Ligand-Directed Template Assembly for the Construction of Gigantic Molybdenum Blue Wheels**

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Abstract:Template-mediated synthesis is a powerful approach to build a variety of functional materials and complex supramolecular systems. However, the systematic study of how templates structurally evolve from basic building blocks, and then affect the templated self-assembly, is critical to understanding and utilizing the underlying mechanism, to work towards designed assembly. Here we describe the templated self-assembly of a series of gigantic Mo Blue (MB) clusters 1–4 using L-ornithine as a structure-directing ligand. We show that by using L-ornithine as a structure director, we can form new template-host assemblies. Based on the structural relationship between encapsulated templates of \{Mo\_12\} (1), \{Mo\_12\_2\} (2) and \{Mo\_36\} (4), a pathway of the structural evolution of templates is proposed. This provides insight into how gigantic Mo Blue cluster rings form and could lead to full control over the designed assembly of gigantic Mo-Blue rings.

Template-mediated synthesis is a versatile approach to fabricate nanostructured materials and supramolecular architectures. Anion templates are widely investigated in biological systems but they are much less explored in supramolecular inorganic chemistry, in comparison to cationic and neutral templates. In the field of polyoxometalates (POMs)—a unique class of anionic discrete metal–oxo clusters with a wide variety of structures and properties—anion templates are essential for their construction. Not only do these anions direct the self-assembly of POMs via a templating effect but also affect the resultant structures and their properties. More recently, nanosized POM clusters have been found as anion templates to direct the self-assembly of larger POMs. One example is the formation of [Mo\_18\_36\_17\_8] upon acidification of molybdate, which allows for the self-assembly of the [Mo\_36\_17\_8] giant Mo Blue wheel after addition of the reducing agent, revealing the role of the [Mo\_17\_8\_17\_36\_18] anion template. In general, three types of interactions can be established between the templates and POMs: hydrogen bonding, electrostatic interactions and coordination, see Scheme 1. To exploit this, we considered if multiple interactions could be combined to build a series of new POM clusters, while elucidating the mechanism of templated self-assembly. In addition, an understanding of the structural evolution of the template species may be derived by trapping fragments/intermediates in the larger host structures.

Herein we describe the template-based self-assembly of a series of Mo Blue (MB) wheels showing a structural evolution 1–4. These compounds are formed by using L-ornithine to direct the assembly electrostatically and via hydrogen bonding to stabilize the template-host architecture (Scheme 1), giving new mechanistic insights. Compound 1 features a framework of [Mo\_12\_Ce\_8] with an [Mo\_4] template cluster, while Compound 2 and 3 share the same [Mo\_12\_Ce\_8] framework, but with different templates: [Mo\_12\_4] for 2 and [PMo\_12\_4] for 3. Compound 4 comprises of two wheels, [Mo\_12\_8\_17\_8] and [Mo\_18\_36\_17\_8], with a [Mo\_36\_17\_8] template trapped in the [Mo\_36\_17\_8] framework. Except for [Mo\_36\_17\_8], the remaining templates are discovered for the first time in MB synthesis and compounds 1–4 are totally new clusters in the structural library of MB.
The [MoO₃] unit is isolated for the first time, although its framework has been seen previously in the [Mo₅O₇] cluster. All compounds were characterized crystallographically and the formulae were determined using an array of techniques (see SI). Compounds 1–4 can be formulated as:

\[ (\text{CH}_3\text{H}_4\text{N}_3\text{O}_2)_2[(\text{MoO}_3\text{O}_2)_{1.5} \subset \text{H}_2\text{Mo}_{10}\text{C}_6\text{O}_{36}(\text{H}_2\text{O})_{16}(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_3] \cdot 160\text{H}_2\text{O} \equiv (\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_4[1\text{a}] \cdot 160\text{H}_2\text{O} \]

\[ \text{Na}_8(\text{CH}_3\text{H}_4\text{N}_3\text{O}_2)_2[(\text{MoO}_3\text{O}_2)_{1.5} \subset \text{H}_2\text{Mo}_{10}\text{C}_6\text{O}_{36}(\text{H}_2\text{O})_{16}(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_3] \cdot 195\text{H}_2\text{O} \equiv \text{Na}_8(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_{12}[2\text{a}] \cdot 195\text{H}_2\text{O} \]

\[ \text{Na}_5(\text{CH}_3\text{H}_4\text{N}_3\text{O}_2)_2[(\text{MoO}_3\text{O}_2)_{1.5} \subset \text{H}_2\text{Mo}_{10}\text{C}_6\text{O}_{36}(\text{H}_2\text{O})_{16}(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_3] \cdot 195\text{H}_2\text{O} \equiv \text{Na}_5(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_{12}[3\text{a}] \cdot 195\text{H}_2\text{O} \]

\[ \text{Na}_{10}(\text{CH}_3\text{H}_4\text{N}_3\text{O}_2)_2[(\text{MoO}_3\text{O}_2)_{1.5} \subset \text{H}_2\text{Mo}_{10}\text{C}_6\text{O}_{36}(\text{H}_2\text{O})_{16}(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_3] \cdot 410\text{H}_2\text{O} \equiv \text{Na}_{10}(\text{C}_2\text{H}_6\text{N}_2\text{O}_2)_{24}[4\text{a}] \cdot 410\text{H}_2\text{O} \]

l-ornithine was initially introduced into a standard version of the lanthanide-doped Mo Blue synthesis system (see SI for details), to establish whether it could assist in trapping an “intrinsic” template that directs the self-assembly process. Crucially, no preformed anion templates, as established in previous studies, such as the Keggin-type [M₂] or Dawson-type [M₁₆] were added, yet crystals of 1 were obtained in two weeks. Single-crystal X-ray structure analysis of 1 reveals a host–guest structure 1a in which α-[MoO₂]³⁻ ([Mo₈]) is encapsulated by the [Mo₁₂,Ce₄] host (Figure 1). [Mo₁₂,Ce₄] is composed of 12 [Mo₈] units, 8 [Mo₅] units, 12 [Mo₄] units and 4 [Ce(H₂O)₄] units functionalized by l-ornithine ligands on the inner surface. Two Ce³⁺ ions are located on the upper rim and separated by one [Mo₈] unit while another two are situated on the opposite side and separated by two [Mo₄] units, giving rise to an elliptical wheel. All the l-ornithine ligands are attached onto [Mo₈] units with the side chain buried in the pitch of [Mo₁₂,Ce₄]. Due to the limited resolution of the X-ray data, only three l-ornithine ligands can be fully located crystallographically. The [Mo₈] template located at the centre of [Mo₁₂,Ce₄] is anchored by a series of N–H···O (3.0205(2)–3.7020(2) Å) and C–H···O (3.1802(2)–3.7795(2) Å) hydrogen bonds, which are formed between the terminal O atoms of [Mo₈] and the methylene and protonated amine groups on the l-ornithine ligands (Figure S6). In addition, the protonated l-ornithine also acts as a charge buffer to reduce the repulsive electrostatic force between the anionic [Mo₈] template and the [Mo₁₂,Ce₄] host. The combination of both hydrogen bonding and electrostatic interaction is thus able to stabilize the template:host architecture.

Under more concentrated reaction conditions, decreasing the ratio of Ce³⁺/MoO₂²⁻ leads to the discovery of compound 2. Single crystal X-ray structure analysis of 2 reveals a host–guest structure 2a in which a [Mo₁₀,Oₓ₂(H₂O)ₙ]³⁻ ([Mo₅]) is trapped by the [Mo₁₀,Ce₄] host (Figure 2a). The host is isostructural to the [Mo₁₀,Ce₄] elliptical ring-shaped structure that is composed of 14 [Mo₈] units, 12 [Mo₅] units, 14 [Mo₄] units and 2 [Ce(H₂O)₄] units, and is functionalized by six protonated l-ornithine ligands on the inner surface. The 2 symmetry-related Ce³⁺ ions are distributed evenly on the two ends of [Mo₁₀,Ce₄], producing an elliptical wheel with outer and inner ring diameter of ~31 and 12 Å, respectively, at its most elongated points. The six l-ornithine ligands are grafted onto six [Mo₈] units via carboxylate groups with the side chain buried in the pitch of [Mo₁₀,Ce₄] (Figure 2a).

Similar to 1a, the [Mo₁₀] template also resides at the centre of [Mo₁₀,Ce₄] and is anchored in place by a large number of N–H···O (2.9338(1)–3.7231(1) Å) and C–H···O (2.9419(1)–3.6863(1) Å) hydrogen bonds formed between the terminal O atoms of [Mo₈] and the l-ornithine ligands.

![Figure 1. View of the molecular structure of 1a. The framework of [Mo₁₀,Ce₄] is presented in polyhedron mode and the entrapped [Mo₈] is shown in ball and stick mode. Color scheme: [Mo₈], yellow polyhedron; [Mo₅], red polyhedron; [Mo₄], blue polyhedron with central pentagonal unit in cyan polyhedron; Ce³⁺, green polyhedron; C, gray ball; N, pink ball.](image-url)

![Figure 2. a) View of the molecular structure of 2a. [Mo₁₀,Ce₄] is shown in polyhedron mode and l-ornithine is presented in ball and stick mode. Color scheme is the same as Figure 1; b) View of the molecular structure of [Mo₅]; the pentagon is highlighted using cyan bonds; c) and d) View of the disordered [Mo₅] in two positions, which are presented in cyan and yellow wire-frames, respectively.](image-url)
host in 3a is isostuctural to 2a but with the [PMo$_{12}$] located in the cavity of [Mo$_{100}$Ce$_2$], in place of [Mo$_3$]. As such, similar hydrogen bonding patterns and electrostatic interactions are observed (Figure S8). Due to the relatively smaller size of [PMo$_{12}$] in comparison to the central cavity of [Mo$_{100}$Ce$_2$], the cluster is disordered over two positions, equally, on either side of the framework cavity, maximizing electrostatic interactions and hydrogen bonding (N–H–O (2.8850(2)–3.7598(2) Å) and C–H–O (3.3208(1)–3.7977(3) Å). Notably, [PMo$_{12}$] adopts the β-configuration instead of the α-isomer (Figure S3b and 3c), due to the β-form being the preferred species under reduced conditions.

The templating effect of encapsulated clusters has been studied in situ by $^{31}$P NMR spectroscopy. Following the synthetic procedure used to produce compound 3, after the addition of all starting materials in D$_2$O, a $^{31}$P NMR spectrum was recorded every 10 min for 1 h. When a low concentration of [PMo$_{12}$] (2.5 mg) was used, much less than the stoichiometry required for the formation of [PMo$_{12}$]$^-$[Mo$_{100}$Ce$_2$], signals resulting from the reduced [PMo$_{12}$]$^-$ (−5.69 and −6.25 ppm for β-[PMo$_{12}$] and α-[PMo$_{12}$], respectively) could be detected after 10 min and then completely disappeared after 1 h (Figure S11c,d). Note that the signals of fully oxidized α-[PMo$_{12}$] are located at −3.35 ppm (Figure S11e).

In contrast, the addition of excess [PMo$_{12}$] (8.0 mg) resulted in the presence of peaks of [PMo$_{12}$] throughout the reaction process but the signal became much less intense after 1 h (Figure S11a,b). This indicates that [PMo$_{12}$] is a template during the self-assembly, which is gradually consumed upon the formation of [PMo$_{12}$]$^-$[Mo$_{100}$Ce$_2$] (3a). Once [PMo$_{12}$] is included as a template, its $^{31}$P NMR signal cannot be observed because of the shielding effect of the paramagnetic [Mo$_{100}$Ce$_2$]. This is also confirmed by the control experiment where compound 3 showed no $^{31}$P NMR response in solution (Figure S12). Accordingly, when an inadequate amount of the template was used, the [PMo$_{12}$] is completely encapsulated by the host and hence the [PMo$_{12}$] is NMR silent. When an excess of template is used, this results in the presence of signals even after 1 h due to the remaining presence of free [PMo$_{12}$] (Figure S11a).

The successful encapsulation of [Mo$_3$], [Mo$_3$] and [PMo$_{12}$] as templates led us to further explore the potential of using l-ornithine as a structure-directing agent to trap different templates, which may in turn give us more insight regarding the formation mechanism of the templated self-assembly of Mo Blue clusters. In the cases of 1–3, lanthanide-doped Mo Blue (LMB) [Mo$_{100}$Ce$_2$] and [Mo$_{106}$Ce$_2$] provide confined environments to enclose templates. In general, LMB-based wheels exhibit a more curved inner surface and elliptical ring shape, and thus a smaller size compared with the archetypal [Mo$_{10}$] wheel. With this in mind, we performed the synthesis without adding lanthanides to see how the change of curvature and size of MB will affect the entrapped template. After a systematic optimization of the synthetic conditions we were able to obtain another templated MB cluster 4, see Figure 4.

Single-crystal X-ray structure analysis reveals that 4 crystallizes in space group P1 and consists of two crystallographically independent wheels in the molecular structure, denoted as 4a$_1$ and 4a$_2$, respectively (Figure 4a and b). 4a$_1$ features a host–guest architecture with a [Mo$_{12}$O$_{42}$(H$_2$O)$_{32}$]$_3$ (Mo$_3$)$_3$] trapped by the [Mo$_3$] host. The [Mo$_{12}$]$_3$ adopts the same framework of the archetypal [Mo$_{10}$]$_3$ that is constructed from 14 sets of [Mo$_3$] units, but with two [Mo$_3$] defect sites on the rim of the wheel (Figure 4b).[10] The [Mo$_3$], which is situated in the center of the [Mo$_{12}$]$_3$ cavity, is structurally equivalent to the well-known and previously described [Mo$_{12}$]$_3$ cluster,[1] as observed in the previously reported [Mo$_{12}$]$_3$[Mo$_{10}$]$_3$.[9] There are also six l-ornithine ligands attached on six [Mo$_3$] units in 4a$_1$. Among them, two pairs of l-ornithine are orientated in tail-to-tail mode, with the terminal amino groups pointing to each other, while the remaining two are arranged freely. [10] Similar to 1–3, the positively charged...
of arrangement means the \([\text{Mo}_{108}]\) can either accommodate \([\text{Mo}_{80}]\) along its lateral axis (4a1) or longitudinal axis (\([\text{Mo}_{80}]\))]. In contrast, the cavity of 4a1 is too large in comparison to \([\text{Mo}_{80}]\) and thus is unable to capture \([\text{Mo}_{80}]\) efficiently. The encapsulation of \([\text{Mo}_{80}]\) in 4a1 further confirms that \([\text{Mo}_{80}]\) is a key template during the self-assembly of Mo Blue, consistent with our previous study.\(^{[9a,b]}\)

The formation of compounds 1–4 with \(L\)-ornithine as a structure-directing agent allows us to propose a potential mechanism of templated self-assembly underpinning the formation of the compounds, see Scheme 2. The process could be described as follows: firstly, the basic building blocks of \([\text{Mo}_{80}]\), \([\text{Mo}_3\]) and \([\text{Mo}_1\]) form in solution. Next, the labile \([\text{Mo}_8]\) units could either transform to the isomeric \(\alpha\{\text{Mo}_{8}\}\) or dimerize with one \([\text{Mo}_1]\) unit to generate the \([\text{Mo}_{17}]\) cluster in situ, which then behaves as a template to drive the self-assembly of 1 and 2 under the direction of \(L\)-ornithine, respectively. If the preformed \([\text{PMo}_{31}]\) is introduced during the synthesis of 2, then the formation of \([\text{Mo}_{17}]\) is prevented and 3 will be constructed with \([\text{PMo}_{31}]\) as the templating species. The dimerization of \([\text{Mo}_{8}]\) to form \([\text{Mo}_{17}]\) presents a new template that can direct the formation of 4a1 together with \(L\)-ornithine. The templated self-assembly revealed here implies that by rationally controlling the sizes, shapes and charges of anionic POM templates with the assistance of structure directors, smaller or larger MB clusters that go beyond the current limitation of sizes and nucleicarities can be constructed, leading to the discovery of unprecedented template species and MB framework clusters.

In summary, we have described the anion-templated self-assembly of MB clusters 1–4 featuring template-host architectures with \(L\)-ornithine as a structure-directing agent. Upon protonation, \(L\)-ornithine not only serves as charge buffer to bind the anionic templates and hosts together, but also provides hydrogen bonding sites to strongly interact with templates, which appears to be essential for the formation of 1–4. The successful construction of 1 unveils the “intrinsic template” of \([\text{Mo}_{80}]\) formed in situ. Under more concentrated conditions, \([\text{Mo}_{17}]\) is trapped as a template to induce the self-assembly of 2, which could be replaced by the preformed \([\text{PMo}_{31}]\), leading to the formation of 3. A \(^{13}P\) NMR study during the synthesis of 3 illustrates the self-assembly is
essentially template-dependent. Moreover, the encapsulation of the $\text{[Mo}_8\text{]}$ cluster in 4a further confirms that $\text{[Mo}_8\text{]}$ is a key template during the self-assembly of the Mo Blue clusters. Due to the structural relationship between $\text{[Mo}_8\text{]}$, $\text{[Mo}_7\text{]}$ and $\text{[Mo}_9\text{]}$, it is reasonable to assume that $\text{[Mo}_9\text{]}$ may be constructed via dimerization of $\text{[Mo}_7\text{]}$, which itself can be built from dimerization of $\text{[Mo}_8\text{]}$, showing a potential stepwise pathway for template assembly in solution.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** anion templation · gigantic cluster · host-guest chemistry · molybdenum blue · polyoxometalates

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