should therefore always have the eclipsed conformation. Of course, for d^4 - d^4 dimers, the eclipsed structure is more simply explained as due to δ bonding, but in d^5 - d^5 dimers and those with more d electrons δ bonding should be essentially (see following paragraph) absent due to occupation of the δ^* orbital. The structures of such molecules should show whether the ligand-ligand interactions in question are attractive enough by themselves to force the eclipsed conformation. One such structure, that of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$, is known,¹⁹ and it is *eclipsed*. Unfortunately, in this case the spatial requirements of the bulky phosphine ligands may dictate the stereochemistry. We hope for the synthesis of complexes that provide more clear-cut examples.

Finally, if one considers the 16 occupied mainly ligand orbitals in Figure 1 (i.e., all but the Mo-Mo σ , π , and δ orbitals) as a group, one finds seven bonding, seven antibonding, and two ($1a_{2g}$ and $1a_{1u}$) nonbonding with respect to Mo-Mo interaction. However, the bonding group averages 23% Mo in character, while the antibonding group averages only 7% Mo. There is thus a net positive contribution to Mo-Mo bonding from this set of orbitals, over and above the strong bonding found in the $4a_{1g}$, $6e_u$, and $2b_{2g}$ levels. The considerable Mo-Mo σ and π components of the $5a_{1g}$ and $5e_u$ orbitals, respectively, are the best example. This phenomenon has no particular importance for $\text{Mo}_2(\text{O}_2\text{CH})_4$ itself, but it has possible structural implications for D_{4h} systems with more d electrons. When, e.g., the δ^* orbital is filled, assuming it is the perfect complement of the δ orbital, the δ bonding present in the latter will be canceled. Some net δ bonding may remain, however, in the lower orbitals. This may partially explain why the Re-Re bond in $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ is only slightly, if at all, longer than in $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$, although the δ^* orbital should be fully occupied in the former and empty in the latter¹⁹ (for another possible explanation, see the discussion of Mo_2 below). The point in general is that, as the δ^* , π^* , etc. orbitals are filled, the metal-metal bond will not necessarily lengthen as fast as might be expected from the simplest considerations. Our preliminary X α -SW results for $\text{Rh}_2(\text{O}_2\text{CH})_4(\text{H}_2\text{O})_2$ suggest that this is one reason that the Rh-Rh distance in the

acetate analogue is shorter than expected for a single bond,^{20,21} although this is all which is obtained from the occupation scheme for the mainly *Rh 4d* orbitals.^{22,23}

Mo₂⁴⁺ and Mo₂. One of the most basic facts about the electronic structure of transition metals is that, as the positive charge on the metal atom increases, the *d* valence orbitals become more stable relative to the *s* valence orbitals. This is why, e.g., the 4*s* orbitals are filled before the 3*d* in the periodic table, but the 4*s* electrons are lost before the 3*d* in forming first-row transition metal ions.²⁴ The energy level diagrams for Mo₂⁴⁺ and Mo₂ (Figures 1 and 6) provide a striking example of this principle; in Mo₂⁴⁺, all of the bonding and antibonding 4*d*-orbital combinations lie below the bonding 5*s* combination, while in Mo₂ the bonding *s* combination is stabilized to the point where it becomes the HOMO. The *d*¹⁰*s*² configuration of Mo₂ is in fact just a doubling of the *d*⁵*s*¹ configuration of atomic Mo. The interesting consequence is that the Mo–Mo bond order actually increases from quadruple in Mo₂⁴⁺ to sextuple in Mo₂! The wave function for the Mo₂ bonding *s* combination, the sixth component of the sextuple bond, is shown in Figure 7. Note that the contours required to achieve good resolution are much smaller than in Figures 2–5; the orbital is much more diffuse and the bonding interaction much weaker than in any of the Mo₂(O₂CH)₄ levels. However, there is clearly some similarity in form with the 5a_{1g} level of the formate (Figure 3), where the Mo contribution is 43% *s* in character.

Although Mo₂ is hypothetical at present, its eventual synthesis and characterization appear possible in view of the recent matrix isolation of Sc₂ and Ti₂, including measurement of their electronic spectra.²⁵ The Mo₂⁴⁺ and Mo₂ results also have a general implication for the electronic structure of the *D*_{4h} complexes: namely, as the metal atoms become more nearly neutral, the possibility of mainly *s* or *p* orbital combinations figuring prominently in the bonding increases. Re₂Cl₄(PEt₃)₄ and Re₂Cl₆(PEt₃)₂ (see last paragraph of preceding section) are certainly more covalent than Re₂Cl₈²⁻, and the reason that the Re–Re bond in the first is not appreciably longer than in the second could be that the extra electrons do not enter the δ* orbital at all, but rather a mainly Re 6*s* or 6*p* orbital which is not strongly antibonding and perhaps is even weakly bonding with respect to Re–Re interaction.¹⁹ Such orbitals would resemble the “σ_n” set originally proposed by Cotton for all the dimers on qualitative grounds.⁷ An explicit calculation on, e.g., Re₂Cl₄(PH₃)₄, is called for to resolve this question.

Photoelectron Spectrum of Mo₂(O₂CH)₄. As shown in Table I, the agreement between the calculated and experimental¹⁶ spectrum is in general excellent. All calculated ionization energies are within 4% of their apparent experimental values, except for the 1b_{2g} level, where the deviation is 8%. The 1b_{2g} experimental position may in fact be somewhat in error, since the peak is asymmetric and the maximum poorly defined. On the basis of the calculated values and the general idea that mainly metal levels should have greater photoelectron intensity than mainly ligand levels,²⁶ it seems clear that the first two experimental peaks (7.7 and 9.5 eV) are mainly due to Mo–Mo δ and π orbitals, respectively, the third (11.6 eV) to Mo–O orbitals, the fourth (12.7 eV) to the Mo–Mo σ orbital, and the last three (14.9, 16.1, and 16.7 eV) to formate-localized levels. It is of course difficult to unambiguously assign a few calculated ionizations in the 10–12-eV region to particular peaks or shoulders, since both experimental and theoretical levels are so closely spaced in this region.

The experimental spectrum up to 14 eV, i.e., through the first four peaks, has been determined independently with essentially the same results.¹⁰ The actual spectral curves for Mo₂(O₂CR)₄, R = H, CH₃, and CF₃, were also compared

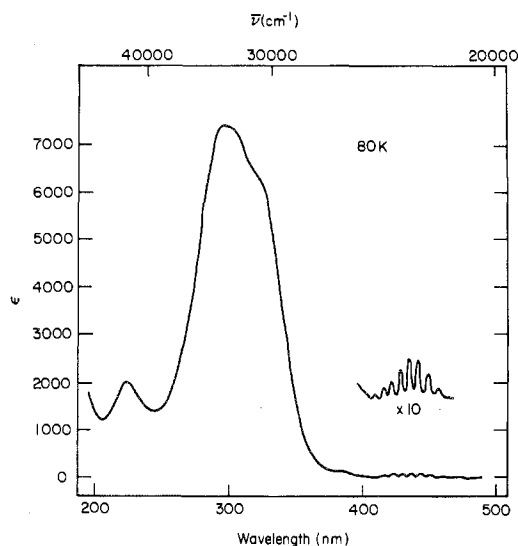


Figure 8. Electronic spectrum of Mo₂(O₂CH)₄ at 80 K in a 4:1 ethanol–methanol glass. The spectrum was scanned at a bandwidth ≤0.2 nm.

directly. The only qualitative change among the three spectra, aside from a uniform energy shift consistent with the relative electronegativities of H, CH₃, and CF₃, is a different structure for the third peak in each. This is consistent with our assignment of that peak mainly to Mo–O bonding levels, whose position should be more sensitive to the R group than should the Mo–Mo levels mainly responsible for the other three peaks.

Electronic Spectrum of Mo₂(O₂CH)₄. The 80-K spectrum of Mo₂(O₂CH)₄ in a 4:1 ethanol–methanol glass is shown in Figure 8; the Gaussian-resolved peak maxima are listed in Table II. Careful examination down to 80 cm⁻¹ shows no further electronic absorption bands. The spectra of Mo₂(O₂CR)₄, R = CH₃, CF₃, C₃F₇, and CH₂CH₃⁺, are virtually the same,^{27–29} although band III, at 3.35 μm⁻¹ in the formate, appears somewhat more sensitive to the R group than the other three bands. The small oscillator strength of band I, at 2.29 μm⁻¹, strongly suggests a dipole-forbidden transition, and careful polarization measurements of this band for single crystals containing Mo₂(O₂CCH₂NH₃)₄⁴⁺, Mo₂(O₂CH)₄, and Mo₂(O₂CCH₃)₄ leave no doubt that this is the case.^{29,30,32} The oscillator strengths of bands II and IV, at 3.08 and 4.44 μm⁻¹, respectively, are similar to the value of 0.02 for the δ → δ* transitions in Re₂Cl₈^{2–31} and Mo₂Cl₈^{4–32}; this and their lack of sensitivity to the R group suggest allowed transitions between metal-localized orbitals. The much larger oscillator strength of band III and its greater sensitivity to R suggest an allowed charge-transfer transition.

The carboxylates thus differ from Mo₂Cl₈⁴⁻, Re₂Cl₈²⁻, and Mo₂(SO₄)₄⁴⁻, for which single-crystal polarized spectra and Xα–SW calculations agree in assigning the lowest spectral band to the δ → δ* transition.^{4,5,30} Here, the polarized spectra completely rule out such an assignment for the 2.29 μm⁻¹ band;^{29,30} the δ → δ* excitation must occur at higher energy. Our predicted δ → δ* energy, 1.47 μm⁻¹, thus appears to be far too low. This was also the case for Mo₂Cl₈⁴⁻, where the comparable theoretical number is ca. 0.9 μm⁻¹, and the experimental δ → δ* energy is 1.88 μm⁻¹.³ If our calculated δ → δ* energy for Mo₂(O₂CH)₄ is the same percentage of the experimental energy as in Mo₂Cl₈⁴⁻, then the experimental band should lie at ca. 3.0 μm⁻¹. As pointed out above, the band at 3.08 μm⁻¹ is in fact a most reasonable candidate for assignment to this transition.

What forbidden transition, then, is responsible for band I in Mo₂(O₂CH)₄? The calculation predicts that the lowest such excitation, δ → π*, should occur at 2.56 μm⁻¹, only slightly

above the observed energy of 2.29 μm^{-1} for band I. Moreover, one would expect the predicted energy to be somewhat high, as the resulting excited state is one of two 1E_g states rather close in energy, the other being from the $6e_u \rightarrow 2b_{1u}$ ($\pi \rightarrow \delta^*$) transition. Since these two states are of the same symmetry, close in energy, and similar in character, they should interact significantly, one going lower and the other higher in energy than predicted by a purely one-electron calculation.³³ The $\delta \rightarrow \pi^*$ assignment is also supported to some extent by the results of analyses of the vibrational structure of band I, which suggest the involvement of a metal-localized transition.^{29,32} Two independent discussions of the vibrational structure, however, disagree as far as the exact nature of the excited state is concerned. Specifically, one suggests a nondegenerate²⁹ and the other a degenerate³² excited state. Only the second, of course, would be consistent with a $\delta \rightarrow \pi^*$ assignment. All of the metal-localized forbidden transitions to excited states suggested by the first analysis (${}^1A_{1u}$, ${}^1B_{1g}$, and ${}^1B_{2g}$)²⁹ are predicted to lie above 3.5 μm^{-1} , and thus we consider them unlikely assignments for band I.

If the $\delta \rightarrow \pi^*$ and $\delta \rightarrow \delta^*$ assignments for bands I and II are correct, the error in the calculated energy for the latter is apparently chiefly in the energy of the δ^* level. This is consistent with the good agreement between the calculated and experimental photoelectron spectrum. The calculated energies of 3.71 and 4.09 μm^{-1} for the $O \rightarrow \delta^*$ transitions (see Table II) may thus also be several tenths of a μm^{-1} too low, leaving $\delta \rightarrow C-O \pi^*$ as the reasonable assignment for band III. Band IV is then assigned to the $\pi \rightarrow \pi^*$ excitation, as in the case of the analogous band in Mo₂Cl₈⁴⁻.³⁴ Both suggestions are consistent with the observed oscillator strengths and R group dependence; moreover, in Mo₂(O₂CPh)₄, where the C-O and aromatic π^* systems should interact, band III appears to shift dramatically (to 2.37 μm^{-1}).²⁷

The careful reader will have noted that we quoted 0.9 μm^{-1} above as the predicted $\delta \rightarrow \delta^*$ transition energy in Mo₂Cl₈⁴⁻, when in fact the number in Table IV of ref 3 is 1.37 μm^{-1} . There are two methods for explicitly calculating the singlet (spin-allowed) component of a particular orbital transition in the X α -SW formalism. The method we did *not* use for Mo₂Cl₈⁴⁻ originally now appears somewhat preferable on theoretical grounds,¹⁴ and so we have employed it here for Mo₂(O₂CH)₄; comparison of the Experimental Sections of the two papers will explain the difference between the two methods. For all transitions *except* $\delta \rightarrow \delta^*$ in both Mo₂Cl₈⁴⁻ and Mo₂(O₂CH)₄, the two methods give the same answer within about 0.1 μm^{-1} , and certainly no assignments are changed according to which is used. This ambiguity serves, however, to illustrate the difficulty of calculating electronic spectra with a basically one-electron method; many-electron effects are necessarily more important than in a calculation of, e.g., dipole moments or ionization energies. Even a perfect calculation of one-electron orbitals and charge distribution is no guarantee of accuracy in predicting the spectrum. Although the X α -SW method has been very successful in this regard for many transition metal complexes,³⁵⁻³⁹ it provides only a tentative assignment here.

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Registry No. Mo₂(O₂CH)₄, 51329-49-8; Mo₂⁴⁺, 11083-49-1; Mo₂, 12596-54-2.

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