Molybdenum Oxides vs. Molybdenum Sulfides: Geometric and Electronic Structures of $\text{Mo}_3X_y^{-}$ ($X$=O, S and $y$=6, 9) Clusters

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In light of the recent attention $\text{MoS}_2$ has received regarding its possibilities for use in the photocatalytic evolution of $\text{H}_2$, we have conducted a comparative computational investigation of some key properties that determine water reactivity such as the molecular structure and water adsorption properties of molybdenum oxide and sulfide clusters. Using density functional theory methods, we have found that while $\text{Mo}_3\text{O}_6^{-}$ and $\text{Mo}_3\text{S}_9^{-}$ assume very similar ring-type isomers, $\text{Mo}_3\text{O}_6^{-}$ and $\text{Mo}_3\text{S}_9^{-}$ clusters are very different with $\text{Mo}_3\text{O}_6^{-}$ having a ring-type structure and $\text{Mo}_3\text{S}_9^{-}$ having a more open, linear-type geometry. The more rigid $\angle(\text{Mo}–\text{S}–\text{Mo})$ bond angle is the primary geometric property responsible for producing such different lowest energy isomers. Additionally, due to a stronger oxide-water hydrogen bond, water is found to adsorb more strongly to $\text{Mo}_3\text{O}_6^{-}$ than to $\text{Mo}_3\text{S}_9^{-}$ although dispersion effects reduces this difference when Molybdenum centers contribute to the binding.

I. INTRODUCTION

Molybdenum sulfide has long been used as an efficient hydrodesulfurization and hydrogenation catalyst. More recently, there has also been an emerging interest in $\text{MoS}_2$ as a photocatalyst for the efficient production of $\text{H}_2$. Li and coworkers have recently reported great enhancements in $\text{H}_2$ evolution on CdS following the loading of a small amount (0.2 wt %) of MoS$_2$ cocatalyst in the presence of sacrificial reagents. However, very little work has been done thus far to understand the interactions between water and molybdenum sulfide clusters at the molecular level.

In the last few years, many studies have been undertaken to investigate Group VI metal oxides using small molecular clusters by both experimental and theoretical means. Focusing on water reactivity, we have recently investigated the interactions of small tungsten oxides and water to understand the associated reaction mechanisms. From those investigations, we have observed that initial water adsorption and subsequent proton mobility are the critical components which characterize the chemistry between small tungsten oxide anion clusters and water.

Prior to computing chemical interaction energies, the geometric as well as the electronic structures of the reactants must first be understood. While there has been a significant amount of research in determining the structure of molybdenum and tungsten sulfides on the nanoscale, the factors that determine the structures and stabilities of small molybdenum sulfide clusters are still not clearly understood. For example, though several published reports on the computation of the structures of anionic and neutral $\text{Mo}_3\text{S}_9$ clusters are available, they show significant differences among each other in their findings regarding the lowest energy isomers. While most of the isomers identified in these studies are based on a central $\text{Mo}_3$ cyclic unit, they vary in the number and location of terminal sulfide, bridging sulfide, and S$_2$ units. As a knowledge of the low-lying geometric isomers is a prerequisite for chemical consideration, more work is warranted to reach definitive results on these important catalytic systems.

In this letter, we initiate studies aimed at understanding the chemistry and structure of molybdenum sulfide clusters via comparison to the more well studied molybdenum oxide clusters. We compare the geometric structures of the $\text{Mo}_3\text{O}_{6(9)}^{-}$ and $\text{Mo}_3\text{S}_{6(9)}^{-}$ clusters. These clusters are of particular interest due to the stoichiometries of the bulk oxide ($\text{O}/\text{Mo} = 3$) and sulfide ($\text{S}/\text{Mo} = 2$) materials. In addition to the calculation of the lowest energy isomers, we investigate the process of water adsorption onto $\text{Mo}_3\text{X}_9^{-}$ clusters.

II. COMPUTATIONAL METHODS

All geometry optimizations and frequency calculations were performed using the B3LYP hybrid density functional method using the Stuttgart-Dresden (SDD) relativistic pseudopotentials to replace the 28 core electrons on molybdenum and an augmented version of the associated double-$\zeta$ basis set to treat molybdenum's 14 remaining electrons. To properly describe anionic wavefunctions, diffuse $s$, $p$, and $d$-functions were added to the molybdenum centers using an exponent ratio of 0.3 to maintain even-tempered basis set behavior, and the augmented triple-$\zeta$ aug-cc-pVTZ basis sets were used for oxygen, sulfur, and hydrogen atoms. Finally, two $f$-type functions ($\zeta_f = 0.338, 1.223$) and one $g$-type function ($\zeta_g = 0.744$) were added to the molybdenum basis set as recommended by Martin and Sundermann. Counterpoise corrections were included to estimate the basis set superposition errors (BSSE) associated with calculating the complexation energies. To estimate the possible errors in B3LYP, the geometries and energies of complexation were also obtained using the B97 functional (via the B972 keyword in Gaussian) and the B97-D functional of Grimme. All calculations were performed using the development version of the Gaussian software.
III. RESULTS

A. Molecular Geometries

The lowest energy isomers for the Mo$_3$X$_6^-$ and Mo$_3$X$_9^-$ clusters are shown in Fig. 1 and Fig. 2, respectively. The molecular symmetries and electronic states are given for each isomer along with their relative energies and key geometric parameters.

Mo$_3$X$_6^-$ – From Fig. 1, the similarities between the most stable oxide and sulfide clusters are readily seen. Both assume configurations consisting of a triangular Mo$_3$ core with each Mo center supporting a terminal Mo=O bond and two bridging Mo—X bonds. The lowest energy isomer for each cluster exhibits C$_{3v}$ symmetry with a $^2A_1$ electronic state. This “ring” geometry scheme is particularly stable for $y=6$; the second lowest energy structure also has a ring configuration making it an excited spin state (quartet) for both systems, lying 0.3 and 0.5 eV higher in energy for Mo$_3$O$_6^-$ and Mo$_3$S$_6^-$ respectively. Given the large difference between the metal-oxide and metal-sulfide bond lengths, it is interesting that for both of the Mo$_3$X$_6^-$ ground doublet states, the metal-metal bonds are nearly equidistant at 2.58 Å. Interestingly, the Mo—Mo distance is shorter than the corresponding distance in molybdenum metal (2.725 Å) suggesting that direct metal-metal bonding may contribute to the stability of these systems.

Mo$_3$X$_9^-$ – While the lowest energy isomers for the oxide and sulfide $y=6$ clusters were found to be very similar, the corresponding oxide and sulfide $y=9$ clusters assume completely different geometric configurations. In Fig. 2, the most stable isomers are shown for the Mo$_3$O$_9^-$ and Mo$_3$S$_9^-$ clusters (ring oxide and open sulfide, bottom) along with the complementary isomer for both systems (open oxide and ring sulfide, top). The lowest energy isomer for Mo$_3$O$_9^-$ is a C$_{2v}$ ring structure with two Mo=O bonds and two Mo—O bonds on each Mo center and no metal-metal bonding (the Mo—Mo distance is 3.45 Å, substantially longer than in molybdenum metal). All metal centers are roughly tetrahedrally coordinated. The lowest energy isomer for Mo$_3$S$_9^-$, however, has an open “linear” structure with only two tetrahedral Mo centers, and one central near-square-pyramidal, penta-coordinate Mo center. Here, both of the tetrahedral Mo centers have two Mo=S and two Mo—S bonds each, while the penta-coordinate Mo has one Mo=S and four Mo—S bonds.

It is quite interesting to see such different structures become favored for the sulfide clusters. In previous work on anionic and neutral Mo$_2$S$_9$, other interesting geometries such as those containing $\eta^2$-S$_2$ units have also been reported. We have found those structures to be significantly higher in energy than the linear structure reported in this letter (particularly, for the anion) and hence these isomers are not shown in this work. We do note, however, that the penta-coordinate –MoS$_5$– bonding motif seen in our ground state structure has been observed experimentally in both molecules and solids.

To understand why the Mo$_3$S$_9^-$ cluster assumes such a different geometry than the Mo$_3$O$_9^-$ cluster we break down the atomization energies into three components: bonding, electron affinity (EA), and geometry effects.
such as ring strain. This is shown below:

\[
E_{\text{Atomization}} = E_{\text{Bonding}} + E_{\text{EA}} + E_{\text{Geometry}}.
\]

To find \( E_{\text{Bonding}} \) we have computed estimations of the \( \text{Mo} \equiv \text{X} \) and \( \text{Mo} - \text{X} \) bond strengths for \( X = O \) and \( S \). This has been done by calculating the binding energies of two different clusters (\( \text{MoX}_3 \) and \( \text{Mo}_2\text{X}_6 \)), which have different numbers of double and single bonds. The structures are represented in Fig. 3.

As \( \text{MoX}_3 \) has 3 double bonds, and \( \text{Mo}_2\text{X}_6 \) has 4 double bonds and 4 single bonds, the bond strengths can be estimated as:

\[
E(\text{Mo} \equiv \text{X}) = \frac{\Delta E_1}{3}
\]

\[
E(\text{Mo} - \text{X}) = \frac{\Delta E_2}{4} - E(\text{Mo} \equiv \text{X}).
\]

Where,

\[
\Delta E_1 : \text{MoX}_3 \rightarrow \text{Mo} + 3\text{X}
\]

\[
\Delta E_2 : \text{Mo}_2\text{X}_6 \rightarrow 2\text{Mo} + 6\text{X}.
\]

The double and single bond strengths for both \( X = O \) and \( X = S \) are given in Table I. We note that while we have used B3LYP to estimate the bond strengths, our estimations for molybdenum oxygen bonds are close to the complete basis set CCSD(T) results obtained by Dixon and coworkers with values of 5.96 eV (137.4 kcal/mol) and 4.21 eV (97.0 kcal/mol) for \( \text{Mo} \equiv \text{O} \) and \( \text{Mo} - \text{O} \) bonds respectively.\(^{46}\)

Values for \( E_{\text{EA}} \) are simply obtained by the difference in zero-point corrected energies of the anion and neutral structures each at their respective optimized geometries. \( E_{\text{Geometry}} \) includes all other effects that contribute to the atomization energy.

For the \( \text{Mo}_3\text{X}_9^- \) clusters, the ring structures each have 6 single and 6 double bonds. The linear structures, however, have 5 double bonds and 8 single bonds. Since a \( \pi \)-bond is significantly weaker than a \( \sigma \)-bond, both \( \text{Mo}_3\text{O}_9^- \) and \( \text{Mo}_3\text{S}_9^- \) would favor a linear structure over a ring structure based solely on bond energies. As shown in Table II, the values for \( E_{\text{Bonding}} \) favors the linear structure by 2.4 eV and 1.9 eV for the oxide and sulfide, respectively. It is quite interesting that, despite the fact that the oxide ring structure is more stable, the oxide cluster has a stronger linear structure bonding stabilization than the sulfide structure. In addition to the bonding, for both oxide and sulfide the \( E_{\text{EA}} \) stabilizes the linear structure over the ring structure. This is not surprising since a linear arrangement allows the charges to be distributed over a greater distance resulting in lower electrostatic repulsion energy. It is also seen that for both isomers \( E_{\text{EA}} \) is larger for \( \text{Mo}_3\text{S}_9^- \) than for \( \text{Mo}_3\text{O}_9^- \), again consistent with simple expectations (e.g., atomic electron affinity of \( S \) vs. \( O \), 2.08 eV vs. 1.46 eV).\(^{47}\)

Once the bonding and electron affinities are accounted for \( (E_{\text{Bonding}} + E_{\text{EA}}) \), the remainder of the adsorption energy in Table II is ascribed to the geometric effects. We see that there are significant geometric effects present in both the ring and linear structures. Both the oxide and sulfide clusters incur rather large energy penalties upon formation of a linear structure, –1.8 eV and –1.7 eV respectively. While this may be partly ascribed to the simplicity of our decomposition scheme, the fact that they are very similar suggests that it is not a significant factor that contributes to the difference between the oxides and sulfides. Formation of a ring structure however, lowers the energy of both clusters, with the oxide being stabilized twice as much as the sulfide cluster. This difference in ring structure stabilization is ultimately responsible for the different lowest energy isomers reported in Fig. 2.

To understand why the ring structure is stabilized so much more for \( \text{Mo}_3\text{O}_9^- \) than for \( \text{Mo}_3\text{S}_9^- \), we focus attention on the bond angles on the Mo centers in Fig. 2. The key difference is that the bond angles around oxygen (\( \text{Mo} - \text{O} - \text{Mo} \)) are quite floppy and can have a large range of values without incurring significant energy penalties while the bond angles around sulfur (\( \text{Mo} - \text{S} - \text{Mo} \)) can occur only in a narrow range. For \( \text{Mo}_3\text{O}_9^- \), the floppy \( \angle(\text{Mo} - \text{O} - \text{Mo}) \) bond angle extends to values as large as 148° as seen in the ring structure. This permits reasonable values without much distortion for the tetrahedral Mo centers (notice the \( \angle(\text{O} - \text{Mo} - \text{O}) \) angle of 103°). The hybridization on the bridging sulfurs, however, prohibits such large bond angles (the \( \angle(\text{Mo} - \text{S} - \text{Mo}) \) angle does not exceed 100°). Consequently, the metal centers in the \( \text{Mo}_3\text{S}_9^- \) ring structure are forced to distort from tetrahedral to assume \( \angle(\text{S} - \text{Mo} - \text{S}) \) angles of around 120°, and the molecule twists in order to alleviate some of the ring strain. The oxide and sulfide linear structures, do not differ significantly (except for the expected lower bond angles around sulfur), a similarity reflected in the geometries as seen in Fig. 2 and the values of \( E_{\text{Geometry}} \) for the linear structures as seen in Table II.

Therefore, we find that while the larger \( \sigma \)-bond:\( \pi \)-bond ratio results in the linear structures being favored over the ring structures based on bond energy estimates, the

\[\text{FIG. 3 – Structures used to estimate the Mo} \equiv \text{X} \text{ and Mo} - \text{X} \text{ bond strengths for } X = O \text{ and } S.\]
most important factor in determining the lowest energy isomer however, is ultimately ring strain due to differences in the $\angle$(X–Mo–X) and $\angle$(Mo–X–Mo) angles.

### B. Water Adsorption

In recent work, we have found H$_2$ elimination to be a rather facile result of reactions between unsaturated gas-phase tungsten-oxide clusters and water. With the emerging interest in the use of MoS$_2$-based catalysts in the photocatalytic production of H$_2$ from water, it is our aim to initiate studies into the manner in which the cluster-water interactions are dependent on the identity of X in Mo$_3$X$_y$ clusters. Our recent work suggests that the energetics and the mode of initial adsorption dictate to a large extent which reaction pathways will be explored. In this section, we compare the formation of H$_2$O···Mo$_3$O$_6$ and H$_2$O···Mo$_3$S$_6$ molecular complexes. To provide a more direct comparison between oxides and sulfides, we focus only on the Mo$_3$X$_6$ clusters in this section since they have similar lowest energy isomers as shown in Fig. 1.

The formation of a molecular complex is largely determined by the cluster’s molecular electrostatic potential (ESP). In Fig. 4, the ESP for both Mo$_3$O$_6$ and Mo$_3$S$_6$ is shown. The blue surface, corresponding to an ESP isosurface value of −0.11, represents regions that are attractive for a positive charge (i.e., water’s hydrogens) and repulsive to a negative charge (i.e., water’s oxygen). While complexes formed through X···H–OH hydrogen bonds are, no doubt, expected to be fairly stable, the ESPs shown in Fig. 4 reveal windows of oxygen accessibility to the positive Molybdenum center. This accessibility permits a stabilizing interaction between the water’s negative oxygen center and the positively charged Mo center at the expense of having to form a bent X···H–OH hydrogen bond.

The shape of the ESP’s gives rise to two predominant modes of adsorption resulting in two different complexes, A and B. Complex A involves 3 points of attraction: two X···H–OH hydrogen bonds and one H$_2$O···Mo interaction, while Complex B involves only 2 points of attraction: two X···H–OH hydrogen bonds. Each complex is shown in Fig. 5 along with the corresponding adsorption difference density ($\Delta \rho^{Ad}$), which is defined as:

$$\Delta \rho^{Ad} = \rho_{\text{Cluster}+\text{H}_2\text{O}} - (\rho_{\text{Cluster}} + \rho_{\text{H}_2\text{O}})$$

Positive values (gray) of $\Delta \rho^{Ad}$ indicate region of density accumulation while negative values indicate region of density depletion. In Fig. 5(a) and 5(b), Complex A $\Delta \rho^{Ad}$ is shown for Mo$_3$O$_6^-$ and Mo$_3$S$_6^-$, respectively. In both figures, the water molecule has an orientation that allows for the 3-points of attraction as described above.

In Fig. 5(c) and 5(d), Complex B $\Delta \rho^{Ad}$ is shown for Mo$_3$O$_6^-$ and Mo$_3$S$_6^-$, respectively. Here, the water molecule is complexed to the cluster via two hydrogen bonds. In Table III, the adsorption energies are given for both types of complexes. In the results shown, counterpoise corrections have been included to estimate the BSSE, although this yields a minimal correction for all adsorption energies (no larger than 0.3 kcal/mol), indicating that our basis set is sufficient for these systems.

**Complex A vs. Complex B** From Table III, it is clear that Complex A is the most favored adsorption configuration for both Mo$_3$O$_6^-$ and Mo$_3$S$_6^-$. This can be clearly seen in Fig. 5 that shows the greater extent of density accumulation between the water and cluster in Complex A relative to Complex B. While the $\Delta \rho^{Ad}$ for Complex B is primarily localized on the oxygen or sulfur groups, the $\Delta \rho^{Ad}$ for Complex A is quite delocalized throughout...
the metal system, indicating that the Complex A–type adsorption processes will be much more sensitive to cluster geometry and spin state. In order to consider the effect of using different density functionals on this energy difference, we have also evaluated the adsorption energies using the B97 functional as well as with B97-D where dispersion effects are included through an empirical correction. It is interesting to note that the empirical dispersion effects reduce the difference in adsorption energies between Complex A and Complex B, particularly for the oxide.

Mo$_3$O$_6^-$ vs. Mo$_3$S$_6^-$ From the relatively large amount of density accumulation between the water and Mo$_3$O$_6^-$ clusters in Fig. 5, it is clear that water adsorbs more strongly to the metal oxides than the metal sulfide clusters. Following inspection of the molecular electrostatic potentials in Fig. 4, the preference of water binding to Mo$_3$O$_6^-$ over Mo$_3$S$_6^-$ (via Complex A) is perhaps a bit surprising as the Mo$_3$S$_6^-$ cluster appears to have a larger “window” of accessibility which would facilitate the stabilizing oxygen-Mo interaction (H$_2$O···Mo). It is interesting to note, however, the inclusion of dispersion effects via the B97-D functional\textsuperscript{42} preferentially stabilizes the Mo$_3$S$_6^-$ Complex A over the Mo$_3$O$_6^-$ Complex A, yielding essentially equivalent binding energies (see parenthetical values in Table III).

IV. CONCLUSIONS

In this computational investigation, we have sought an understanding of the chemistry and structure of molybdenum sulfide clusters via comparison to the more well studied molybdenum oxide clusters. We have compared the geometric structures of the Mo$_3$O$_{(6,9)}^{-}$ and Mo$_3$S$_{(6,9)}^{-}$ clusters. These structures are of particular interest due to the stoichiometries of the bulk oxide (O/Mo = 3) and sulfide (S/Mo = 2) materials. From this work the following conclusions may be drawn:

- The lowest energy isomers for the Mo$_3$X$_6^-$ clusters are very similar despite the inherent differences in the Mo–S and Mo–O bond lengths.
- The lowest energy isomers for the Mo$_3$X$_9^-$ clusters (higher S/Mo ratio than in bulk) are completely different, with the Mo$_3$O$_9^-$ cluster favoring a cyclic metal framework and the Mo$_3$S$_9^-$ cluster favoring an open structure. This is a result of differences in the $\angle$(Mo–X–Mo) bond angles imposing a greater ring strain in the Mo$_3$S$_9^-$ ring structure.
- Water complexation to the Mo$_3$X$_6^-$ clusters can result in two main adsorption configurations, a more stable complex A with two hydrogen bonds and one H$_2$O···Mo interaction, and a less stable complex B with just two hydrogen bonds.
- Due to the larger atomic charges and greater hydrogen bonding, molybdenum oxide clusters adsorb water more strongly than molybdenum sulfide clusters, although this difference in Complex A binding is reduced with the inclusion of dispersion.

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\begin{itemize}
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