J. Phys. Chem. A **2007,** *111,* 1683−1687

Inversed Stability Order in Keggin Polyoxothiometalate Isomers: A DFT Study of 12-Electron Reduced α, *β*, *γ*, *δ*, and ϵ $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ Anions

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Received: October 7, 2006; In Final Form: December 23, 2006

Density functional theory calculations have been carried out to investigate 12-electron reduced α, β, γ, δ, and ϵ Keggin-like $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ polyoxothiometalates (POTMs), which show that the stability order is $\alpha < \beta < \gamma < \delta < \epsilon$ that is perfectly inverse to the well-known trend of the classical Keggin polyoxometalates. Energy decomposition analysis reveals that the enhanced stabilities of γ, δ, and ϵ isomers originate the favorable arrangements of their $Mo_{12}O_{12}S_{12}(OH)_{12}$ shell, in which the edge-sharing $[Mo^V_2(\mu\text{-}S)_2O_2]$ fragment plays a fundamental role in stabilizing the overall structure. Both frontier orbital analysis and Mayer indexes exhibit that a Mo−Mo single bond is formed inside the $[Mo^V_2(\mu\text{-}S)_2O_2]$ fragment, which leads to the localization of the two reduced electrons. As compared with experimentally discovered cyclic $[(C_9H_3O_6)@Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$, all Keggin POTM structures are less stable due to their disfavored cage framework and the disadvantageous host−guest interaction. However, the ϵ-type Keggin POTM that has the largest similarity to the cyclic species is possibly available in the presence of appropriate templates.

Introduction

Polyoxothiometalates (POTMs)[1] represent a new emerging family of compounds in which polyoxometalates (POMs)[2] are decorated with sulfur atoms. As successful examples of incorporation of the metal−sulfur chemistry[3,4] into the fascinating structural architecture of the POMs,[5] POTMs are of special potential to be the new generation of POMs with excellent electronic properties.[6]

The original approach toward POTMs was based on the direct sulfurization of the POMs,[7] and this method generally resulted in the collapse of the POMs' framework,[8] and only four clusters with 1∼2 sulfur atoms were reported.[7−9] Recently, Sécheresse and co-workers[1] have developed a new strategy based on the reactivity of the oxothio cations $[M_2S_2O_2]^{2+}$ (M = Mo, W), by which a new class of cyclic POTMs[10] with 6∼16 sulfur atoms has been prepared. POTMs are nowadays a fast growing area, some of which have grown to nanoscopic domains.[11] However, the introduction of more sulfur atoms on the surface of caged POMs remains very difficult, and there is no caged POTM containing more than 6 sulfur atoms inside the metal−oxygen shell available to date.[12] For Keggin-type[13] POTMs, only α-$[PW_{11}MSO_{39}]^{4-}$ (M = Nb, Ta)[7] and γ-$[SiW_{10}M_2S_2O_{38}]^{6-}$(M = Mo, W)[14] have been documented.

Thanks to the development of density functional theory (DFT) methods and computer techniques, high-level calculations of large metal systems such as the POMs have been carried out recently.[15] Considerable progress has been achieved in describing and rationalizing their fundamental properties such as redox, acidity, magnetic and spectroscopic properties, metal−metal coupling, reactivity behavior, and decomposition gateway, etc.[15,16] In contrast, much less attention has been paid to the POTM analogues, and DFT studies were only performed on Keggin-type γ-$[SiW_{10}M_2X_2O_{38}]^{n-}$ (M = Mo, W; X = S, O)[17] and cyclic $Mo_{12}O_{12}S_{12}(OH)_{12}(H_2O)_6$.[18] Inspired by the synthetic works of Sécheresse et al.,[1] we are interested in the structure and stability of caged sulfur-rich POTMs. The $[Mo_2S_2O_2]^{2+}$ cations readily assemble cyclic POTMs in the presence of various substrates;[10] however, can they form a caged skeleton if the appropriate template is available? Do caged POTMs bear more stable sulfur atoms? What is the key factor in the control of the formation of caged POTMs? In this paper, we address these questions by DFT studies on the five isomers of $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$. Comparison to the 12-centered cyclic POTM species has been made and provides useful guidelines for the rational design synthesis of these unique complexes.

Computational Details

All the calculations were performed at the DFT level with the DMol^3 program[19] in the Materials Studio of Accelrys Inc. The exchange and correlation energies were calculated using the Perdew and Wang functionals (GGA-PW91)[20] within the generalized gradient corrected approximation (GGA). The double numerical basis set augmented with *d*-polarization and *p*-polarization functions (DNP) was utilized, and ionic cores of the metal were described by the effective core potential (ECP). For the numerical integration, a fine quality mesh size was used, and the real space cutoff of the atomic orbital was set at 5.5 Å. The convergence criteria for structure optimization and energy calculations were set to FINE with the tolerance for density convergence in SCF, energy, gradient, and displacement of 1×10^{-6} e/Å,^{3} 2×10^{-5} au, 4×10^{-4} Å, and 5×10^{-4} Å, respectively. Both spin restricted (singlet) and unrestricted calculations (triplet) were carried out for all the clusters.

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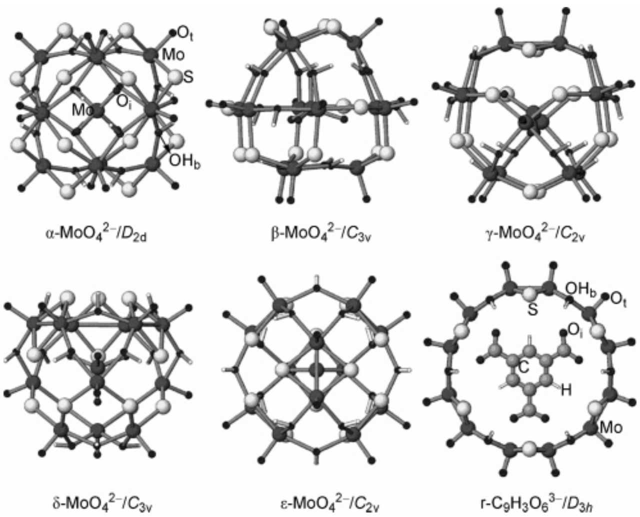
10.1021/jp066585m CCC: $37.00



α-MoO_4^{2-}/D_{2d} β-MoO_4^{2-}/C_{3v} γ-MoO_4^{2-}/C_{2v}

δ-MoO_4^{2-}/C_{3v} ε-MoO_4^{2-}/C_{2v} r-$C_9H_3O_6^{3-}/D_{3h}$

Figure 1. Ball-and-stick representations of α, β, γ, δ, and ϵ $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ isomers and $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$. The guest molecules were used to denote the overall anion. Three types of oxygens are given, terminal (O_t), interior (O_i), and bridging (OH_b). X is the central heteroatom Mo.

Results and Discussion

The five POTM isomers of $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ were derived from the five classical Baker−Figgis[21] cap-rotation isomers of the Keggin-type $[(MoO_4)Mo_{12}O_{36}]^{2-}$[22] via substitution of 24 bridging oxygen atoms by 12 sulfur atoms and 12 hydroxyls. The introductions of 12 extra hydrogen atoms as well as the 12 reduced electrons in the skeleton aims at mimicking the composition and valence state of classical cyclic sulfur-rich POTMs.[10a−e] The most stable isomers are shown in Figure 1, in which the α structure is a triplet while the others are singlets. The β/C_{3v}, γ/C_{2v} and δ/C_{3v} isomers maintain the ideal symmetries as observed in Keggin POMs,[21,23] while the symmetries of α and ϵ are lowered from T_d to D_{2d} and C_{2v}, respectively. However, the energy differences (1.8 and 1.3 kcal/mol for the α and ϵ isomers, respectively) and the structural deviations (<0.02 Å, see Table 1) are very small, demonstrating that the α and ϵ isomers actually have approximate T_d symmetry.

In each isomer, there are three kinds of oxygen atoms [interior oxygen (O_i), terminal oxygen (O_t), and bridging hydroxyl oxygen atoms (OH_b)] and two types of molybdenum atoms (tetrahedral Mo in the center and octahedral Mo addenda in the cage shell), as shown in Figure 1. Mulliken population analysis shows that the interior oxygen atoms bear the largest negative charges (−0.640 to −0.659, see Supporting Information) and that the hydroxyl oxygen atoms carry more negative charge than the terminal ones (−0.564 to −0.617 vs −0.453 to −0.492), similar to the natural charge distribution of the Keggin POMs.[24] In contrast, the bridging sulfur atoms are very close to charge neutrality (−0.115 to 0.078), and this reveals that the Mo addenda accept more transferred charge from sulfur atoms than from oxygen atoms. It is well-known that the Mulliken charges in some cases have little meaning, but in general, the charge differences are much more believable. As observed in the Keggin POMs,[24,25] the Mulliken charge (0.555−1.687) of the Mo sites is much less than the formal +5 or +6 oxidation states in this paper; however, the charge difference between the two kinds of Mo ions is close to 1.0 (0.931−1.010), exhibiting that central and shell Mo atoms are in oxidization states of +6 and +5, respectively.[26] It should be noted that in each isomer the $Mo_{12}O_{12}S_{12}(OH)_{12}$ cage and the inner MoO_4^{2-} subunit are well-separated as indicated by large $Mo_{shell}-O_i$ distances (2.625−2.879 Å) with a very small bond order[27] (0.12−0.27, see Supporting Information), and thus, all five Keggin POTM isomers can be viewed as host−guest encapsulation compounds assembled by trapping of one charged MoO_4^{2-} guest molecule into a neutral $Mo_{12}O_{12}S_{12}(OH)_{12}$ host and can be reformulated as $[MoO_4^{2-}@Mo_{12}O_{12}S_{12}(OH)_{12}]$ (abbreviated as $MoO_4^{2-}@Mo_{12}S_{12}$). This feature is in line with the well-known clathrate model[28] of the classical Keggin POMs.

Our calculations show the gradually increased relative stability (ΔE_t, Table 2) order of $\alpha < \beta < \gamma < \delta < \epsilon$, which is perfectly inverse to the traditional trend of classical Keggin POM isomers. The β-$MoO_4^{2-}@Mo_{12}S_{12}$, obtained by 60° rotation of one $[Mo_3O_{10}(\mu\text{-}S)_3]$[29] cap of the α isomer, gains 1.7 kcal/mol in stability. When two or more caps are rotated, edge-sharing $[Mo^V_2(\mu\text{-}S)_2O_2]$ fragments appear. The γ, δ, and ϵ isomers, having 1, 3, and 6 $[Mo^V_2(\mu\text{-}S)_2O_2]$ fragments, respectively, are of substantially lower energy (8.7−126.6 kcal/mol) than the α partner, with the energy decrease of about 16 kcal/mol per $[Mo^V_2(\mu\text{-}S)_2O_2]$ fragment on average. Conversely, for the classical oxidized Keggin POMs, the well-established stability order is $\alpha > \beta > \gamma > \delta > \epsilon$.[16a,23,30,31] Kepert[31a] and Pope[31b] have noted that $[M^{VI}_2(\mu\text{-}O)_2O_2]$ (M = Mo, W) played a crucial role in destabilizing the γ, δ, and ϵ Keggin isomers, arising from the electrostatic repulsion caused by short $M^{VI}-M^{VI}$ contacts. López and Poblet[23] theoretically verified that the energies of γ, δ, and ϵ $[PW_{12}O_{40}]^{3-}$ are notably enhanced (9−51 kcal/mol) as compared to the α and β isomers, with the energy increase of about 8−9 kcal/mol per $[W^{VI}_2(\mu\text{-}O)_2O_2]$ fragment. Hence, the $[M^V_2(\mu\text{-}S)_2O_2]$ and $[M^{VI}_2(\mu\text{-}O)_2O_2]$ fragments play opposite roles in the assembly of Keggin POTMs and POMs, respectively.

It should be noted that for the stable γ, δ, and ϵ $MoO_4^{2-}@Mo_{12}S_{12}$ isomers, the computed Mo−Mo distances inside the $[Mo^V_2(\mu\text{-}S)_2O_2]$ fragment (2.857−2.899 Å, Table 1) are close to the experimental data (∼2.83 Å) of the POTM molybdates.[10a,b,14] Orbital analysis exhibits that the HOMOs (Figure 2) of the three isomers are strongly localized inside $[Mo^V_2(\mu\text{-}S)_2O_2]$ fragments and that a weak single σ_{M-M} bond is formed between two Mo atoms as indicated by Mayer indexes of 0.68−0.69 (Table S2 in the Supporting Information). Similar property is also found theoretically in dimeric $[Mo_2S_2O_2(H_2O)_6]^{2+}$,[32] caged γ-$[SiW_{10}M_2S_2O_{38}]^{6-}$ (M = Mo, W),[17] and cyclic $[Mo_{12}O_{12}S_{12}(OH)_{12}(H_2O)_6]$.[18] The localization of reduced electrons and the formation of a single M−M bond in the $[M^V_2(\mu\text{-}S)_2O_2]$ (M = Mo, W) fragment are general features of POTMs[1] that might be responsible for the stabilizing effect of the $[Mo^V_2(\mu\text{-}S)_2O_2]$ in this study. In contrast, for the classical oxidized Keggin POMs, there is no M−M bond formed inside the edge-sharing fragment. For instance, for the γ-$[PMo_{12}O_{40}]^{3-}/C_{2v}$, δ $[PMo_{12}O_{40}]^{3-}/C_{3v}$, and ϵ $[PMo_{12}O_{40}]^{3-}/T_d$, there is no M−M bond formed inside $[Mo^{VI}_2(\mu\text{-}O)_2O_2]$ at the GGA-PW91/DND level, as indicated by the long Mo−Mo distances (2.962−3.017 Å) and very small bond orders (0.10−0.12, Table S4 in the Supporting Information). Moreover, the energies of the three Keggin isomers are 11.8−59.5 kcal/mol higher than α $[PMo_{12}O_{40}]^{3-}/T_d$. This result is in accordance with the recent work of López[23] on Keggin tungstates and confirms Kepert and Pope's attribution.[31] It should be noted that the single Mo−Mo bond is also observed experimentally in the reduced ϵ Keggin core of the $\{Mo_{16}\}$,[33] $\{Mo_{37}\}$,[34] $\{Mo_{43}\}$,[35] and $\{Mo_{12}Ni_4\}$[36] systems as characterized by the short Mo−Mo distance (2.55−2.77 Å) inside the $[Mo^V_2(\mu\text{-}O)_2O_2]$ dumbbells. In view of the structural and electronic similarities, it can be inferred that $[Mo^V_2(\mu\text{-}O)_2O_2]$ has a stabilizing effect similar to the $[Mo^V_2\text{-}$

TABLE 1: Optimized Distances[a] (Å) of the Five $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ Isomers, ϵ-$[(NbO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$, and $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$[b]

anions/symmetry	X−O$_i$[c]	Mo−O$_i$	Mo−O$_t$	Mo−S	Mo−O(H)	Mo−Mo
α-MoO_4^{2-}/D_{2d}[d]	1.810	2.719−2.731	1.700	2.342−2.379	2.108−2.120	3.911−4.145
α-MoO_4^{2-}/T_d[d]	1.810	2.724	1.700	2.362	2.113	3.914−4.138
β-MoO_4^{2-}/C_{3v}	1.811	2.625−2.879	1.701	2.289−2.431	2.091−2.145	3.713−4.121
γ-MoO_4^{2-}/C_{2v}	1.812	2.658−2.818	1.707	2.331−2.367	2.122−2.155	2.857−4.283
δ-MoO_4^{2-}/C_{3v}	1.813	2.670−2.816	1.707	2.320−2.327	2.135−2.164	2.874−4.267
ϵ-MoO_4^{2-}/C_{2v}	1.811	2.725−2.735	1.709	2.326	2.159	2.891−3.899
ϵ-MoO_4^{2-}/T_d	1.811	2.755	1.708	2.326	2.159	2.892−3.899
ϵ-NbO_4^{3-}/D_{2d}	1.906	2.612	1.717	2.328	2.160	2.881−3.806
$C_9H_3O_6^{2-}/D_{3h}$		2.349	1.708−1.721	2.341−2.349	2.096	2.816−2.832
expt[e]		2.35−2.43	1.67−1.69	2.31−2.33	2.06−2.10	2.82−2.84

[a] Observed intervals are given. [b] Guest molecules are used to denote the overall anions. [c] X is a heteroatom (X = Mo or Nb). Averaged data are given. [d] Unrestricted computation for the open-shell configuration (triplet). [e] X-ray data of $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$ from reference 10a.

TABLE 2: Five Kinds of Relative Energies[a] (kcal/mol) of the Five Most Stable $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ Isomers, ϵ-$[(NbO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$, and $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$[b]

anions	ΔE_t	ΔE_{host}	ΔE_{guest}	ΔFIE	ΔE_{eval}
α-MoO_4^{2-}/D_{2d}	0.00	0.00	0.0	0.0	0.00
β-MoO_4^{2-}/C_{3v}	1.7	3.5	0.1	−1.9	1.5
γ-MoO_4^{2-}/C_{2v}	8.7	7.4	−0.6	1.9	9.3
δ-MoO_4^{2-}/C_{3v}	59.8	58.6	0.0	1.2	59.8
ϵ-MoO_4^{2-}/C_{2v}	126.6	133.1	0.0	−6.5	126.6
ϵ-NbO_4^{3-}/D_{2d}		100.4		240.7	341.1
$C_9H_3O_6^{3-}/D_{3h}$		202.3		51.6	253.8

[a] Defined as the energy of α subtracting that of the others. [b] The guest molecules are used to denote the overall anions.

(μ-S)$_2$O$_2$] analogue. Detailed studies exhibit that the five fully 12-protonated reduced $[PMo^{V}_{12}O_{28}(OH)_{12}]^{3-}$ Keggin-type isomers share the same order of $\alpha < \beta < \gamma < \delta < \epsilon$ (Table S5 in the Supporting Information), confirming the significant roles of the $[Mo^{V}_2(\mu\text{-}O)_2O_2]$ and $[Mo^{V}_2(\mu\text{-}S)_2O_2]$ fragments in stabilizing the reduced Keggin POMs and POTMs, respectively.

For further clarification of the differences among the five Keggin POTMs, a simple energy analysis is performed. The host−guest interaction energy (*FIE*) is evaluated by the energy difference between the encapsulation complex $MoO_4^{2-}@Mo_{12}S_{12}$ (E_t) and the sum of the host cage $Mo_{12}O_{12}S_{12}(OH)_{12}$ (E_{host}) and guest subunit MoO_4^{2-} (E_{guest}), as expressed by eq 1

$$E_t = FIE + E_{host} + E_{guest} \qquad (1)$$

The computed energetic data of the β, γ, δ, and ϵ isomers relative to those of the α isomer are given in Table 2, where a positive value denotes a favored energy. Several points can be drawn from the values in this table. (1) The difference in spatial arrangement of the host (ΔE_{host}) is mainly responsible for the relative stability (ΔE_t). Besides the dominant contribution of the ΔE_{host} in the γ isomer (7.4 kcal/mol ΔE_{host} vs 8.7 kcal/mol ΔE_t, 75%[37]), the ΔE_t values of the other three isomers (β, δ, and ϵ) are almost completely from their ΔE_{host}. (2) The influence of the host−guest interactions (ΔFIE) to ΔE_t is small. For the less stable β structure, ΔFIE is a minor but still important factor (35%[38]), while for the γ isomer, the value is considerably reduced to 19%. In the cases of more stable δ and ϵ isomers, the contribution of ΔFIE is only 2−5% and can be completely neglected. (3) The ΔE_{guest} contributes little to ΔE_t. The subtle energy differences between five guest molecules (ΔE_{guest}, −0.6 to 0.1 kcal/mol) are completely in line with the small structural differences (Mo−O$_i$ angle ranges 1.810−1.813 Å and Mo−O$_i$−−X angle ranges 109.3−110.9°), exhibiting that the five MoO_4^{2-} values are almost identical for the isomers. Thus, it is clear that the intrinsic stabilities of β, γ, δ, and ϵ isomers, especially the γ, δ, and ϵ ones, stem form their neutral $Mo_{12}O_{12}S_{12}(OH)_{12}$ host in favorable arrangement. Despite the inverse stability order, this result compares well with that of the classical Keggin POM isomers,[23,31] in which the instabilities of the β, γ, δ, and ϵ isomers originate in their disfavored $M_{12}O_{36}$ host frameworks. The similar origin of relative stability in both Keggin POMs and Keggin POTMs sheds new insight into the nature of these encapsulation complexes.

Compared with structural properties of cyclic POTMs,[1] it is not surprising that the five Keggin POTM isomers have such a unique stability order. Apparently, the most stable ϵ-type $MoO_4^{2-}@Mo_{12}S_{12}$ shows a striking similarity to the experimentally discovered cyclic 12-center[10a−e] POTM species. For instance, despite the significant difference in shapes (cage vs ring), both caged ϵ $[MoO_4@Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ and cyclic $[(C_9H_3O_6)@Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$ (abbreviated as $C_9H_3O_6^{3-}@Mo_{12}S_{12}$,[10a] Figure 1) have the $Mo_{12}O_{12}S_{12}(OH)_{12}$ host assembled by six $[Mo^{V}_2(\mu\text{-}S)_2O_2]$ fragments via 12 bridging hydroxyl linkers (μ-OH). At the GGA-PW91/DNP level, $C_9H_3O_6^{3-}@Mo_{12}S_{12}$ possesses D_{3h}[39] symmetry, and the computed structural parameters (Table 1) compare well with the X-ray data.[10a] Similar to ϵ $MoO_4^{2-}@Mo_{12}S_{12}$, the HOMOs of the cyclic $C_9H_3O_6^{3-}@Mo_{12}S_{12}$ are also strongly localized inside the $[Mo^{V}_2(\mu\text{-}S)_2O_2]$ fragment (Figure 2), and the formation of six Mo−Mo bonds can be identified by the Mayer index of 0.64−0.68. Interestingly, the cyclic host is observed 69.2 kcal/mol more stable than the ϵ one, indicating the favorable arrangement of $Mo_{12}O_{12}S_{12}(OH)_{12}$ in the cyclic framework rather than in the caged one. In the meantime, the *FIE* term is also favored in the cyclic anion with 58.1 kcal/mol, further reflecting the large stability of the cyclic POTM species.

Because of the different shape and composition of guest molecules, it is difficult to directly compare the energetic properties of the cyclic and caged POTMs. In an alternative way, the relative stability is evaluated by the sum of E_{host} and *FIE* (E_{eval}, eq 2), in which the influence of the guest has been approximately neglected. The computed energies (ΔE_{eval}) of β, γ, δ, and ϵ $MoO_4^{2-}@Mo_{12}S_{12}$ and $C_9H_3O_6^{3-}@Mo_{12}S_{12}$ relative to α-$MoO_4^{2-}@Mo_{12}S_{12}$ are given in Table 2 and plotted in Figure 3. As can be seen, for β, γ, δ, and ϵ Keggin POTMs, ΔE_{eval} is almost equal to ΔE_t with the largest deviation of 0.6 kcal/mol, showing the validity of the method. By this approach, the cyclic $C_9H_3O_6^{3-}@Mo_{12}S_{12}$[40] is estimated to be 127.2 kcal/mol more stable than ϵ $MoO_4^{2-}@Mo_{12}S_{12}$, revealing the significant experimental preference of the $[Mo_2S_2O_2]^{2+}$ cation to assemble the cyclic skeleton.[1,10]

$$E_{eval} = E_{host} + FIE \qquad (2)$$

However, is there any possibility of $[M_2S_2O_2]^{2+}$ cations forming caged POTMs? It has been observed that the nature

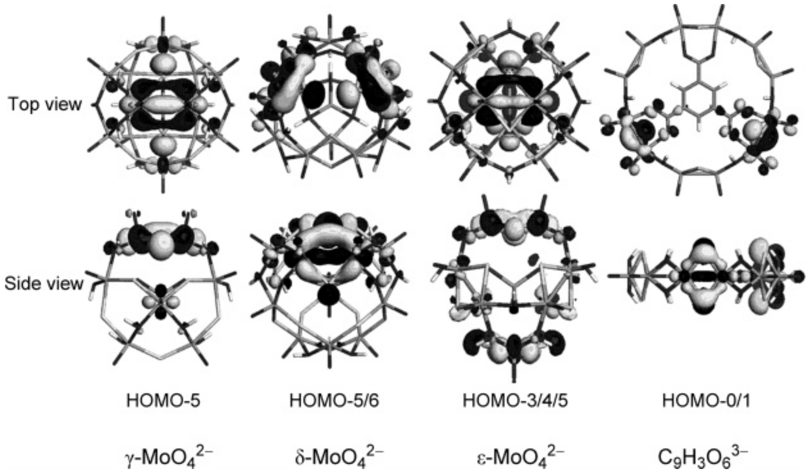


Figure 2. Localization of the single Mo−Mo bond inside the $[Mo^{V}_{2}(\mu\text{-}S)_2O_2]$ fragments in the frontier orbitals of the γ, δ, and ϵ $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ isomers and $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$. The guest molecules were used to denote the overall anions.

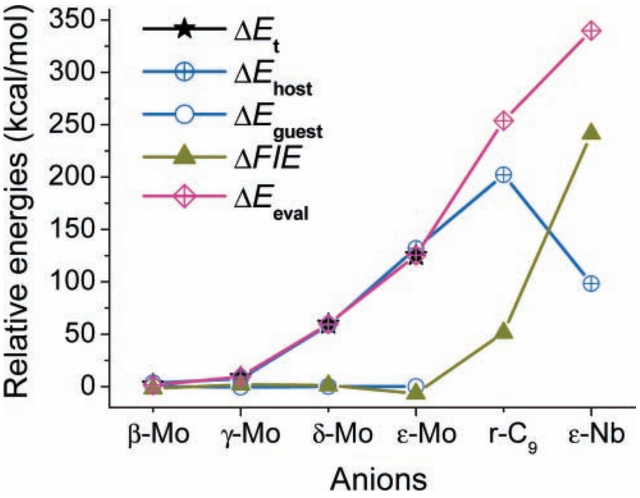


Figure 3. Five kinds of relative energies as functions of six structures. The β, γ, δ, and ϵ Mo denote β, γ, δ, and ϵ $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$, respectively. The ϵ Nb and C_9 denote ϵ $[(NbO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$ and $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$, respectively.

of the heteroatom X, the overall charge of the anion as well as the shape and symmetry of the guest molecule are key factors affecting the assembly of POM compounds.[15b] To search for a stable caged Keggin POTMs, we studied the energetically favored ϵ-type $Mo_{12}O_{12}S_{12}(OH)_{12}$ cage by incorporation of a large and highly charged NbO_4^{3-} guest. At the GGA-PW91/DNP level, the most stable ϵ $[(NbO_4^{3-})Mo_{12}O_{12}S_{12}(OH)_{12}]$ (denoted as ϵ-NbO_4^{3-}@$Mo_{12}S_{12}$) has D_{2d} symmetry that is 1.3 kcal/mol lower than the T_d symmetric compound. As compared to the ϵ MoO_4^{2-}@$Mo_{12}S_{12}$, the host−guest interaction (*FIE*) of ϵ NbO_4^{3-}@$Mo_{12}S_{12}$ is markedly lowered (247.2 kcal/mol). On the basis of this simple evaluation of ΔE_{eval}, ϵ NbO_4^{3-}@$Mo_{12}S_{12}$ is 214.5 and 87.3 kcal/mol more stable than ϵ MoO_4^{3-}@$Mo_{12}S_{12}$ and $C_9H_3O_6^{3-}$@$Mo_{12}S_{12}$, respectively, exhibiting that the favored host−guest interaction caused by the appropriate guest molecule size and charge can effectively compensate the disadvantages of the $Mo_{12}O_{12}S_{12}(OH)_{12}$ in cage arrangement. As a result, in the presence of the highly charged NbO_4^{3-} template, the assembly of $[Mo_2S_2O_2]^{2+}$ dications into the ϵ cage is, from a thermodynamic viewpoint, possible. Further studies exploring the influences of guest molecules are in progress.

Conclusion

The five sulfur-rich polyoxothiometalates $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ derived from the classical Keggin-type $[(MoO_4)Mo_{12}O_{36}]^{2-}$ isomers have been investigated at a level of density functional theory. It was found that the nature of these polyoxothiometalates is quite different from that of the classical Keggin polyoxometalates. The calculations led to the following rules: (1) The stability of the five $[(MoO_4)Mo_{12}O_{12}S_{12}(OH)_{12}]^{2-}$ isomers increases in an order of $\alpha < \beta < \gamma < \delta < \epsilon$ that is perfectly inverse to the well-known trend of oxidized Keggin polyoxometalates. (2) Molecular orbital analysis shows that HOMOs of the γ, δ, and ϵ isomers are strongly localized inside the $[Mo^{V}_{2}(\mu\text{-}S)_2O_2]$ fragment that leads to the formation of the Mo−Mo single bond. (3) Energy analysis reveals that the differences in relative stability of the five polyoxothiometalate isomers mainly stems from their $Mo_{12}O_{12}S_{12}(OH)_{12}$ host shell in different arrangements, in which the edge-sharing $[Mo^{V}_{2}(\mu\text{-}S)_2O_2]$ fragment is energetically favorable. (4) The $[Mo_2S_2O_2]^{2+}$ dications prefer to form a cyclic structure rather than a caged one; however, the discovery of a caged ϵ structure is possible in the presence of a suitable template.

Acknowledgment. This work was supported by the National Natural Science Foundation of China. We thank the reviewers for constructive suggestions.

Supporting Information Available: Total electronic energies of polyoxothiometalate anions, single-point energies of $Mo_{12}O_{12}S_{12}(OH)_{12}$, XO_4^{n-} (X = Mo, Nb), and $C_9H_3O_6^{3-}$. Mulliken charge and Mayer indexes of the polyoxothiometalate anions. Total electronic energies, relative energy, bond length (Å), and Mayer indexes of short Mo−Mo distances inside the $[Mo_2(\mu\text{-}O)_2O_2]$ fragment for the five Keggin $[PMo_{12}O_{40}]^{3-}$ isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(38) Evaluated by $|\Delta FIE|/(|\Delta FIE| + \Delta E_{host} + |\Delta E_{guest}|)$.

(39) The energy difference between the D_{3h} and C_1 structures is less than 0.01 kcal/mol at the GGA-PW91/DNP level.

(40) The cyclic $[Mo_{12}O_{12}S_{12}(OH)_{12}(H_2O)_6]/D_{6h}$ cannot be used as a reference due to the neglect of solvent effects. In the gas phase, the interior six water molecules inside this neutral cluster form strong hydrogen bonds, and the resulted S_6 symmetric structure is quite different from the X-ray one. However, isolated ion modeling for cyclic $[(C_9H_3O_6)Mo_{12}O_{12}S_{12}(OH)_{12}]^{3-}$ and other anion studies in the paper is suitable. Work is in progress to address this issue.