Polyoxometalates

Exploring the Molecular Growth of Two Gigantic Half-Closed Polyoxometalate Clusters \{Mo_{180}\} and \{Mo_{130}Ce_6\}

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Abstract: Understanding the process of the self-assembly of gigantic polyoxometalates and their subsequent molecular growth, by the addition of capping moieties onto the oxo-frameworks, is critical for the development of the designed assembly of complex high-nuclearity cluster species, yet such processes remain far from being understood. Herein we describe the molecular growth from \{Mo_{150}\} and \{Mo_{120}Ce_6\} to afford two half-closed gigantic molybdenum blue clusters \{Mo_{180}\} (1) and \{Mo_{130}Ce_6\} (2), respectively. Compound 1 features a hat-shaped structure with the parent wheel-shaped \{Mo_{150}\} being capped by a \{Mo_{10}\} unit on one side. Similarly, 2 exhibits an elliptical lanthanide-doped wheel \{Mo_{130}Ce_6\} that is sealed by a \{Mo_{10}\} unit on one side. Moreover, the observation of the parent uncapped \{Mo_{150}\} and \{Mo_{130}Ce_6\} clusters as minor products during the synthesis of 1 and 2 strongly suggests that the molecular growth process can be initialized from \{Mo_{150}\} and \{Mo_{120}Ce_6\} in solution, respectively.

Polyoxometalates (POMs) are a unique class of discrete metal-oxo clusters with a diversity of structures and properties.\(^1\) The almost unlimited combination of anion templates and basic building blocks in solution results in an extensive library of POM clusters with a range of extraordinary structures. As such, particular attention has been paid to the grand goal of the rational design and synthesis of gigantic POM clusters, building on prior structural and mechanistic data.\(^4\) This is because, in general, gigantic POM clusters are constructed from a precisely ordered arrangement of building blocks which appear structurally to be fundamental to this class of compounds. For example, the molybdenum blue (MB) clusters such as \{Mo_{150}\}, \{Mo_{176}\}, and \{Mo_{130}\}, are constructed from basic \{Mo\}, \{Mo\}, and \{Mo\} building blocks.\(^{1-4}\) and gigantic polyoxotungstates such as \{W_{22}Mn_{84}\} and \{W_{50}Co_{36}\} are generated via the connection of \{W_{16}\} (\(X = 8-15\)) building blocks.\(^{4,6}\) Nevertheless, it is rare to see reports on the use of gigantic preformed POMs as “big building blocks” to construct even higher nuclearity clusters, or to achieve high-order assemblies.\(^{16}\) Two prominent examples are the molecular growth of \{Mo_{120}\} from the smaller \{Mo_{150}\}\(^{15a}\) and in situ growth of metal-oxo clusters such as \{Cu_{10}\} and \{Fe_{10}\} within the cavity of the ring shaped \{P_{4}W_{12}\}.\(^{18a}\) In principle, molecular growth based on gigantic POM clusters will not only result in novel clusters with high structural diversity, but also leads to the opportunity of introducing new building blocks/functionalities that cannot be discovered via traditional synthesis methods, opening up an alternative pathway to build functional POM-based materials.\(^5\) Meanwhile, it is important to understand the way in which the additional fragments initialize the molecular growth process. This is particularly important to improve the understanding of the initial nucleation of POM clusters in solution, as well as the metal-centered assemblies found in biological systems.\(^{5,15}\) In this context, the investigation of clusters that can be grown/ assembled by molecular growth processes is warranted.

Within the MB family of gigantic isopolyoxomolybdates clusters the \{Mo\} units are relatively reactive and can be easily coordinated by carboxylic acids, or replaced by electrophiles, such as lanthanides, to afford amino acid-functionalized\(^6\) or lanthanide-doped\(^6\) MB species. More importantly, we hypothesized that the inward terminal O atoms on the \{Mo\} units could provide interactive sites to support further growth from the inner surface, as evidenced by the molecular growth from \{Mo_{176}\} to \{Mo_{248}\}.\(^{5a}\) Inspired by this, we set out to explore the molecular growth using a smaller MB, such as \{Mo_{154}\}, and lanthanide-doped MB as the parent scaffolds, to see how different sizes and curvatures of the pristine rings may affect the resulting clusters. Herein, we report two novel MB clusters \{Mo_{180}\} (1) and \{Mo_{130}Ce_6\} (2) constructed via the molecular growth from \{Mo_{150}\} and \{Mo_{130}Ce_6\}, respectively. Compounds 1 and 2 exhibit unprecedented half-closed structural motifs arising from the asymmetric growth of cap-like \{Mo_{150}\} and \{Mo_{130}\} units present on just one side of \{Mo_{150}\} and \{Mo_{130}Ce_6\}, respectively (Scheme 1).

Compound 1 was prepared by reducing an acidified solution of Na$_2$MoO$_4$ and l-ornithine in H$_2$O while 2 was obtained from reduction of an acidified suspension of cerium polymolybdate in H$_2$O. l-ornithine was introduced as cationic structure-directed agent during the self-assembly which not only balances the overall charge of 1 but, also facilitates the further growth of capped fragment by adjusting the orientation and conformation of the \{Mo\} units. All the compounds were characterized crystallographically and the formula assignments are fully supported by using an extensive array of analytical techniques (see Supporting Information). Compounds 1–2 can be formulated as \{Eqs. (1)–(2)\}:

\[\text{Eq. (1):} \quad \text{Comp. 1} \quad \{Mo_{150}\} \quad \text{Comp. 2} \quad \{Mo_{130}Ce_6\}\]

\[\text{Eq. (2):} \quad \text{Comp. 1} \quad \{Mo_{180}\} \quad \text{Comp. 2} \quad \{Mo_{130}Ce_6\}\]

\[\{Mo_{150}\} \quad \{Mo_{130}Ce_6\}\]
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Scheme 1. Schematic representation of molecular growth from [Mo150] to 1 and from proposed intermediate “Mo150Ce6” to 2. [Mo0] yellow polyhedron, [Mo1] red polyhedron, [Mo2] blue polyhedron with central pentagonal unit in cyan polyhedron, CeIII green polyhedron, C gray ball, N blue ball.

\[
\text{Na}_5 (\text{C}_5 \text{H}_{11} \text{N}_2 \text{O}_2)_2 \cdot \text{H}_2 \text{O} \cdot [\text{Mo}_{130} \text{O}_{396} (\text{H}_2 \text{O})_{73} (\text{C}_5 \text{H}_{12} \text{N}_2 \text{O}_2)_7] \cdot 250 \text{H}_2 \text{O} \\
\equiv \text{Na}_5 (\text{C}_5 \text{H}_{11} \text{N}_2 \text{O}_2)_2 \cdot 250 \text{H}_2 \text{O}
\]

\[
\text{Ce}_{15} (\text{C}_5 \text{H}_{10} \text{N}_2 \text{O}_2)_{14} (\text{H}_2 \text{O})_{23} \cdot 180 \text{H}_2 \text{O} \equiv \text{Ce}_{15} [2 \text{a}] \cdot 180 \text{H}_2 \text{O}
\]

The single-crystal X-ray structural analysis reveals that 1 crystallizes in the space group P1 – 1 and not only has a ring topology, but has another cluster grafted to the rim of the ring giving a hat-like [Mo114] (1a), composed of 17 [Mo0] units, 15 [Mo1] units, and 14 [Mo2] units (Figure 1a,b). Compound 1a could be divided into two parts, that is, the rim of hat, [Mo150], and the cap, [Mo30]. The [Mo150] adopts the same framework of archetypal [Mo154] discovered by Müller et al. that is constructed from 14 sets of [Mo11] units but with two [Mo0] sites with defects on the rim of the wheel (Figure 1c). In total, there are five [Mo0] units on the lower rim and seven [Mo1] units on upper rim of [Mo150]. The [Mo30] cap is situated on top of [Mo150] and is connected to the main ring via 7-based [Mo0] units. The [Mo114] is built from three [Mo0] units which are linked with two edge-sharing [Mo0] units and one corner-sharing [Mo0] unit (Figure 1d). It should be noted that edge-sharing [Mo0] units are also the basic building blocks for the spherical inorganic Fullerene Keplerate structure, [Mo132], and have never before been observed in the structure of MB wheels. In addition, seven l-ornithine ligands are found to be grafted onto the seven [Mo0] units with the side chain buried in the pitch of [Mo150]. Among them, two pairs of l-ornithine are arranged in tail-to-tail mode with the terminal amino groups pointing to each other while another pair of l-ornithine ligands adopt a head-to-head arrangement (Figure S4).

The geometry and shape of 1a resembles that of half of a [Mo114] cluster. To make a better comparison, we have simplified both the structures and placed an emphasis on pentagonal [Mo0] units as shown in Figure 2. For example, in Figure 2e, the 20 pentagons found in half of the [Mo114] cluster are shown tiled in three layers (A–C) with an 8-8-4 arrangement. The 8 pentagons in layer B stack between 4 pairs of pentagons in layer A and each pentagon in layer C further pack between 4 pairs of pentagons in layer B. Therefore, the general rule is that pentagons in three layers are connected in a ratio of 2:2:1 (Figure 2b,e). Applying this rule to 1a, the ideal arrangement of pentagons in the three layers should be 7-7-3.5. In consideration of steric hindrance and spatial constraints, only three pentagons are built in layer C and each of them are located between two pentagons in layer B with the position corresponding to a pentagon being left vacant, see the VS (vacant site) in Figure 2a. Notably, this unoccupied or “defect” site superimposes on the position of the missing [Mo0] units on [Mo114], indicating that both the brim and cap of 1a have adjusted their structures to dissatisfy the non-defect-based [Mo154] and the 3.5 pentagons to

Figure 1. a) Top view of the molecular structure of 1a in polyhedron representation. [Mo0] yellow polyhedron, [Mo1] red polyhedron, [Mo2] blue polyhedron with central pentagonal unit in cyan polyhedron. l-ornithine is omitted for clarity. b) Side view of hat-like 1a in ball and stick mode. Mo color code same as in (a); O gray. The inserted purple ball is to highlight void space within 1a. c) and d) Polyhedron representation of [Mo150] (c) and [Mo30] (d).
promote the formation of 1a. Similar to that of [Mo368], symmetry breaking occurs between layer B and C in 1a, and the local symmetry of [Mo150] dramatically reduces from ideal D_{3d} to C_{1}, in the cap. Accordingly, the positively curved interior surfaces of [Mo368] transform to negative curvatures in the cap. There are two domains of negative curvatures formed between [Mo30] units and [Mo6] pentagons in layer B and C (Figure 2d and Figure S5). One domain contains two negative curvatures while another one comprises three negative curvatures (Figure S5).

In principle, the torus-shaped [Mo368] and [Mo368] can mainly support the in-plane growth of capping moieties along the direction of interior rim defined by [Mo150] units, as shown by the molecular growth from [Mo368] to [Mo368] which has a “flying saucer-like” shape (Figure 2c,f).[4a,5a] In view of [Mo368], longitudinal growth is favored owing to the pumpkin-shaped central parts (layer A + B, composed of 16 pentagons; Figure 2e).[6] In this respect, it is interesting to observe the molecular growth of the capping [Mo368] along the longitudinal axis of the [Mo248]. After a detailed analysis of the topological structure of 1a, we found that the [Mo30] units in 1a play a key role in directing the longitudinal growth. As shown in Figure 3a and Figure 3b, each Mo atom of the corner-shared [Mo2] in both [Mo368] and [Mo368] uses two O atoms in the equatorial plane to link with adjacent [Mo30] pentagons (green lines in Figure 3) and the third O atom to do so (Figure 3d). This type of connectivity means that the [Mo30] unit in the [Mo30] is prone to deviate from the positive camber defined by adjacent two pentagons, and thus facilitate the longitudinal growth instead of horizontal growth.

The successful synthesis of compound 1 promotes us to explore the potential of using smaller MB as scaffold to realize the molecular growth. To do this, we selected a lanthanide-doped Mo Blue (LMB) as the candidate.[9] In general, LMBs are prepared using strong electrophiles such as Ce^{IV}, Pr^{III}, and Eu^{III} ions to replace [Mo2] units on the parent [Mo150]. The resulting LMB generally exhibits smaller dodecameric or decameric frameworks in comparison with tetradecameric [Mo150]. Since the Ln^{III} ions are significantly smaller than [Mo30] unit, the substitution of the [Mo30] units with Ln^{III} ions causes the contraction of the wheel, and consequently increases the curvature on the inner surface of the ring. Therefore, the incorporation of lanthanide ions not only adjusts the available number of [Mo30] units but also tunes the curvature and size of the MB. With this in mind, we envision that LMBs may provide a great chance to cap “species” differently from the iso-POMs such as [Mo368] and [Mo368].

After a systematic optimization of the synthetic conditions we were able to obtain the half-closed compound 2. Single-crystal X-ray structure analysis reveals that 2 crystallizes in space group Pnma and features an elliptical ring structure of [Mo120Ce6] capped by a [Mo10] unit on one side (Figure 4). The parent [Mo120Ce6] could be regarded as a dodecamer that is composed of 12 [Mo30] units, 6 [Mo2] units, 12 [Mo30] units, and 6 Ce^{III} ions.[8a] The Six Ce^{III} ions are distributed on both upper and lower rim of the wheel in an unsymmetrical arrangement, i.e., 4 of them are located symmetrically on one side while another 2 stay on the same
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[11] Unpublished results: We have obtained the crystal structures of L-ornithine functionalized [Mo150], [Mo148], and [Mo146] during the optimization of the synthesis of L. All these compounds share the same framework of archetypal [Mo154] but with 2, 3, and 4 [Mo4] missing defect units, respectively.

Manuscript received: March 21, 2017
Accepted manuscript online: May 15, 2017
Version of record online: 

Communications


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**Big building blocks:** Two half-closed gigantic polyoxometalate (POM) clusters \{\text{Mo}_{180}\} and \{\text{Mo}_{130}\text{Ce}_6\} have been constructed by molecular growth from \{\text{Mo}_{150}\} and \{\text{Mo}_{120}\text{Ce}_6\}, respectively, demonstrating the concept of using gigantic clusters as “big building blocks” to build high-nuclearity clusters.