



Cite this: *Chem. Sci.*, 2022, **13**, 1146

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 15th September 2021
Accepted 11th December 2021

DOI: 10.1039/d1sc05111c
rsc.li/chemical-science

Introduction

Polyoxometalates (POMs) are a material class of early transition metal oxygen cluster anions, with Mo^{VI}, W^{VI}, and V^V as the most described metals. The counter ions on the other hand range from hydrogen atoms over small inorganic cations to complex molecules.^{1,2} If the cluster includes heteroanions such as PO₄³⁻ or SO₄²⁻ they are called heteroPOMs, otherwise isoPOMs.³ The first reported POM was the nowadays-called Keggin-type [PM₁₂O₄₀]³⁻, which was also, in its form of phosphothungstic acid, the first one where the structure could be determined from powder X-ray diffraction data in 1933.^{4,5} In the last decades POMs were intensively investigated, showing a huge range of structural varieties and properties. The structures can not only differ in size of cluster, ranging from 6 to over 300 metal oxide building blocks, but also by the incorporation of organic molecules and the usage of POMs as building units for metal-organic frameworks.^{3,6-8} The resulting varying properties make them useful for a wide range of applications, *e.g.* in catalysis,³ energy storage³ and medicine^{7,9,10} or as ion-exchangers¹¹ sensors,⁵ and electrochromic devices.¹²

POMs are usually synthesized in aqueous solutions, containing the respective metal oxoanions. For the condensation reactions the pH of the solution plays a crucial role and has to be adjusted by the usage of acids. The syntheses are done at different conditions, ranging from ambient temperature over reflux to hydrothermal conditions.³ The use of alternative

methods is scarce. Yan and co-workers used microwaves to synthesize POMs out of sodium molybdate.^{13,14} In a solid-state synthesis, the Keggin-type POM as K₃PM₁₂O₄₀ (M = Mo, W) could be synthesized *via* heating a mixture of MO₃, K₂CO₃ and K₂HPO₄ at 500 °C for 30 h.¹⁵

In the last decade mechanochemistry has gained a lot of interest as a synthetic method. The term is used for chemical reactions induced by mechanical energy and performed in hand mortars as well as ball, planetary and vibration mills.¹⁶ Mechanochemical reactions are increasingly used thanks to their easy handling, short reaction times, high conversion rates, a small production of waste, based on a high atom economy and the small amount of solvents used.¹⁷⁻²⁰ Moreover, by using little quantities of liquids (liquid assisted grinding, LAG) the reaction outcome can be influenced regarding the yield, reaction times and the nature of the product. Mechanochemistry offers the possibility to create new compounds, not or only difficult achievable from solution.²¹⁻²⁷ Thanks to the solid-state nature of the process, it is possible to follow *in situ* the reaction and several setups where developed, using X-ray diffraction, spectroscopy or temperature devices.²⁸⁻³⁴

Although POMs are used in mechanochemical synthesis, *e.g.* to exchange the cation^{35,36} or to encapsulate the POM inside of a metal-organic framework (MOF),³⁷⁻⁴⁰ there is, to the best of our knowledge, no description of a direct mechanochemical synthesis. Such an alternative route could make the use of strong acids obsolete as well as decrease reaction times and the energy consumption. Beside that, a different synthetic route could lead to new and unknown structures. Moreover, the relatively higher stability of solid products may be an advantage against a possible reorganization of POMs in solution. Therefore, the goal of this work was to produce POMs mechanochemically from the scratch and to investigate the reaction process by using *in situ* methods.

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† Electronic supplementary information (ESI) available: Experimental procedures, including a chemical list, synthesis protocols, and the structure solution and refinement description with plots of the Rietveld refinements followed by a discussion of the observed results. CCDC 2067564-2067567. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc05111c



Results and discussion

Mechanochemical synthesis

Most syntheses from solution are starting from molybdate, MoO_4^{2-} . To follow these routes in a solid-state synthesis would be difficult, since, depending on the desired POM, specific conditions regarding the solvent, pH, temperature and pressure are needed. Instead we wanted to use MoO_3 and add O^{2-} by using compounds who have good leaving group, *e.g.* carbonates with CO_3^{2-} . Our reactions are done in a vibration ball mill, where the reaction mixture is weighted together with steel balls into a steel jar, which is closed and mounted into a vibrating holder. Any gas formation during reaction would therefore be observed as a pressure release at the end of the reaction itself. The details of all lab syntheses can be found in the ESI.† The first idea was to create simple POMs with only one atom species. The isoPOM heptamolybdate $[\text{Mo}_7\text{O}_{24}]^{6-}$ is a well known member of the POM family. Other than most POMs it can be directly synthesized from solutions of MoO_3 in ammonium hydroxide by evaporation.⁴¹ This simple approach and high tendency to self-assembly made it an ideal candidate to prove if our approach could work. The isoPOM heptamolybdate could be produced within the compounds $(\text{NH}_4)_6\text{K}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (**1a**, **1b**). They are formed already by neat grinding of MoO_3 and NH_4KHCO_3 , but, as visible in the reaction equation in Fig. 1, for the full formation the addition of a small amount of water (30 μL to 500 mg) is needed. The respective Rietveld refinements can be found in the ESI.† Within 30 min a pure and highly crystalline compound could be produced.

In the next step we wanted to introduce heteroatoms in the POM structure. The Strandberg-type POM, $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{4-}$, has a comparably high ratio of heteroatoms which is why we choose it as a first candidate. It could be realized within

$(\text{NH}_4)_5\text{HP}_2\text{Mo}_5\text{O}_{23} \cdot 3\text{H}_2\text{O}$ (**2**) and $(\text{NH}_4)_6\text{P}_2\text{Mo}_5\text{O}_{23} \cdot 5.5\text{H}_2\text{O}$ (**3**), by grinding MoO_3 , NH_4HCO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ in a ratio of 5 : 3 : 2 and 5 : 4 : 2, respectively (Fig. 1). The addition of water (100 μL and 50 μL , respectively) was necessary for the formation of a pure and highly crystalline product. The reaction times varied from 30 to 60 min. For **2** a structure from literature was used for the Rietveld refinement while the structure of the new compound **3** could be solved from PXRD data (see ESI†).

With the proof that even heteroPOMs can be synthesized, the Keggin-type POM, as probably the best known representatives of the POM material class, was an attractive candidate to be synthesized by our method. Its synthesis requires strong acidic conditions, which can not be applied in an mechanochemical synthesis. Nevertheless, the Keggin-type POM containing compounds $(\text{NH}_4)_3\text{K}_3\text{PMo}_{12}\text{O}_{40}$ (**4a**, **4b**) could both be synthesized by grinding MoO_3 , the respective bicarbonate and dihydrogen phosphate together (Fig. 1). It was necessary to add a mixture of water and ethanol to the reaction. With no solvent or ethanol alone almost no reaction could be observed, while with water as the only liquid the formation of a side product, with very broad peaks which could not be identified, was promoted. With 3 h the synthesis took much longer than the other ones presented in this paper. To prove the correct phase, we did Rietveld refinements (Fig. S3†). In both syntheses, a small amount of MoO_3 can still be detected, 3 wt% and 2 wt%, respectively. Milling a longer time or with heavier balls did not help to fully complete the reaction, since it promoted the formation of the unidentified side product as well.

Our results show that the formation of POMs *via* mechanochemistry can be a valid alternative. The isoPOM heptamolybdate could be synthesized within 30 min by ball milling with a small amount of water. The products were highly crystalline powders. The Rietveld refinements prove the purity of the compounds and no further cleaning step was needed. For the heteroPOMs a small variation of the amounts of the starting materials is enough to get full control over the formed product. By using the respective stoichiometric ratio always the exact POM is formed. Using liquid assisted grinding the Strandberg-type POM was produced as a highly crystalline and pure product within maximum 60 min. The Rietveld refinements do not show any additional reflections. For the Keggin-type POM the synthesis was more complicated. The balance had to be found between a high conversion rate and the production of a second phase. By choosing the correct parameter it was possible to synthesize the Keggin-type POM within 3 h with high purity.

In situ investigations

In our experiments we used MoO_3 instead of MoO_4^{2-} , which is mostly used in solution based syntheses. Also we worked under much milder conditions. In no synthesis strong acids were added to the mixture. To enable the full potential of the mechanochemical synthesis of POMs a better understanding of the mechanisms is needed. For this reason, we investigated *in situ* the formation of the three POMs which we synthesized.

Both syntheses for the heptamolybdate in **1a** and **1b** were followed *in situ* and very similar pathways could be observed,

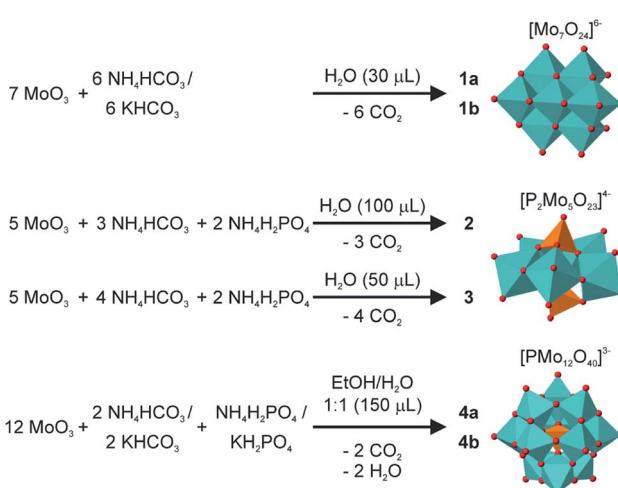


Fig. 1 Reaction equations for the mechanochemically synthesized POMs in this work. For all syntheses a vibration ball mill Pulverisette 23 (Fritsch GmbH, Germany) and a total load of 500 mg was used. The reaction times varied between 30 min and 3 h. $[\text{Mo}_7\text{O}_{24}]^{6-}$ – heptamolybdate, $[\text{P}_2\text{Mo}_5\text{O}_{23}]^{4-}$ – Strandberg-type, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ – Keggin-type; turquoise: molybdenum, orange: phosphorus, red: oxygen.

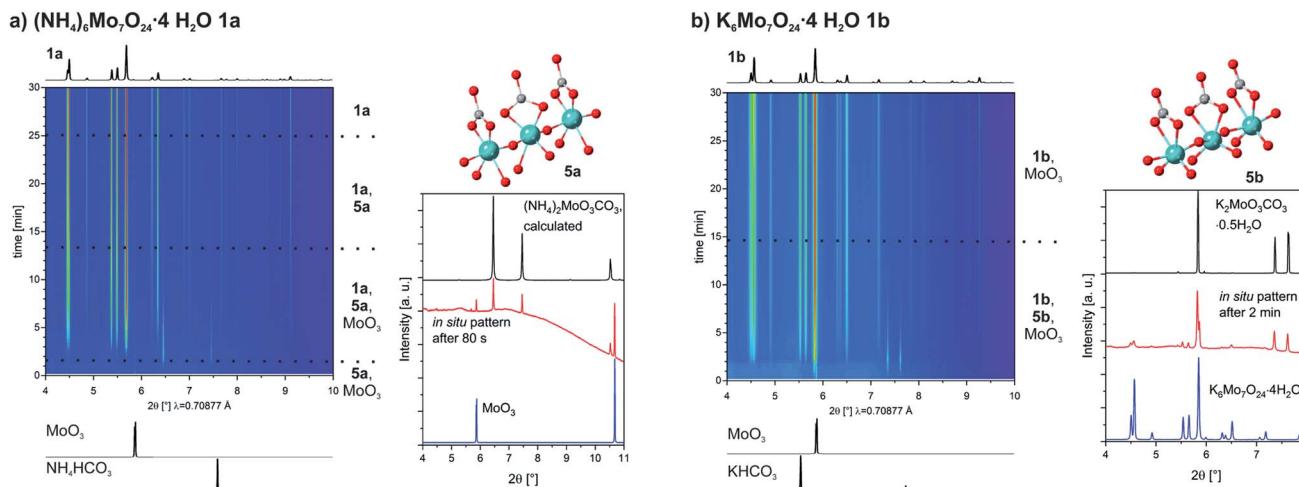


Fig. 2 2D-plot of the *in situ* investigation of the respective synthesis using PXRD (left), and comparison of the observed intermediate compound with a novel synthesized structure (right) for (a) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ **1a** and (b) $\text{K}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ **1b**. The molybdenum network for the intermediate is shown on the right for **5a** and **5b**, respectively.

(Fig. 2a and b, left). Among the reagents we could observe diffraction peaks of MoO_3 from the very beginning, while no peak of the respective bicarbonates are visible at any time during the milling. In both cases an intermediate phase is formed immediately. During the synthesis the reflections of this phase vanish, while the ones of the product evolve. In the case of **1b**, the peaks of MoO_3 get very weak in the first minutes but can still be detected until the end. The lab synthesis instead produced a pure compound. We used the setup of the Materials Science beamline at the SLS, Paul Scherrer Institute in Switzerland.⁴² Due to the machinery of the *in situ* setup, where the powder is measured in a special probing area, there is the possibility of caking powder in this area, when additional liquid is used. This is possibly the reason for this observed slight difference. For both reactions we were able to identify the intermediates, which are novel molybdenum carbonates, namely and respectively $(\text{NH}_4)_2\text{Mo}_3\text{CO}_3$ (**5a**) and $\text{K}_2\text{Mo}_3\text{CO}_3 \cdot 0.5\text{H}_2\text{O}$ (**5b**). Both structures were solved from PXRD data. A detailed description, including crystallographic details and the Rietveld refinements can be found in the ESI.[†]

For **1b** we were able to isolate the intermediate by reacting MoO_3 with K_2CO_3 (1 : 1, LAG H_2O). In the potassium molybdenum carbonate **5b**, molybdenum is coordinated by three oxygen atoms and bidentate by a carbonate ligand, resulting in a 1D chain structure (Fig. 2b, right). A comparison with an *in situ* powder pattern after 2 min clearly confirms this as the found intermediate.

For **1a** the ammonium molybdenum carbonate **5a** could only be synthesized within a mixture with **5a** as the main compound with 66 wt% (see ESI[†]). The motif is similar to **5b** (Fig. 2a, right), except that no water of crystallization is present. The comparison between a calculated powder pattern of **5a** and the powder pattern after 80 s of the *in situ* investigation of **1a** is proving that it is the quickly formed intermediate. In both cases the formation of the heptamolybdate happened *via* the formation of

a molybdenum carbonate. The carbonate coordinates to the molybdenum, activating the MoO_3 and then CO_2 is evolved.

For the Strandberg-type POM we followed *in situ* the formation of **2**. To prevent caking we halved the amount of water used. However, at the end the powder was wet and caked in the probing area of the *in situ* jar. Nevertheless, the reaction is proceeding and our gained data can still shed light on the reaction pathway. The 2D plot of the time-resolved powder patterns is shown in Fig. 3. As observed for the heptamolybdates, MoO_3 can be detected from the start. The additional reflections can not be assigned to the other starting materials,

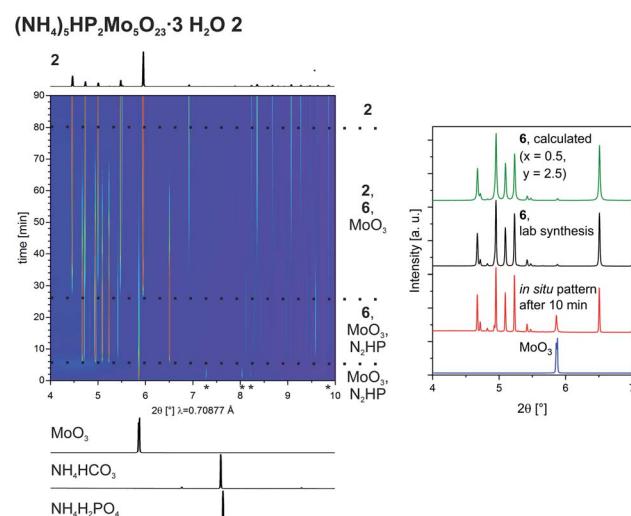


Fig. 3 2D-plot of the *in situ* investigation for the synthesis of $(\text{NH}_4)_5\text{HP}_2\text{Mo}_5\text{O}_{23} \cdot 3\text{H}_2\text{O}$ **2** using PXRD (left, * = position of the peaks of $(\text{NH}_4)_2\text{HPO}_4(\text{N}_2\text{HP})$), and comparison of the observed intermediate compound with the pattern of the novel synthesized structure $(\text{NH}_4)_{6-x}\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23} \cdot y\text{H}_2\text{O}$ **6** and of the calculated pattern of this compound using $x = 0.5$, $y = 2.5$ (right). The pattern from the lab synthesis does also contain peaks for $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$.

but to $(\text{NH}_4)_2\text{HPO}_4$. Its reflections can be detected until 9 min of milling, showing that there is also an interaction between the non-metallic starting materials. After 6 min another intermediate is fast forming. We identified it as a new ammonium phosphomolybdate containing the Strandberg-type POM $((\text{NH}_4)_{6-x}\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}\cdot y\text{H}_2\text{O}$ **6**). After 36 min also **2** can be detected and its peaks get more intense with time while at the same time the ones of **6** start to vanish. After 80 min, all peaks of the intermediate and the ones of MoO_3 vanish, and the reaction is completed.

For a certain period, the unknown intermediate and MoO_3 are the only two phases visible. We were not able to isolate the intermediate, but were able to identify it as another ammonium phosphomolybdate containing the Strandberg-type POM. The formula is $(\text{NH}_4)_{6-x}\text{H}_x\text{P}_2\text{Mo}_5\text{O}_{23}\cdot y\text{H}_2\text{O}$ (**6**, $x = 2-0$, $y = 2-4$). The competition with the very similar compounds **2** and **3** prevented a pure synthesis. The details are described in the ESI.† In Fig. 3, on the right a comparison between an *in situ* pattern after 10 min and patterns from **6** (from the lab synthesis and calculated with $x = 0.5$, $y = 2.5$) is showing that **6** is the observed intermediate.

To investigate the formation of the Keggin-type POM we followed the synthesis of **4a** *in situ* (Fig. 4, on the left). To lower the amount of caking we reduced the amount of liquid to 50 μL . Nevertheless, at the end the powder was caked and after 4 h the synthesis did not proceed anymore but was also not completed. As seen before, also this reaction proceeds with the formation of intermediates. At the beginning only peaks of MoO_3 can be detected. No other starting materials could be observed. After 1.5 min **6** is formed as an intermediate, as in the synthesis of **2**, followed by the formation of **2** after 3.5 min. Shortly after the

peaks of **6** are vanished. The peaks of **2** get less intense with time as well and are very weak after 4 h. The product **4a** can be detected for the first time after 18 min. In the following hours it is formed more and its crystallinity improves, as visible from the more intense and sharper diffraction peaks. After 4 h, no changes can be observed. The reaction is not complete, very likely because of the observed caking.

In all conducted syntheses we could observe intermediates, formed before the final product evolves. In the syntheses of heptamolybdate, molybdenum carbonates are formed intermediately. These compounds where not described before, probably based on the reactivity of the carbonate ion and, for **5a**, the short life time. During the synthesis of the Keggin-type POM the Strandberg-type POM is formed as an intermediate. The intermediates differ for the isoPOM and the heteroPOM reactions, but they have in common that they include a bigger amount of the basic anion, either carbonate or phosphate (Fig. 5). In all reactions a pressure release could be observed when the jar was opened, showing the evolution of CO_2 . Therefore, the formation of molybdenum carbonates seems to be possible also in the heteroPOM reactions. Nevertheless, the respective compounds could not be observed during the ball milling. Based on the small amount of carbonate during the reactions, it might be possible that the formed amount is too small or the reaction is too fast. Grinding only MoO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, neat or as LAG with water, did not lead to a reaction. $(\text{NH}_4)_2\text{HPO}_4$ instead reacts with MoO_3 even without the addition of ammonium carbonate, indicating that also the ammonium-ion and the acidity play an important role. Based on these results we can deduce that MoO_3 is activated by a nucleophilic attack. The activated species react with each other or with more starting material to form the final POM.

A comparison to the classical, solution based synthesis of POMs is difficult, since there mostly the more aggressive molybdate MoO_4^{2-} is used. The formation process is supposed to happen *via* condensation and addition reactions.⁴³ In the *in situ* investigations of our mechanochemical reactions we could not observe any MoO_4^{2-} species or its condensation products, except for heptamolybdate, which is the final product of the synthesis of **1a** and **1b**. Additionally, NH_4MoO_4 was formed as a side product in the synthesis of **5a**. Nevertheless, our results suggest that different mechanisms lead to the POM formation

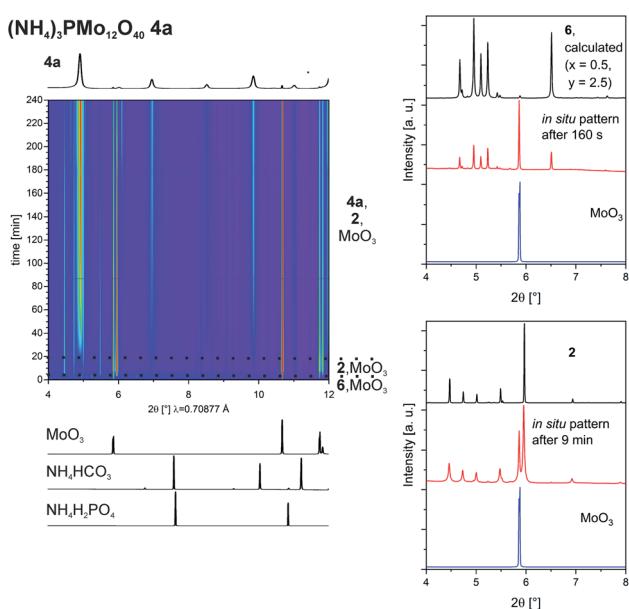


Fig. 4 2D-plot of the *in situ* investigation of the formation of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ **4a** using PXRD (left), and comparison of the observed intermediate compounds with the calculated pattern of the novel structure **6** (with $x = 0.5$, $y = 2.5$), after 160 s (middle) and with **2**, after 9 min (right).

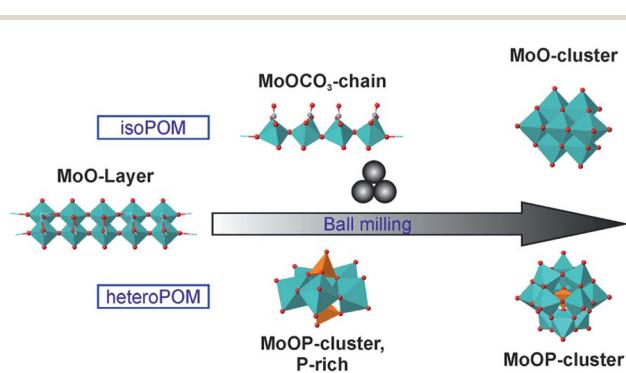


Fig. 5 Formation scheme for the mechanochemical synthesis of POMs.



in the mechanochemical reaction than in the solution based methods.

With the possibility, to synthesize POMs *via* mechanochemistry, come several opportunities. The short reaction times lower the energy consumption of the process. The absence of strong acids, the low amount of liquids and the high atomic economy are a huge asset for less waste production and go towards green chemistry.⁴⁴ As typical in mechanochemical reactions, the yield only depends on the possibility to remove the powder from the jar since the conversion is almost complete. Moreover, new compounds can also be stabilized in these conditions, as demonstrated by the synthesis of two new POMs containing the Strandberg-type POM and especially with the two new ammonium molybdenum carbonates. Host-guest compounds instead, where POMs are encapsulated into MOFs are already done mechanochemically. Now it might be possible, to create the POM on the side, while the MOF and the host-guest structure is formed. This might not only safe one production step, it also might allow the encapsulation of different POMs and create different structures. Also the new field of POMs as secondary building-units in MOFs is open for mechanochemical tries.

Conclusion

Our results show that POMs can be formed mechanochemically from simple building blocks. Under mild conditions and in a fast and easy manner we could synthesize iso- and hetero-POMs with varying counter ions. *In situ* investigations revealed that the formation goes *via* metal oxygen clusters, incorporating the basic anions of the starting materials. This first mechanistic insight shows that the molybdenum oxide is activated by a nucleophilic attack before the final product is formed. This new route to polyoxometalates provides a big range of possibilities, from synthesizing POMs in short times, to finding new structures or to find new ways to encapsulate them into porous frameworks.

Author contributions

Manuel Wilke planed and conducted the research and wrote the manuscript. Nicola Casati participated in the data analysis and supported the writing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful for the funding received from the European Union's Horizon 2020 Research and Innovation Programme under the Marie Skłodowska-Curie grant agreement No. 701647.

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