# Structure and Bonding Analysis of Some Xenophilic Transition Metal Clusters

**Zhitao Xu and Zhenyang Lin***

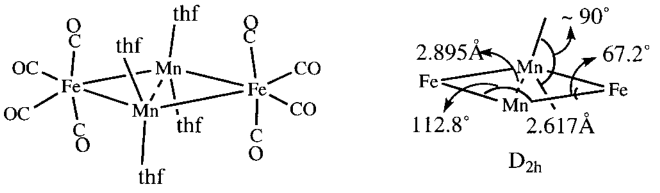
**Abstract:** Ab initio quantum chemical calculations have been used to study the metal–metal interactions in a new emerging class of transition metal clusters. These xenophilic clusters consist of two entirely different types of metal complex fragments in terms of the ligand accepting and donating properties. Simple bonding models based on a local metal frontier orbital approach are proposed to account for their electronic and magnetic behavior. Through our detailed analyses, we find that the paramagnetic properties of these clusters are determined by the coupling among those metal centers bonded to π-donating ligands.

**Keywords:** ab initio calculations • bond theory • clusters • electronic structure • iron • manganese

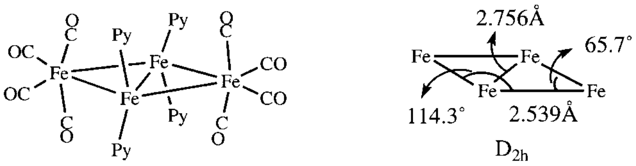
## Introduction

In a recent highlight article,[1] Gade pointed out that the way we teach transition metal cluster chemistry is based on its partition into two paradigms of metal–metal bonded systems, one containing mainly π-acceptor ligands such as carbonyls, nitrosyls, phosphines, and/or cyclopentadienyl groups, and the other containing mainly π-donor ligands such as halides, oxides, chalcogenides, etc. The former type of clusters comprises transition metal centers with zero or even negative formal oxidation states, while the latter contains transition metals in low positive oxidation states.[2,3]

Another new type of transition metal cluster is emerging in which metal complex fragments of the two totally different regimes are directly bonded to each other.[4–7] Harakas and Whittlesey proposed the term xenophilic for this class of clusters to characterize the nature of the combination of different types of metal complex fragments.[7] Some typical clusters of this emerging third type highlighted by Gade are shown in structures **1**–**4**.[1] Unlike the majority of carbonyl clusters, these clusters have open-shell electronic structures. For example, magnetic moment measurements show that **2** has a triplet ground state while **1** appears to have a quintet ground state. To account for the electronic structures of these clusters, a more detailed theoretical study into their metal–metal bonding is required. In this paper, we attempt to provide qualitative metal–metal bonding pictures[8] for these clusters with the aid of ab initio calculations[9] to rationalize their magnetic and electronic behavior.



**1**



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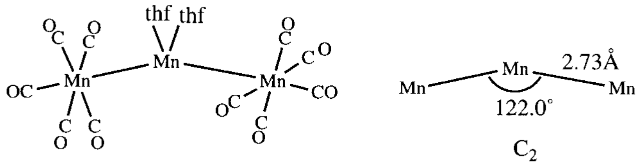

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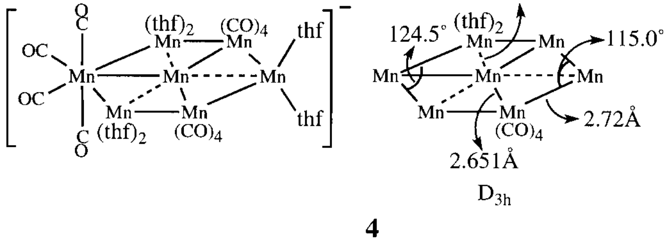

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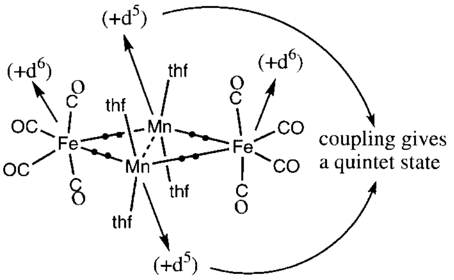
## Results and Discussion

**$[\{(thf)_2MnFe(CO)_4\}_2]$ (1) and $[\{(py)_2FeFe(CO)_4\}_2]$ (2)**: Examining the structure of $[\{(thf)_2MnFe(CO)_4\}_2]$, one can see that the cluster consists of two $Mn(thf)_2$ and two $Fe(CO)_4$ fragments.[7] $Fe(CO)_4$ has π-acceptor ligands while $Mn(thf)_2$ contains hard donor ligands. Metal complexes containing π-acceptor ligands normally conform to the 18-electron rule.[10] Assuming that the two Fe centers satisfy the 18-electron rule, one can immediately conclude that each Fe uses two valence electrons to form two formal covalent σ bonds with the two Mn centers. In other words, each Fe center can be viewed as an octahedral complex with a $d^6$ electronic configuration when the two Fe–Mn bonds are considered as two metal–ligand bonds. Since these two Fe centers have a noble-gas-like electronic configuration, one would expect that the $d^6$ electrons would be relatively inactive due to the presence of carbonyl ligands and would not contribute anything to the cluster's paramagnetic property. As there are four Fe–Mn σ bonds, each Mn atom has to contribute two electrons to form two Fe–Mn σ bonds, and consequently retains five d electrons for the Mn–Mn interaction, a $d^5$–$d^5$ interaction, which then gives the resulting quintet ground state. A schematic bonding model is illustrated in Scheme 1. Here, we employ classical Lewis dot electronic structures[10] to represent the relevant bonding model. This kind of representation is only for the purpose of clarity and simplicity. It should be noted that Harakas and Whittlesey gave a similar covalent model to account for the cluster's magnetic behavior.[7]



Scheme 1. Schematic Lewis dot bonding model for **1**.

The question here is how these two Mn $d^5$ centers in **1** interact with each other. Figure 1 illustrates the relevant d–d orbital interaction between these two Mn centers. For the sake of clarity, we do not depict those d–d molecular orbitals based on Fe centers, which are quite low-lying due to the stabilization effect from the π* orbitals of carbonyl ligands. In the figure, the $d_{xy}$ fragment orbital of each Mn center has been used to form Mn–Fe σ bonds (the Cartesian coordinate system is depicted in Figure 1). Our ab initio results indicate that this is indeed the situation. Therefore, the $d^5$ electrons available for the Mn–Mn interaction have to occupy the remaining four d orbitals. In these four d orbitals, $d_{xz}$ is the lowest in energy, since it has zero overlap with all the metal–ligand (Mn–thf) and metal–metal (Mn–Fe) σ bonds. The $d_{yz}$ orbital is the highest in energy because it overlaps with the ligand's σ orbitals, resulting in its antibonding character.

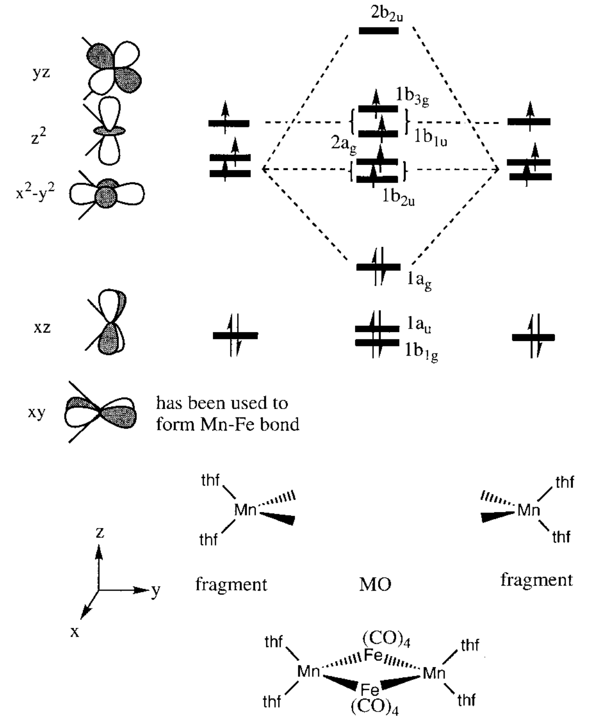


Figure 1. The d–d orbital interaction diagram derived for the two Mn centers of $[\{(thf)_2MnFe(CO)_4\}_2]$. The molecular orbitals derived from the available Fe d orbitals are low-lying and omitted from the figure for the sake of clarity.

Now we come to consider the orbital interaction between the two Mn centers. The $d_{xz}$–$d_{xz}$ orbital interaction gives rise to both $1b_{1g}$ and $1a_u$ molecular orbitals, which are approximately nonbonding due to the nature of their δ overlap. The interaction between the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals from both Mn centers results in one strongly σ-bonding ($1a_g$), two roughly nonbonding ($1b_{2u}$ and $2a_g$), and one strongly antibonding ($2b_{2u}$) molecular orbitals (Figure 1). The $d_{yz}$–$d_{yz}$ orbital interaction gives rise to one weakly bonding ($1b_{1u}$) and one weakly antibonding ($1b_{3g}$) orbital due to their π-overlap nature. It is the two roughly nonbonding ($1b_{2u}$ and $2a_g$) and the two $d_{yz}$–$d_{yz}$ orbitals ($1b_{1u}$ and $1b_{3g}$) that are singly occupied, giving a quintet ground state. The energy-level ordering of these four singly occupied orbitals shown in Figure 1 is only qualitative. One would expect that their orbital energies are close to each other.

Our ab initio calculation results show that the ground state of a $[\{(H_2O)_2MnFe(CO)_4\}_2]$ model cluster is indeed a quintet state ($^5A_g$) in which the four singly occupied orbitals are $b_{1u}$, $b_{2u}$, $a_g$ and $b_{3g}$, consistent with the qualitative orbital pattern shown in Figure 1. Figure 2 shows the spatial plots[8] of these four singly occupied molecular orbitals derived from our HF calculations. The two molecular orbitals ($1b_{1g}$ and $1a_u$) derived from the linear combinations of $d_{xz}$ bases are found in orbitals 119 and 120 in our calculations. The $1a_g$ bonding molecular orbital is found in orbital 123. These three molecular orbitals, which are doubly occupied (see Figure 1), are plotted in Figure 3.

The Mulliken spin density analysis (Table 1) reveals that the spin density of each Mn atom is 1.93. This result indicates

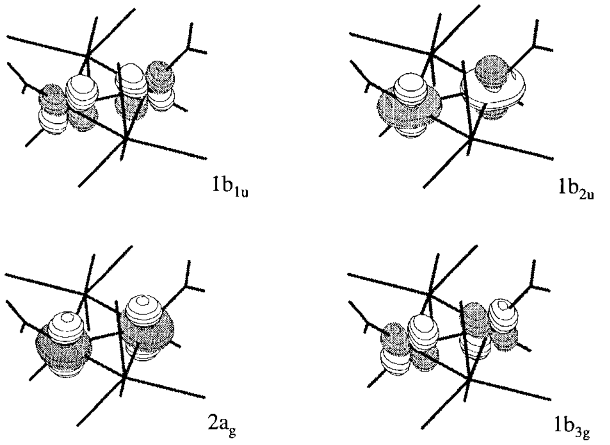


Figure 2. Spatial plots of the four singly occupied molecular orbitals of $[\{(H_2O)_2MnFe(CO)_4\}_2]$ derived from ab initio calculation at the HF level. The orbital symmetry labels of these molecular orbitals are those of Figure 1.

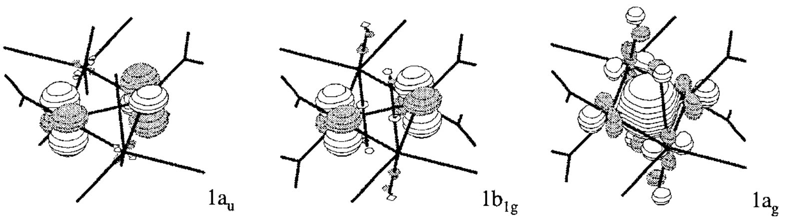


Figure 3. Spatial plots of the three doubly occupied molecular orbitals of $[\{(H_2O)_2MnFe(CO)_4\}_2]$ derived from the $d_{xz}$ and $d_{x^2-y^2}$ bases (see also Figure 1 for the symmetry labels).

that the four unpaired electrons are almost exclusively localized on the two Mn centers. This result also provides strong support for our assumption that the $d^6$ electrons on each Fe center are inactive. The atomic charges on Mn and Fe atoms are +1.08 and +0.62, respectively. A less positive Fe center is reasonable because of its noble-gas-like electronic configuration. Table 1 shows that the positive charges carried by the metal atoms are counterbalanced almost exclusively by the eight carbonyl ligands. The atomic charges are mainly dictated by the metal–carbonyl bond polarity.

Cluster $[\{(py)_2FeFe(CO)_4\}_2]$[5] (**2**) is isostructural with the $[\{(thf)_2MnFe(CO)_4\}_2]$ (**1**) cluster. One would expect the molecular orbital pattern of **2** to be similar to that of **1**. The former cluster has two more valence electrons than the latter. Therefore, a triplet ground state is expected for **2**. Our ab initio calculation on the $[\{(NH_3)_2FeFe(CO)_4\}_2]$ model cluster gives a $^3B_{2u}$ ground state, corresponding to the $(b_{1u})^1(b_{3g})^1$ electronic configuration. Earlier extended Hückel molecular orbital calculations did not give a similar electronic configuration.[5] The two singly occupied orbitals are derived from the in-phase and out-of-phase linear combinations of the $d_{yz}$ bases (see Figure 1) that have metal–ligand antibonding character. The Mulliken analysis (Table 1) gives a spin density of 0.96 on each Fe center of the two $Fe(NH_3)_2$ fragments. Once again, the result implies that the two unpaired electrons are localized on the two Fe centers bonded to the N containing ligands. The atomic charges for the iron atoms in the $Fe(NH_3)_2$ fragments are also greater than those in the $Fe(CO)_4$ fragments. The carbonyls carry the most negative charges, approximately −0.4 each (see Table 1).

**$[Mn_3(thf)_2(CO)_{10}]$ (3)**: This cluster consists of one $Mn(thf)_2$ and two $Mn(CO)_5$ fragments.[6] Here, one can easily assume that the two terminal Mn centers conform to the 18-electron rule. In other words, two Mn–Mn σ bonds can be assumed for the trinuclear V-shape cluster. If one considers the two Mn–Mn σ bonds as two Mn–L bonds, the two terminal Mn centers can once again be viewed as normal octahedral complexes with a $d^6$ electronic configuration. Due to their noble-gas-like electronic configuration and the presence of strong π accepting ligands, the $d^6$ electrons are inactive, as seen in the two rhombic clusters discussed above.

For the $Mn(thf)_2$ fragment, the Mn center has to contribute two valence electrons to form the two Mn–Mn σ bonds mentioned above. The remaining five d electrons should be localized on the central Mn center. From our analysis of the $Mn(thf)_2$ fragment above, we can immediately deduce that the remaining five electrons will occupy four metal d orbitals, as one of the five d orbitals in the metal center has been utilized for the Mn–Mn bonding.

The orbital pattern of the $Mn(thf)_2$ fragment should be similar to that presented in Figure 1. Although no magnetic and spectroscopic properties are available for this cluster, we

Table 1. The average atomic charges and spin densities derived from Mulliken analyses at the HF(BLYP) level.

| | Average atomic charge | | | | | |
|---|---|---|---|---|---|---|
| $[\{(H_2O)_2MnFe(CO)_4\}_2]$ | Mn | Fe | $O(H_2O)$ | H | C | O |
| | +1.08 | +0.62 | −0.92 | +0.47 | 0.00 | −0.43 |
| $[\{(NH_3)_2FeFe(CO)_4\}_2]$ | Fe | $Fe_{(CO)}$ | N | H | C | O |
| | +1.00 | +0.48 | −1.07 | +0.37 | +0.06 | −0.44 |
| | (+0.86) | (+0.61) | (−0.96) | (+0.35) | (−0.15) | (−0.26) |
| $[Mn_3(H_2O)_2(CO)_{10}]$ | Mn | $Mn_{(CO)}$ | $O(H_2O)$ | H | C | O |
| | +1.46 | +0.50 | −0.94 | +0.48 | +0.15 | −0.40 |
| | (+1.24) | (+0.67) | (−0.80) | (+0.41) | (−0.04) | (−0.22) |
| | Atomic spin density [a] | | | | | |
| | $[\{(H_2O)_2MnFe(CO)_4\}_2]$ | | $[\{(NH_3)_2FeFe(CO)_4\}_2]$ | | $[Mn_3(H_2O)_2(CO)_{10}]$ | |
| | Mn | Fe | Fe | $Fe_{(CO)}$ | Mn | $Mn_{(CO)}$ |
| | 1.93 | 0.01 | 0.96 | 0.00 | 2.96 | 0.00 |
| | | | (0.84) | (0.03) | (2.59) | (0.07) |

[a] The spin densities for all ligand atoms are almost zero.

predict that it has an $S = {}^3/_2$ ground state. Detailed ab initio calculations show that the ground state is a quartet $^4B$ (based on the $C_2$ point group), corresponding to the occupation of the three singly occupied fragment orbitals shown in the left-hand side of Figure 1. The total spin density (see Table 1) on the central Mn atom is 2.96, indicating the almost exclusive localization of the three unpaired electrons. The central Mn atom has an atomic charge of $+1.46$. The atomic charge of each terminal Mn atom is $+0.50$. These results suggest that the Mn–Mn bonds are highly polarized. This property might explain the experimental observation that the cluster is partially decomposed in solution.[6] Again, the atomic charges are mainly dictated by the metal–carbonyl bond polarity (see Table 1).

**$[Mn_7(thf)_6(CO)_{12}]^-$ (4)**: This heptanuclear planar cluster contains one uncoordinated Mn, three $Mn(CO)_4$, and three $Mn(thf)_2$ fragments.[6] If we again assume that each Mn center of three $Mn(CO)_4$ fragments satisfies the 18-electron rule, we can immediately propose the *formal* bonding description shown in Figure 4. Each Mn atom in the three $Mn(CO)_4$ fragments uses 3 valence electrons to form 3 Mn–Mn σ bonds with its adjacent Mn atoms. Indeed, one can see that these three Mn(central)–Mn bonds are shorter than the other three Mn(central)–Mn bonds. The Mn centers of $Mn(CO)_4$ are analogous to pentagonal-bipyramidal $d^4$ transition metal complexes if the three Mn–Mn σ bonds are viewed as equivalent to three M–L bonds. Since the Mn centers in the three $Mn(thf)_2$ fragments have coordination environments similar to those discussed for **1** and **3**, we expect that they have similar fragment orbital patterns. For convenience, these fragment orbitals are again shown in Figure 4. The central Mn atom contributes three electrons using s, $d_{x^2-y^2}$ and $d_{xy}$ atomic orbitals to form three Mn–Mn σ bonds with the three $Mn(CO)_4$ fragments. The remaining five d electrons occupy $d_{xz}$, $d_{yz}$ and $d_{z^2}$ orbitals (see Figure 4). Here, we tentatively assign the extra electron from the negative molecular charge to the central Mn atom for convenience.

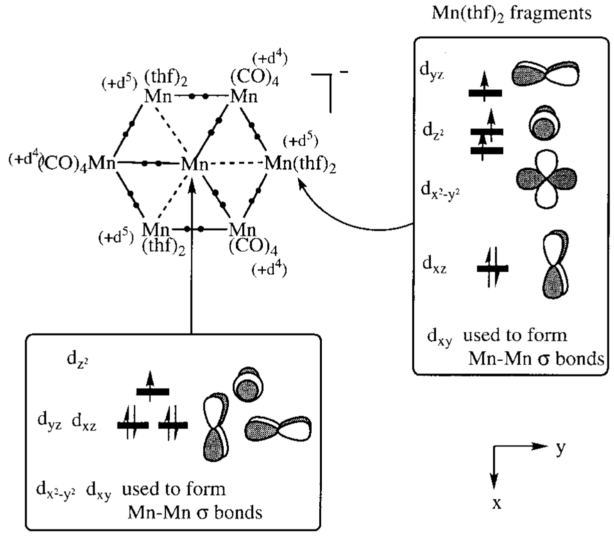


Figure 4. Schematic bonding model for $[Mn_7(thf)_6(CO)_{12}]^-$.

In addition to the formal valence bond picture illustrated in Figure 4, the metal–metal interaction of this cluster can be derived by consideration of the orbital interaction among the frontier fragment orbitals of the central Mn and the $Mn(thf)_2$ fragments. Here, the d electrons in the $Mn(CO)_4$ units are again assumed to be inactive. The magnetic behavior of the cluster depends on how the spin–spin coupling occurs among the three $S = {}^3/_2$ centers and the $S = {}^1/_2$ uncoordinated central atom.

Detailed and accurate molecular orbital calculations must be performed in order to obtain the ground-state electronic structure of this cluster. It is not feasible to do ab initio calculations for such a large cluster given the capacity of our current computer resources. We can only present some qualitative analyses here. One would expect that the three sets of $d_{x^2-y^2}$ and $d_{z^2}$ orbitals (see Figure 4) from the three $Mn(thf)_2$ fragments would interact with the central Mn's $d_{z^2}$, $p_x$, and $p_y$ orbitals. This interaction may lead to three weakly bonding molecular orbitals accommodating 6 metal electrons, and therefore leaving an unpaired electron. If this is the case, one expects a quintet ground state ($S = 2$) with four unpaired electrons in which the other three unpaired electrons come from the three sets of the singly occupied $d_{yz}$ orbital. One can conclude that the heptanuclear cluster should have a ground state between $S = 2$ and $S = 5$.

## Summary

The structure and bonding in this new type of xenophilic transition metal cluster can be understood in terms of a simple molecular orbital approach. In this simple approach, one first assumes that metal centers bonded to π-accepting ligands conform to the 18-electron rule. By doing so, one can easily determine the number of metal–metal σ bonds in the cluster and, consequently, the number of electrons required to form these metal–metal σ bonds from the metal centers. The remaining available electrons on those metal centers bonded to π-donor ligands are then considered to contribute to the magnetic behavior for a given cluster. A similar approach, called the local metal frontier orbital approach,[12] has been used in analyzing metal–metal interactions in transition metal clusters with π-donor ligands. Using this approach, we have successfully explained the magnetic properties of clusters **1** and **2**. We also predict that cluster **3** should have a quartet ground state and that cluster **4** has a ground state between $S = 2$ and $S = 5$. Through our detailed analyses, we find that the paramagnetic properties of these clusters (**1**–**4**) are determined from the coupling among those metal centers bonded to π-donating ligands.

## Calculation Details

Molecular orbital calculations for clusters **1**–**3** were carried out at the HF level by the Gaussian 94 program package[9] on Silicon Graphics workstations. For clusters **2** and **3**, density functional theory calculations at the BLYP level were also performed. Both the HF and BLYP results were qualitatively consistent with each other. Therefore, no additional BLYP calculation was carried out for **1**. Owing to the large size of these clusters, the capacity of our computers prevented us from performing geometry optimization calculations. Since we only focus on the bonding analyses for these new clusters, single-point molecular orbital calculations should be acceptable in obtaining the details of their electronic structures. The standard 6-311G basis set, available within the Gaussian 94 package, was used for all atoms in our calculations. The use of the triple-$\zeta$ basis set was good enough to produce accurate molecular orbitals for analyses.

Clusters **1**–**3** were modeled by replacing THF with $H_2O$ and Py with $NH_3$ for theoretical simplicity. The O–H bond length was fixed at 0.96 Å and N–H at 1.0 Å. The tetrahedral angle was used for both $H_2O$ and $NH_3$. In the calculations, $D_{2h}$ symmetry was used for both **1** and **2**, and $C_2$ for **3**. Average bond lengths of experimental data are used for both metal–metal and metal–ligand bonds. The metal–metal bond lengths and related bond angles are shown in **1**–**4**. The detailed metal–ligand bond parameters used for calculations are given in the following paragraph.

For cluster **1**, the average Mn–O and Fe–C distances were 2.100 and 1.747 Å, respectively. Within the $Mn(thf)_2$ fragments, the average O-Mn-O bond angle was 91.4°. Within the $Fe(CO)_4$ fragments, the average OC-Fe-CO bond angles were 103.5° and 141.6° (the axial carbonyls bend away from the equatorial ones). The C–O distance in the carbonyls was fixed at 1.15 Å. For cluster **2**, the average Fe–N and Fe–CO bond lengths were 2.14 Å and 1.71 Å, respectively. The N-Fe-N bond angle was 90.0°, while the average OC-Fe-CO bond angles were 99.6° and 148°. For cluster **3**, the Mn–CO bond length was 1.818 Å. The OC(axial)-Mn-CO(equatorial) bond angle was 92.5 Å and the OC(eq)-Mn-CO(eq) angle was fixed at 90.0°.

The molecular orbitals (Figures 2 and 3) obtained from HF results were plotted using the Molden v3.2 program written by G. Schaftenaar.[11]

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