Metal–Metal, Metal–Ligand, and Ligand–Ligand Interactions in $[Mo_2(O_2CH)_4]$ and $[Mo_2Cl_8]^{4-}$

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Summary Comparison of calculated electronic structures for $[Mo_2(O_2CH)_4]$ and $[Mo_2Cl_8]^{4-}$ reveals two important types of interactions between the Mo–Mo and Mo–ligand bonds.

WE present here results of an SCF–Xα–SW calculation[1] for molybdenum(II) formate, which typifies the dinuclear carboxylates, the largest known class of compounds exhibiting strong metal–metal bonding. Although the calculated results for $[Mo_2(O_2CH)_4]$ in many ways resemble those which we recently reported[2] for $[Mo_2Cl_8]^{4-}$, the comparison reveals two remarkable features of the relationship between metal–metal and metal–ligand bonding in dinuclear molecules of D_{4h} symmetry, one of which has structural implications.

Figure 1 compares SCF valence energy levels of $[Mo_2(O_2CH)_4]$ and $[Mo_2Cl_8]^{4-}$ having more than 20% metal character. The energy ordering and % metal *vs.* ligand character of the levels are qualitatively similar for the two molecules, except for the partitioning of Mo–Mo σ and π bonding among the different a_{1g} and e_u levels, respectively. In $[Mo_2Cl_8]^{4-}$, most of the σ and π bonding is found in the upper $4a_{1g}$ and $5e_u$ pair of orbitals, while in $[Mo_2(O_2CH)_4]$ the main σ and π levels are the lower energy pair (again $4a_{1g}$ and $5e_u$). In this respect $[Mo_2(O_2CH)_4]$ resembles $[Re_2Cl_8]^{2-3}$ more than $[Mo_2Cl_8]^{4-}$.

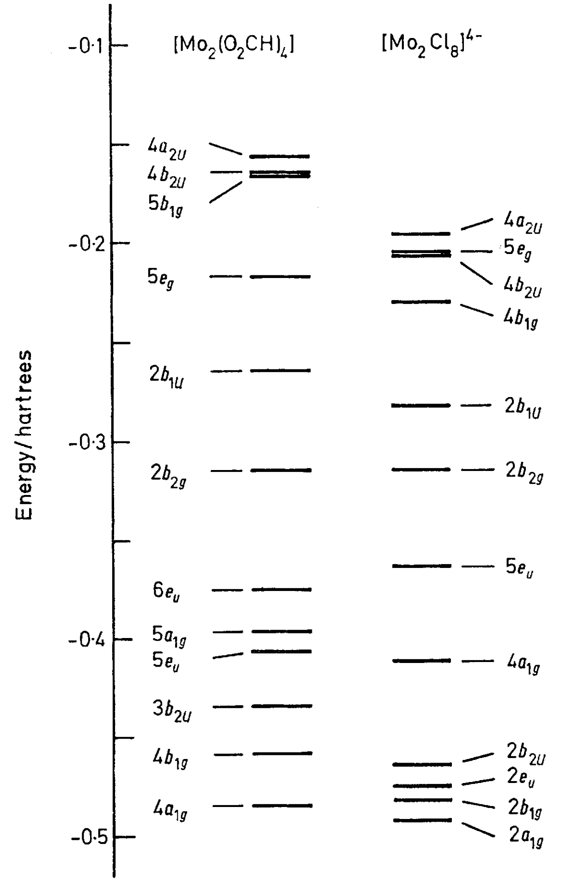

FIGURE 1. Valence energy levels of $[Mo_2(O_2CH)_4]$ and $[Mo_2Cl_8]^{4-}$ with > 20% Mo character. Each $[Mo_2Cl_8]^{4-}$ level has been stabilized by −0·16 hartree to make the energy of the highest occupied $2b_{2g}$ level the same for both molecules.

This difference is explicable in terms of the influence of Mo–ligand bonding on the Mo–Mo interaction, as revealed by contour maps of relevant wavefunctions. Some Mo–ligand π interaction is present in most of the a_{1g} and e_u levels in both molecules; if this π bonding is interior, *i.e.* on the side of the Mo–ligand direction near the Mo–Mo bond, its presence 'steers' charge into the region between the metals and thus enhances Mo–Mo bonding and Mo character in the level; if the π bonding is exterior, it has the opposite effect. The wavefunction maps show that in both molecules the a_{1g} or e_u levels with predominantly metal and ligand character are, respectively, the ones where interior and exterior metal–ligand π bonding dominate. Thus the differing level distribution of Mo–Mo σ and π bonding is at least partially due to the differences in ligand-orbital hybridization between the HCO_2 and 2-Cl systems.

Figure 2 is the wavefunction map for the lower energy $5e_u$ level of $[Mo_2(O_2CH)_4]$, illustrating the interior type of Mo–O π bonding. It also exemplifies an even more interesting aspect of the relationship between metal–metal and metal–ligand bonding, namely the merging of the interior Mo–O π bonds on the two halves of the dimer with each other and the metal–metal bond, giving rise to a multicentre interaction which, in particular, is *attractive* between the two oxygen atoms of the same carboxylate ligand. This phenomenon is also seen in other formate levels and in $[Mo_2Cl_8]^{4-}$ (see, *e.g.*, Fig. 2 of ref. 2), but is overall stronger in the formate. Consistently, the Cl–Cl distance across the Mo–Mo bond in $[Mo_2Cl_8]^{4-}$ is 3·36(2) Å,[4] considerably shorter than the van der Waals contact of 3·60 Å.

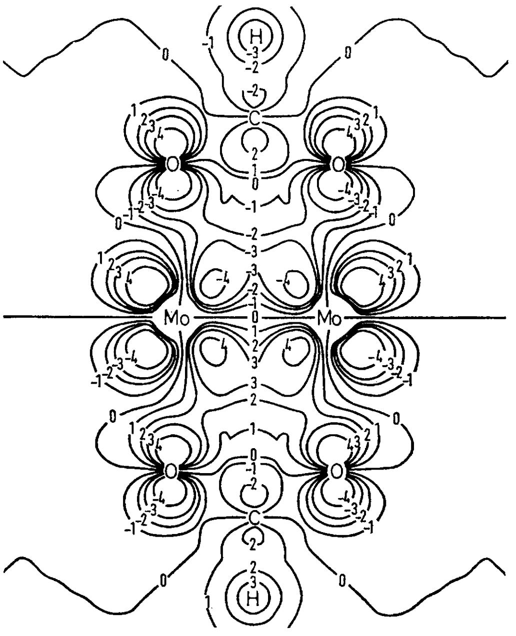

FIGURE 2. Contour map of the $5e_u$ level wavefunction for $[Mo_2(O_2CH)_4]$. The contour values and area covered are the same as for Fig. 3 in ref. 2.

Such attractive ligand–ligand interactions in an M_2L_8 molecule will only be important if the ML_4 units are eclipsed. The eclipsed conformation invariably observed even for nonbridged d^4–d^4 dimers has always been explained as due to metal–metal δ bonding,[5] and our calculations on both $[Mo_2Cl_8]^{4-}$ and $[Mo_2(O_2CH)_4]$ confirm the importance of this effect.[2] However, ligand–ligand interactions of the above type may also contribute to the stability of the eclipsed *vs.* staggered arrangement. The structures of d^5–d^5 dimers, where the antibonding δ^* orbital should be filled[6] and δ bonding therefore absent, should show whether such interactions are strong enough by themselves to force the eclipsed conformation. One such structure, that of $[Re_2Cl_4(PEt_3)_4]$, is known,[7] and it is eclipsed. Unfortunately, in this case the steric requirements of the bulky phosphine ligands may require the eclipsed arrangement. We hope d^5–d^5 dimers will be synthesised where steric factors are unimportant to provide a clear-cut test of these ideas.

We have prepared $[Mo_2(O_2CH)_4]$ directly from $[Mo_2(O_2CMe)_4]$ and formic acid, a simpler procedure than that described previously.[8] Its electronic spectrum is virtually identical to that of all other molybdenum(II) carboxylates;[9]

hence our theoretical analysis should be equally valid for the whole series. These results will be presented in more detail after completion of calculations necessary to provide a thorough comparison of theoretical and experimental ionization[10] and transition energies. Preliminary indications are that the lowest electronic transition near 23,000 cm^{-1} is a forbidden $\delta \rightarrow \pi^*$ or $\pi \rightarrow \delta^*$, rather than an allowed $\delta \rightarrow \delta^*$, process, as a result of configuration interaction.

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