

Protonation and inter-cluster aggregation of $\{\text{Mo}_{138}\}$

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Introduction

The last decade saw an explosion of research on the mixed-valence giant-cluster polyoxomolybdates, among which the ring-shaped $\{\text{Mo}_{154}\}$ anion has the largest number of derivatives. Their synthetic conditions depend on acidity, temperature, reaction time, concentration of Mo, reducing reagent, and other chemical components present in the system. We focused on the effect of the acidity on determining the nuclearity of $\{\text{Mo}_{154}\}$ family polyoxometalates, preliminary the result of which was reported in the PF activity report last year. During a further experiment for a more thorough survey, we found that depending on the pH of the mother liquor a certain cluster crystallizes into several crystals with different degree of protonation and/or in a different type of inter-cluster connections.

Results and Discussions

From a 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 controlled to pH at 3.0-4.5, 3.3 and 3.0, respectively.

Compound **1** crystallized in monoclinic $C2/m$ with $a = 30.3344(4) \text{ \AA}$, $b = 49.5012(7) \text{ \AA}$, $c = 29.0565(4) \text{ \AA}$, and $\beta = 96.785(1)^\circ$ at 35 K. A total of 261,331 reflections were measured, of which 67,335 were unique with $R_{\text{int}} = 0.0891$. The current agreement factor is: $R1 = 0.0654$ for 41,686 reflections with $I > 2\sigma(I)$ and $wR2 = 0.2151$ for all reflections. Compound **2** crystallized in monoclinic $C2/m$ with $a = 26.9098(6) \text{ \AA}$, $b = 42.9546(14) \text{ \AA}$, $c = 29.4850(9) \text{ \AA}$, and $\beta = 94.283(1)^\circ$ at 123K. A total of 137,116 reflections were measured, of which 31,749 were unique with $R_{\text{int}} = 0.1090$. The current agreement factor is: $R1 = 0.0703$ for 18,739 reflections with $I > 2\sigma(I)$ and $wR2 = 0.2305$ for all reflections. Compound **3** crystallized in monoclinic $C2/m$ with $a = 27.7619(5) \text{ \AA}$, $b = 42.6994(10) \text{ \AA}$, $c = 30.2459(7) \text{ \AA}$, and $\beta = 95.858(1)^\circ$ at 123K. A total of 185,876 reflections were measured, of which 44,232 were unique with $R_{\text{int}} = 0.0871$. The current agreement factor is: $R1 = 0.0616$ for 22,308 reflections with $I > 2\sigma(I)$ and $wR2 = 0.1969$ for all reflections.

Synchrotron X-ray diffraction of these samples revealed that compounds **1**, **2** and **3** contains giant clusters with equal nuclearity, $\{\text{Mo}_{138}\}$. While $[\text{Mo}_{138}\text{O}_{407}(\text{OH})_{240}(\text{OH})_{29}]^{43-}$ in **1** is isolated from its neighboring anions, $[\text{Mo}_{138}\text{O}_{409.8}(\text{OH})_{240.8}(\text{OH})_{17.4}]^{37-}$ in **2** and $[\text{Mo}_{138}\text{O}_{408.5}(\text{OH})_{247.5}(\text{OH})_{12}]^{25-}$ in **3** are connected to four neighboring anions through 16 linker O atoms to form two-dimensional layer structure. Moreover, the anion in **3** is more extensively protonated than the anion in **2**,

reflecting the more acidic condition from which the crystals were precipitated. These results indicate that the degree of protonation of the 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 $\{\text{Mo}_{138}\}$ anion in **1**.

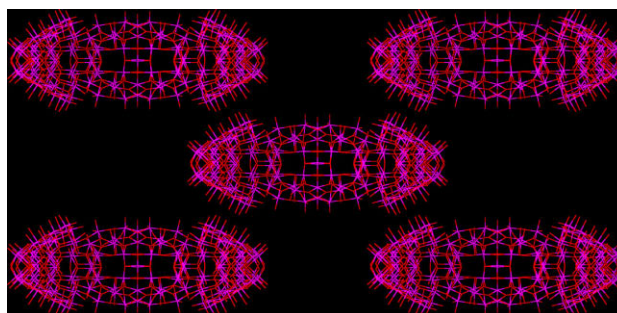


Figure 2. Packing diagram of compound **1** showing the discrete nature of the $[\text{Mo}_{138}\text{O}_{476}]$ cluster.

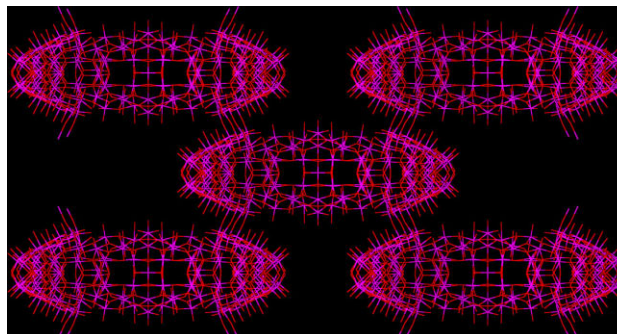


Figure 3. Packing diagram of compounds **2** and **3** showing the two-dimensional layer structure.

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