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Investigating the Autocatalytically Driven Formation of Keggin-based Polyoxometalate Clusters

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SUMMARY

The term self-assembly is used to describe the formation of many molecules and supramolecular architectures but often the precise mechanism is neglected. Here we have investigated the kinetics of the self-assembly of the simplest heteropolyoxoanion, the Keggin ion $[\text{XMo}_{12}\text{O}_{40}]^{x-}$. This study used variable temperature UV/vis spectroscopy to show that the Keggin ion can catalyse its own formation via an autocatalytic cycle. Kinetic investigations with real-time monitoring of the $[\text{XMo}_{12}\text{O}_{40}]^{x-}$ family's formation reaction revealed key traits of autocatalytic systems including kinetic saturation and concentration dependence of the incubation period. We explored the effect of the heteroatom on the kinetics of the autocatalytic process by investigating and comparing the formation rates of $\{\text{AsMo}_{12}\}$ and $\{\text{SiMo}_{12}\}$. Finally, real-time ESI-MS studies of the reaction mixtures assist the identification of the species involved in the formation process of the Keggin species and these were explored using a stochastic model which confirms our experimental observations.

INTRODUCTION

Polyoxometalates (POMs) have been widely studied, largely due to the fact they cover a vast range of shapes, sizes, and properties.¹⁻⁴ One of the fundamental aspects of POMs is their ability to self-assemble to discrete molecular structures, despite the presence of building block libraries that could combinatorially form an infinite number of alternative structures. These discrete structures range from small clusters such as the {Mo₈} (0.7 nm), the {Mo₁₂} Keggin (1.0 nm) and the {Mo₃₆} (2.1 nm), all the way up to the high nuclearity nanosized species of {Mo₁₃₂} Keplerate (2.9 nm), {Mo₁₅₄} (3.6 nm) Molybdenum blue wheel and the protein sized, and largest of all POMs, {Mo₃₆₈} (5.5 nm). Although the process of self-assembly still isn't fully understood, recent studies have shown that both the {Mo₃₆} and the {PMo₁₂} Keggin are involved in the assembly of larger POM structures via a template mediated process as part of a set of autocatalytic reactions, but it is not known how the smaller clusters form (Figure 1).⁵ This is important since the Keggin species is the oldest known POM archetype which was first discovered in 1826.⁶ However, it wasn't until over a century later that its structure was determined by X-ray crystallography in 1933⁷ and it's now, after almost another century has passed, that the intrinsic formation mechanism is being investigated. The lack of earlier mechanistic insights did not prevent the investigation of its chemical reactivity along with other heteropolyanions which are by far the most explored subset of the POM family.⁸⁻¹² These can be described as metal oxide clusters that incorporate heteroatoms such as PO₄³⁻ and SO₄²⁻.¹³

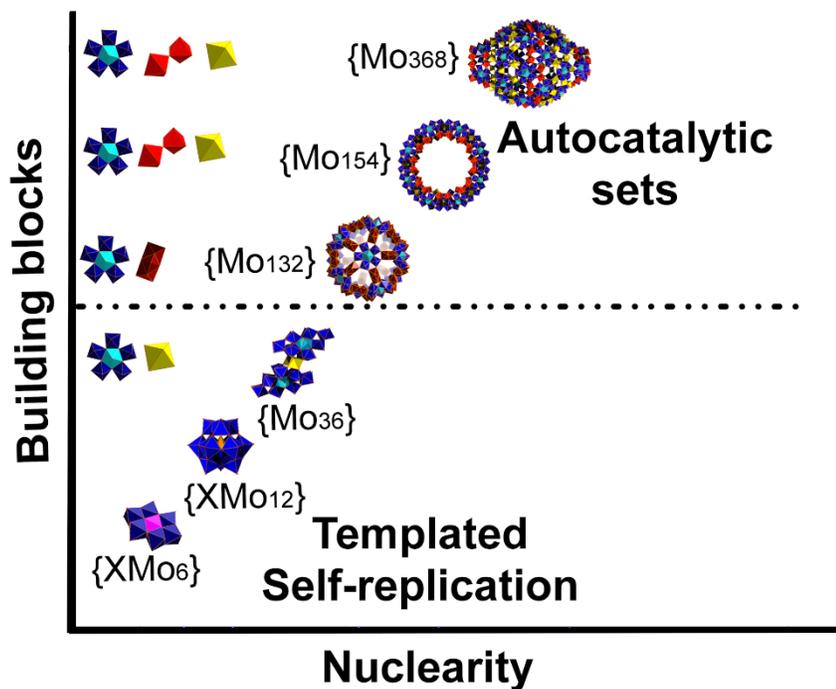


Figure 1. Polyhedral representation of fundamental building units involved in the formation of polyoxoanions and size dependent mechanistic effects that govern their formation.

Investigations into the self-assembly and dynamics of these POM systems has often involved the use of high-resolution mass spectrometry, specifically electrospray (ESI-MS) and cryospray (CSI-MS), as these ionization techniques are mild enough to prevent undesirable fragmentations and allow well-defined identification of structurally related species within the reaction systems. These studies, along with theoretical studies, have allowed us to gain insight into how these complex systems fundamentally behave and how the identified clusters isomerize, speciate and reassemble.^{14–21} Decades of extensive investigations on POM's accompanied by detailed structural characterizations has allowed the discovery of numerous species. The breakdown into various subgroups such as iso-/hetero-polyanions, molybdenum blues/browns and identification of fundamental virtual building blocks, has been essential for the deeper understanding POM's chemical reactivity.

Although extensive studies have probed the self-assembly at the conceptual level or theoretical studies have characterised the bonding involved,^{22–25} it has been difficult to devise a mechanistic and experimental paradigm to investigate the mechanism of the formation. Previously it has been shown that the large polyoxometalates just as the $\{\text{Mo}_{154}\}$ wheel and $\{\text{Mo}_{132}\}$ ball shaped clusters are formed by a network⁵ of mutually catalytic reactions – a so called autocatalytic set^{26–28} – and this explains why these clusters are even possible and represent magic numbers of stable compounds from the infinite number conceivable. This is important since it hints at the first example of the transfer of templated-based information at the molecular level in an inorganic system outside of biological ones.^{29,30} Thus, this work is part of our extended exploration effort which is based on the hypothesis that the formation of smaller POM based species involves template driven autocatalytic cycles which controls further combinatorial explosion in the reaction mixture making possible the formation of nanosized molecular constituents via cross-catalysed processes, Figure 1.⁵

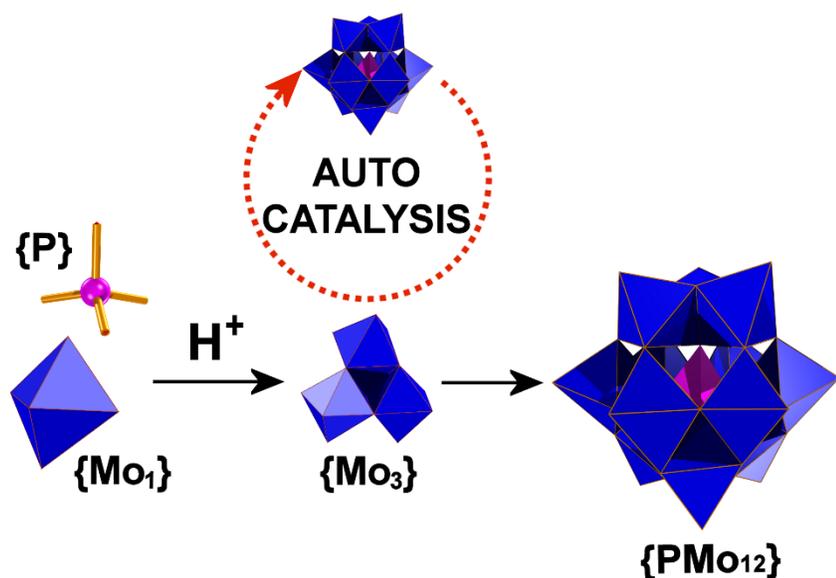


Figure 2. Formation of $\{\text{PMo}_{12}\}$ Keggin species via an $\{\text{PMo}_3\}$ templated autocatalytic cycle.

Autocatalytic processes are reactions in which a product of the reaction acts as a catalyst for its own formation. One of the characteristic traits of template autocatalytic systems^{31–34} is the existence of an induction period, followed by an exponential rise in rate.³⁵ More specifically, a marked increase of the reaction rate takes place as a function of time followed by a considerable decrease upon formation of substantial amount of product. This decrease is caused by a combination of two factors, the depletion of the reactants, and in the case that

the templating step requires more than one reactant, the number of templates can exceed the number of reactants, meaning that multiple reactants are unlikely to react with a single template, known as kinetic saturation. The use of the term autocatalytic is appropriate only for chemical systems considered under constant temperature and pressure. Crucially, the identification of autocatalytic and self-replication effects does not depend only on the detection of an induction period but rather on a collection of signatures associated with this process, such as exponential (sigmoidal) product vs. time curve with induction period, rate increase and elimination of induction period upon seeding of the reaction mixture with pre-formed product followed by kinetic saturation of the system and deceleration of the species' formation.

In this work we hypothesised that the template-mediated autocatalysis of POMs provides crucial information in relation to the driving force that directs the assembly of these chemical systems, Figure 1. That is the formation of discrete products out of a plethora of infinite combinations is only possible due to the selective utilisation of building blocks that can be recognised and take part in the autocatalytic cycle, such as $\{\text{Mo}_1\}$, $\{\text{Mo}_2\}$, $\{\text{Mo}_3\}$, $\{\text{XMo}_3\}$ and $\{\text{Mo}_6\}$, able to carry specific chemical and structural information. Given the importance of lower nuclearity species, due to their involvement in larger autocatalytic sets and cross-catalysed systems that produce nanosized high nuclearity molecular metal oxides, we envisaged to investigate and identify the autocatalytic behaviour of different species that belong to the Keggin family of molecular metal oxides with the general formula $[\text{XMo}_{12}\text{O}_{40}]^{X-}$ ($X = \text{P}, \text{As}$ or Si) – $[\text{AsMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$, see Figure 2.

It is important to note here that in the cases of self-assembled complex multinuclear systems such as the family of polyoxometalates, it is not possible to de-couple and investigate individually the numerous equilibria established in the reaction mixture which dynamically alter the presence and the relevant concentrations of the constituents involved. Thus, autocatalytic cycles, self-replication processes and templated catalytic cycles co-exist and feed into one-another within the same system. The ability though to determine and monitor over time the presence and concentrations of the species at the beginning of the reaction (t_0) and of the final product at the end of the reaction (t_f) allows us to observe the overall behaviour of the system, identify

conceptually the underlying phenomena and the unique effects which are masked by the vagueness of self-assembly terminology.

Preliminary results indicated previously that the formation of the $\{\text{PMo}_{12}\}$ anion is part of an autocatalytic pathway and very fast kinetics. The use of a stopped-flow UV-vis apparatus was necessary in this case to monitor the reaction kinetics which was carried out by mixing freshly prepared solutions of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{H}_3\text{PO}_4 / \text{HClO}_4$ allowing us to identify the characteristic signature of autocatalytic systems⁵ provided the first hint that autocatalysis might be common and not an artefact among the members of the Keggin family. The obtained information offers a unique opportunity for the exploration of the other members of the Keggin family and allows us to determine if the autocatalytic traits and the fast kinetics are inherent properties of the whole Keggin family.

RESULTS AND DISCUSSION

Here we will discuss our experimental efforts to monitor the formation mechanism of the $\{\text{AsMo}_{12}\}$ and $\{\text{SiMo}_{12}\}$ species where the use of a conventional UV/Vis detection system, equipped with a temperature control system, proved to be sufficient. The choice of these Keggin species was based on the size and charge difference of the incorporated $\{\text{XO}_4\}^{n-}$ templates and the consistency of the experimental conditions that drives their formation. This allowed a direct comparison to be made and helped us reach some conclusions in relation to the underlying chemical processes that take place during their formation. The first set of data obtained for a reduced version of the $[\text{AsMo}_{12}\text{O}_{40}]^{3-}$ Keggin, where freshly prepared solutions of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, ascorbic acid and $\text{Na}_2\text{HAO}_4 \cdot 7\text{H}_2\text{O}$ were mixed inside a 10 mm cuvette at quantities of 0.5, 1.5 and 2 mL, respectively. The pH value of the reaction mixture at $t=0$ falls in the range of 3.6-3.8 which are the optimum conditions for the Keggin species formation. The use of reducing agent allowed us to monitor over time the concentration of the final product. In the absence of reducing agent, the final product exhibits a shoulder in the 200-300 nm region of the UV-vis spectrum where other smaller fragments can contribute making it impossible to monitor unambiguously the formation process of the Keggin species. The reaction was carried out at 5 °C as we recorded in real time the λ_{max} of the UV-vis signal centred at 800 nm (Figure 3). Interestingly the increase of

the concentration of the species formed in solution as a function of the time followed a sigmoidal trend, which is indicative of an underlying autocatalytic process.

To investigate further the potential effect of the heteroatom on the catalytic cycle and determine if the autocatalysis is a general property of the Keggin family and not heteroatom specific, we investigated the formation reaction of the reduced $\{\text{SiMo}_{12}\}$ Keggin in a similar manner. The same UV/Vis set up was used under the same experimental conditions. This time freshly prepared solutions of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, ascorbic acid and Na_2SiO_3 were used. Although this reaction was carried out at twice the concentration, the reaction is much slower when compared to the formation of $\{\text{AsMo}_{12}\}$ Keggin species.

The characteristic incubation period was detected in a similar fashion, providing evidence that the formation reaction of this system also proceeds via an autocatalytic cycle (Figure 3B).

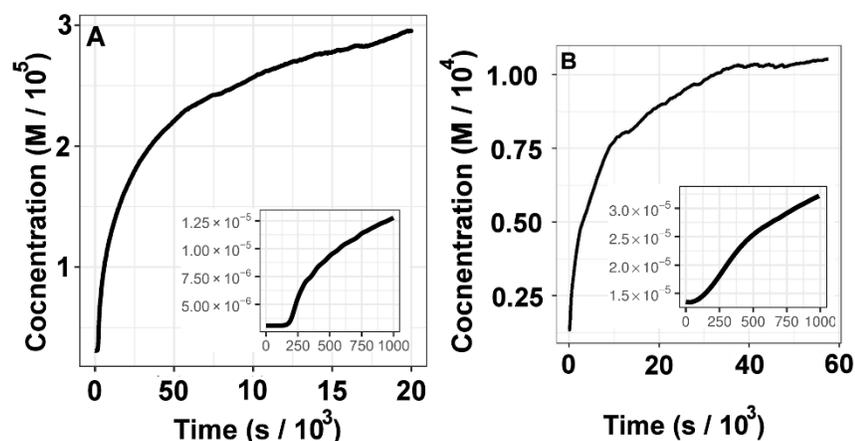


Figure 3. (A) Concentration vs. time profile of $\{\text{AsMo}_{12}\}$ (in H_2O at 5°C), initial concentrations $[\text{Mo}] = 0.02 \text{ M}$, $[\text{H}^+] = 0.028 \text{ M}$, $[\text{As}] = 5 \times 10^{-3} \text{ M}$. Inset of graph showing lag period at the start of the reaction. **(B)** Concentration vs. time profile of $\{\text{SiMo}_{12}\}$ (in H_2O at 5°C), initial concentrations $[\text{Mo}] = 0.02 \text{ M}$, $[\text{H}^+] = 0.028 \text{ M}$, $[\text{Si}] = 5 \times 10^{-3} \text{ M}$. Inset of graphs shows lag period at the start.

To verify further the kinetic behaviour of the underlying autocatalytic cycle, we carried out the same reactions using the same stock solutions at various increasing temperatures, to test whether would result in an increase in the rate of the reaction, therefore leading to an increase in the concentration of the species produced as a function of the time. This also allowed us to verify that the presence of the incubation period was not an

experimental artefact. Indeed, the temperature increase of the reaction mixture gradually eliminated the lag period that had been observed in the system due to the increased production rate of $\{\text{AsMo}_{12}\}$ species, further supporting the hypothesis of an autocatalytic system (Figures 4A and 4B). Since the presence of the incubation period is a necessary but not a sufficient requirement on its own to verify the presence of template autocatalysis, it was envisaged that the autocatalysis occurs via a molecular recognition process where the presence of a species is required in order to act as a template for the further formation of another cluster in the reaction mixture. A key feature of autocatalytic systems is that during the initial stages of the reaction, the process occurs primarily via an uncatalysed pathway which is the cause of the observed lag time.^{32,33,36} However, once a critical concentration of the catalyst is formed in solution, the explosive growth of the autocatalytic cycle is observable. Therefore, introduction of pre-synthesised $\{\text{AsMo}_{12}\}$, at the beginning of the reaction, ($t = 0$), should result in the elimination of the induction period in the rate profile for the reaction, and an increase of the initial rate. To verify our hypothesis, a fixed volume of the preformed $\{\text{AsMo}_{12}\}$ solution (0.05 mL) was added at incrementally increasing concentrations to the original mixture and the reaction was followed with UV-vis spectroscopy once more as a function of the time. This pre-synthesised $\{\text{AsMo}_{12}\}$ was made at six different concentrations – 1.19×10^{-7} , 3.83×10^{-7} , 5.73×10^{-7} , 7.65×10^{-7} , 1.16×10^{-6} and 1.53×10^{-6} M. The most significant change when there is addition of a seed is the gradual elimination of the lag period (Figure 4C), providing further support and reinforcing the hypothesis that the $\{\text{AsMo}_{12}\}$ is formed via a template mediated process whereby the cluster is part of equilibria involved in autocatalytic sets. As shown in Figure 4D, auto-catalyst saturation occurs after addition of 1.16×10^{-6} M of preformed $\{\text{AsMo}_{12}\}$, inducing maximisation of the self-propagated rate of $\{\text{AsMo}_{12}\}$, as expected. These results encouraged us to further investigate the behaviour of the $\{\text{SiMo}_{12}\}$ system at various temperatures, in a similar way to described previously for the $\{\text{AsMo}_{12}\}$, and more specifically on the incubation period. Indeed, the temperature increase led to the gradual elimination of the incubation period due to the increased production rate of the $\{\text{SiMo}_{12}\}$ Keggin species (Figures S1 and S2)).

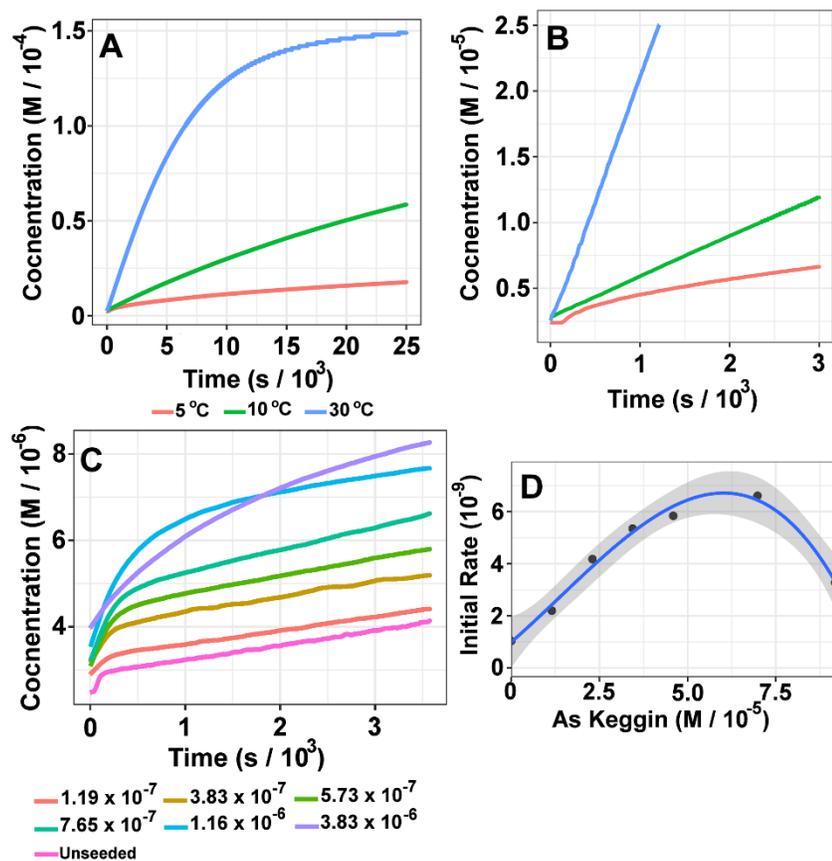


Figure 4. (A) Concentration vs. time profile of {AsMo₁₂} H₂O, initial concentrations [Mo] = 0.01 M, [H⁺] = 0.014M. The data represents the concentration profile vs. time of the same reaction at different temperatures (B) Inset of Graph (A), showing disappearance of lag period upon increased temperature. (C) Concentration vs. time profile of {AsMo₁₂} (in H₂O at 5 °C), initial concentrations [Mo] = 4 × 10⁻³ M, [H⁺] = 5.65 × 10⁻³ M. The data represents the concentration profile vs. time of the same reaction mixture seeded with preformed {AsMo₁₂} at 1.15 × 10⁻⁵ M. (D) Kinetic saturation of {AsMo₁₂} autocatalyst. Formation rate vs. concentration of {AsMo₁₂} injected in the reaction mixture (in H₂O at 5 °C). The injected [Mo] concentration of the seed shown in (D) was 1.15 × 10⁻⁵, 2.3 × 10⁻⁵, 3.9 × 10⁻⁵, 4.6 × 10⁻⁵, 6.9 × 10⁻⁵ and 8.05 × 10⁻⁵, respectively. The experimental data points represent the initial rate of the system. An increase is observed at the beginning before reaching a plateau (saturation) where the rate increase by a factor of six before dropping off after the saturation point.

Finally, the additional verification of the presence of autocatalytic cycle in the system involved the seeding of the reaction mixture with preformed {SiMo₁₂}, much like the {AsMo₁₂}, but at an increased concentration and

volume. This pre-synthesised $\{\text{SiMo}_{12}\}$ was then made up to 5 different solution concentrations – 4.78×10^{-7} , 9.12×10^{-7} , 1.92×10^{-6} , 2.87×10^{-6} and 3.83×10^{-6} M. Again, the reaction inside the cuvette remained the same but 0.05mL additions of the seed were injected at the incrementally increased concentrations. Upon addition of the preformed $\{\text{SiMo}_{12}\}$, an increased formation rate was observed at the beginning of the reaction, leading to the elimination of the lag period (Figure S3(A)) and kinetic saturation of the system upon addition of 9.12×10^{-7} M of preformed $\{\text{SiMo}_{12}\}$ (Figure S3(B)) providing further support that this member of Keggin species also catalyses its own formation via a template mediated process.

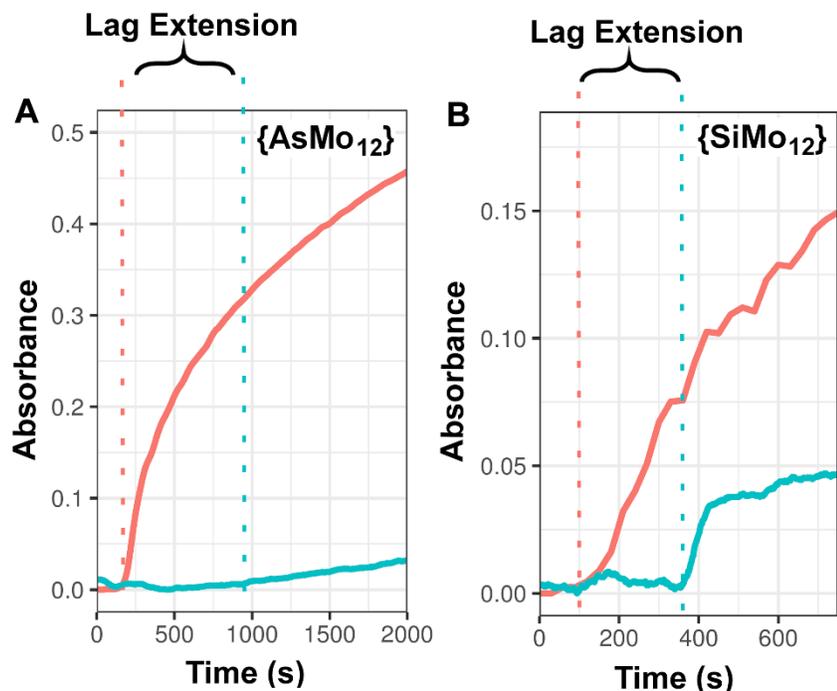


Figure 5. Representation of the effect of the [Mo] on the induction period for: **A** $\{\text{AsMo}_{12}\}$ and **B** $\{\text{SiMo}_{12}\}$, respectively. Colour code: light blue, $[\text{Mo}] = 3 \times 10^{-4}$; light red, $[\text{Mo}] = 3 \times 10^{-3}$.

Additionally, we embarked on exploring further the incubation periods observed during the formation of the Keggin species. More specifically, we explored the effect of the concentration on the length of the observed lag. More specifically, the lag time has increased from 180 to 900 sec in the case of $\{\text{AsMo}_{12}\}$ and from 130 to 380 sec in the case of $\{\text{SiMo}_{12}\}$ by reducing the initial concentrations of molybdenum by an order of magnitude according to Figure 5.

Based on the above observations, it is quite intriguing the fact that all members of the Keggin family exhibit autocatalytic traits. However, the autocatalytic behaviour is markedly different. This is potentially due to the interplay between the size and overall negative charge of the $\{XO_4\}$ ($X = P, Si, As$) anionic templates. The bigger size and larger overall negative charge of the $\{XO_4\}$ template, seems to slow down the autocatalytic cycle. It is interesting the fact that autocatalytic processes constitute a favourable resource for the formation also of smaller nuclearity molecular metal oxides and its manifestation does not depend on the type of the heteroatom. However, the rate of the autocatalytic cycle can be manipulated and is directly related to the size and charge of the heteroatom.

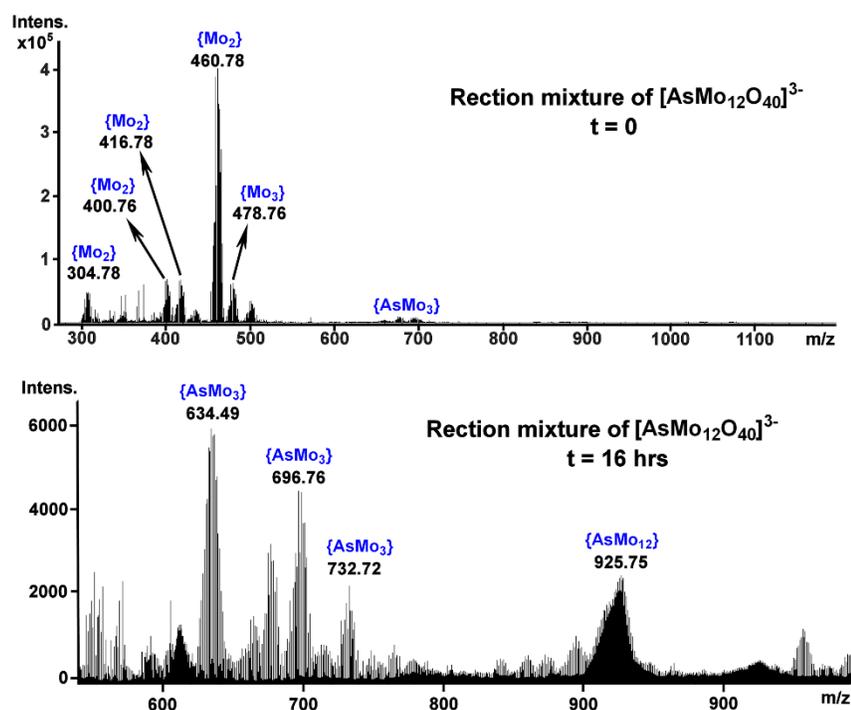


Figure 6. Negative mode electrospray ionization mass spectrum (ESI-MS) of the $\{AsMo_{12}\}$ reaction mixture in H_2O at $t = 0$ hrs (TOP) and $t = 16$ hrs (BOTTOM). See also Figures S4-S8.

Real-time monitoring of reaction mixture by ESI-MS

After establishing evidence to support a template autocatalytic reaction mechanism driving the formation of the Keggin species, we sought to refine the mechanistic steps in the process. A key point required clarification in our effort to shed light upon the formation mechanism of the Keggin family members, was the identification

of species that are involved in the detected autocatalytic set. In order to explore this, we employed electrospray ionisation mass spectrometry (ESI-MS) and detected the species that are present in the reaction mixture upon mixing of the starting materials ($t = 0$) and after 16 hrs (Figure 6). Interestingly, at $t = 0$ the only species that are detectable were singly charged $\{\text{Mo}_2\}$ units such as $[\text{Mo}_2\text{O}_7\text{H}]^-$, $[\text{Mo}_2\text{O}_7\text{Na}(\text{H}_2\text{O})_4]^-$, $[\text{Mo}_2\text{O}_7\text{Na}(\text{H}_2\text{O})_5]^-$ and $[\text{Mo}^{\text{VI}}_2\text{O}_9\text{Na}_3(\text{H}_2\text{O})_3\text{H}_2]^-$ centred at 304.78, 400.76, 416.78 and 460.78 m/z , singly charged $\{\text{Mo}_3\}$ unit, $[\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}_2\text{O}_9\text{Na}_2\text{H}_2]^-$ centred at 478.76 m/z and amounts of $\{\text{AsMo}_3\}$ units such as $[\text{Mo}^{\text{VI}}_3\text{O}_9(\text{AsO}_4)\text{Na}_2(\text{H}_2\text{O})]^-$, $[\text{Mo}^{\text{VI}}_3\text{O}_{10}(\text{AsO}_4)\text{Na}_4(\text{H}_2\text{O})]^-$ and $[\text{Mo}^{\text{VI}}_3\text{O}_{10}(\text{AsO}_4)\text{Na}_4(\text{H}_2\text{O})_3]^-$ centred at 634.49, 696.76 and 732.60 m/z respectively. After 16 hrs, solution studies revealed the presence of $\{\text{AsMo}_3\}$ units such as $[\text{Mo}^{\text{VI}}_3\text{O}_9(\text{AsO}_4)\text{H}_2]^-$, $[\text{Mo}^{\text{VI}}_3\text{O}_9(\text{AsO}_4)\text{NaH}]^-$, $[\text{Mo}^{\text{VI}}_3\text{O}_9(\text{AsO}_4)\text{Na}_2(\text{H}_2\text{O})]^-$, $[\text{Mo}^{\text{VI}}_3\text{O}_{10}(\text{AsO}_4)\text{Na}_4]^-$, $[\text{Mo}^{\text{VI}}_3\text{O}_{10}(\text{AsO}_4)\text{Na}_4(\text{H}_2\text{O})]^-$, $[\text{Mo}^{\text{VI}}_3\text{O}_{10}(\text{AsO}_4)\text{Na}_4(\text{H}_2\text{O})_2]^-$ and $[\text{Mo}^{\text{VI}}_3\text{O}_{10}(\text{AsO}_4)\text{Na}_4(\text{H}_2\text{O})_3]^-$ centred at 572.61, 594.58, 634.49, 678.60, 696.76, 716.59 and 732.60 m/z and the doubly charged $[\text{AsMo}^{\text{VI}}_{11}\text{Mo}^{\text{V}}\text{O}_{39}\text{H}]^{2-}$ Keggin anion centred at 925.75 m/z value (See also Figures S4-S8). These results suggest that not only do the $\{\text{Mo}_2\}$ and $\{\text{Mo}_3\}$ units form rapidly in solution, but also show that building blocks of other sizes did not form at comparable concentrations. These observations informed the construction of the kinetic model described below. It is important to note here that the ESI-MS solution studies are extremely useful into revealing information about the stability or the presence of species in the reaction mixture or exclude the presence of other POM species that might form in solution but cannot determine the concentration of the individual species which would allow us to study individually the different equilibria that co-exist in solution.

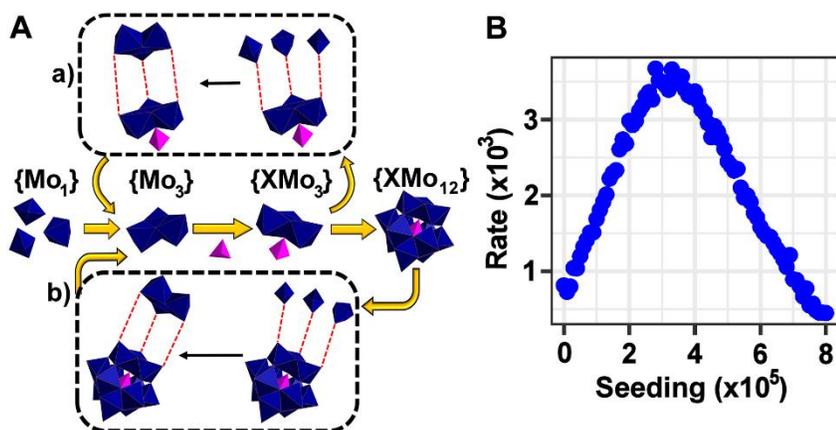


Figure 7. A) Hypothesized embedded autocatalytic cycles. a) The final $\{\text{XMo}_{12}\}$ Keggin product and the $\{\text{XMo}_3\}$ subunit are responsible for the templating of more $\{\text{Mo}_3\}$ building blocks. b) The subsequent templating of more $\{\text{Mo}_3\}$ subunits allow for an exponential production of the $\{\text{XMo}_{12}\}$ Keggin. B) A dynamic model of the

reaction pathway hypothesized in Figure 7A is consistent with the observed kinetic saturation. Details of the model can be found in the SI. See also Figures S9 and S10.

Modelling of the reaction pathway

A consistent feature of the dynamics observed here, for all the $\{\text{PMo}_{12}\}$, $\{\text{AsMo}_{12}\}$ and $\{\text{SiMo}_{12}\}$, clusters is the observation of kinetic saturation of the initial rate upon seeding, which is shown for the $\{\text{AsMo}_{12}\}$ in Figure 4D. To better understand the dynamics behind this phenomenon, we implemented a computational model of the proposed reaction pathway based on the evidence provided by the conducted solution studies using temperature-controlled UV-vis and ESI-MS at different time intervals. Briefly, in this model all reactions proceed as either bimolecular or unimolecular reactions. This indicates that the formation of the $\{\text{Mo}_3\}$ building block from molybdate occurs in two steps with an $\{\text{Mo}_2\}$ intermediate, which can degrade back into molybdate or further reactions with other molybdate to form $\{\text{Mo}_3\}$. We model the template catalysis of species by including a reaction where a molybdate can first attach to the template surface, and then proceed to add more molybdate in a step wise fashion, each step of which is reversible. We included both $\{\text{XMo}_3\}$ and $\{\text{XMo}_{12}\}$ as templates for the formation of $\{\text{Mo}_3\}$, as hypothesized in Figure 7A. This is because based on the experimental evidence collected these compounds are produced in abundance while other species are not, in order to explain the autocatalytic properties observed, some of these species must be involved in the process. Using this model, we explored the effect of increasing the initial amount of $\{\text{XMo}_{12}\}$, the results are shown in Figure 7B (See also Figures S9 and S10).

The model is consistent with the kinetic saturation seen in the physical experiments and can be explained by the template mechanism.^{37,38} When the initial amount of the template is low relative to the amount of molybdate, templates accelerate the formation of $\{\text{Mo}_3\}$ which is then reactions to form more of the $\{\text{XMo}_{12}\}$ template and adding more $\{\text{XMo}_3\}$ increases this rate. This is true until the number of template surfaces becomes too large for the initial amount of molybdate. At that point, individual molybdates attach to templates but are unlikely to react with other molybdates (because they are themselves attached to templates), this means the net formation of the $\{\text{XMo}_{12}\}$ is reduced because of the time required for the unreacted molybdate to dissociate from the template and reaction with other template complexes. The fact that both the $\{\text{XMo}_3\}$ and

$\{XMo_{12}\}$ can serve as templates by bringing together 3 x $\{Mo_1\}$ to form additional $\{Mo_3\}$ building blocks and finally Keggin species, means that the amount of $\{XMo_{12}\}$ at which this happens is much lower than the initial amount of molybdate.

CONCLUSIONS

In conclusion, we identified the presence of autocatalytic traits in the formation of the Keggin family of polyoxometalate species such as $\{AsMo_{12}\}$ and $\{SiMo_{12}\}$. Real-time monitoring UV/Vis studies have shown that the formation of Keggin species proceeds via a templated autocatalytic mechanism exhibiting an early uncatalyzed stage leading to an incubation period of ~ 200 sec as well as kinetic saturation effects in the presence of pre-formed catalyst, confirming the presence of an embedded autocatalytic cycle and an underlying molecular template process. Another interesting observation is the influence of the heteroatom on the autocatalytic cycle of the Keggin species. More specifically, there is an interplay between ionic radius and the overall charge on the $\{XO_4\}^{n-}$ central component and the operational rate of the autocatalytic cycle. The higher overall charge and smaller ionic radius seems to be beneficial for the operation rate of the autocatalytic cycle. The $\{As^V O_4\}^{3-}$ templated Keggin appears to form at faster rates than the $\{Si^{IV} O_4\}^{4-}$ templated one even though the As-heteroatom exhibits larger ionic radius if compared to the Si^{IV} . In the case of $\{P^V O_4\}^{3-}$ (reported previously) which carries the same charge but with smaller radius than the $\{As^V O_4\}^{3-}$, appears to be considerably faster among the investigated $\{XO_4\}^{n-}$ templated species. Finally, the unveiled knowledge and embedded processes within this family of inorganic clusters, provides crucial evidence for the deeper understanding of the underlying chemical processes usually vaguely described as “self-assembly”. Most importantly, this observation not only contributes to the better understanding of the masked chemical processes but also can be extrapolated and used constructively for the discovery of new forms of materials. The underlying processes can now be manipulated at the molecular level and be used as functional modules leading to the design of extended and interactive chemical operations where the outcome is determined by the combination of the modules used.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Leroy Cronin (lee.cronin@glasgow.ac.uk).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The published article includes all data analyzed during this study.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <DOI>

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AUTHOR CONTRIBUTIONS

The idea was conceived by LC and HM. DL carried out the reactions and analyzed the data with help from HM. CM developed the model. All the authors helped write the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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