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Synthesis, structures and theoretical investigation of three polyoxomolybdate-based compounds: self-assembling, fragment analysis, orbital interaction, and formation mechanism

Yi-Ping Tong, a Guo-Tian Luo, b Jin Zhen, a You Shen a and Wen-Yan Lin c

Three Mo 12- and Mo 12-based polyoxoanion compounds (1–3), contain [Mo 6 O 26 ] 4+ and [(SiO 4 ) (Mo 12 O 36 )] 4+ anions, have been successfully synthesized by one-pot hydrothermal method, and characterized structurally by X-ray crystallographic method. 1, [Cu(L') 2 ][Mo 6 O 26 ] (L' = 1-methylimidazole), contains rarely observed Mo 6 -based oblate shell [Mo 6 O 26 ] 4+ polyoxoanion, while 2, [L' 1 ][SiMo 12 O 40 ][L' 2 ]·5H 2 O (L' = benzotriazole) and 3, [L''H][SiMo 12 O 40 ]·2H 2 O, Mo 12 -based spherical shell α-Keggin [(SiO 4 )(Mo 12 O 36 )] 4+ polyoxoanions. Very interesting, SiO 4 4- fragment is disordered in 2 and that in 3 is ordered. The observation that 1–3 are different in polyoxoanion structures and crystallized in order in the same solution system is very rare so far for POM synthetic chemistry and very interesting for understanding the formation mechanism and self-assembling process of Mo-based polyoxoanions. The fragment analysis based on the clathrate structural model, i.e. [Mo 6 O 26 ] 4+ anion modeled as [MoO 4 ] 4- @MoO 18 , and [(SiO 4 ) (Mo 12 O 36 )] 4+ anion modeled as [SiO 4 ] 4- @[Mo 12 O 36 ] 4- and/or [SiO 4 ] 4- @[Mo 5 O 12 ] 6+ @[MoO 8 ] 4- , and orbital interaction analysis based on extended Hückel theory calculation have been successfully employed to account for the formation mechanism and self-assembling process of fragments and two Mo-based polyoxoanions in 1–3. The calculated large charge transfer and/or high electronic polarization item between fragments provide electronic structural information of structural stability and interpret the fragment-fragment self-assembling process.

Polyoxometalate (POM) chemistry has been in existence for more than a century and still attracts much attention due to their potential applications in catalysis, medicine, magnetism, optics, conductivity, and so forth. 1–4 Polyoxometalate-based compounds are regarded as one of the most promising materials potentially. 5,6 However, how to design and assemble the POM materials with desired structures and functions remains a great challenge. One of the important reasons is that, in addition to the external chemical stimuli, the formation mechanism and self-assembling of different POM topological structures also plays a key role in the assembly process. 7–10 As being well-known, the basic parent structures (topology) for POM compounds are diversified, including following anion structures, Keggin series, Dawson series, Silverton series, Waugh series, Lindqvist series and Anderson series. 11 The most typical and important topology is the M 12 -based POM, which has the highest formation tendency in POM compounds, and therefore is particularly worth considering. These M 12 -based POM topology is [(XO 4 ) (Mo 12 O 36 )] -based Keggin series (α-, β-, γ-, δ- and ε-type). 11,12 Obviously the α-Keggin is the most important, though it has been investigated for decades. 12,13 In this work, we focus on the one-pot synthesis, structures and theoretical analyses of three polyoxomolydodate-based compounds, 14,15 [Cu(L') 2 ][Mo 6 O 26 ] (1, C 24 H 46 Cu 2 Mo 6 N 16 O 26 ·L' = 1-methylimidazole, Scheme 1), [L' 1 ][SiMo 12 O 40 ][L' 2 ]·5H 2 O (2, C 24 H 39 Mo 12 N 2 O 4 Si, L' = benzotriazole, Scheme 1), and [L''H][SiMo 12 O 40 ]·2H 2 O (3, C 23 H 29 Mo 12 N 2 O 2 Si), together with clathrate structural model discussion 16 and extended Hückel theory calculation 17 for self-assembling, fragment analysis, orbital interaction, and formation mechanism. Owing to the fact that 1–3 are diversified in polyoxoanion structures and therefore is rarely observed in the same one-pot solution system so far for POM synthetic chemistry. Thus this provides special chance for looking into the formation mechanism and self-assembling process of Mo-based polyoxoanions.

L': 1-methyl-imidazole
L'": benzotriazole

Scheme 1 Organic ligand structures.

Among the three compounds, 1 is a rarely observed Mo 6 -based polyoxomolybdate polyoxoanion structure, while 2 and 3 are all Mo 12 -based [(SiO 4 ) (Mo 12 O 36 )] 4+ -type (α-Keggin) polyoxoanion compounds. 11,16 However, the α-Keggin polyoxoanion in 2 is crystallographically different from that of 3, as the four O atoms of SiO 4 4- in 2 are disordered over.
eight positions, while that in 3 are ordered.

Compounds 1–3 were obtained by one-pot hydrothermal reaction of CuO, H$_2$MoO$_4$ and hydrofluoric acid with L‘ and L” ligands, and characterized crystallographically (Table S1 in the Supporting Information). The resulting solution was filtrated and kept to unchanged for a few weeks in room temperature for slow vaporization. Very interestingly, 1–3 were crystallized from the same solution in order (1 first, then 2, and 3 last), which imply that the polymerization process of Mo into polyoxoanions should form similar intermediates (fragments) or building blocks in solution, and further self–assembling of these fragments gives rise to different polyoxoanions.

For the [Mo$_8$O$_{26}$]$^{4+}$ polyoxoanion and two different but symmetrically equivalent Cu(II)-central coordination cations (Fig. 1a). Each of the Cu(II) centers lies in a distorted square geometry and is coordinated by four nitrogen atoms from the L’ ligands. The Cu–N bond distances and angles around Cu(II) are 2.005–2.024 Å, and the N–Cu–N angles are 92.3(4)–176.0(4)° (Table S2 in Supporting Information). In the axial direction the Cu(II) centers are also weakly coordinated by two terminal O atoms from adjacent [Mo$_{8}$O$_{26}$]$^{4+}$ anions with Cu–O distances being very long 2.479 Å (Fig. 1b). Each [Mo$_8$O$_{26}$]$^{4+}$ anionic unit coordinate to two adjacent [Cu(L’)]$_2$$^{2+}$ cations via two symmetry-related terminal O atoms, featuring repeating [Cu(L’)]$_2$$^{2+}$ [Mo$_8$O$_{26}$]$^{4+}$ [Cu(L’)]$_2$$^{2+}$ one-dimensional (1D) chains structure (Fig. 1b). The two elongated axial Cu–O linkages are marked and can be easily accounted for by the John–Teller effect of $d^4$ electron configuration Cu(II).

For the [Mo$_{8}$O$_{26}$]$^{4+}$ anion of 1, it is oblate shell in shape with a circular ring-shape Mo$_8$O$_{18}$ fragment or moiety caped by two MoO$_5^{2-}$ fragments or moieties below and above in a centro symmetric arrangement. Among the eight Mo atoms, six Mo atoms from the Mo$_8$O$_{18}$ fragment are identical with each other, being arranged in a circular ring-shape, and obviously different from another two Mo atoms of MoO$_5^{2-}$ fragments. In the Mo$_8$O$_{18}$ fragment, each Mo atom has two terminal O atoms (O$_t$), and linked to two adjacent Mo atoms via two bridging O atoms (µ$_3$-O$_b$), featuring repeating –MoO$_{2b}$–O$_t$–MoO$_{2b}$– units. While for the MoO$_3^{2-}$ fragment, each MoO$_4^{2-}$ has a terminal O atom (O$_t$) and three µ$_2$- bridging O atoms (µ$_2$-O$_b$), which bridge MoO$_3^{2-}$ fragment and Mo$_8$O$_{18}$ circular ring fragment.

Fig. 1 ORTEP drawing of 1 with 30% thermal ellipsoids (a) and view of a 1D linear chain of 1 (b). The dot line means weak coordinative bonding interaction between [Cu(L’)]$_2$$^{2+}$ and [Mo$_8$O$_{26}$]$^{4+}$. Hydrogen atoms are omitted for clarity.

Compound 2 consists of a [Mo$_8$O$_{26}$]$^{4+}$ polyoxoanion and two different but symmetrically equivalent Cu(II)-central coordination cations (Fig. 2). Each of the Cu(II) centers lies in a distorted square geometry and is coordinated by four nitrogen atoms from the L’ ligands. The Cu–N bond distances and angles around Cu(II) are 2.005–2.024 Å, and the N–Cu–N angles are 92.3(4)–176.0(4)° (Table S2 in Supporting Information). In the axial direction the Cu(II) centers are also weakly coordinated by two terminal O atoms from adjacent [Mo$_{8}$O$_{26}$]$^{4+}$ anions with Cu–O distances being very long 2.479 Å (Fig. 1b). Each [Mo$_8$O$_{26}$]$^{4+}$ anionic unit coordinate to two adjacent [Cu(L’)]$_2$$^{2+}$ cations via two symmetry-related terminal O atoms, featuring repeating [Cu(L’)]$_2$$^{2+}$ [Mo$_8$O$_{26}$]$^{4+}$ [Cu(L’)]$_2$$^{2+}$ one-dimensional (1D) chains structure (Fig. 1b). The two elongated axial Cu–O linkages are marked and can be easily accounted for by the John–Teller effect of $d^4$ electron configuration Cu(II).

For the [Mo$_{8}$O$_{26}$]$^{4+}$ anion of 1, it is oblate shell in shape with a circular ring-shape Mo$_8$O$_{18}$ fragment or moiety caped by two MoO$_5^{2-}$ fragments or moieties below and above in a centro symmetric arrangement. Among the eight Mo atoms, six Mo atoms from the Mo$_8$O$_{18}$ fragment are identical with each other, being arranged in a circular ring-shape, and obviously different from another two Mo atoms of MoO$_5^{2-}$ fragments. In the Mo$_8$O$_{18}$ fragment, each Mo atom has two terminal O atoms (O$_t$), and linked to two adjacent Mo atoms via two bridging O atoms (µ$_3$-O$_b$), featuring repeating –MoO$_{2b}$–O$_t$–MoO$_{2b}$– units. While for the MoO$_3^{2-}$ fragment, each MoO$_4^{2-}$ has a terminal O atom (O$_t$) and three µ$_2$- bridging O atoms (µ$_2$-O$_b$), which bridge MoO$_3^{2-}$ fragment and Mo$_8$O$_{18}$ circular ring fragment.

Fig. 2 ORTEP drawing of 2 with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Compound 2, i.e. [L’H]$_2$[SiMo$_{12}$O$_{40}$]·5[L”]·5H$_2$O, consists of one α-Keggin [SiMo$_{12}$O$_{40}$]$^{3+}$ polyoxoanion, four protonated L” cation (L”H$^+$), five neutral lattice L” molecules, and five lattice waters (Fig. 2). L”H$^+$ acts as counterion in the crystalline solid. There are very complicated linkages of hydrogen bonding between the four ions/molecules, which link these into rigid solid crystal (Table S3 in the Supporting Information). It is noteworthy that the central SiO$_4^{4+}$ fragment or moiety is disordered over eight O positions, and some L”H$^+$/L” locate on crystallographic special positions and are highly disordered, thus the treatments for these disordered units are very difficult, and fortunately the good
quality of the single crystals leads finally to a very satisfactory refinement results with $R_1 = 0.0514$ and $wR_2 = 0.1479$.
For 3, i.e. [L"H][SiMo$_{13}$O$_{36}$]\_2H$_2$O, it consists of one $\alpha$-Keggin [SiMo$_{13}$O$_{36}$]$^+$ polyanion, four protonated L"$^-$ cations (L"H$^+$), and two lattice waters (Fig. 3). The [SiMo$_{13}$O$_{36}$]$^+$ anion is a typical $\alpha$-Keggin structure, and its SiO$_4^-$ fragment is ordered, which is wholly different from the disordered case in 2. The L"$^-$H$^+$ cation acts as counterion in the crystalline solid, and there are very complicated hydrogen bonding systems between the three ions/molecules, which link these into rigid solid crystal (Table S3 in the Supporting Information).

For the $\alpha$-Keggin [SiMo$_{13}$O$_{36}$]$^+$ polyanion in 2 and 3, it is a spherical anion in shape, containing a spherical shell (Mo$_{12}$O$_{36}$ fragment or moiety) and an encapsulated central core (SiO$_4^-$ fragment or moiety). In Mo$_{12}$O$_{36}$ shell unit, each Mo atom has a terminal O atom (O$_t$), and linked to four adjacent Mo atoms via four bridging O atoms ($\mu_2$-O$_b$), thus, twelve Mo atoms are linked into a spherical network, featuring repeating –O$_{t}$-Mo-C-O$_{b}$- – linkages. In SiO$_4^-$ coral fragment, each O atom acts as $\mu_1$-bridging O atom (O$_{b}$-Mo), bridges to three adjacent Mo atoms of the spherical shell, featuring four Si–O$_{t}$-Mo$_{12}$O$_{36}$ shell fragments.

To better understand the structures, formation and self-assembling mechanism, it is necessary to decompose the polyanion clusters in 1, 2 and 3 into its fragment constituents. For [Mo$_{13}$O$_{36}$]$^{2-}$ anion in 1, there are, intuitively, two capped MoO$_5^{2-}$ fragments and one ring-shaped Mo$_{12}$O$_{36}$ fragment (Scheme 2a, 2b), thus [Mo$_{13}$O$_{36}$]$^{2-}$ anion can also be presented as [MoO$_5^{2-}$]$_2$@Mo$_{12}$O$_{36}$ based on the clathrate structural model.$^{16}$

While for [SiMo$_{13}$O$_{36}$]$^+$ anion in 2 or 3, there are an encapsulated SiO$_4^+$ fragment and one shell Mo$_{12}$O$_{36}$ fragment (Scheme 2a), and the shell Mo$_{12}$O$_{36}$ fragment can be further identified as four trimeric (Mo$_3$O$_9$) fragments, which are located in the Si–O bond axial direction of tetrahedral SiO$_4^+$ fragment and bond to the central SiO$_4^+$ fragment via $\mu_3$-O$_b$ atoms, or as one ring-shaped Mo$_{12}$O$_{36}$ fragment and two capped trimeric (Mo$_3$O$_9$) fragments (Scheme 2c). Thus the [SiMo$_{13}$O$_{36}$]$^+$ anion can also be presented intuitively as [SiO$_4^+$]@[Mo$_3$O$_9$]$_3$, or [SiO$_4^+$]@[Mo$_3$O$_9$]$_2$@[Mo$_3$O$_9$]$_2$, or [SiO$_4^+$]@Mo$_3$O$_9$, based on the clathrate structural model. Among the three fragment models, [SiO$_4^+$]@[Mo$_3$O$_9$]$_3$ and [SiO$_4^+$]@Mo$_3$O$_9$,@Mo$_3$O$_9$ models will be selected for following discussion as they appear to be more acceptable and more intuitive than [SiO$_4^+$]@Mo$_3$O$_9$, based on the clathrate structural model. Moreover in [SiO$_4^+$]@Mo$_3$O$_9$,@Mo$_3$O$_9$ model, it contains ring-shaped [Mo$_3$O$_9$]$_3$, and such fragment is also observed in [Mo$_3$O$_9$]$^{2+}$ anion of 1, in agreement with the fact that 1–3 were crystallized from the same solution, implying that similar intermediates (fragments) or building blocks have been formed in the reaction process. There are also other possible fragment species, but the present fragment decomposition analyses for the two polyanions in 1–3 are the most intuitive, and understandable, and should be reasonable and acceptable.

In general, the Mo(VI) and other $d^+$-metal are polyanion...
formers par excellence is clearly due to the fact that they have a favorable combination of ionic radius, charge, and empty d orbitals for metal-oxygen π-bonding. Though the full understanding of the formation mechanism and self-assembling processes of the polyoxoanions is still a challenge, as the intermediates or building blocks of the reaction process are hard to measure experimentally and usually presumed theoretically,18 fragments or moieties of molecules are often related to the intermediates or building blocks of the reaction process. In the present cases, 1–3 were obtained from the same solution system, therefore implying that similar intermediates or building blocks should be formed in the polymerization reaction process and further self-assembling of these intermediates leads to two different polyoxoanions. Here we focus on the fragment decomposition of two obtained polyoxoanions in 1–3, and deep analysis of fragment orbital interaction of the clathrate structural model based on extended Hückel theory calculation, in order to reveal the self-assembling and formation mechanism of the two polyoxoanion in 1–3. According to the structural model and the fragment orbital interaction method,19 the structural stability is ascribed to both charge transfer and the polarization between two fragments. In other words the formation process and stability of two polyoxoanions appear entirely an electronic consequence of the large, highly electron transfer or electronic polarization between fragments.

In the beginning, a MoO$_4$ or MoO$_6$ polyhedral can be reasonably assumed based on the knowledge of coordination chemistry, and a followed polymerization process of these MoO$_4$ or MoO$_6$ polyhedral units to form polyoxoanion structures can be expected. Then the formations of monomeric MoO$_{4}^{2-}$ fragment, trimeric Mo$_3$O$_9$ fragment, ring-shaped Mo$_{18}$O$_{36}$ fragment, spherical shell-shaped Mo$_{20}$O$_{36}$ fragment, and other fragment species may be quite possible in the polymeric reaction process (Scheme 2a). The further self-organizations of these fragment species with each other or other heteratomic species, e.g. SiO$_{4}^{4-}$, etc., lead to the formation of the final polyoxoanions in 1–3. A diagram for the self-assembling and formation mechanism of these fragments and final polyoxoanions in 1–3 are shown in Scheme 2b and 2c.

In terms of theoretical calculations of two anions and relative fragments, together with analyses of orbital interactions, charge transfer, electronic polarization of fragments, employed extended Hückel theory method,17,20 the structures of the two polyoxoanions in 1–3 can be reasonably interpreted. In theory, no charge transfer and no electronic polarization mean no covalent interaction between fragments, and large charge transfer and electronic polarization mean covalent interaction between fragments. For the [MoO$_{12}$]$_{6}^{6-}$@MoO$_{18}$ fragment model of the [MoO$_{26}$]$_{6}^{6-}$ anion in 1, the charge donation from two capped monomeric MoO$_{4}^{2-}$ fragments to a ring-shaped Mo$_{18}$O$_{36}$ fragment is 2.38 electrons and electronic polarization in the Mo$_{18}$O$_{36}$ fragment is 18.3 orbital% larger than in the two MoO$_{4}^{2-}$ fragments (Table 1), while for [SiO$_{4}^{4-}$@MoO$_{18}$] fragment model of the [SiMo$_{12}$O$_{36}$]$^{4-}$ anion in 2 and 3, the calculated charge donation from SiO$_{4}^{4-}$ fragment to Mo$_{18}$O$_{36}$ shell fragment is 2.91 electrons and correspondingly a larger electronic polarization occurs in the Mo$_{18}$O$_{36}$ fragment than in SiO$_{4}^{4-}$ fragment (33.2 orbital%) (Table 1). The large charge transfer and obvious polarization process observed in both the [MoO$_{26}$]$_{6}^{6-}$ and [SiMo$_{12}$O$_{36}$]$^{4-}$ anions accounted for another facts that there are very large interaction energy between the fragments (-888 kcal/mol for the former and -1555 kcal/mol for the latter), and the larger the charge transfer and/or polarization item, the larger the interaction energy. The charge transfer from two MoO$_{4}^{2-}$ fragments to the Mo$_{18}$O$_{36}$ fragment, or the formal charge (4-) of two MoO$_{4}^{2-}$ fragments delocated over the MoO$_{18}$ and Mo$_{18}$O$_{36}$ fragments of the whole [MoO$_{26}$]$_{6}^{6-}$ anion leads a large reorganization of the Mo$_{18}$O$_{36}$ fragment. Being similar, the large charge transfer, or the formal charge (4-) of the SiO$_{4}^{4-}$ fragment delocated over the SiO$_{4}^{4-}$ fragment and Mo$_{18}$O$_{36}$ fragments of the whole [SiMo$_{12}$O$_{36}$]$^{4-}$ anion leads a large reorganization of the Mo$_{18}$O$_{36}$ fragment. 

![Table 1](image-url)

<table>
<thead>
<tr>
<th>[MoO$<em>{12}$]$</em>{6}^{6-}$ in 1</th>
<th>[SiMo$<em>{12}$O$</em>{36}$]$^{4-}$ in 2 and 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net charge donation / electrons</td>
<td>2.38</td>
</tr>
<tr>
<td>[(MoO$<em>{12}$]$</em>{6}^{6-}$@MoO$_{18}$)</td>
<td>(SiO$<em>{4}^{4-}$@MoO$</em>{18}$)</td>
</tr>
<tr>
<td>Electronic polarization / orbital%</td>
<td>18.3 (Mo$<em>{12}$O$</em>{36}$@MoO$_{12}$)</td>
</tr>
<tr>
<td>Interaction energy between the fragments / kcal/mol</td>
<td>-888</td>
</tr>
</tbody>
</table>

*The data is based on G98 calculation.*

Somewhat differently for [SiO$_{4}^{4-}$@MoO$_{18}$] fragment model of the [SiMo$_{12}$O$_{36}$]$^{4-}$ anion, the calculated charge donation from two capped trimeric (Mo$_{3}$O$_{9}$) fragment to the ring-shaped Mo$_{18}$O$_{36}$ fragment is 0.11 electrons and electronic polarization in Mo$_{18}$O$_{36}$ fragment is ca. 72.4 orbital% larger than in the [MoO$_{18}$]$_{2}^{2-}$ fragments. Though the charge transfer is so little (0.11), the high polarization (72.4 orbital%) provides stabilization to the Mo$_{18}$O$_{36}$ – [MoO$_{12}$]$_{6}^{6-}$ fragment assembling process, which is different from the cases of Mo$_{3}$O$_{9}$ – SiO$_{4}^{4-}$ fragment assembling process and Mo$_{18}$O$_{36}$ – [MoO$_{12}$]$_{6}^{6-}$ fragment assembling process where the charge transfer contributes mainly to the fragment assembling interaction. The interaction energy for MoO$_{18}$ – [MoO$_{12}$]$_{6}^{6-}$ fragment assembling process is ca. -1278 kcal/mol. Obvious charge transfer from the SiO$_{4}^{4-}$ fragment to the ring-shaped Mo$_{18}$O$_{36}$ fragment (1.37 electrons) and significant electronic polarization of ring-shaped Mo$_{18}$O$_{36}$ fragment over the SiO$_{4}^{4-}$ fragment (29.1 orbital%) have been also observed (Table 1). Fig. 4 shows fragment molecular orbital (MO) interaction of the [MoO$_{26}$]$_{6}^{6-}$ anion. For this anion, all of the 4d orbitals of the central Mo(VI) atoms are unoccupied, while the occupied frontier orbitals are all from the oxo orbitals. The LUMO is 4d orbital of Mo atoms, and the HOMO is the p orbitals of the terminal oxo atoms, which are predominantly from the HOMO-9 (p of terminal oxo, 40.3%) and HOMO-13 (p of terminal oxo, 24.7%) orbitals.
of the Mo₅O₁₈ fragment. Owing to orbital interaction of the two MoO₄²⁻ fragments, the HOMO-9 orbital of the Mo₅O₁₈ fragment is destabilized, it becomes the HOMO of the [Mo₃O₂O₆]⁴⁺ anion. Differently the HOMO-1 orbital, is an admixture of Mo₅O₁₈ fragment orbitals (the HOMO-14, p of terminal oxo, 26.5%, and HOMO-3, p of terminal oxo, 23.4%) with bridging oxo orbitals (p, 12.3%) of two MoO₄²⁻ fragments. However the HOMO-1 and frontier orbitals of [SiMo₁₂O₃₆]⁴⁻ anion. An admixture from bridging oxo orbitals of the SiO₄⁴⁻ fragment are relatively larger in the occupied orbitals than in the unoccupied orbitals, and thus a relatively larger energy increase can be expected in occupied orbitals than in unoccupied orbitals. For the SiO₄⁴⁻ fragment since the Si(IV) atom has a tetrahedral geometry, the four sp³-hybrid Si(IV) orbitals bond to four O atoms (σ-orbitals). These orbitals are doubly occupied, and are formally delocalized over the oxo ligands of the Mo₁₂O₃₆ shell fragment. The orbital energies of σ-Si(IV)–O bondings of the SiO₄⁴⁻ fragment should be shifted to very low values, hence these orbitals will be buried deeply into the occupied oxo orbitals of the [SiMo₁₂O₃₆]⁴⁺ anion, and are far below the frontier HOMO orbital of the [SiMo₁₂O₃₆]⁴⁺ anion, an indicative that these bonding interactions are highly stabilized in the [SiMo₁₂O₃₆]⁴⁺ anion, and that it appears to be a weaker covalent interaction, between the Mo₁₂O₃₆ and SiO₄⁴⁻ fragments in the [SiMo₁₂O₃₆]⁴⁺ anion, which is in agreement with the experimental observation that SiO₄⁴⁻ fragment in 2 is disordered.

Conclusions

To summarize, we herein report the one-pot synthesis, structures of three polyoxomolybdate-based compounds (1–3) containing MoO₄²⁻ and MoO₃³⁻-based polyoxoanions, i.e. [Mo₅O₂₆]⁴⁻ and [(SiO₄)₃(MoO₃₂)]⁴⁺. 1 contains rarely observed Mo₉-based [Mo₅O₂₆]⁴⁻ polyoxoanion, while 2 and 3 consist of Mo₁₂-based [(SiO₄)₃(MoO₃₂)]⁴⁺ polyoxoanions. That three compounds are different in the polyoxoanion structures and crystallize in order in the same solution system is very rarely observed so far for POM synthetic chemistry and very interesting for understanding the formation mechanism and self-assembling process of Mo-based polyoxoanions. The fragment analysis and orbital interaction analysis successfully account for the formation mechanism and self-assembling process of fragments and two Mo-based polyoxoanions in 1–3. The calculated large charge transfer and/or high electronic polarization item between fragments provide successfully electronic structural information for interpretation of structural stability and the fragment‐fragment self‐assembling process.

Acknowledgements

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Notes and references


4 (a) S. Favette, B. Hasenknopf, J. Vaissermann, P. Gouzerh and C. Ganzhou 341000, China


6 One-pot hydrothermal syntheses of 1-3: a mixture of CuO (0.081 g, 1 mmol), H2MoO4 (0.81 g, 5 mmol), L-


15 Crystal data: For I, C12H12Cu2MoN6O12Si, M = 983.73, monoclinic, space group P21/c, a = 13.1126(15) Å, b = 16.706(19) Å, c = 17.1279(15) Å, β = 123.896(6)°, V = 3105.6(5) Å3, Z = 4, D(calc) = 2.167 cm−3, μ = 2.382 mm−1, F(000) = 1908, GOF = 1.007, R1 = 0.0573, wR1 = 0.1441. A total of 15868 reflections were collected, of which 4529 (Rint = 0.1043) were unique. For 2, C12H20Cu2MoN6O12Si, M = 2985.65, monoclinic, space group C2/m, a = 23.1711(13) Å, b = 15.7546(9) Å, c = 12.0657(7) Å, β = 94.9904(10)°, V = 4415.84(4) Å3, Z = 2, D(calc) = 2.245 g cm−3, μ = 1.765 mm−1, F(000) = 2900, GOF = 1.061, R1 = 0.0514, wR1 = 0.1479. A total of 16040 reflections were collected, of which 4941 (Rint = 0.0240) were unique. For 3, C24H24Cu2MoN6O12Si, M = 2335.95, triclinic, space group P-1, a = 11.6044(6) Å, b = 13.1169(4) Å, c = 20.4496(9) Å, V = 2779.28(18) Å3, Z = 2, D(calc) = 2.791 g cm−3, μ = 2.749 mm−1, F(000) = 2220, GOF = 1.037, R1 = 0.0382, wR1 = 0.0825. A total of 53969 reflections were collected, of which 14351 (Rint = 0.0481) were unique.Intensity data were collected on a Bruker SMART CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) X-ray source using omega-20 scans. The structures were solved by direct methods and refined by full-matrix least-squares fitting on F2 by SHELXTL-97. All nonhydrogen atoms were located from the initial solution and refined with anisotropic thermal parameters.
20 Calculation details: The input data of [Mo$_8$O$_{26}$]$^{4-}$ anion and its [MoO$_4$]$^{2-}$ and [MoO$_4$]$^{2-}$ fragments in 1, and [SiMo$_{12}$O$_{40}$]$^{4-}$ anion and its [SiO$_4$]$^{4-}$, [Mo$_{12}$O$_{36}$], [Mo$_6$O$_{18}$] fragments in 2 and 3, are from the same crystal data, and are selected for respective electronic structure calculations based on extended Hückel theory method, and the default parameters of the employed Gaussian98 software. These calculated results are further analysed and compared to each other so as to understand the orbital interactions, charge transfer, electronic polarization between fragments employed the AOMix program. The solvent effect and basis set are not needed for considering in the extended Hückel theory calculations.
Graphical Abstract

Synthesis, Structures and Theoretical Investigation of Three Polyoxomolybdate-based Compounds: Self-assembling, Fragment Analysis, Orbital Interaction, and Formation Mechanism

Yi-Ping Tong, Guo-Tian Luo, Jin Zhen, You Shen, and Yan-Wen Lin

Three Mo₈⁶⁻ and Mo₁₂-based compounds, containing [Mo₈O₂₆]⁴⁻ and [(SiO₄)(Mo₁₂O₃₆)]⁴⁻ polyoxoanions, were synthesized from a solution system. It is very rare and very interesting in POM synthetic chemistry. Both fragment analysis and orbital interaction analysis were employed to explain the formation and self-assembling mechanism of the polyoxoanions.