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Comparison of polyoxo and polyoxothiometallate rings: a theoretical approach

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The electronic structures of a synthesized oxothiomolybdate ring and its hypothetic oxo analog were studied by DFT calculations. Different intermediate structures, which can appear during ring formation, were analyzed and their stabilities systematically compared. No significant difference between the two systems has been found in the ring assembly processes from elementary bricks $[Mo_2O_2X_2(H_2O)_6]^{2+}$ (X = S, O). It is suggested that the assembly of the oxo ring can be perturbed by the coexistence of two close-in-energy isomers for the oxo dication $[Mo_2O_4(H_2O)_6]^{2+}$, having short and long Mo–Mo distances.

Introduction

Polyoxoanions (POA) have attracted much attention in recent years. An extensive body of experimental data has been accumulated on these large metal-oxygen clusters, usually formed by Mo, W and V. Polyoxometallates can find potential applications in different fields such as catalysis, electronic and magnetic materials, and medicine.[1–4] Different possibilities for fine-tuning polyoxoanion properties in view of the design of new materials have been considered in the literature. Many of them include the substitution of transition metal ions or the grafting of organic or organometallic fragments.[5] A very attractive possibility to modify the chemical properties arises from the substitution of one, or several, terminal or bridging oxo ligands by isoelectronic sulfur atoms. This opens up new perspectives in combining the properties of oxides and sulfides. However, direct reaction of hydrogen sulfide or sulfido ions with a POA generally results in reduction of the metal centers and cleavage of the M–O–M bonding of the framework. Moreover, these methods are inadequate for the design of new sulfur-rich compounds.[6]

An original approach to form sulfur-containing polyoxoanions, developed by Secheresse *et al.*, is based on self-condensation under acido-basic conditions of the $[Mo_2O_2S_2]^{2+}$ fragment.[7] The first compound prepared by this method was the cyclic oxothio compound $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$.[7a] Six $\{Mo_2O_2S_2\}$ units are connected to each other by hydroxo double bridges and a water molecule, delimiting a central cavity of 11 Å in diameter (Fig. 1). Two types of Mo–Mo bonds are present in the wheel: short Mo–Mo bonds within the building blocks (≈2.80 Å) and long Mo–Mo ones (≈3.30 Å) between them. The condensation reaction is performed by the controlled addition of potassium hydroxide to an acidic aqueous solution of the oxothio cation $[Mo_2O_2S_2(H_2O)_6]^{2+}$. However, the Mo_{12} oxothiometallate ring has no pure oxo analog. Several attempts to obtain a polyoxo ring under similar conditions have not been successful. This suggests that some fundamental difference exists in the assembly process of oxo and oxothio structures.

In the present paper we study the condensation reaction of the binuclear oxo and oxothio cations $[Mo_2X_2O_2]^{2+}$ (X = O, S) on the basis of quantum-chemical DFT calculations. Numerous calculations of the electronic structure of POA are reported in the literature. In particular, DFT calculations of rather large polyoxoanion clusters, sometimes substituted by 3d transition metals, have become available during the past 20 years.[8] However, to our knowledge, a single theoretical study considers mixed oxothio systems.[8h] In the present work, we firstly consider the electronic structure of the elementary building blocks $[Mo_2X_2O_2(H_2O)_6]^{2+}$ and the resulting cyclic structures $[Mo_{12}X_{12}O_{12}(OH)_{12}(H_2O)_6]$ (X = O, S). Then we study complexes of different nuclearity that can appear during the condensation process. The electronic structures of oxo and oxothio compounds will be systematically compared.

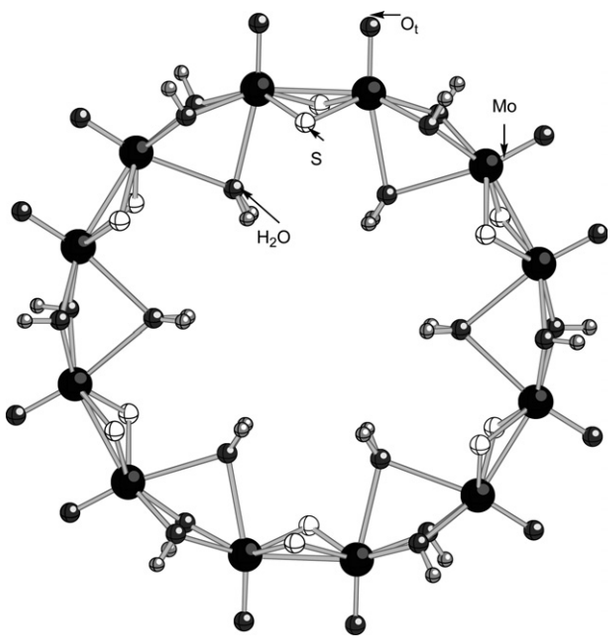

Fig. 1 Ball-and-stick representation of the cyclic oxothio compound $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$.

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Theoretical details

Calculations were carried out with the ADF 2.3 program.[9] Triple-zeta basis sets were taken to describe the valence electrons of all atoms with added polarization functions for oxygen and sulfur atoms. Core electrons up to and including the 3d, 1s and 2p ones were frozen for molybdenum, oxygen and sulfur atoms, respectively. Scalar relativistic corrections were explicitly included *via* the frozen-core potential. The LDA approximation was employed, with the exchange-correlation potential of Vosko, Wilk, and Nusair.[10] Gradient corrections to exchange (Becke)[11] and correlation (Perdew)[12] were also incorporated in a perturbative way, based on the local SCF density.

Spin-unrestricted calculations of the broken symmetry and triplet states for the dimer building blocks $[Mo_2X_2O_2(H_2O)_6]^{2+}$ (see below) were performed with the B3LYP method[13] implemented in the Gaussian-98 package.[14] We used the Huzinaga–Dunning double-ζ basis set[15] for oxygen, sulfur and hydrogen atoms and the Hay and Wadt effective core potentials[16] with relativistic effects and double-ζ basis set for molybdenum. A polarization function was added for oxygen and sulfur atoms.

The geometry optimizations were performed in internal coordinates and positions of hydrogen atoms were frozen. Constraints of the symmetry group were taken into account if a molecule possessed a particular symmetry. Optimization procedures were performed in spin-restricted calculations of singlet states, as well as in the spin-unrestricted calculations of the broken symmetry and triplet states of $[Mo_2X_2O_2(H_2O)_6]^{2+}$.

Results and discussions

$[Mo_2O_2X_2(H_2O)_6]^{2+}$(X = O, S): first approach

Under acidic conditions, the elementary units $[Mo_2O_2X_2]^{2+}$ exist in the form of the hydrated dication $[Mo_2O_2X_2(H_2O)_6]^{2+}$ (Fig. 2). In our first approach, the metal-bonded dimers were analyzed within the spin-restricted approach. The optimization procedure for the hydrated dication led to the geometrical parameters and Mulliken charges summarized in Table 1. It can be seen the Mo–Mo distance in the mixed oxothio dication is close to the experimental value (2.80 Å) for the short Mo–Mo bond in the cyclic structure. We must note that the Mo_2X_2 core is bent as in many other compounds containing this fragment.[17]

The dimer HOMO presents an antibonding combination of Mo $4d_{xy}$ and O_2 (S_2) σ orbitals (Fig. 3). The bent geometry of the bridge weakens the antibonding combination and allows a direct overlap of the two d_{xy} orbitals of molybdenum atoms. The substitution of oxygen by sulfur increases the covalence with Mo atoms: the overlap population between the bridge and the metal passes from 0.11 for X = O to 0.19 for X = S. One could also mention the important difference found in the Mo Mulliken charges in the oxo and thio dimers (Table 1). This feature reflects the difference in electronegativity between sulfur and oxygen atoms and the more diffuse character of sulfur orbitals.

Table 1 The main optimized geometric parameters (distances in Å, angles in °) and Mulliken charges on the molybdenum atoms of the minima obtained for $[Mo_2O_2X_2(H_2O)_6]^{2+}$(X = O, S)

X	Mo–Mo	Mo–X	Mo–X–Mo	Q_{Mo}
O	2.54	1.95	82.0	1.80
S	2.81	2.33	74.3	1.30

$[Mo_{12}O_{12}X_{12}(OH)_{12}(H_2O)_6]$

The calculations of the full structures have been performed in order to compare the stabilities of oxygen and sulfur rings. The D_{6h} symmetry group was assumed in the geometry optimizations. Stable minima have been found for both structures. Table 2 gives main characteristics of each compound. As for the experimental cyclic oxothio system, two types of Mo–Mo bonds were found: one short within the building blocks and one long between them. The geometry, the Mulliken charges values for metal centers, and the composition of the HOMO (Fig. 4) show that the integrity of the building blocks is maintained in the wheel. One can note that the optimized distances between the blocks and the size of the cavity are overestimated in comparison with the experimental structure for the oxothio compound. It is suggested that this difference is due to the higher symmetry imposed in the optimization procedure. The two cyclic structures are strongly stabilized (and the pure oxo wheel by 40 kcal mol^{-1} more than the mixed oxothio wheel) compared to the six individual non-interacting building blocks.

Formation of the wheel

As both oxo and oxothio rings appear to be stable, we looked for differences that can appear during the assembly process. This process can consist of two steps: the association of building blocks and the elimination of excess water molecules. Fig. 5 presents three different ways to link two entities. All three structures were optimized under the appropriate symmetry constraints. Stable minima were obtained for the three intermediates with X = O and S. Again, as for the closed rings, the geometry and the electronic structure of the building blocks are maintained. The *trans* configuration [Fig. 5(b)] is more stable than the *cis* configuration [Fig. 5(a)] by 0.34 eV for X = S and by 0.39 eV for X = O. It is even more stable (3.0 eV for X = S and 3.3 eV for X = O) than the configuration in which the coordination number of Mo is equal to five [Fig. 5(c)]. For the latter the energy of four water molecules was added in order to compare the total energies.

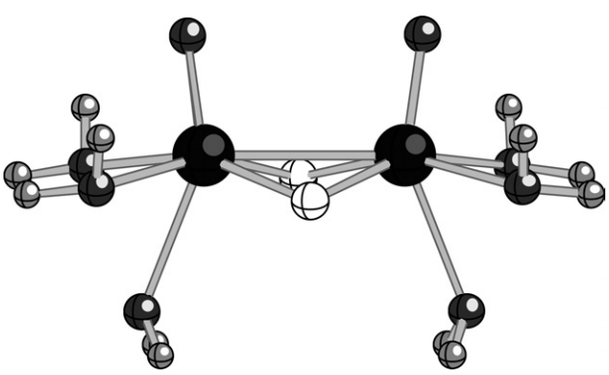

Fig. 2 Ball-and-stick representation of the dimer building block $[Mo_2O_2X_2(H_2O)_6]^{2+}$ (X = O, S).

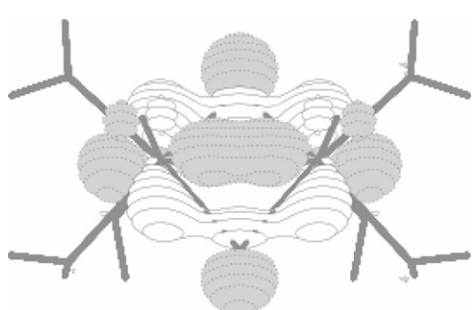

Fig. 3 Composition of the HOMO for the building blocks $[Mo_2O_2X_2(H_2O)_6]^{2+}$ (X = O, S).

Table 2 The main optimized distances (in Å) and Mulliken charges on the molybdenum atoms for the cyclic compounds $[Mo_{12}O_2X_2(H_2O)_6]$ (X = O, S).

X	Mo–Mo	Mo–OH_2	Mo–X	Mo–OH	R_{cavity}	Q_{Mo}
O	3.47, 2.59	2.61	1.96	2.11	11.4	1.83
S	3.50, 2.84 (≈3.30, 2.80)[a]	2.63	2.36	2.11	12.3 (≈11[a])	1.35

[a] Experimental values.

During the assembly process several water molecules are eliminated, leaving only those needed for the connection of two elementary units $[Mo_2O_2X_2]^{2+}$. The remaining water molecules play the role of a "template" for ring formation. In order to study the elimination step, we considered the reaction:

trans configuration (n blocks)
$\rightarrow$ *template* configuration (n blocks) + $(n-1)H_2O$.

Fig. 6 shows the *template* and *trans* configurations for $n = 3$. Up to $n = 3$, the elimination of water molecules and stabilization of the template structure is disadvantaged for both O and S. For $n = 4$, the system *template* + $3H_2O$ is favored by 0.35 eV for X = S and by 0.43 eV for X = O. Again, no qualitative difference between oxo and oxothio systems can be found at this stage.

A difference between the two compounds can also appear if for one of them the reaction goes in the direction of polymerization:

$$[Mo_{12}X_{12}O_{12}(OH)_{10}(H_2O)_{16}] + 2OH^- + [Mo_2X_2O_2(H_2O)_6]^{2+} \rightarrow [Mo_{14}X_{14}O_{12}(OH)_{12}(H_2O)_{18}] + 4H_2O,$$

and not cyclization:

$$[Mo_{12}X_{12}O_{12}(OH)_{10}(H_2O)_{16}] + 2OH^- \rightarrow [Mo_{12}X_{12}O_{12}(OH)_{12}(H_2O)_6] + 10H_2O.$$

Although the calculations favor the polymerization reactions, the behavior of oxo and oxothio compounds is clearly similar. This incorrect result may be due to the absence of entropic factors in our calculations.

Another reason for the non-formation of the cyclic oxo compound can result from the important difference of Mulliken charges on the molybdenum atoms in the building block $[Mo_2O_2X_2]^{2+}$ (Table 1). We can suppose that the oxo dication, with more electrophilic molybdenum atoms, reacts not with two, but with three hydroxo ligands, to form the compound shown in Fig. 7. In order to verify this hypothesis, geometry optimizations of this structure were done for X = O, S and the energies were compared with those for the system *trans*

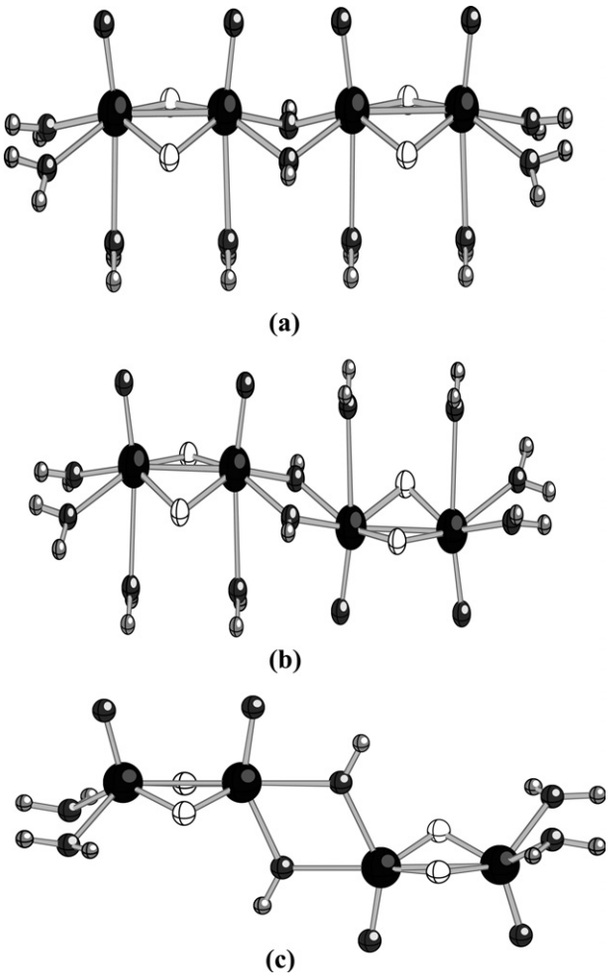

Fig. 5 Ball-and-stick representations of different ways to link two building blocks: (a) *cis* configuration, (b) *trans* configuration and (c) configuration with penta-coordinated Mo atoms.

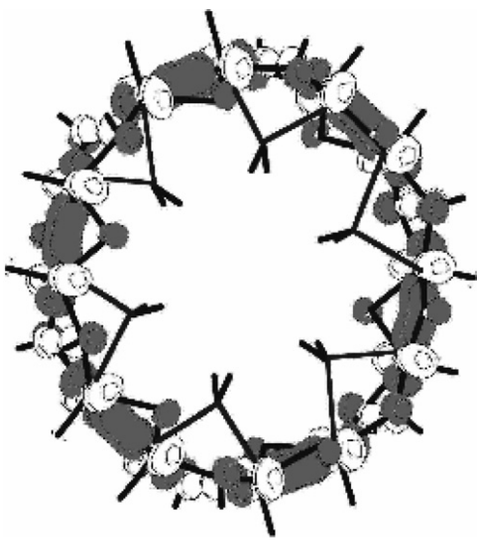

Fig. 4 Composition of the HOMO for the cyclic compound $[Mo_{12}X_{12}O_{12}(OH)_{12}(H_2O)_6]$ (X = O, S).

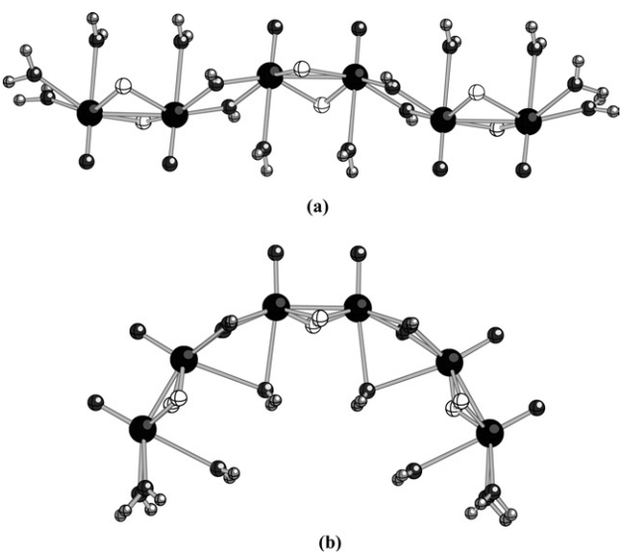

Fig. 6 Ball-and-stick representations of the *template* and *trans* configurations for $n = 3$.

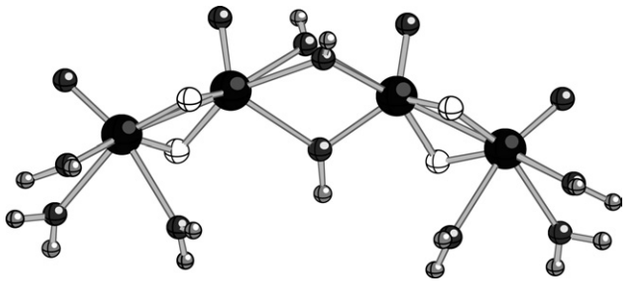

Fig. 7 Ball-and-stick representation of the compound formed by the reaction between three hydroxo ligands and the building blocks.

$(n = 2) + (OH)^- - 2H_2O$. In this case, we did not find any difference between sulfur- and oxygen-containing compounds.

Of course, our treatment considers the relative stabilities of different intermediates only in the gas phase. The inclusion of medium effects into theoretical models can modify the results.

$[Mo_2O_2X_2(H_2O)_6]^{2+}$(X = O, S): second approach

As the studies of the intermediate steps of the condensation process as well as the calculations of the final rings did not explain the non-formation of the cyclic oxo structures, we decided to consider in more detail the ground states of the building blocks. This second approach was motivated by the numerous publications on the isomerism between the μ-η^2:η^2-peroxo and bis(μ-oxo) bimetallic complexes.[18] These studies were connected with the problem of molecular oxygen activation in biological and synthetic catalytic system. It has been shown that the possibility of coexistence of the two isomers depends on the number and nature of the terminal ligands. In particular, isomerism was well-documented for Cu dimers with tetra- and penta-coordinated metal atoms. The eventual isomerism was also discussed for dimers with octahedrally coordinated atoms but with non-oxygen bridges.[19] In our case, if two isomers can exist for the ring building blocks, a rapid equilibrium between two forms can perturb the condensation reaction. In particular, we looked for isomers with longer Mo–Mo distances. The problem of the existence of isomers for $[Mo_2O_2X_2]^{2+}$ dications inserted into γ-Keggin polyoxoanions was recently discussed by Rohmer and Benard.[8h] These authors have shown that the potential surfaces of reduced oxothio heteropolyanions of general formula γ-$[SiW_{10}Mo_2X_2O_{38}]^{6-}$ possess two minima corresponding to different Mo–Mo distances. This phenomenon can be seen as a manifestation of the bond-stretch isomerism.[20] However, the appearance of two minima for the γ-Keggin POA resulted from the redistribution of electronic density between the Mo dimer and W–O framework. In both cases the clusters are described by a spin-restricted singlet wave function.

Following previous work on bis(μ-oxo) bimetallic complexes[18] we paid special attention to the correct description of metal-metal bond. For large metal-metal separations the intercenter electronic coupling becomes weaker and the singlet state must be described by a multiconfigurational approach. Although the real multiconfigurational state is not accessible by DFT calculations, important information can be obtained by the broken symmetry technique developed by Noodleman and colleagues.[21] Introducing asymmetry in the spin density at the two metal centers of the $[Mo_2O_2X_2(H_2O)_6]^{2+}$ (X = O, S) dication, it is possible to obtain a broken-symmetry state with one electron localized on each metal center. This corresponds to a fictive state, which, if we know the energy of the triplet state, gives access to the energy of the singlet state. We looked for a broken-symmetry state for $[Mo_2O_2X_2(H_2O)_6]^{2+}$ dimers using the mixed B3LYP exhange-correlation functional, which is known to give the best DFT results for this state.[22]

Broken-symmetry optimizations were realized for X = O and S, taking a large metal-metal separation as the starting point. For X = S, we did not succeed in obtaining a broken-symmetry state. The optimization process always converged to the spin-restricted solution with a short Mo–Mo bond. The spin-restricted B3LYP calculations for the oxo dimer resulted in the same Mo–Mo equilibrium distance of 2.54 Å as was obtained before (Table 1). However, we were also able to obtain a stable broken-symmetry state with a more important Mo–Mo separation of 2.97 Å. This difference between sulfur and oxygen dimers can be explained by the stronger covalent interaction in Mo–S, which does not allow molybdenum atoms to break away. It is often supposed that the broken-symmetry state geometry corresponds closely to that of the true singlet state. The energy of the broken-symmetry state for X = O is just 0.013 Hartree (≈8 kcal mol^{-1}) higher than that of the first minimum (Table 1). As it has been mentioned before, the broken state is a fictive state, and, in order to estimate the energy of the real singlet state, we also performed calculations of the triplet state. Surprisingly, the triplet state lies even lower than the broken-symmetry state. However, the very small energy difference between the two states (≈0.8 kcal mol^{-1}) indicates that the energies of the broken-symmetry and singlet states must also be very close. A stable triplet state can also be found for the short Mo–Mo bond isomer, but its energy is much higher than the corresponding singlet energy (≈34 kcal mol^{-1}). We can suppose that the interconversion between the two forms, with short and long Mo–Mo distances, is possible. This new equilibrium can modify the condensation process on the oxo dication $[Mo_2O_4(H_2O)_6]^{2+}$ and could explain why the $[Mo_{12}O_{24}(OH)_{12}(H_2O)_6]$ wheel is not formed.

Since polyoxoanions and oxothioanions are formed by tungsten we also considered $[W_2O_2X_2(H_2O)_6]^{2+}$ dimers. No isomers have been found in this case, the behavior of oxo and oxothio dimers being identical. This result suggests that both systems can form dodecanuclear wheels.

Concluding remarks

In this study we tried, on the basis of quantum-chemical microscopic modeling, to describe the acido-basic condensation process occurring on the dinuclear oxo or oxothio cation $[Mo_2X_2O_2]^{2+}$ (X = O, S) to give the cyclic compounds $[Mo_{12}X_{12}O_{12}(OH)_{12}H_2O)_6]$. It is shown that the mechanism proposed is correct for the two systems. Electronic structures of the oxo and oxothio compounds are systematically compared. For oxothio compound, the Mo–S interaction is more covalent due to the electronegativity of sulfur atom. This suggests that the equilibrium between two forms, with short and long metal-metal bonds, existing only for $[Mo_2O_4(H_2O)_6]^{2+}$, can play a role during the formation of the wheel. The systematic comparison of oxo and oxothio compounds allows us to understand the electronic and geometric modifications introduced by substitution of oxygen bridging ligands by sulfur atoms and thus contributes to a rationalization of the properties of polyoxoanions. However, the importance of the present work goes beyond the description of the condensation process. The isomerism in molybdenum oxo dimers appears to be an interesting possibility meriting further theoretical and experimental studies.

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