

Molecular growth and intermolecular condensation of $\{\text{Mo}_{154-x}\}$

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Introduction

During the past decade, chemistry of molybdenum oxide giant clusters with nano-sized ring shape, where the Mo atoms are in the +5/+6 mixed valence state, has exploded to give numerous kinds of compounds of this family [1]. These compounds show extraordinarily high nuclearity (typically more than 100 metal atoms with more than 400 oxygen atoms) that depends on the preparative conditions, which then influence to their structures. However, almost all the preparative procedures vary from sample to sample and thus a comprehensive survey of the formation conditions of these compounds is still lacking. Here we have prepared a series of $\{\text{Mo}_{154-x}\}$ compounds from precisely controlled preparative procedures. Single crystal synchrotron radiation X-ray diffraction of these samples revealed the pH dependence of the molecular growth and intermolecular condensation reactions of the Mo nano-rings.

Results and Discussions

From an survey on the pH dependence of the synthetic conditions, we have obtained three kinds of compounds, **1**, **2** and **3**, which were obtained from solutions carefully controlled to pH at 2.2, 1.7 and 1.4, respectively.

Compound **1** crystallized in monoclinic $C2/m$ with $a = 42.0599(7) \text{ \AA}$, $b = 40.0450(5) \text{ \AA}$, $c = 22.5450(3) \text{ \AA}$, and $\beta = 94.587(1)^\circ$ at 123K. A total of 219,779 reflections were measured, of which 47,374 were unique with $R_{\text{int}} = 0.0636$. The current agreement factor is: $R1 = 0.0593$ for 37,460 reflections with $I > 2\sigma(I)$ and $wR2 = 0.0709$ for all reflections. Compound **2** crystallized in monoclinic $C2/c$ with $a = 59.1887(5) \text{ \AA}$, $b = 47.1521(5) \text{ \AA}$, $c = 31.8640(3) \text{ \AA}$, and $\beta = 109.695(1)^\circ$ at 123K. A total of 369,563 reflections were measured, of which 103,302 were unique with $R_{\text{int}} = 0.0800$. The current agreement factor is: $R1 = 0.0903$ for 50,188 reflections with $I > 2\sigma(I)$ and $wR2 = 0.1552$ for all reflections. Compound **3** crystallized in monoclinic $C2/m$ with $a = 33.4487(5) \text{ \AA}$, $b = 53.5509(10) \text{ \AA}$, $c = 26.6748(10) \text{ \AA}$, and $\beta = 107.175(1)^\circ$ at 123K. A total of 374,815 reflections were measured, of which 73,161 were unique with $R_{\text{int}} = 0.0754$. The current agreement factor is: $R1 = 0.1026$ for 44,475 reflections with $I > 2\sigma(I)$ and $wR2 = 0.1444$ for all reflections.

Synchrotron X-ray diffraction of these samples revealed that compounds **1**, **2** and **3** contains giant clusters formulated as $\{\text{Mo}_{142}\text{O}_{490}\}$, $\{\text{Mo}_{148}\text{O}_{499}\text{O}_{12/2}\}$ and $\{\text{Mo}_{150}\text{O}_{514}\text{O}_{4/2}\}$, respectively. While $\{\text{Mo}_{142}\text{O}_{490}\}$ in **1** is isolated from its neighboring anions, $\{\text{Mo}_{148}\text{O}_{499}\text{O}_{12/2}\}$ in **2** is connected to six neighboring anions through 12 linker O atoms (12/2 means that each of these 12 atoms are

shared by an adjacent anion). $\{\text{Mo}_{150}\text{O}_{514}\text{O}_{4/2}\}$ in **3** is connected to two neighboring anions into a chain structure. These results indicate that the nuclearity of these anions can be directly controlled by the acidity of the mother liquor while the mechanism of intermolecular condensation involves other factors, such as the structures of the constituent nano-clusters.

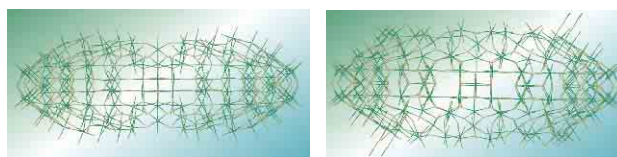


Figure 1. Structures of the $\{\text{Mo}_{142}\}$ anion in **1** (left) and $\{\text{Mo}_{150}\}$ anion in **3** (right). Increase in the nuclearity results in the thickness of the nano-ring, while the radii are kept almost constant.

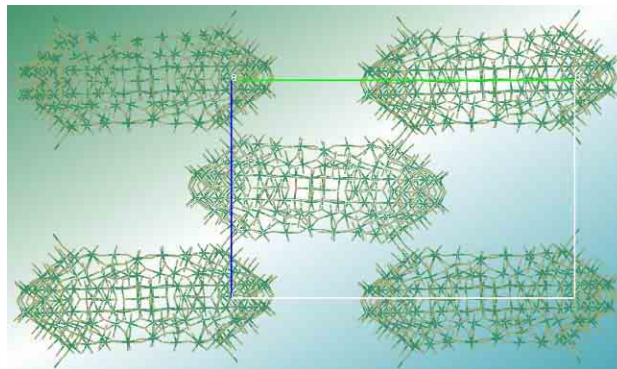


Figure 2. Packing diagram of compound **2** showing a slice of its three-dimensional network structure.

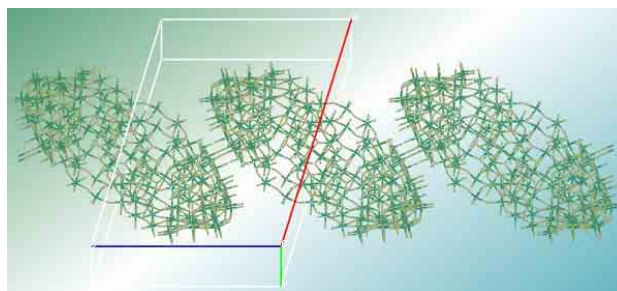


Figure 3. Packing diagram of **3** showing the one-dimensional chain structure.

References

- [1] See, for example, A. Müller, R. Maiti, M. Schmidtman, H. Bögge, S. K. Das and W. Zhang, *Chem. Commun.*, 2126-2127 (2001).

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