Controlling the Reactivity of the \([\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}\) Inorganic Ring and Its Assembly into POMZite Inorganic Frameworks with Silver Ions

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Abstract: The construction of pure-inorganic framework materials with well-defined design rules and building blocks is challenging. In this work, we show how a polyoxometalate cluster with an integrated pore, based on \([\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}\) (abbreviated as \([\text{P}_8\text{W}_{48}]\)), can be self-assembled into inorganic frameworks using silver ions, which both enable reactions on the cluster as well as link them together. The \([\text{P}_8\text{W}_{48}]\) was found to be highly reactive with silver ions resulting in the in situ generation of fragments, forming \([\text{P}_8\text{W}_{48}\text{O}_{135}]^{58-}\) and \([\text{P}_8\text{W}_{2}\text{O}_{135}]\) in compound (1) where these two clusters cosynthesize and are connected into a POMZite framework with 11 \(\text{Ag}^+\) ions as linkers located inside clusters and 10 \(\text{Ag}^+\) linking ions situated between clusters. Decreasing both the concentration of \(\text{Ag}^+\) ions, and the reaction temperature compared to the synthesis of compound (1), leads to \([\text{P}_8\text{W}_{48}\text{O}_{160}]\) in compound 2 where the \([\text{P}_8\text{W}_{48}]\) clusters are linked to form a new POMZite framework with 9 \(\text{Ag}^+\) ions per formula unit. Further tuning of the reaction conditions yields a cubic porous network compound (3) where \([\text{P}_8\text{W}_{48}]\) clusters as cubic sides are joined by 4 \(\text{Ag}^+\) ions to give a cubic array and no \(\text{Ag}^+\) ions were found inside the clusters.

Polyoxometalate (POM)-based materials are a family of compounds known for their rich structural diversity and properties.[1] Over the years many synthetic strategies have been developed to control the self-assembly of the POMs as effective anionic molecular inorganic building blocks.[5,3] One of the most recent successes of this strategy was made possible by using the superluminal cyclic heteropolyanion \([\text{P}_8\text{W}_{45}\text{O}_{184}]^{18-}\) (abbreviated as \([\text{P}_8\text{W}_{45}]\)) as a building block for the construction of intrinsically porous all-inorganic framework materials, named POMZites.[4] Polyoxometalate-based framework materials, or POMZites, are an emerging class of configurable all-inorganic porous materials.[5] Porous materials such as zeolites or metal–organic frameworks, MOFs, are ordered networks whose building units are linked with strong interactions via ionic, covalent, and coordination bonds.[6] Silver ions are often used as a flexible linkers in coordination chemistry.[7] For instance, silver-linked molybdenum oxide POMs are very stable, both in the solid and liquid phases.[8] Further, silver ions play a remarkable role in chemical reactions and crystallization processes acting both as counterions and structure directors. In this work, we demonstrate that by using silver ions as linkers, two new porous polyoxotungstates (POTs) can be derived from \([\text{P}_8\text{W}_{48}]\), which was isolated originally by Contant and Tezé in 1985.[9] The \([\text{P}_8\text{W}_{48}]\) cluster has a symmetry of point group \(D_{2h}\) and is a highly stable and versatile oligomer formed from the aggregation of four subunits of the hexaviacant \([\text{P}_8\text{W}_{2}\text{O}_{49}]^{12-}\) polyanion derived from the phosphotungstic acid Dawson-type cluster \([\text{P}_6\text{W}_{12}\text{O}_{40}]^{2-}\).[10] In 2005, Kortz et al. reported the first Cu-containing \([\text{P}_8\text{W}_{48}]\) assembly, thus proving this molecule to be a large superlacunary polyanion precursor.[11] Since then, a series of novel structures based on \([\text{P}_8\text{W}_{48}]\) clusters have been reported in the literature including \([\text{Cu}_{20}]\) clusters,[12] \([\text{V}_3]\) aggregates,[13] \([\text{Fe}_{16}]^{14+}\) and Ln-containing clusters,anions,[13] as well as organoruthenium-based composites.[10] All of these structures were based on transition metal complexes with the superlacunary \([\text{P}_8\text{W}_{48}]\) cluster acting as a ligand.[17] Herein, we present a unique method of extending the \([\text{P}_8\text{W}_{48}]\) as POMZites.

The \([\text{P}_8\text{W}_{48}]\) cluster can be viewed as a drum-like structure formed by the condensation of four \([\text{P}_8\text{W}_{2}\text{O}_{49}]\) subunits. Around the corners of the \([\text{P}_8\text{W}_{12}\text{O}_{49}]\) subunits on the top and bottom faces, there are eight sites where \([\text{W}_4]\) units or other transition metal ions can be added to form new locations for further growth to extend the structures. The tungsten occupancy on these new growth points is significant, and can be differentiated from other transition metal ions like \(\text{Co}^{2+}\) or \(\text{Mn}^{2+}\).[18] Although these growth points have been noted as being occupied by both tungsten and other transition metals in previous publications,[16–18,20] no extended structures built upon these foundations have been reported.

Our work demonstrates the formation of higher nuclearity clusters built up from the superlacunary \([\text{P}_8\text{W}_{48}]\) cluster by extension of these growth sites (Scheme 1). The reaction of \([\text{P}_8\text{W}_{48}]\) and a high concentration of \(\text{Ag}^+\) ions as starting materials led to the formation of \([\text{Li}_{4}\text{K}_{5}\text{Ag}_{2}][\text{H}_{39}\text{P}_{18}\text{W}_{36}\text{O}_{125}]\)15
[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{40}]_m\cdot\text{Cl}_2\cdot 50\text{H}_2\text{O} \text{ (1)}, when an aqueous solution (adjusted to pH 1.53 by concentrated HNO₃) containing LiNO₃, K₂Ln₂[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{40}]_x\text{ and AgNO}_3 was heated at 80°C for about 30 min. The solution was left to cool to room temperature, and after two weeks well-defined colorless block crystals started to form in solution; those crystals were harvested after further two weeks. The critical conditions for synthesizing compound (1) are: i) heating [P₆W₆O₃₅] in the presence of Ag⁺ ions at high concentration; ii) ensuring the ratio of [P₆W₆O₃₅] to Ag⁺ ions in the synthesis is ca 1:30. A similar procedure without heating, and with a lower concentration of silver ions so the cluster to silver ion ratio is 1:12, gives Li₉K₁₃Ag₁₆[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{40}]· 50\text{H}_2\text{O} \text{ (2)}. As is common in POM chemistry, the pH is also a decisive parameter that affects the crystallization process. Under reaction conditions similar to that for (2), but with a slightly lowered pH, compound Li₉K₁₃Ag₁₆[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{40}]· 170\text{H}_2\text{O} \text{ (3)}, with a cubic structure, was obtained.

Compound (1) crystallizes in a monoclinic system with the space group P2₁/m. A [P₆W₆O₃₅] base with six [W₁] units, at the joining corners between the four [P₆W₆O₃₅] units, was identified in the structure. An additional lacunary Keggin [PW₆] or a lacunary Dawson [P₂W₁₂] subunit was found to add on the six [W₁] units (Figure 1), which are identified as growth points (Figure S1, see the Supporting Information). Since co-crystallization occurs with these two clusters, the [PW₆] and [P₂W₁₂] add-on units co-occupy the same location by sharing the first six W atoms with full occupancy (Figure S2). The remaining W atom sites that separately belong to the [PW₆] and [P₂W₁₂] units are 50% occupied. Most oxo ligands with full occupancies on the [PW₆] unit are shared by the [P₂W₁₂] unit. The remaining unshared oxo sites with half occupancies on [PW₆] and [P₂W₁₂] units were also found and refined (Figure S1). A well-defined disorder model, which includes a 1:1 ratio of [PW₆] and [P₂W₁₂] units, confirms the co-crystallization of the [P₆W₆O₃₅] and [P₆W₆O₃₅] clusters. Both clusters have the same [P₆W₆O₃₅] base and have roughly similar sizes for the [PW₆] and [P₂W₁₂] parts. The formation of high-nuclearity [P₆W₆O₃₅] and [P₆W₆O₃₅] clusters is only possible with a high concentration of Ag⁺ ions and heating/refluxing during the synthesis process before crystallization.

A careful analysis of the cluster structure found in compound (1) revealed that the central cavity of the [P₆W₆O₃₅] base is filled with Ag⁺ ions which form a [Ag₉] aggregate with two Cl⁻ ions as cores, which is similar to the observation in other Ag-POM clusters.\(^{[17]}\) One more Ag⁺ ion was found to support and stabilize key [W₁] growth sites, similar to the [Ag₉] cluster, from within the central cavity of the cluster (Figure S2). The remaining 10 Ag⁺ ions per formula were found to link clusters which form a 3D network with a complex topology. The silver ions appear to use all the linking models of [W₁] that are possible for the POMzite archetypes.\(^{[9]}\) The packing diagram in Figure S3 shows that the space between clusters accommodates silver ions at locations inside and between the clusters.

Compound Li₉K₁₃Ag₁₆[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{40}]· 50\text{H}_2\text{O} \text{ (2)}, was synthesized under reaction conditions similar to (1), but at room temperature and with a lower concentration of AgNO₃. In the single-crystal structure determination, major silver ion positions are clearly defined with occupancies between 0.55 and 1.0. The structure can be described as [P₆W₆O₃₅] rings that are packed in a layer-by-layer mode. Within a single layer, the [P₆W₆O₃₅] rings are virtually coplanar with ring center-to-center distances being about 22.9 and 24.2 Å in the two distinct dimensions. Each layer has a thickness of around 11.3 Å. The [P₆W₆O₃₅] rings either within or between layers are linked by Ag⁺ ions (total 9 per formula, Figure S4) and the gaps and cavities are further filled by K⁻ counterions. The closest contact between clusters is bridged by a Ag⁺ ion with an O–O separation of about 2.86 Å. Layers of the [P₆W₆O₃₅] rings are displaced and are stacked in an AB fashion (see Figure 2). There are three additional tungsten atoms with partial occupancies across six growth sites in the [P₆W₆O₃₅] ring in
comparison to the above description of (1). This confirms the existence of the growth points of the [P₆W₁₈O₆₆] in solution starting with either a minor tungstate impurity in the starting material, or the decomposition of a small amount of [P₆W₁₈O₆₆] during the reaction. In contrast to the Ag⁺ cluster found in the cavity of [P₆W₁₈O₆₆] rings in (1), the corresponding positions in (2) are instead occupied by K⁺ ions. The network structure of (3) is best described as a “truncated cuboctahedron” (or great rhombicuboctahedron); in other words, the molecular paneling of [P₆W₁₈O₆₆]⁻⁻ units into the network can essentially be viewed as cubic (Figure 3), a topology shared by some other notable materials. Strikingly, this topology is analogous to that of the prominent LTA (Linde Type A) zeolite framework, with a pore size of 0.4 nm. Both compound (3) and POMzite-3[20] [M₉₉(H₂O)₉₉,P₆W₁₈O₆₆] have approximately spherical voids with an internal diameter of 0.21 nm (that is, void volume of 0.48 nm³, see Figure 3) and are accessible through the integrated pores of the six surrounding [P₆W₁₈O₆₆]⁻⁻ anions[20] LTA, compound (3), and POMzite-3 frameworks crystallize in the same cubic Pm₃m space group and differ only in the tiling around the central cubo-octahedral cavity[19,20].

Structural control between the two distinct structures, (1) and (2), was achieved by varying reaction temperatures and the concentration of Ag⁺ ions, whilst maintaining the same pH 1.53. Compound (1) was obtained by heating at 80°C for 30 minutes with a much higher concentration of Ag⁺ ions that replaces the K⁺ ions in the [P₆W₁₈O₆₆] cavity of the starting materials and produces more [PW₄] and [P₂W₆O₁₈] fragments, which fully fill the growth sites on the [P₆W₁₈O₆₆] base. This leads to the formation of molecular clusters [P₆W₁₈O₆₆] and [P₆W₁₈O₆₆] which co-crystallize in compound (1). The synthesis of (2) under similar conditions but with a lower concentration of Ag⁺ ions and without heating yields some partially filled growth points but with no extended POM framework, such as [P₆W₁₈O₆₆] and [P₂W₆O₁₈] as in (1). Under such conditions Ag⁺ ions cannot substantially replace the K⁺ ions in the [P₆W₁₈O₆₆] cavity of the starting materials and no significant amount of [PW₄] or [P₂W₆O₁₈] fragments are produced. Compound (3), synthesized with the reaction conditions of (2), but with a lower pH of 1.45, has no growth points filled with [W₈] units. This is because lower pH is not favorable for [PW₈] to disassemble to produce fragments or even [W₈] units. Also lower pH is not favorable for Ag⁺ ions to coordinate to oxo ligands because oxo has a higher affinity to protons. Therefore, fewer Ag⁺ ions are included in (3) and hence fewer O-Ag-O bridges are formed between the [P₆W₁₈O₆₆] clusters, generating a less dense cubic framework compared with compounds (1) and (2) (Figure S5).

In conclusion, by varying the reaction conditions—the temperature, pH and the concentration of Ag⁺ ions—it is possible to control the synthesis of lacunary [PW₄] and
Experimental Section

General experimental remarks: All chemicals were purchased from commercial sources and used without further purification. CDCDC 1892362, 1892363 and 1892364 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of LiK3Ag6H2P2W9O34H2O (1): In a 25 mL round-bottomed flask, LiNO3 (84 mg, 1.2 mmol) was dissolved in 12 mL of H2O, then K2Li[H2P2W9O34·92H2O (102 mg, 6.9 × 10−3 mmol) was added and dissolved. The solution was adjusted to pH 1.53 by using HNO3 (70%), then AgNO3 (35.7 mg, 0.21 mmol) was added. The mixture was then heated at 80°C for 30 min then cooled down to room temperature. After two weeks well-behaved block colorless crystals started to form in solution.

The products were isolated after several weeks. The chlorine came from the trace amount in the starting materials. Yield: 0.06 g. Characteristic IR bands (in cm−1): νa(H2O), 3439 (br), 1626 (m); νa(Ag-O), 1384 (s); νa(P-O), 1134 (s); νa(P-O), 1015 (w), 926 (br). Elemental analysis calc (found) for Ag2ClH2LiK3Ag6H2P2W9O34·92H2O: Ag 11.5 (11.6), W 60.1 (60.3), K 1.88 (1.74). Li 0.28 (0.29). TGA water loss from room temperature to 400°C, calc (found): %: 4.6 (5.2).

Synthesis of LiK2Ag(H2P2W9O34H2O) (2): In a 25 mL flask, LiNO3 (84 mg, 1.2 mmol) was dissolved in 12 mL of H2O, then K2Li[H2P2W9O34·92H2O (102 mg, 6.9 × 10−3 mmol) was added. The solution was adjusted to pH 1.53 by using HNO3 (70%), then AgNO3 (13.7 mg, 0.08 mmol) was added. The mixture was then stirred at room temperature for 5 min. After three weeks well-behaved block, colorless crystals started to form in solution. These were isolated after several weeks. Yield: 0.12 g. Characteristic IR bands (in cm−1): νa(H2O), 3416 (br), 1626 (m); νa(Ag-O), 1412 (w); νa(P-O), 1134 (s), 1081 (s); νa(W-O), 1015 (w), 926 (br). Elemental analysis calc (found) for Ag2H2LiK2Ag(H2P2W9O34·92H2O·Ag2ClH2LiK3Ag6H2P2W9O34·92H2O): Ag 2.7 (2.9), W 54.9 (55.1), K 2.92 (3.17), Li 0.43 (0.43). TGA water loss from room temperature to 400°C, calc (found): %: 19.0 (19.5).

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Conflict of interest

The authors declare no conflict of interest.

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