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Fate of a Giant $\{Mo_{72}Fe_{30}\}$-Type Polyoxometalate Cluster in an Aqueous Solution at Higher Temperature: Understanding Related Keplerate Chemistry, from Molecule to Material

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Supporting Information

ABSTRACT: When the giant icosahedral $\{Mo_{72}Fe_{30}\}$ cluster containing compound $[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]\cdot 150H_2O$ (**1**) is refluxed in water for 36 h, it results in the formation of nanoiron molybdate, $Fe_2(MoO_4)_3$, in the form of a yellow precipitate; this simple approach not only generates nanoferric molybdate at a moderate temperature but also helps to understand the stability of $\{Mo_{72}Fe_{30}\}$ in terms of the linker−pentagon complementary relationship.

Metal oxide based nanocapsules of the type $\{(M^{VI})M^{VI}_5\}_{12}\{Mo^V_2\}_{30}$ ($\equiv\{M^{VI}_{72}Mo^V_{60}\}$) and $\{(M^{VI})M^{VI}_5\}_{12}\{M'\}_{30}$ (M = Mo or W; M′ = VO^{2+}, Fe^{3+}, or Cr^{3+}),[1] also called Keplerates, have attracted considerable interest because of their structural aesthetics and importance in diverse disciplines, e.g., chemical science, molecular physics, magnetochemistry, biological sciences, materials science, and even mathematics.[2,1b] In polyoxometalate (POM) chemistry, the concept of "transferable" building blocks (for example, the pentagonal unit $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$) is the key point to understanding the formation of very large cluster entities of diverse architectures, e.g., Keplerates, giant wheels, etc.[2f] Most of the Keplerate POMs are soluble in water (polar solvent) because of their charge and hydrophilic surface (a layer of water ligands). In order to understand the chemistry of Keplerates, especially in an aqueous solution, it is necessary to learn the formation of pentagonal units $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ (see eq 1), which is the basic and common unit of all sorts of Keplerates. The number of these pentagonal units in a Keplerate cluster is always 12 because it is an icosahedral object.

$$6[MoO_4]^{2-} + 3H^+ + 6H_2O \rightarrow [Mo_6O_{21}(H_2O)_6]^{6-} + 3OH^- \qquad (1)$$

In the case of the $\{Mo_{132}\}$-type Keplerate, $[\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo^V_2O_4(CH_3COO)\}_{30}]^{42-}$, the linker is $\{Mo^V_2(O_t)_2(\mu_2\text{-}O)_2(\mu_2\text{-}CH_3COO)\}^+$, which plays an important role in the formation of this pentagonal unit (eq 1). In a recent report,[3] Müller and co-workers have demonstrated that the addition of such dinuclear $\{Mo_2\}$ linkers to a dynamic library containing a molybdate solution of the correct pH results in formation of the $\{Mo_{132}\}$-type Keplerate by spontaneous self-assembly, meaning that once the linker is added to the molybdate solution, the required pentagonal $\{(Mo)Mo_5\}$ building block $[Mo_6O_{21}(H_2O)_6]^{6-}$ is "immediately" formed. In the present report, we address this issue of linker−pentagon correlation in the context of the stability of the $\{Mo_{72}Fe_{30}\}$-type Keplerate in boiling water. In the case of the $\{Mo_{72}Fe_{30}\}$-type Keplerate, $[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]\cdot 150H_2O$ (**1**), 12 pentagonal $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ units are separated from one another by 30 $\{Fe^{III}O_5(H_2O)\}$ linkers, which are stabilized by acetate ligands, $\{Mo_2\}$ dimers, and water ligands.[4] Several research groups have been interested in this cluster (Figure 1) in the context of materials science (magnetism, catalysis, membrane formation, aggregation in solution, etc.).[2c,5,6] Recently, the aqueous chemistry of the $\{Mo_{72}Fe_{30}\}$-type Keplerate was explored at room temperature by Liu and co-workers, who have shown that the clusters of $\{Mo_{72}Fe_{30}\}$ self-assemble in an aqueous solution into blackberry-type supramolecular structures of 10−100 nm range.[6] Here we report the aqueous chemistry of the $\{Mo_{72}Fe_{30}\}$ cluster containing compound **1** at its refluxing condition.

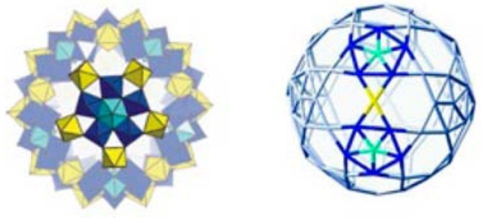

Figure 1. Left: polyhedral representation of the $\{Mo_{72}Fe_{30}\}$ cluster. Right: stick representation of the $\{Mo_{72}Fe_{30}\}$ cluster.

When an aqueous solution of compound **1** is refluxed for 36 h, it results in the formation of nanoparticles of ferric molybdate, $Fe_2(MoO_4)_3$, in the form of a yellow precipitate. The nanocrystalline product of $Fe_2(MoO_4)_3$ was collected, washed with deionized water, and dried at room temperature. All of the peaks of the powder X-ray diffraction (PXRD) pattern of this product (Figure S4, Supporting Information, SI) are indexed to monoclinic ferric molybdate, which is in good agreement with relevant literature values. The obtained nanomaterial of ferric molybdate is additionally characterized by energy-dispersive X-ray spectroscopy (EDS) and ICP elemental analysis of molybdenum and iron (see the SI). The morphology and micro/nanostructure of the obtained ferric molybdate material

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have been investigated by field-emission scannning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). Parts a and b of Figure 2 show the FESEM pictures of the as-synthesized product that demonstrates both micro- and nanostructures of $Fe_2(MoO_4)_3$ with relatively good distribution. The TEM image of the as-prepared product, which further confirms the result of SEM, is shown in Figure 2c. Both micro- and nanostructures of $Fe_2(MoO_4)_3$, shown in parts a and b and part c of Figure 2 (FESEM and TEM images, respectively), have been found to be obtained from a single phase of ferric molybdate, as demonstrated by selected-area electron diffraction (SAED) patterns from TEM images. The clear interlaced stripes (Figure 2d) further confirm its single-crystalline nature.

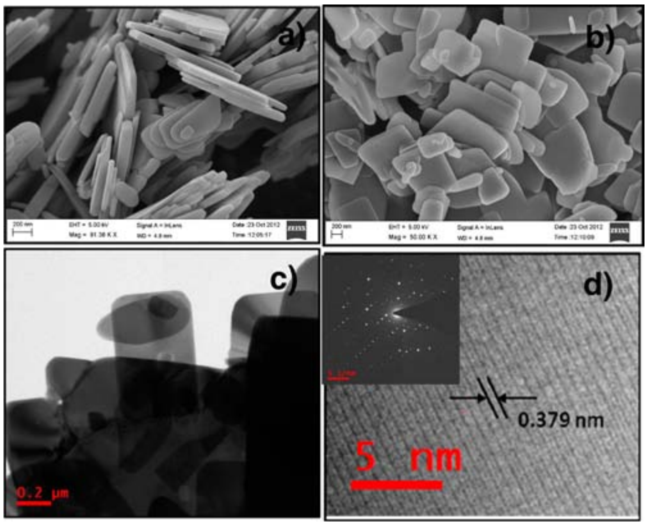

Figure 2. (a and b) FESEM and (c) TEM images of $Fe_2(MoO_4)_3$ particles obtained from $\{Mo_{72}Fe_{30}\}$. (d) HRTEM image of $Fe_2(MoO_4)_3$ particles and the corresponding SAED pattern, shown in the inset.

Thus, the cage of the $\{Mo_{72}Fe_{30}\}$ cluster (compound **1**) collapses in boiling water, leading to the formation of ferric molybdate, meaning thereby that the pentagonal $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ units in the concerned cage are detached from the Fe^{3+} linkers, leading to disintegration of the cage, whereby the pentagon transforms back to a tetrahedral molybdate. This fact clearly indicates that the linker $\{Fe^{III}O_5(H_2O)\}$ happens to be unstable, probably because of the unfastening of acetate ligands (an acetate ligand coordinates to an Fe^{III} linker and a Mo^{VI} center of the pentagon in a bidentate fashion) in the refluxing condition (boiling water). This is supported by the fact that when an aqueous solution of compound **1** is refluxed in the presence of an excess of acetic acid for 36 h, the $\{Mo_{72}Fe_{30}\}$ cluster remains intact, and it does not precipitate ferric molybdate (see the SI for details). When the linker gets unbalanced in the refluxing condition (in the absence of an excess of acetic acid), the detached pentagon $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ is not stable anymore and transforms to MoO_4^{2-} ions for the formation of stable $Fe_2(MoO_4)_3$ because in the dynamic library the detached Fe^{3+} species are already present. In the case of the $\{Mo_{132}\}$-type Keplerate, the pentagonal unit $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ is instantly generated to form an icosahedral object (12 pentagons and 30 linkers), when a suitable linker $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ is added to the molybdate solution acidified to pH 4 with acetic acid.[3] In the present study, we have demonstrated another way around in the sense that an icosahedral object ($\{Mo_{72}Fe_{30}\}$ cluster) destabilizes its linkers under the influence of an external stimulus (higher temperature at boiling water) and the detached pentagons, which do not exist anymore because of the lack of a suitable linker, are converted to the molybdates, deposited to the dynamic library. This fact of the stability of the giant $\{Mo_{72}Fe_{30}\}$ cluster in its refluxing condition is schematically presented in Figure 3.

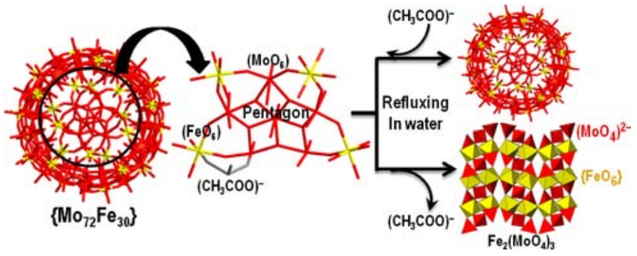

Figure 3. Schematic representation demonstrating the overall theme of the present work.

Thus, the $[(Mo)Mo_5O_{21}(H_2O)_6]^{6-}$ pentagons are formed by the induction of an appropriate linker from the dynamic library of aqueous molybdate solutions of the correct pH, and the same pentagons disappear when the concerned linker is taken away. So far, we have shown that the ligated acetate anion in the $\{Mo_{72}Fe_{30}\}$ icosahedral object plays an important role as far as stability is concerned. The cluster is stable even at boiling water when an excess amount of acetate is present.

In order to gain more insight into the linker–pentagon correlation, we have further investigated the synthesis data. We found that, when we reflux 2.0 g of the $\{Mo_{72}Fe_{30}\}$ compound, the maximum yield of ferric molybdate is 0.55 g (average taken from many syntheses), which is 52% based on iron from the overall reaction $\{Mo_{72}Fe_{30}\} \rightarrow 15[Fe_2(MoO_4)_3]$. Even if we increase the refluxing time from 36 h to 5 days, the yield remains constant (around 50%). These experiments suggest that when around 50% of the $\{Mo_{72}Fe_{30}\}$ compound decomposes to $[Fe_2(MoO_4)_3]$ at the refluxing condition, it generates a considerable amount of acetate anions (in principle, 1 g of the $\{Mo_{72}Fe_{30}\}$ compound should afford 0.038 g of acetate) in a reaction medium. It is then logical to argue that these released acetate anions do not allow the remaining 50% of the $\{Mo_{72}Fe_{30}\}$ compound to fall apart because we have seen that the $\{Mo_{72}Fe_{30}\}$ compound remains intact and does not form ferric molybdate in the presence of added acetic acid even under boiling conditions. The extra acetate anions (released from decomposition of the $\{Mo_{72}Fe_{30}\}$ cluster) shift the equilibrium of the reaction $\{Fe-Mo\}^{n+} + CH_3COO^- \rightarrow \{Fe-Mo(CH_3COO)\}^{(n-1)+}$ to the right side, which, in turn, stabilizes the linker to keep the cluster intact. This important role of the acetate anion to stabilize the linker, and thereby the $\{Mo_{72}Fe_{30}\}$ cluster, can further be corroborated by designing and performing the following experiment.

We performed the same experiment (refluxing 2.0 g of the $\{Mo_{72}Fe_{30}\}$ compound in 50 mL of water) in the presence of added hydrochloric acid (1.0 mL, 1.0 M) for 36 h, and we could obtain 0.94 g of $[Fe_2(MoO_4)_3]$, which is an almost quantitative yield (98%) based on the $\{Mo_{72}Fe_{30}\} \rightarrow 15[Fe_2(MoO_4)_3]$ reaction. In this experiment, the acetate anions that come out to deteriorate the linker, followed by the collapse of some amount of cluster cages, get immediately protonated, resulting in the depletion of free acetate anions in the reaction mixture, which is mandatory for the survival of the rest of the cluster cages. In this way, all released acetate anions get protonated and none of the clusters survive. This accounts for the quantitative yield of ferric molybdate in the case of the refluxing $\{\mathrm{Mo_{72}Fe_{30}}\}$ compound in water containing hydrochloric acid (see the SI for detailed experiments and spectral characterization of the products). The solution (filtrate), after the separation of ferric molybdate nanoparticles from the reaction mixture, obtained by refluxing the $\{\mathrm{Mo_{72}Fe_{30}}\}$ compound in water (which gives a 50% yield of ferric molybdate), in principle, should contain the remaining 50% intact/unreacted $\{\mathrm{Mo_{72}Fe_{30}}\}$ compound. We could not isolate, so far, a pure phase from this solution. However, when this solution (filtrate) is evaporated to dryness, a greenish-yellow microcrystalline powder is obtained. The IR spectrum and PXRD pattern of this crude product reveal the presence of the $\{\mathrm{Mo_{72}Fe_{30}}\}$ molecule as a major component in this microcrystalline solid (see the SI, section S6). The filtrate, after the separation of ferric molybdate from the reaction mixture obtained by refluxing the $\{\mathrm{Mo_{72}Fe_{30}}\}$ compound in water containing hydrochloric acid, does not contain any intact/unreacted $\{\mathrm{Mo_{72}Fe_{30}}\}$ compound (see section S8 in the SI).

In summary, we have shown that a $\{\mathrm{Mo_{72}Fe_{30}}\}$-type icosahedral Keplerate cluster containing compound **1**, upon refluxing in water for 36 h, disintegrates by 50% to nanoparticles of ferric molybdate, retaining the remaining 50% in solution. We have rationalized this fact by a complementary relationship between the linker (which is $\{\mathrm{Fe^{III}O_5(H_2O)}\}$ in the present case) and the pentagonal unit $[\mathrm{(Mo)Mo_5O_{21}(H_2O)_6}]^{6-}$ of the icosahedral object (Keplerate). We have demonstrated that the acetate anions play a crucial role to stabilize the linker because in the presence of an extra acetate anion the $\{\mathrm{Mo_{72}Fe_{30}}\}$ Keplerate does not disintegrate (the linker remains stable) even in boiling water. In the absence of added acetate anion, under refluxing condition, the $\{\mathrm{Mo_{72}Fe_{30}}\}$ Keplerate decomposes to ferric molybdate and released acetate anions are used to retain the rest of the Keplerates (survival by making the linker stable). It is evident from the present work and the work reported by Müller and his group that isolation of the so-called pentagon $[\mathrm{(Mo)Mo_5O_{21}(H_2O)_6}]^{6-}$ is very unlikely because, due to its high charge, the pentagon exists only as a complementary associate of the linker. In order to generalize this concept of linker−pentagon complementarity, we will be working on the stability of the $\{\mathrm{Mo_{72}Fe_{30}}\}$ cluster in boiling water in the presence of other anions (sulfate, phosphate, oxalate, etc.) including solution Raman studies, which will be reported in a full paper.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystallographic details, FESEM and TEM images, IR and PXRD patterns, and SAED studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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