Supporting information - A new route to polyoxometalates via mechanochemistry

Manuel Wilke*^a and Nicola Casati^a

^a Laboratory for Synchrotron radiation - Condensed Matter, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland, manuel.wilke@psi.ch, +41-56-310-5346

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Experimental Procedures

Chemicals

 MoO_3 (99.5+%, Strem Chemicals), NH_4HCO_3 (for analysis, 99%, Acros Organics), $(NH_4)_2CO_3$ (for analysis, Acros Organics), $NH_4H_2PO_4$ (ACS reagent >99.00%, Honeywell Fluka), $KHCO_3$ (ACS reagent, Acros Organics), K_2CO_3 (ACS reagent, 99+%, Acros Organics), KH_2PO_4 (min. 99.5%, Appli Chem) and ethanol (absolute, extra pure, Pharmpur) were used without purification. Milli-Q water was gained from a Milli-Q Direct 8 water purification system (Merck, Germany).

Syntheses

For all lab syntheses, a vibration ball mill Pulverisette 23 (Fritsch GmbH, Germany) was used. In a standard synthesis a total load of 500 mg was used and three stainless steel balls (diameter: 7 mm, weight: 1.4 g) were added to the reaction mixture in a 10 mL stainless steel jar. The frequency applied was 40 Hz if not stated otherwise.

Synthesis of $(NH_4)_6/K_6Mo_7O_{24} \cdot 4H_2O$ (**1a**, **1b**) MoO₃ and NH₄HCO₃ or KHCO₃ were weighted into a stainless steel jar, with a molar ratio of 7:6. The balls and 30 µL of H₂O were added and the mixture was milled for 30 min. By opening the jar, pressure was released. A white, slightly wet powder was obtained and dried in air.

Synthesis of $(NH_4)_5HP_2Mo_5O_{23} \cdot 3H_2O\ 2$ MoO₃, NH₄HCO₃ and NH₄H₂PO₄ were weighted into a stainless steel jar, with a molar ratio of 5:3:2. Three stainless steel balls and 100 µL of H₂O were added and the mixture was milled for 30 min. By opening the jar, pressure was released. A blue, wet powder was obtained and dried in air. Using less water was possible if the milling time was increased.

Synthesis of $(NH_4)_6P_2Mo_5O_{23} \cdot 5.5H_2O$ **3** MoO₃, NH₄HCO₃ and NH₄H₂PO₄ were weighted into a stainless steel jar, with a molar ratio of 5:4:2. Using 50 µL of H₂O and 60 min of milling time gave the product with the best crystallinity in the powder pattern. By opening the jar, pressure was released. A white, wet powder was obtained and dried in air.

Synthesis of $(NH_4)_3/K_3PMo_{12}O_{40}$ (4a, 4b) MoO₃, NH₄/KHCO₃ and NH₄/KH₂PO₄ were weighted into a stainless steel jar, with a molar ratio of 12:1:1. For the best result 150 µL of a 1:1 mixture of ethanol and water was added to the mixture. Using less liquid or only ethanol lead to a much smaller conversion while using only water leads to the formation of an unknown side product with very broad reflections. The milling time was 3 h. In both cases, a small amount of MoO₃ was still present. Longer milling times or heavier balls promoted the formation of the side product. For 4a using 50 Hz instead of 40 Hz gave a more crystalline product, while for 4b the side product formation was promoted. When the jar was opened, a little pressure release could be observed. A blue to green wet powder was obtained.

Synthesis of $(NH_4)_2MoO_3CO_3$ **5a** The compound could not be synthesized pure, always **1a** and NH₄MoO₄ in its C2/m modification were present. In addition, the lifetime of **5a** is very short and a measurement had to happen at the same day of the synthesis, otherwise **1a** and NH₄MoO₄ were the only products. The sample we used for the structure solution was produced by weighting MoO₃ and $(NH_4)_2CO_3$ into a stainless steel jar with a molar ratio of 1:1. Three stainless steel balls and 50 µL of H₂O were added and the mixture was milled for 15 min. A pale yellow powder was obtained and dried in air.

Synthesis of $K_2MoO_3CO_3 \cdot 0.5 H_2O$ **5b** MoO₃ and K_2CO_3 were weighted into a stainless steel jar with a molar ratio of 1:1. Three stainless steel balls and 50 µL of H₂O were added and the mixture was milled for 30 min. A white, slightly wet powder was obtained and dried in air.

Synthesis of $(NH_4)_{6-x}H_xP_2Mo_5O_{23} \cdot yH_2O$ **6** (x = 2-0, y = 2-4) The compound could not be synthesized pure. In the best attempt, MoO₃, $(NH_4)_2HCO_3$ and $NH_4H_2PO_4$ were weighted into a stainless steel jar with a molar ratio of 1:1:1. Three stainless steel balls and 50 µL of H₂O were added and the mixture was milled for 60 min. The synthesis resulted in unreacted $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ as side products. The identification of the product and its composition are discussed within the Results and Discussion section.

Structure Solution and Refinement



Figure S1: Final Rietveld refinement and difference plots of mechanochemical synthesized $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ **1a** (**left**) and $K_6Mo_7O_{24} \cdot 4H_2O$ **1b** (**right**); Rwp(1a) = 3.21, GOF(1a) = 7.52; Rwp(1b) = 2.82, GOF(1b) = 6.74.

For the known compounds **1a**, **1b**, and **2** structures from the literature (ICSD Collection Code: 4153, 8080, and 6200) were used for the Rietveld refinements.^{1,2} The Rietveld refinement plots can be found in the Figures S1 and S2, respectively. For **4a** and **4b** we choose as reference the structures of $(NH_4)_{2.6}(H_3O)_{0.4}/K_{2.7}(H_3O)_{0.3}PMo_{12}O_{40}$ (ICSD collection code 212 and 210).³ Since, especially for the potassium derivative, there is no hint that we have any exchange of our cation, we replaced all hydronium ions with NH_4^+ or K^+ , respectively. As discussed in the main article, the powder patterns contain 2-3 wt.% MoO₃. The plots are depicted in Figure S3. All refinements were done using Topas (version 6, Bruker AXS, Germany).



Figure S2: Final Rietveld refinement and difference plots of mechanochemical synthesized $(NH_4)_5HP_2Mo_5O_{23} \cdot 3H_2O$ 2 (Rwp = 3.86, GOF = 7.80)

For the novel compounds **5a**, **5b**, **3**, and **6** the deposition Numbers 2067564-2067567 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

The structures of **3**, **5a**, and **5b** were solved using the charge flipping, simulated annealing and Rietveld routine implemented in Topas. For **3** the Strandberg-type POM $[P_2Mo_5O_{23}]^{4-}$ as present in **2** was given as a



Figure S3: Final Rietveld refinement and difference plots of mechanochemical synthesized $(NH_4)_3 PMo_{12}O_{40}$ **4a** (left, Rwp = 3.00, GOF = 8.13; x(MoO_3) = 3 wt.%) and K_3 PMo_{12}O_{40} **4b** (right, Rwp = 3.25, GOF = 9.80; x(MoO_3) = 2 wt.%).

rigid body. During the Rietveld refinement its atomic positions were refined with restrains in the coordination bond lengths and angles. In all compounds the amount of crystal water present was judged on existing voids and goodness of the fit. The crystal data and refinement parameters for all three phases are listed in Table S1. The Rietveld refinements are shown in Figure S4-S6. As stated in the syntheses description, **5a** could not be isolated, its structure was solved from the gained mixture, with **5a** as the main product with an amount of 66.2 wt.%.



Figure S4: Final Rietveld refinement and difference plots of mechanochemical synthesized $(NH_4)_6P_2Mo_5O_{23} \cdot 5.5H_2O$ **3**.



Figure S5: Final Rietveld refinement and difference plots of mechanochemical synthesized (NH₄)₂MoO₃CO₃ 5a; x(1a) = 24.3 wt.\%, x((NH₄)₂MoO₄) = 9.5 wt.\%.



Figure S6: Final Rietveld refinement and difference plots of mechanochemical synthesized $K_2MoO_3CO_3 \cdot 0.5 H_2O$ 5b.

	3	5a	5b
Empirical formula	$H_{70}Mo_{10}N_{12}O_{57}P_4$	$CH_8MoN_2O_6$	$C_2H_2K_4Mo_2O_{13}$
Color	white	pale yellow	white
Formula weight $/g \text{ mol}^{-1}$	2233.96	240.03	582.32
Crystal system	triclinic	orthorhombic	monoclinic
Space group	P-1	Pbca	$P2_1/c$
a/Å	15.48976(5)	15.4230(2)	11.00097(6)
b/Å	14.69350(5)	10.8984(1)	7.70975(4)
c/Å	16.48594(6)	7.72642(6)	15.43453(9)
$\alpha/^{\circ}$	109.6004(3)	90	90
$\beta/^{\circ}$	59.5381(3)	90	104.0801(5)
$\gamma/^{\circ}$	84.7342(3)	90	90
V/\AA^3	2884.10(2)	1298.71(2)	1269.75(1)
Z	2	8	4
$D_{calc}/g\;cm^{-3}$	2.572	2.455	3.046
R _{wp}	3.73	5.12	5.18
R _{Bragg}	2.43	5.65	4.14
GOF	5.30	9.12	4.45

Table S1: Crystal data and structure refinement parameters of $(NH_4)_6P_2Mo_5O_{23} \cdot 5.5H_2O$ **3**, $(NH_4)_2MoO_3CO_3$ **5a**, and $K_2MoO_3CO_3 \cdot 0.5H_2O$ **5b**.

6 could not be isolated and its structure not fully be solved. As written in the syntheses section, the best way of getting **6** as a main compound was grinding MoO₃, (NH₄)₂HCO₃ and NH₄H₂PO₄ together in the ratio 1:1:1. Side products are unreacted NH₄H₂PO₄ and (NH₄)₂HPO₄. The indexing gave with very high scores P2₁/c, a = 17.4361 Å, b = 9.8989 Å, c = 32.9017 Å, β = 94.969° as possible unit cell. The charge flipping routine in Topas gave the positions of 10 heavy atoms in the asymmetric unit. Based on their arrangement it was clear that **6** contains two times the Strandberg-type POM. With a volume of 5657 Å³ its unit cell is a doubling of the unit cells of **2** and **3**, who contain the same POM. Additionally, grinding the same reagents together but with more water can also lead to the production of **3** instead of **6**, with the same amount of side products. Based on the synthesis conditions, the indexed unit cell and the charge flipping results, we believe that **6** is a compound like **2** and **3**, with a different amount of ammonium and water, (NH₄)_{6-x}H_xP₂Mo₅O₂₃ · yH₂O (x = 2-0, y = 2-4). For a structure idea we used the Strandberg-type POM from **3** as rigid body and x = 0.5. The amount of water was assumed by voids present and the resulting Rwp, which gave y = 2.5. The resulting Rietveld refinement plot is shown in Figure S7 and the crystal data and refinement parameters are listed in Table S2.



Figure S7: Final Rietveld refinement and difference plots of mechanochemical synthesized $(NH_4)_{6-x}H_xP_2Mo_5O_{23}\cdot yH_2O$ **6** with x = 0.5, y = 2.5; $x(NH_4H_2PO_4) = 21.4$ wt.%, $x((NH_4)_2HPO_4) = 7.9$ wt.%.

Table S2: Crystal data and structure refinement parameters of $(NH_4)_{6-x}H_xP_2Mo_5O_{23} \cdot yH_2O$ **6**, refined as $(NH_4)_{5.5}H_{0.5}P_2Mo_5O_{23} \cdot 2.5H_2O$.

	6
Empirical formula	$H_{55}Mo_{10}N_{11}O_{51}P_4$
Color	pale blue
Formula weight	2108.78
$/{ m g}~{ m mol}^{-1}$	
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.4444(1)
b/Å	9.90967(8)
c/Å	32.9178(3)
$\beta/^{\circ}$	94.995(8)
$V/Å^3$	5668.83(8)
Z	4
$D_{calc}/g\;cm^{-3}$	2.47
R _{wp}	4.92
R_{Bragg}	5.23
GOF	10.06

Results and Discussion

Mechanochemical Synthesis

The mechanochemical syntheses of 1a, 1b, 2, 3, 4a, and 4b were discussed in the main article.

As visible in the Rietveld refinement plot, the syntheses of **5b** leads to a pure and highly crystalline compound. However, it was not possible to isolate the ammonium molybdenum carbonate **5a**. MillingMoO₃ with $(NH_4)_2CO_3$ (1:1, LAG H₂O) or NH₄HCO₃ (1:2, LAG H₂O) leads to a mixture of **1a**, NH₄MoO₄ in its C2/m modification and **5a**. The impossibility to synthesize **5a** pure is very likely based on the high reactivity of CO₃²⁻ and the protons from the ammonium ion, followed by an evolution of CO₂. Measuring the product shortly after the reactions was mandatory; when the measurement was more than one day after the reaction almost no reflections of **5a** could be observed anymore.

As written in the main article, **6** could not be synthesized pure. In the structure solution and refinement part above we describe how we could find a probable composition. The only time **6** could be synthesized with a full conversion of all reagents was a LAG synthesis using water and grinding MoO₃, $(NH_4)_2HCO_3$ and $NH_4H_2PO_4$ together with a ratio of 10:7:4. A mixture of 49 wt.% **2**, 39 wt.% **3** and 12 wt.% **6** was the result. The results show that the competition with the very similar compounds **2** and **3** prevented a pure synthesis.

The Crystal Structures of 3, 5a, 5b, and 6

The structure of **3** is shown in Figure S8. It is very similar to the structure of **2**, described by Fischer et al.² **3** contains the same Strandberg-type POMs, but here two independent clusters are present in the asymmetric unit. As a result, the symmetry decrease to triclinic. The Strandberg-type POM is constructed by five edge and corner connected distorted MoO_6 -octahedra and two PO_4 -tetrahedra. Ammonium-ions and water molecules lie between the POMs and connect them via hydrogen bonds.

The structure of **5a** is depicted in Figure S9. The Mo-atom is coordinated by the $CO_3^{2^-}$ -ion as a bidentate ligand and by four oxygen atoms, resulting in a strongly distorted octahedral coordination ($d_{Mo-O} = 1.79(2)$ -2.18(2) Å, angle_{O-Mo-O} = 72.0(8)-110.4(6)°). These octahedra are connect via one corner forming an infinite {MoO₃CO₃}-chain. These chains are arranged in a layer-like manner along the a-axis. The ammonium-ions are located between these layers, connecting the {MoO₃CO₃}-chain via hydrogen bonds.

In Figure S10 the structure of **5b** is shown. There are two individual Mo-atoms, both coordinated by the bidentate ligand CO_3^{2-} and by four oxygen atoms. Both octahedra are strongly distorted with Mo-O-distances of 1.67(1)-2.26(2) Å for Mo1 and 1.75(2)-2.31(1) Å for Mo2 and O-Mo-O angles of $59.9(7)-111.0(7)^{\circ}$ for Mo1 and $62.3(7)-105.5(7)^{\circ}$ for Mo2. As in **5a** the octahedra are connect via one corner and form an infinite $\{MoO_3CO_3\}$ -chain. There are four K-atoms acting as coordination center. All of them are coordinated by 9 oxygen atoms, stemming from both carbonate ligands, the MoO_3-octahedra and the water molecule. The water ligand is only coordinating to potassium and not to molybdenum. The KO_9-polyhedra share their corners and edges and connect thereby the $\{MoO_3CO_3\}$ -chains.

Figure S11 contains our structural proposal for **6**, refined as $(NH_4)_{5.5}H_{0.5}P_2Mo_5O_{23} \cdot 2.5H_2O$. It is similar to **2** and **3** and contains as well the Strandberg-type POM. As in **3** there are two Strandberg-type POMs present in the asymmetric unit and water molecules and ammonium ions lay between the POMs, connecting them via hydrogen bonds.



Figure S8: Structure of $(NH_4)_6P_2Mo_5O_{23} \cdot 5.5H_2O$ **3** shown along the b-axis (**left**) and structure of the two Strandberg-type POMs present in **3** (**right**). Turquoise: molybdenum; orange: phosphorus; red: oxygen; purple: nitrogen; gray: carbon; white: hydrogen.



Figure S9: Structure of $(NH_4)_2MoO_3CO_3$ **5a** shown along the c-axis (**left**), connection of the MoO₆-octahedra within the chain (**middle**) and structure of a MoO₆-octahedron. Turquoise: molybdenum; red: oxygen; purple: nitrogen; gray: carbon; white: hydrogen.



Figure S10: Structure of $K_2MoO_3CO_3 \cdot 0.5 H_2O$ **5b** shown along the b-axis (**left**), connection of the MoO_6 -octahedra within the chain (**middle left**), structure of the two MoO_6 -octahedra (**middle right**), and structure of the KO_9 -polyhedra (**right**). Turquoise: molybdenum; red: oxygen; purple: potassium; gray: carbon; white: hydrogen.



Figure S11: Structure of $(NH_4)_{6-x}H_xP_2Mo_5O_{23} \cdot yH_2O$ **6**, refined as $(NH_4)_{5.5}H_{0.5}P_2Mo_5O_{23} \cdot 2.5H_2O$, shown along the b-axis.

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