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Bonding in $Mo_3M'S_4$ Cubane-Type Clusters: Variations in Electronic Structure When M′ Is a Main Group or Transition Metal

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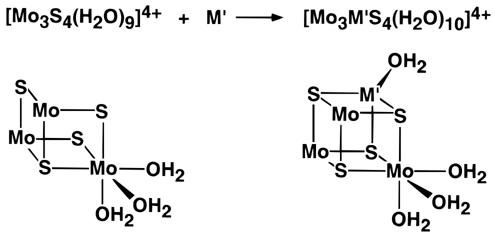
The results of Fenske−Hall molecular orbital calculations for cubane-type clusters having $Mo_3M'S_4$ cores show that the electronic structures of the clusters depend on the nature of M′. When M′ is a main group metal, as in $[Mo_3(SnCl_3)S_4(NCS)_9]^{6-}$, $Mo_3SnS_4(S_2PEt_2)_6$, or $[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$, the heterometal is oxidized upon incorporation into the cluster; no M′−Mo bonds are formed, and electrons are transferred from M′ to an orbital localized on the Mo_3S_4 incomplete cubane core. When M′ is a transition metal, as in $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$, $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$ (tacn = 1,4,7-triazacyclononane), or $Mo_3CoS_4(CO)(Cp')_3$ (Cp′ = methylcyclopentadiene), M′ is not oxidized but instead shares electron density with the Mo_3S_4 core through the formation of metal−metal bonds with the Mo_3 triangle. The relatively high stretching frequencies observed for CO ligands bound to the Ni and Pd centers in the Mo_3NiS_4 and Mo_3PdS_4 clusters arise from the nature of the bonding in the clusters, not from the oxidation of the Ni and Pd atoms. Since the same heterometal orbitals are used both to form the M′−Mo bonds and to back-donate to the CO ligand, the Mo_3 orbitals and the CO π^* orbitals compete for M′ electron density. The CO orbitals do not compete effectively for metal electron density in the Ni and Pd clusters, and this results in weak back-donation to the CO π^* orbitals and relatively high CO stretching frequencies. Although it has been proposed that the Mo_3NiS_4 cluster may serve as a model for NiMoS hydrodesulfurization (HDS) catalysts, the fact that the Ni center in this cluster is not electron rich suggests that it may not provide a suitable model. The electron density at the heterometal can be increased slightly by increasing the donor ability of the ligands attached to the Mo atoms.

Introduction

Bimetallic cubane-type clusters are of interest as potential models for active sites in both biological and hydrodesulfurization (HDS) catalysts.[1−5] We have previously carried out molecular orbital calculations on $Mo_2M'_2S_4$ clusters[6] and developed qualitative bonding schemes for a number of other heterometal cubanes.[7] The synthesis and structure of several bimetallic clusters with an $Mo_3M'S_4$ core (M′ = a 3d, a 4d, or a main group metal) have also been reported.[4,5,8−13] As shown in Scheme 1, the $Mo_3M'S_4$ cubane-type clusters are usually formed by incorporating a heterometal, M′, into the incomplete cubane-type aqua ion cluster $[Mo_3S_4(H_2O)_9]^{4+}$ to form the cubane-type cluster $[Mo_3M'S_4(H_2O)_{9+x}]^{n+}$ (x = 1−3, depending on coordination geometry of the heterometal).[14] (For clarity, only three H_2O ligands are shown in Scheme 1, but all of the Mo atoms have three H_2O ligands.) Once the heterometal has been inserted into the cluster, the H_2O ligands attached to the Mo atoms may be replaced by other donor ligands (e.g. NCS^-, Cp′). The H_2O ligand on the heterometal can also be replaced by different ligands and is commonly substituted with a CO group.

Scheme 1



Qualitative bonding schemes have been developed for the incomplete cubane-type clusters $[Mo_3S_4(Cp)_3]^+$ [15] (Cp = cyclopentadiene) and $[Mo_3S_4(CN)_9]^{5-}$,[16] and molecular orbital

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calculations have been performed on several other incomplete cubane-type clusters[17,18] and related clusters.[19−21] Molecular orbital calculations have also been reported for clusters with Mo_3FeS_4, Mo_3NiS_4,[22] and W_3SnS_4 cores,[23] but no detailed study of the bonding in clusters having an $Mo_3M'S_4$ core has been reported. In this paper we report the results of Fenske−Hall[24] molecular orbital calculations on a group of $Mo_3M'S_4$ clusters and attempt to answer several questions that have arisen in the literature regarding the electronic structure and reactivity of these clusters. First, although the oxidation state of the Mo atoms in the incomplete clusters is accepted to be Mo^{4+}, the oxidation states of the heterometal and Mo atoms in the cubane-type clusters have become the subject of debate.[5,9] The discussion is centered around a possible two-electron oxidation of the heterometal when it is incorporated into the incomplete cluster. Evidence for such an oxidation comes primarily from the relatively high CO stretching frequencies reported for the CO ligand attached to Ni in $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ (2060 cm^{-1})[8] and to Pd in $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$ (tacn = 1,4,7-triazacyclononane) (2085 cm^{-1}).[5] Second, it has been proposed that clusters such as $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ might serve as structural and possible functional models for the active surface sites of NiMoS HDS catalysts.[25] It therefore becomes important to understand how the electronic structure of these clusters is related to other cubane-type clusters and, in particular, how the electronic environment of the heterometal differs in the various clusters.

We report here the calculated electronic structures of $[Mo_3(SnCl_3)S_4(NCS)_9]^{6-}$,[12] $Mo_3SnS_4(S_2PEt_2)_6$,[26] $[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$,[13] $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$,[8] $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$,[4] and $Mo_3CoS_4(CO)(Cp')_3$ (Cp′ = methylcyclopentadiene).[11] Ignoring metal−metal bonds, the Mo atoms in all of the clusters are bound to three core sulfur atoms and three ligands and therefore have pseudo-octahedral coordination geometry. The Sn atoms in the clusters are also bound to three sulfur atoms and three ligands and exhibit the same pseudooctahedral geometry, while the Ni, Pd, and Co atoms are bound to three core sulfur atoms and one ligand and have pseudo-tetrahedral coordination geometry. The long Sn−Mo distances in the Sn clusters (averaging 3.72 Å) rule out bonds between the Sn and Mo atoms, while the Mo−M′ distances in the Ni, Pd, and Co cubanes (2.68, 2.85, and 2.70 Å, respectively) indicate the presence of Mo−M′ bonds.

The first section below provides a brief account of the calculational details. This is followed by a description of the electronic structure and bonding in the $Mo_3S_4L_x$ incomplete cubane clusters. The incomplete clusters generally have six metal electrons, corresponding to each Mo atom having a formal 4+ oxidation state, but there are several recently synthesized incomplete clusters which have seven,[18,27] eight,[28,29] and even nine[30] cluster electrons. A description of the bonding in the incomplete cubane clusters provides a starting point for the study of the bonding in the cubanes. The next section discusses the electronic structures of $[Mo_3(SnCl_3)S_4(NCS)_9]^{6-}$, $Mo_3SnS_4(S_2PEt_2)_6$, and $[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$. It is clear in these complexes that the Sn center is oxidized upon incorporation in the incomplete cubane core(s). This is followed by an analysis of the bonding in $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$, $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$, and $Mo_3CoS_4(CO)(Cp')_3$. Comparisons between the electronic structures of the Sn and the Ni, Pd, and Co clusters indicate that the Ni, Pd, and Co atoms are not formally oxidized when they are incorporated in the cubane clusters. Finally, the last section discusses how variations in the donor ability of the ligands on the Mo atoms effects the electronic environment of the heterometal in the Ni, Pd, and Co clusters and considers whether $Mo_3M'S_4$ clusters can indeed serve as models for HDS catalysts.

Calculational Details

The results described for the clusters were obtained using Fenske−Hall molecular orbital calculations. The molecular structures of $[Mo_3(SnCl_3)S_4(NCS)_9]^{6-}$,[12] $Mo_3SnS_4(S_2PEt_2)_6$,[26] $[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$,[13] $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$,[8] $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$,[4] and $Mo_3CoS_4(CO)(Cp')_3$[11] have all been determined by X-ray diffraction. With the exception of $Mo_3SnS_4(S_2PEt_2)_6$, atomic positions for the $Mo_3M'S_4$ cores of these clusters were idealized to C_{3v} (or D_{3d} for the double-cubane $[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$) symmetry from the known structures.

The last section in the paper reports ligand effects on the electronic structures of a series of nine clusters: $[Mo_3M'S_4(CO)L_x]^{n+}$ (M′ = Ni, Pd, Co; L = H_2O, $x = 9$; L = tacn, $x = 3$; L = Cp′, $x = 3$. Of the nine possible cluster combinations with the metals and ligands listed here, only $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$, $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$, and $Mo_3CoS_4(CO)(Cp')_3$ have been structurally characterized. The remaining six cluster combinations were constructed by substituting the above-mentioned Mo-attached ligands (L) to a $Mo_3M'S_4CO$ cluster core containing the various heterometals (M′). The atomic positions of the ligands were then optimized by performing molecular mechanics calculations using the 1.01 Universal Force Field[31−33] as implemented through Cerius^2.[34] The atomic positions of the $Mo_3M'S_4CO$ cores were frozen during the optimizations and movement was restricted to the ligand atoms only.

Atomic charges, orbital populations, and overlap populations were calculated by Mulliken population analysis.[35] Bond orders were calculated using the method of Sannigrahi and Kar.[36] All atomic basis functions were generated by the Xα program of Herman and Skillman[37] using the method of Bursten, Jensen, and Fenske.[38] An exponent of 2.2 was used for the 5s and 5p functions of both Mo and Pd; an exponent of 2.0 was used for the 4s and 4p functions of both Ni and Co. An exponent of 1.2 was used for hydrogen.

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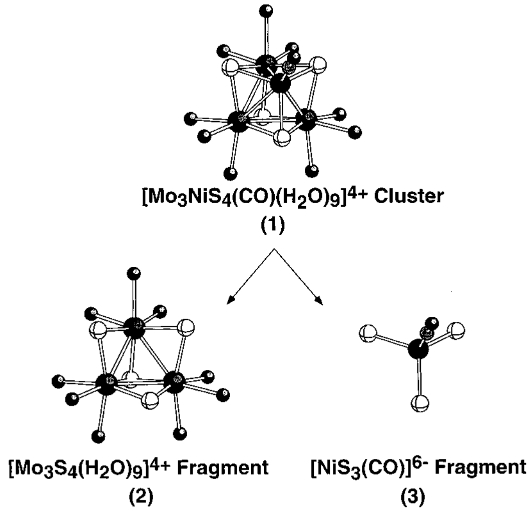
Scheme 2



Results and Discussion

When studying metal−metal bonding, it is useful to break down a cluster into characteristic components or fragments. Metal−metal bond formation can then be viewed in terms of molecular orbitals (MO's) associated with each fragment. This approach has proven to be useful in studies of both metal carbonyl[39−41] and metal−sulfur cubane[6,42] clusters, where strong metal−ligand interactions can be separated out from the weaker metal−metal interactions. The formation of metal−metal bonds in the cubane clusters requires the use of metal orbitals that are also used for metal−ligand bonding. The pseudotetrahedral (Ni, Pd, Co) and pseudo-octahedral (Sn) heterometals and the pseudo-octahedral Mo metals are coordinatively saturated before the formation of metal−metal bonds, and the energy and orientation of the metal-based orbitals used in forming metal−metal bonds are therefore dictated by the stronger metal−sulfur/ligand interactions. Previous calculations on related $Mo_2M'_2S_4L_x$ clusters used MoS_3L_3 fragments with approximate O_h symmetry and $M'S_3L$ fragments with approximate T_d symmetry to describe the metal−ligand interactions.[6] In the current study, we found it more convenient and descriptive to use the incomplete cubane-type cluster, $Mo_3S_4L_x$, as one fragment, and $M'S_3L_x$ as the other. These fragments are illustrated in Scheme 2 using $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ (**1**) as an example. Here the cubane cluster (**1**) is broken down into $[Mo_3S_4(H_2O)_9]^{4+}$ (**2**) and $[NiS_3(CO)]^{6-}$ (**3**) fragments. The use of these types of fragments allows us to view the formation of Mo−M′ bonds most intuitively.

In the following discussions we focus on interactions between frontier metal-based fragment orbitals. In all the clusters discussed here these frontier orbitals are at least 80% metal in character and are separated by at least 1 eV from lower energy molecular orbitals which are high in sulfur character. We therefore focus on the metal portion of these frontier orbitals and show only the metal components of the orbitals in the figures.

Mo_3S_4 Core. Because the Mo_3S_4 core of the incomplete cubane fragment remains intact upon formation of the cubane cluster, it is useful to describe and understand the bonding in this core before including it in a description of the bonding in the overall cubane-type cluster. In a qualitative orbital analysis of their incomplete cubane-type cluster $[Mo_3S_4Cp_3]^+$, Dahl et al.[15] predicted that there are nine cluster orbitals involving direct metal−metal interactions: four bonding (two a_1 + e) and five antibonding (a_2 + two e) delocalized trimetal orbitals (the three lowest-energy orbitals are occupied by the six metal electrons). We also found these groups of metal-based orbitals in the Mo_3S_4 core fragments we studied (such as the metal-based orbitals of $[Mo_3S_4(NCS)_9]^{5-}$ shown on the right-hand side of Figure 1) but consider it more descriptive to label these nine orbitals as three strongly bonding ($1a_1$ + 1e), one weakly bonding ($2a_1$), two weakly antibonding (2e), and three strongly antibonding (a_2 + 3e). There are also six higher-energy unoccupied Mo-based orbitals which are not involved in metal−metal interactions but are strongly Mo−ligand antibonding. Only the six lower-energy orbitals are shown in Figure 1 because they are the orbitals involved in metal−metal bonding in the cubanes. When the incomplete clusters contain three Mo^{4+} centers, six metal electrons occupy the three strongly bonding orbitals ($1a_1$ and 1e*)* to form three Mo−Mo bonds; the weakly bonding $2a_1$ orbital remains unoccupied.

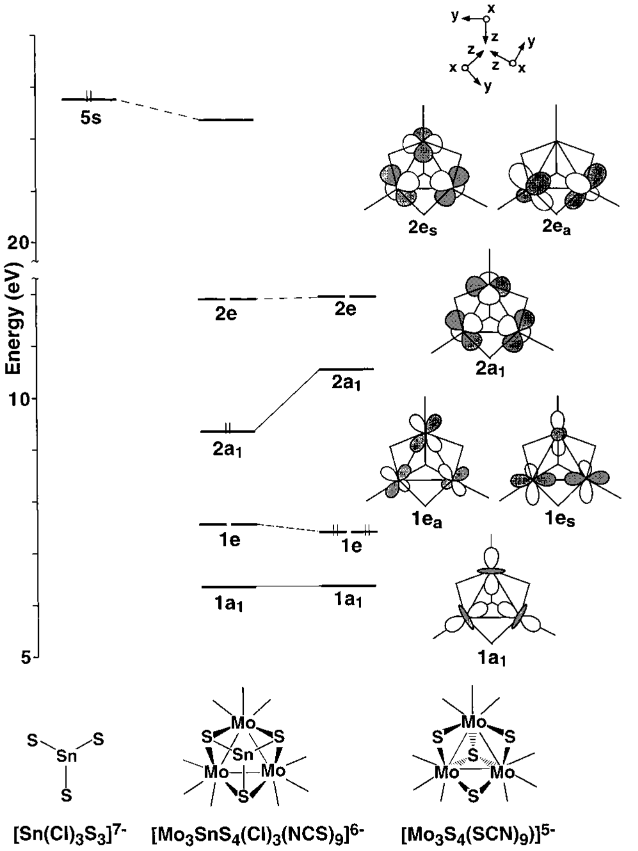


Figure 1. Calculated energy level diagram for $[Mo_3(SnCl_3)S_4(NCS)_9]^{6-}$ and for the $[SnCl_3S_3]^{7-}$ and $[Mo_3S_4(NCS)_9]^{5-}$ fragments.

Dahl also predicted that it would be possible to have clusters with more than six metal-based electrons, and as mentioned earlier, several incomplete clusters have indeed been synthesized with more than six electrons. Results of theoretical studies for these clusters[19−21,43] are consistent with Dahl's predictions regarding metal−metal bonding. In the eight- and nine-electron complexes, the seventh and eighth electrons occupy the higher-energy $2a_1$ orbital (composed of Mo $d_{x^2-y^2}$ atomic orbitals in the coordinate system defined in Figure 1) that contributes to

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Mo−Mo bonding, and the ninth electron occupies the weakly antibonding 2e orbital. The seven-electron complex is different in that the seventh electron occupies the antibonding 2e orbital while the bonding $2a_1$ orbital remains empty. Although occupation of the 2e orbital by a single electron does not appear to lead to a true Jahn−Teller distortion, a small distortion of the Mo_3 triangle is seen in the crystal structure of the seven-electron cluster.[18] It is important to point out that the eight- and nine-electron cluster cores have the general formula Mo_3XCl_3 (X = S, O, Cl) while the seven-electron cluster has an Mo_3S_4 core. Substituting bridging chlorine atoms for bridging sulfur atoms appears to have a noticeable effect on the ordering of the unoccupied energy levels, namely, the unoccupied $2a_1$ orbital is stabilized to a lower energy than that of the unoccupied 2e orbital. This effect is not limited to bridging atoms, however, since terminal thiocyanate ligands also lower the energy of the $2a_1$ orbital (see Figure 1).

The bridging S atoms play an important role in the formation of the cubane-type clusters since they form the M′−S bonds that complete the primary framework of the cubane. When the heterometal inserts into the incomplete cluster to form the cubane, it occupies the pocket formed by these S atoms. As discussed below, formation of the M′−S bonds removes electron density from the Mo_3S_4 core. This loss of electron density from the core can be compensated for in one of two ways, either a formal oxidation of the heterometal and transfer of two electrons into the Mo_3S_4 core or the formation of covalent Mo−M′ bonds. Heterometal oxidation occurs when M′ is a main group metal, while Mo−M′ bonds are formed when M′ is a transition metal.

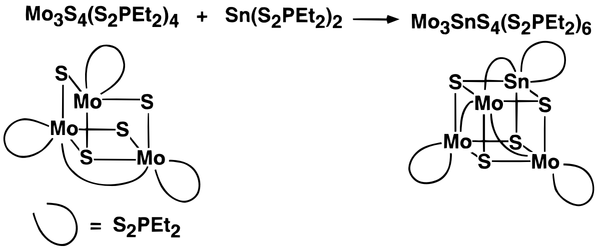
$[Mo_3S_4(SnCl_3)(NCS)_9]^{6-}$. One of the first heterometals to be incorporated into the incomplete cubane-type cluster was Sn. $[Mo_3S_4(SnCl_3)(NCS)_9]^{6-}$ is one of the more recent Sn complexes to be synthesized. The energy levels for this complex and for the component $[Mo_3S_4(NCS)_9]^{5-}$ and $[SnCl_3S_3]^{7-}$ fragments are shown in Figure 1. Charges for the fragments are calculated using oxidation states of Mo^{4+}, Sn^{2+}, and S^{2-}. These are consistent with the oxidation states of the species used in the preparation of the complex (eq 1).

$$[Mo_3S_4(H_2O)_9]^{4+} + SnCl_2 \xrightarrow[NaNCS]{HCl} [Mo_3S_4(SnCl_3)(NCS)_9]^{6-} \quad (1)$$

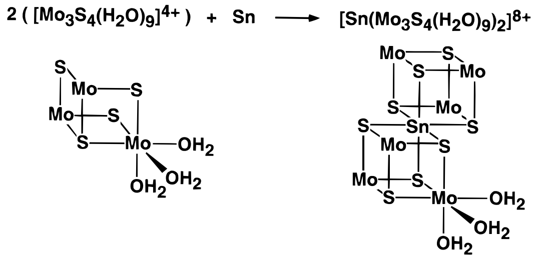
The calculated electronic structure of the cubane shows clearly that the Sn center is oxidized upon incorporation into the cluster. The HOMO of the Sn fragment is the 5s orbital of the Sn^{2+} center. When inserted into the incomplete cluster to form the cubane, the Sn atom donates two electrons from the 5s orbital to the Mo-based $2a_1$ LUMO of the incomplete cluster (thus the Sn atom is oxidized, $Sn^{2+} \rightarrow Sn^{4+}$). The cubane HOMO is an Mo_3-based orbital with little contribution from the Sn orbitals, and the Mo_3S_4 core essentially becomes an eight-electron system. The cluster HOMO is a bonding orbital with a_1 symmetry, consisting primarily of Mo $d_{x^2-y^2}$ atomic orbitals. The bonding character of the MO comes from the overlap of the $d_{x^2-y^2}$ orbitals in the plane of the three Mo atoms. There is virtually no contribution from the Sn atomic orbitals to any of the bonding metal-based cluster orbitals, and the occupied orbitals of the cluster closely resemble those of the eight-electron incomplete cubane clusters.

$Mo_3SnS_4(S_2PEt_2)_6$. As illustrated in Scheme 3, $Mo_3SnS_4(S_2PEt_2)_6$ is synthesized differently than the previous cluster.[26] In the incomplete cluster the bidentate ligands bind to one five-coordinate and two six-coordinate Mo atoms. When the Sn atom inserts to form the cubane cluster, all the metal atoms become six coordinate as the ligands rearrange to give a new bridging network between the Sn and Mo atoms. Since the Mo_3SnS_4 core and the overall electronic structure of this cubane cluster are similar to the core and electronic structure of $[Mo_3S_4(SnCl_3)(NCS)_9]^{6-}$, the energy level diagram for this cluster is not illustrated. Just as in $[Mo_3S_4(SnCl_3)(NCS)_9]^{6-}$, two electrons are transferred from the Sn 5s orbital to an unoccupied a type orbital of the Mo_3 triangle. Since the geometry of the bridging ligands lowers the point group of the cluster to C_s, the cluster HOMO now has a′ rather than a_1 symmetry as in the previous cluster. Even with the lowered symmetry and the corresponding increase in freedom for mixing among the orbitals, the HOMO is still composed primarily of Mo-based $d_{x^2-y^2}$ atomic orbitals and is similar to the HOMO of $[Mo_3S_4(SnCl_3)(NCS)_9]^{6-}$. Unlike the previous cluster, however, the Mo_3 triangle is not uniform (one Mo−Mo bond is 0.2 Å longer than the other two). While this structure might suggest that the two transferred electrons occupy an e orbital, thus forcing a Jahn−Teller distortion, our results suggest that this is not the case. The structure appears to result instead from the arrangement of the bridging ligands. The two shorter Mo−Mo bonds are bridged by S_2PEt_2 ligands, while the long Mo−Mo bond is not. The ligand arrangement and the a′ character of the HOMO indicate that the distortion of the Mo_3 triangle results from the constriction imposed by the bridging ligands.

Scheme 3



Scheme 4



$[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$. Tin has also been incorporated into the double cluster $[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$. While the previous two clusters are synthesized using Sn(II), the synthesis of the this cluster begins with Sn metal. As illustrated in Scheme 4, the double cluster is formed when Sn metal reacts with 2 equiv of the incomplete cluster. The calculated energy level diagram for this cluster is not illustrated, since the structure of each cubane component and the electronic structure of these components resemble those of the Sn clusters discussed above. The distinguishing feature of the electronic structure of the double cubane is the transfer of two electrons to *each* Mo_3S_4 core so that the Sn atom is oxidized by a total of four electrons ($Sn^0 \rightarrow Sn^{4+}$). In the double cubane, the transferred electrons occupy two Mo-based orbitals that are simply linear combinations of the $2a_1$ orbitals of each Mo_3S_4 core. These two orbitals are the HOMO and SHOMO (second-highest occupied molecular orbital) of the double cluster. Since this cluster has D_{3d} symmetry, the HOMO and SHOMO have a_{1u} and a_{1g} symmetry,

Table 1. Calculated Bond Orders in $Mo_3M'S_4$ Clusters and Incomplete Cubane Mo_3S_4 Fragments

	$Mo_3M'S_4$		Mo_3S_4
	M′−Mo	Mo−Mo	Mo−Mo
$[Mo_3(SnCl_3)S_4(NCS)_9]^{5-}$	0.019	0.983	0.765
$Mo_3SnS_4(S_2PEt_2)_6$	0.002	0.991	0.740
$[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$	0.024	1.039	0.804
$[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$	0.432	0.777	0.774
$[Mo_3PdS_4(CO)(tacn)_3]^{4+}$	0.401	0.763	0.771
$Mo_3CoS_4(CO)(Cp')_3$	0.561	0.682	0.684

respectively. Although these MO's are formally bonding and antibonding between the two Mo_3 triangles, the triangles are physically too far apart from each other for any interaction to occur. As a result, the two cluster MO's lie close in energy and are both actually nonbonding between the triangles.

Two common features of all three Sn clusters are the absence of Sn−Mo metal bonding and the reduction of the Mo_3S_4 core. In each cluster there is no significant mixing of the Sn- and Mo-based metal orbitals, and the electrons that are transferred from the Sn atom occupy a Mo-based a-type cluster orbital (or two a-type cluster orbitals in the double cubane) that is Mo−Mo bonding. The absence of Sn−Mo bonding is also reflected by the calculated Sn−Mo bond orders in each cluster. The values shown in Table 1 for average Sn−Mo bond orders are negligible. The average Mo−Mo bond orders in both the cubane clusters and their respective incomplete Mo_3S_4 fragments are also shown in Table 1, and in contrast to the absence of Mo−Sn bonds, the Mo−Mo bond orders increase by about 30% from the Mo_3S_4 fragment to the cubane. This is consistent with the Mo−Mo bonding nature of the a-type orbitals occupied in the cubanes and the lack of Sn participation in the occupied metal-based orbitals.

To examine the effects of the two-electron reduction of the Mo_3S_4 core in more detail, we also carried out calculations on a reduced incomplete cluster $[Mo_3S_4(H_2O)_9]^{2+}$. The results of these calculations show that, although the two extra electrons formally occupy a Mo-based orbital, the bulk of the extra negative charge actually resides on the equatorial S atoms, with the charge on the Mo atoms remaining virtually unchanged. Reducing the Mo_3S_4 core thus increases the nucleophilicity of the equatorial S atoms and provides the increased electron density necessary to form M′−S bonds. (This same effect was observed by Müller et al. in their studies of a similar W_3S_4 cluster.[23]) In the Sn cubane clusters the oxidation of the Sn center provides the extra electron density, and it appears that the transfer of electrons from Sn to the Mo_3 network is necessary to form Sn−S bonds and maintain the integrity of the Mo_3S_4 core. Attempts at synthesizing the single cubanes with Sn^{4+} species or the double cubane with anything more oxidized than Sn^0 have not been successful. Indeed, many cubanes formed from the $[Mo_3S_4(H_2O)_9]^{4+}$ incomplete cluster decompose upon air oxidation. The double-cubane $[Sn(Mo_3S_4(H_2O)_9)_2]^{8+}$, for example, decomposes to give the starting incomplete cluster and a single $[Mo_3SnS_4]^{6+}$ aqua cluster which has not been characterized[8].

To better understand the oxidation of the double cubane, we also carried out a calculation on an oxidized double-cluster $[Sn(Mo_3S_4(H_2O)_9)_2]^{10+}$. A similar, but opposite, result from that of the reduction calculation shows that, although the electrons are formally removed from a Mo-based orbital, it is actually the sulfur atoms that lose electron density. This is accompanied by a decrease in Sn−S bond order and an increase in Mo−S bond order. Thus, when electrons are removed from Mo-based orbitals of the Mo_3S_4 core, the cluster compensates by moving electron density from the M′−S bonds (in reality, breaking those bonds) back into the Mo_3 network to form, once again, the initial incomplete cluster with no Sn−S bonds.

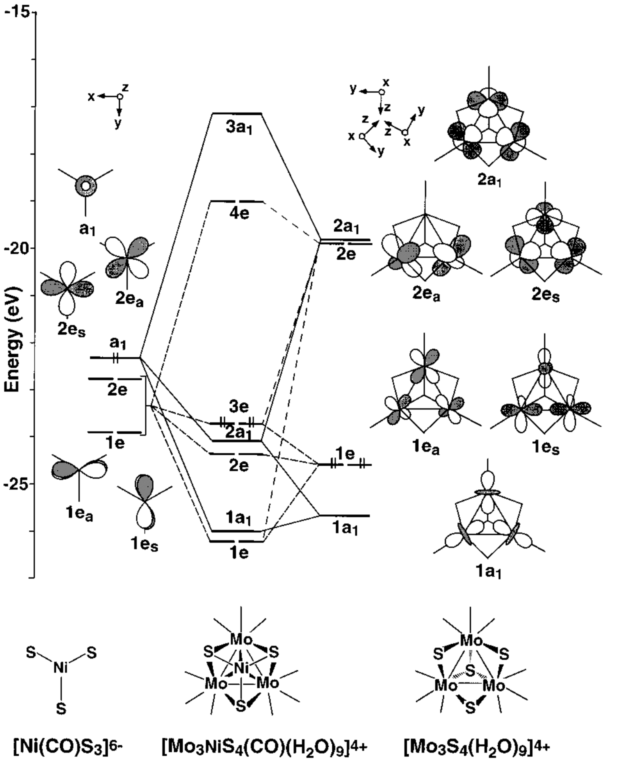


Figure 2. Calculated energy level diagrams for $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ and for the $[Ni(CO)S_3]^{6-}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ fragments.

In summary, the results of calculations on three separate Sn-containing clusters suggest that the Mo_3S_4 core cluster requires an additional two electrons in order to form M′−S bonds. In the Sn clusters these electrons are provided by transfer of electrons from Sn to the Mo_3S_4 core. Although the three Sn cubanes differ structurally, they all are characterized by oxidation of the Sn atom and the absence of any Sn−Mo bonding. The HOMO in each cubane cluster is an a-type Mo−Mo bonding orbital that was unoccupied in the incomplete cluster. Occupation of this orbital increases the bonding within the Mo_3 network and leads to the increase in electron density on the S atoms needed to form Sn−S bonds. This same bonding picture is probably appropriate to describe the bonding in similar $Mo_3M'S_4$ clusters where M′ is another main group metal.[44−48] As discussed below, however, this picture is not appropriate to describe the bonding in the cubane clusters incorporating transition metals such as Ni, Pd, or Co.

$[Mo_3M'S_4(CO)L_x]^{n+}$. Calculations were carried out for $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$, $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$, and $Mo_3CoS_4(CO)(Cp')_3$. Since the electronic structures of these three clusters are similar, only $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ is discussed in detail. The calculated energy level diagrams for $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ and the $[Mo_3S_4(H_2O)_9]^{4+}$ and $[NiS_3(CO)]^{6-}$ fragments are illustrated in Figure 2. (The charges on the

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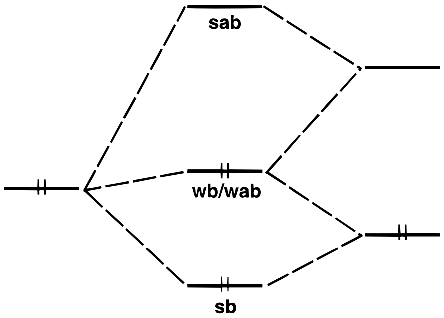

Figure 3. Qualitative energy level diagram for the orbitals resulting from a three-orbital−four-electron interaction. The orbitals are strongly bonding (sb), weakly bonding or weakly antibonding (wb/wab), and strongly antibonding (sab). Interactions between groups of M′ and Mo_3 orbitals in the $Mo_3M'S_4$ clusters lead to a similar nine-orbital−twelve-electron energy level diagram where the sb, wb/wab, and sab orbitals are replaced by groups of three sb orbitals, three wb/wab obitals, and three sab orbitals, respectively.

fragments correspond to the same formal oxidation states assigned to the components of the overall cluster: Mo^{4+}, S^{2-}, Ni^0.) The Ni- and Mo-based fragment orbitals are quite close together in energy, allowing for good interaction between the metal-based orbitals on the two fragments. The Ni cluster (as well as the Pd and Co clusters) has 16 metal-based electrons and six metal−metal bonds. Formation of Mo−Ni bonds requires the use of both the higher-energy unoccupied $2a_1$ and 2e orbitals and the lower-energy occupied orbitals of the Mo_3 fragment. Unlike the lower-energy orbitals, which form the Mo−Mo bonds and lie in the Mo_3 plane, the higher-energy ($2a_1$, 2e) fragment orbitals lie out of the Mo_3 plane.

The metal-based energy levels for $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ appear as four distinct groups: a group of eight occupied orbitals that are both Ni and Mo based; three unoccupied orbitals that have both Ni and Mo character; three unoccupied Mo−Mo antibonding orbitals; and six high-energy Mo-based nonbonding orbitals. The latter two groups of orbitals are too high in energy to be displayed on the diagram. Based on earlier qualitative models for metal−metal bonding in clusters having an $M_3M'S_4$ core,[7] we would expect the 16 cluster electrons to occupy six delocalized metal−metal bonding orbitals and two metal−metal nonbonding orbitals localized on the Ni atom. While earlier studies of $Mo_2Ni_2S_4L_x$ clusters[6] clearly show a group of occupied Ni-based nonbonding orbitals below the metal−metal bonding orbitals, the $Mo_3NiS_4L_x$ cluster does not. There are eight occupied metal orbitals in the $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ cluster, but the identity of the nonbonding orbitals is not immediately evident.

Because both the fragments and the overall cluster have C_{3v} symmetry a high degree of mixing takes place among fragment orbitals possessing the same symmetry. While this complicates the interpretation of the cluster orbitals involved in metal−metal bonding, the system can be greatly simplified by viewing it as an extension of a three-orbital−four-electron system.[49] In the simple three-orbital system (Figure 3), the orbitals combine to form a strongly bonding (sb) MO, a weakly bonding or weakly antibonding (wb/wab) MO, and a strongly antibonding (sab) MO. In our extension of this system, the cubane can be viewed as a nine-orbital−twelve-electron system (not counting the two Ni nonbonding orbitals) where the orbitals occur in groups of three (refer to Figure 2). This extension leads to a group of three strongly bonding cluster MO's (1e and $1a_1$), a group of three weakly antibonding cluster MO's ($2a_1$ and 3e) and a group of three strongly antibonding cluster MO's (4e and $3a_1$) (the bonding/antibonding labels are in reference to the interaction between the heterometal and the Mo atoms). The two cluster orbitals not included in these groupings are the 2e orbitals. These orbitals are primarily Ni based and are linear combinations of the 1e and 2e Ni fragment orbitals. Although the orbitals do contain Mo character, the orientation of the Mo orbitals does not allow for overlap with the Ni orbitals, and the net effect is a Ni−Mo nonbonding e orbital. The energetic placement of these nonbonding orbitals above the bonding 1e and $2a_1$ orbitals is a consequence of the large stabilization of the bonding orbitals resulting from the formation of three Mo−Mo bonds.

The bonding/antibonding character of the middle group of cluster orbitals ($2a_1$ and 3e) is affected by the relative energies of the M′ and Mo_3 fragment orbitals. As the M′ fragment orbitals increase in energy relative to the Mo_3 fragment orbitals, the middle group of cluster orbitals becomes more bonding (or in our case, less antibonding) between the heterometal and the Mo_3 triangle. Conversely, as the M′ fragment orbitals decrease in energy relative to the Mo_3 fragment orbitals, the middle group of cluster orbitals becomes less bonding (or in our case, more antibonding) between the heterometal and the Mo_3 triangle. This effect is seen very clearly in a comparison of the orbital structures and bond orders in the Ni, Pd, and Co clusters. The energies of the M′ fragment orbitals increase in the order Pd < Ni < Co. The Pd fragment orbitals lie closest in energy to the occupied Mo_3S_4 fragment orbitals and thus mix least strongly with the unoccupied Mo_3S_4 fragment orbitals. In contrast, the Co fragment orbitals lie considerably higher in energy than either the Pd or Ni fragment orbitals and mix most strongly with the unoccupied Mo_3S_4 fragment orbitals. As a result, the antibonding character of the 3e and $2a_1$ cluster orbitals decreases in the order Pd > Ni > Co. As can be seen from the calculated Mo−M′ bond orders shown in Table 1, this leads to considerable variation in the strength of the Mo−M′ bonds. While we might expect the better 4d−4d overlap to lead to stronger Mo−M′ bonds in the Pd cluster, the net Mo−M′ bonding interaction actually increases in the order Pd < Ni < Co. The differences in orbital energies appear to be more important here than differences in 4d−4d and 4d−3d orbital overlap.

Comparisons of the Mo−Mo bond orders listed in Table 1 show that the net Mo−Mo bonding interactions in the Ni, Pd, and Co clusters appear to depend on the nature of the Mo_3S_4 core and show little change between the cubanes and the corresponding Mo_3S_4 fragments. This effect contrasts sharply with the increase in Mo−Mo bond orders in the Sn clusters which resulted from the complete transfer of electrons from the Sn atom to the Mo_3S_4 core.

The character of the cluster orbitals of both the incomplete cubane and the $Mo_3M'S_4$ clusters (M′ = Ni, Pd, Co) is consistent with results of cyclic voltammetry experiments performed by Shibahara et al.[22] on $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, and $[Mo_3Fe(H_2O)_{10}]^{4+}$. Three consecutive, reversible one-electron reduction peaks are observed for the incomplete cubane, and our results indicate that these three electrons should occupy the 2e and/or the $2a_1$ orbitals of the Mo_3S_4 cluster. Since stable nine-electron incomplete cubane clusters actually exist, it is not surprising that these reductions are reversible. In contrast, the Ni cubane cluster (where 16 "metal" electrons completely fill the metal−metal bonding and nonbonding orbitals) displays an irreversible three-electron reduction. In this cluster the reduction will place the three added electrons into an e-type orbital which is strongly antibonding with respect to Mo−Ni interactions. This

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will disrupt the integrity of the metal−metal bonding framework and is consistent with the observed irreversibility. This irreversible behavior would also be expected for the 16 "metal" electron Pd and Co clusters. On the other hand, the Fe cluster studied by Shibahara undergoes three consecutive, *reversible* one-electron reductions. Since this cluster only has 14 "metal" electrons, reduction of the cluster by three electrons will add two electrons to a counterpart of the weakly antibonding 3e cluster orbital found in the Ni cluster and only one electron to a higher-energy strongly antibonding orbital. Adding only one electron to an antibonding orbital is probably enough to distort the geometry of the molecule but not enough to destroy the integrity of the metal−metal bonding network.

In summary, our results show that the electronic structures of the $Mo_3M'S_4$ cubane clusters depend on the nature of M′. Differences in electronic structure depend on both the relative energies of the Mo_3 and M′ orbitals and on the type of valence orbitals associated with M′. A main group metal inserts into the incomplete cluster and is clearly oxidized, losing electrons from its relatively high-energy s orbital (and p orbitals in the double cubane) to the Mo_3S_4 portion of the cluster. The transferred electrons are localized in the Mo_3S_4 triangle and occupy an Mo_3 bonding orbital. The reduction of the Mo_3S_4 core provides the electron density needed to form the S−Sn bonds. In contrast, when M′ is a transtion metal both the lower energy and the orientation of the valence d orbitals enable M′ to participate in Mo−M′ bonds and the metal electrons to occupy cluster MO's delocalized throughout the metal framework. The participation of both Mo and M′ orbitals and electrons in these cluster MO's provides the electron density needed to form S−M′ bonds. The Ni, Pd, and Co clusters are all characterized by three bonding Mo−M′ orbitals, two nonbonding orbitals localized primarily on M′, and three weakly antibonding Mo−M′ orbitals. The relative energies of the Mo_3 and M′ orbitals affect the character of the orbitals and lead to the strongest Mo−M′ bonds in the Co cluster.

Oxidation States in the Ni, Pd, and Co Clusters. There has been considerable discussion of the formal oxidation states of the heterometals in the $Mo_3M'S_4$ clusters, particularly for clusters containing Ni or Pd. The relatively high CO stretching frequencies observed for the $[Mo_3M'S_4L_x(CO)]^{n+}$ clusters (2060 and 2085 cm^{-1} for M′ = Ni^8 and Pd,[5] respectively) have led several researchers to suggest that Ni and Pd are oxidized to Ni^{2+} and Pd^{2+} upon formation of the cubane clusters. Although Sykes noted that the properties of the Ni in the Mo_3NiS_4 cluster appear to lie somewhere between those of Ni^0 and Ni^{2+},[9] he assigned a 2+ oxidation state to the Ni atom in $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$. This assignment, originally based on comparisons with CO stretching frequencies in the hydrogenase from *Chromatium vinosum*, is no longer valid, however, since the relevant stretching frequency in the hydrogenase has recently been reassigned to a CN^- ligand attached to an Fe atom rather than a CO ligand attached to a Ni atom.[50] The assignment of oxidation states in the Pd cluster is also not clear-cut. Hidai et al.[5] noted that while the CO stretching frequency is higher in this cluster than in known Pd^0 species, it is also significantly lower than CO stretching frequencies in known Pd^{2+} complexes. In addition, the tetrahedral coordination geometry of the Pd atom in the cluster is generally associated with Pd in a zero oxidation state; four-coordinate Pd^{2+} is usually square planar.[51] To further complicate the issue, the CO stretching frequency in $Mo_3CoS_4(CO)(Cp')_3$ is significantly lower than the corresponding value in either $[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$ or $[Mo_3PdS_4(CO)(tacn)_3]^{4+}$ and does not suggest oxidation of the Co atom.

While it is extremely difficult to assign formal oxidation states to metal atoms involved in delocalized cluster bonding, the calculated electronic structures of the clusters discussed in this paper make it clear that the $Mo_3M'S_4$ cubanes fall into two distinct classes. In the Sn clusters (and presumably in other $Mo_3M'S_4$ cubanes where M′ is a main group metal) Sn is unambiguously oxidized when a pair of electrons is transferred to the Mo_3S_4 core. In contrast, the calculated electronic structures of the Ni, Pd, or Co clusters indicate that it is not appropriate to describe M′ as formally oxidized in these clusters. The complete transfer of electrons seen in the Sn clusters is clearly not observed in the Ni, Pd, or Co clusters. Instead, all of the occupied cluster molecular orbitals exhibit a significant amount of mixing between the M′ and Mo atomic orbitals. With the exception of the two nonbonding molecular orbitals, all the metal-based cluster MO's are delocalized throughout the entire Mo_3M' framework. The degree to which the charge distributions in the orbitals are polarized toward the M′ or Mo atoms depends on both the separation between the energy levels of the M′ and Mo fragment orbitals and the amount of overlap between these orbitals, but none of the orbitals is localized on the Mo_3 portion of the cluster.

If the heterometal is not formally oxidized, what factors lead to the relatively high CO stretching frequencies in the Ni and Pd clusters? The answer to this question really lies in the fact that the heterometals in these clusters share electron density not only with their tetrahedrally coordinated ligands but also with the three Mo atoms. As discussed earlier, the Mo_3S_4 core requires extra electron density to form the M′−S bonds in the cubane. In the Sn clusters, oxidation of the Sn atom provides this extra electron density, and two electrons are transferred into a cluster orbital localized on the Mo_3S_4 core. In the clusters where M′ is a transition metal, the extra electron density is provided by the formation of three Mo−M′ bonds and the participation of both Mo and M′ orbitals in cluster orbitals that are delocalized throughout the entire Mo_3M' framework. As is clear from the diagrams of the heterometal fragment orbitals shown in Figure 2, the formation of Mo−M′ bonds in the $Mo_3M'S_4$ clusters requires the use of the d_{xz} and d_{yz} orbitals ($1e_a$ and $1e_s$ in Figure 2) of the heterometal. At the same time, however, these are also the M′ orbitals that overlap with the CO 2π orbitals and therefore participate in back-bonding with the CO 2π orbitals. The dual role of the d_{xz} and d_{yz} orbitals leads to a direct competition between the metal framework and the CO ligand for electron density. It is the participation of the heterometal $1e_a$ and $1e_s$ orbitals in the delocalized cluster orbitals, not the oxidation of the heterometal, that reduces the electron density available for π back-bonding and leads to the relatively high CO stretching frequencies observed for the Ni and Pd clusters. As noted earlier, the energy of the heterometal orbitals increases in the order Pd < Ni < Co. The considerably lower CO stretching frequencies in the Co cluster can be traced to the fact that the Co orbitals lie at much higher energy than either the Pd or Ni orbitals and actually lie 4 eV closer to the CO π^* orbitals. The CO 2π orbitals thus compete more effectively for electron density in the Co cluster than in either the Ni or the Pd cluster. The calculated populations for the CO 2π orbitals in the Co, Ni, and Pd are listed in Table 2. The much larger 2π population in the Co cluster reflects the higher energy of the Co orbitals and the more effective competition

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Table 2. CO Stretching Frequencies and Calculated CO Mulliken Populations in $Mo_3M'S_4$ Clusters

species	CO stretch (cm^{-1})	5σ	2π	ref
CO	2143	2.00	0.00	51
$[Mo_3NiS_4(CO)(H_2O)_9]^{4+}$	2060	1.384	0.214	8
$[Mo_3PdS_4(CO)(tacn)_3]^{4+}$	2085	1.408	0.322	5
$Mo_3CoS_4(CO)(Cp')_3$	1943	1.406	0.529	11

of the 2π orbitals for electron density and is consistent with the lower CO stretching frequency observed for this cluster.

In summary, the high CO stretching frequencies measured for the Ni and Pd clusters are not the consequence of an oxidized heterometal but rather are the result of the dual role of the heterometal d_{xz} and d_{yz} orbitals in the cluster. Since these orbitals are used both in the formation of the Mo−M′ bonds and in back-bonding to the CO ligand, the metal framework of the cluster and the CO ligand compete for electron density. In a very simplified picture, the Mo_3 framework might be viewed as a tridentate π acceptor ligand in competition with CO. The relatively high CO frequencies in the Ni and Pd clusters reflect the fact that the higher-energy CO 2π orbitals do not compete effectively with the lower-energy Mo_3 framework orbitals for electron density. Back-bonding increases in the Co cluster because the Co orbitals lie higher in energy, relative to the Mo_3 orbitals, than the Ni or Pd orbitals. This competition for electron density is also apparent in the structures of the Ni and Pd clusters, since, as noted earlier by Hidai,[5] the Mo−Ni and Mo−Pd distances lengthen noticeably when the π acceptor CO ligand replaces a donor ligand.

Ligand Effects and $Mo_3M'S_4$ Clusters as Models for HDS Catalysts. Several recent studies showed that the heterometal in the $Mo_3M'S_4$ clusters exhibits quite interesting reactivity. Hidai et al. observed the uptake of ethylene and various alkynes by the Pd atom in the $[Mo_3PdS_4(Cl)(tacn)_3]^{3+}$ cluster and found that the cluster actually catalyzes the addition of alcohols to alkynic acid esters and the cyclization of alkynoic acids to enol lactones.[5,52] Shibahara also observed uptake of ethylene by Ni in a series of related Ni clusters.[53] The reactivity of the Ni center prompted Jacobsen et al. to suggest that the $Mo_3M'S_4$ clusters may serve as models for HDS catalyst surfaces.[25]

The reactivity at the heterometal center will, in part, be determined by the electronic environment of the metal, and the results of the calculations presented here show that the heterometal site in the Pd and Ni clusters is indeed unique. The participation of the Pd or Ni orbitals in the delocalized Mo_3M' cluster orbitals leaves the heterometal much less electron rich than might be expected for a metal bound to three donor S ligands. In addition, the weak back-bonding to Pd or Ni should increase the lability of the CO ligand. The fact that the Ni and Pd centers in these clusters are not electron rich, however, calls into question their suitability as models for HDS catalysts. All of the model transition metal complexes and clusters which have actually been shown to activate and/or break C−S bonds contain one or more electron-rich metal centers.[54] Nevertheless, the very delocalized nature of the electronic structure of these clusters suggests that changing the donor ability of the ligands on the Mo atoms will have an effect on the electronic environment at the heterometal. Stronger donor ligands should lead to increased electron density on the heterometal and an increase in back-bonding to the CO ligand.

Table 3. Variations in Calculated CO 2π Mulliken Populations and Heterometal Charges as Mo−Bound Ligands Are Changed

	CO 2π orbital	heterometal charge
Ni clusters		
$Mo_3NiS_4(CO)(H_2O)_9{}^{4+}$	0.214	−0.042
$Mo_3NiS_4(CO)(tacn)_3{}^{4+}$	0.257	−0.110
$Mo_3NiS_4(CO)(Cp')_3{}^{+}$	0.283	−0.169
Pd clusters		
$Mo_3PdS_4(CO)(H_2O)_9{}^{4+}$	0.279	+0.035
$Mo_3PdS_4(CO)(tacn)_3{}^{4+}$	0.322	−0.070
$Mo_3PdS_4(CO)(Cp')_3{}^{+}$	0.349	−0.113
Co clusters		
$Mo_3CoS_4(CO)(H_2O)_9{}^{3+}$	0.443	+0.039
$Mo_3CoS_4(CO)(tacn)_3{}^{3+}$	0.490	0.000
$Mo_3CoS_4(CO)(Cp')_3$	0.530	−0.063

To test this idea we carried out calculations on a series of nine $Mo_3M'S_4(CO)L_x$ clusters (all combinations of M = Ni, Pd, Co and $L_x = (H_2O)_9$, $(tacn)_3$, Cp'_3). Since only three of these combinations have been synthesized and characterized structurally, the arrangements of the Mo-bound ligands in the remaining six clusters were determined via molecular mechanics optimizations (see Calculational Details). The calculated heterometal charges and CO 2π populations for all nine clusters are shown in Table 3. The trends in these charges and populations indicate that the donor ability of the Mo-bound ligands increases in the order H_2O < tacn < Cp′. (This trend also reflects the relative ligand field strengths of the ligands in these clusters. Although it is expected that tacn should be the strongest ligand among these three, steric crowding of the tacn ligand around each Mo atom may lead to longer Mo−N bonds and a lower effective donor strength[55]). As the effective donor strength of the Mo-attached ligands increases, the Mo−M′ bonds become less polarized toward the Mo atoms, more electron density remains on the heterometal, and more back-donation to the CO ligand is observed.

These results indicate that it may be possible to tune the electron density at the heterometal by changing the ligands attached to the Mo atoms. It should be noted, however, that the effects of changing the ligands on the Mo atoms are smaller than the effects of changing the heterometal from Pd or Ni to Co. The fact that the donor ability of the Mo ligands correlates with the relative electron density at the heterometal also suggests that the reactivity of the heterometal may be influenced by the donor ability of the Mo ligands. We will consider this subject further as we continue to study the electronic structure of the $Mo_3M'S_4$ clusters and attempt to relate differences in electronic structure to differences in binding and activation of ligands at the heterometal in these clusters.

Conclusions

The results of calculations on several $Mo_3M'S_4L_x$ cubane clusters show that the electronic structures of the clusters depend on the nature of M′. When M′ is a main group metal such as Sn, the calculated electronic structures of the clusters show clearly that the heterometal is oxidized upon incorporation into the cluster. No Sn−Mo bonds are formed, and electrons are transferred from the Sn atom to an orbital localized on the Mo_3S_4 incomplete cubane core. When M′ is a transition metal (Ni, Pd, or Co), on the other hand, M′ is not oxidized but instead shares electron density through the formation of metal−metal bonds with the Mo_3 triangle.

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The relatively high stretching frequencies observed for CO ligands bound to the Ni and Pd centers in Mo_3NiS_4 and Mo_3PdS_4 clusters have previously been attributed to the oxidation of the heterometals to Ni^{2+} and Pd^{2+}. Our results offer an alternative explanation for the high CO stretching frequencies. A common feature of the Ni, Pd, and Co clusters is the formation of Mo−M′ bonds. The heterometal d_{xz} and d_{yz} orbitals are used both to form these metal−metal bonds and to back-bond to the CO $2\pi^*$ orbitals. This leads to a competition between the Mo_3 orbitals and the CO π^* orbitals for M′ electron density. Since the Ni and Pd orbitals lie close in energy to the Mo_3 triangle and are significantly lower in energy than the CO orbitals, the CO orbitals do not compete effectively for metal electron density in the Ni and Pd clusters. This results in weak back-donation to the CO π^* orbitals and relatively high CO stretching frequencies. The Co orbitals are much higher in energy than those of either Ni or Pd and are therefore closer in energy to the CO $2\pi^*$ orbitals. The CO π^* orbitals therefore compete much more effectively for M′ electron density in the Co cluster; this results in stronger back-donation to the CO ligand and a lower stretching frequency.

Although it has been proposed that the Mo_3NiS_4 cluster may serve as a model for NiMoS HDS catalysts, the fact that the Ni center in this cluster is not electron rich suggests that it may not provide a suitable model. The very delocalized nature of the electronic structure of these clusters does suggest, however, that the electron density at the heterometal may be increased by substituting ligands with better donating ability at the Mo atoms. Calculations for $Mo_3M'S_4(CO)L_x$ model clusters showed that as the donor ability of L increases both the electron density on M′ and the back-donation to CO increase. The effects of changing the ligands attached to the Mo atoms are much smaller, however, than the effects of changing M′ from Pd or Ni to Co.

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