Host-Guest Chemistry of Inorganic Porous Platforms

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ABSTRACT

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Complexes made by hosts that completely surround their guests provide a mean to stabilize reactive chemical intermediates, transfer biologically active cargo to a diseased cell, and construct molecular scale devices. By the virtue of inorganic host-guest self-assembly, the nucleation processes in the cavity of a \{P_8W_{48}\}-archetype phosphotungstate has afforded a nanoscale 16-Ga^{III}-32-oxo cluster that contain the largest number of Ga^{III} ions yet found in polyoxometalate chemistry. Catalytic activity via thus “Metal-Oxo Cluster within Cluster” Assembly has been preliminarily investigated. Besides, the hybrid aggregates composed of the inorganic \{P_8W_{48}\} and orgainc cyclic moiety has been studied.
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“In the realm of ideas everything depends on enthusiasm... in the real world all rests on perseverance”

Johann Wolfgang von Goethe

Dedicated to my parents
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# Table of Contents

**Chapter 1** ........................................................................................................................................... 11

**Introduction** ......................................................................................................................................... 11

1.1 Supramolecular Chemistry- Beyond the Molecular Frontier ......................................................... 11

1.2 Host-Guest Chemistry .......................................................................................................................... 12

1.3 Polyoxometalates .............................................................................................................................. 14

   1.3.1 Historical Background .................................................................................................................. 14

   1.3.2 Composition and Classification .................................................................................................. 16

   1.3.3 Proposed Formation Mechanism ................................................................................................ 18

   1.3.4 Typical Structural Types ........................................................................................................... 19

   1.3.5 Lacunary Wells-Dawson Derivatives ......................................................................................... 22

   1.3.6 Wheel Cluster \{P₈W₄₈\} ................................................................................................................. 27

   1.3.7 Transition Metal-Incorporated POMs ......................................................................................... 30

   1.3.8 Applications ............................................................................................................................... 30

1.4 Objectives ............................................................................................................................................ 31

**Chapter 2** ............................................................................................................................................ 33

**Experimentation** ................................................................................................................................. 33

2.1 Materials ............................................................................................................................................. 33

2.2 Characterization Techniques ............................................................................................................. 34

   2.2.1 Fourier Transform Infrared (FTIR) Spectroscopy ....................................................................... 34

   2.2.2 Nuclear Magnetic Resonance (NMR) Spectroscopy ................................................................... 34

   2.2.3 Single Crystal X-ray Diffraction (SXRd) .................................................................................... 35
2.2.4 Thermogravimetric Analysis (TGA) ................................................................. 35
2.2.5 Gas Chromatography-Mass Spectrometry (GC-MS) ............................................ 35
2.2.6 Dynamic Light Scattering (DLS) ........................................................................ 35
2.2.7 Transmission Electron Microscopy (TEM) .............................................................. 36
2.2.8 Electrospray Ionization Time-of-Flight Mass Spectrometry (ESI-TOF-MS) ........... 36
2.2.9 Elemental Analyses (Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) and (C, H, N)) .......................................................... 36
2.2.10 UV-vis Spectroscopy ......................................................................................... 36

2.3. Synthetic Procedures ............................................................................................. 37
2.3.1 Synthesis of K_{28}Li_{5}[H_{7}P_{8}W_{48}O_{184}]-92H_{2}O salt ........................................ 37
2.3.2 Synthesis of K_{11}Li_{9}(NH_{4})_{4}[Ga_{16}(OH)_{32}(P_{8}W_{48}O_{184})]-112H_{2}O ........ 38
2.3.3 Synthesis of [2+2] Macrocycle ......................................................................... 39
2.3.4. Synthesis of \{P_{8}W_{48}\} & [2+2] Macrocycle ....................................................... 39

Chapter 3 ....................................................................................................................... 41

Group IIIAGuest in \{P_{8}W_{48}\} Archetypal Polyoxotungstate Host: Catalytic Prospects via Metal-Oxo Cluster within Cluster Assemblies .................................................. 41

3.1 Introduction and Literature Review ........................................................................ 41
3.2 Results and Discussion ......................................................................................... 44
3.2.1 \{P_{8}W_{48}\} ...................................................................................................... 44
3.2.1.1 ESI-TOF-MS of \{P_{8}W_{48}\} ........................................................................ 45
3.2.2 \{Ga_{16}-P_{8}W_{48}\} .......................................................................................... 47
3.2.3 SXRD of \{Ga_{16}-P_{8}W_{48}\} ............................................................................ 47
3.2.4 Bond Valence Sum of \{Ga_{16}-P_{8}W_{48}\} ......................................................... 51
3.2.5 $^{31}$P and $^{71}$Ga NMR of $\{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\}$ .......................................................... 52
3.2.6 FTIR Spectroscopy of $\{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\}$ .............................................................. 53
3.2.7 Elemental Analyses of $\{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\}$ ............................................................ 55
3.2.8 UV Spectrum of $\{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\}$ ................................................................. 55
3.2.9 TGA of $\{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\}$ ................................................................. 56
3.3 Catalysis of $\{\text{Al}_{16}-\text{P}_8\text{W}_{48}\}$ ........................................................................ 57
  3.3.1 Thioether Oxidation Reaction .......................................................... 57
  3.3.2 Catalytic Results ........................................................................ 57
3.4 Conclusions and Outlook .................................................................. 61

Chapter 4 .............................................................................................. 62

Inorganic-Organic Hybrid Hydrophilic Assemblies in Aqueous Solutions........ 62
  4.1 Introduction and Literature Review .................................................. 62
  4.2 Results and Discussion ................................................................... 64
    4.2.1 $\text{P}_8\text{W}_{48}$ & [2+2] Macrocycle .................................................. 64
    4.2.2 DLS of $\{\text{P}_8\text{W}_{48}\}$ & [2+2] Macrocycle .......................... 64
    4.2.3 TEM of $\{\text{P}_8\text{W}_{48}\}$ & [2+2] Macrocycle .................. 67
    4.2.4 FTIR Spectroscopy of $\{\text{P}_8\text{W}_{48}\}$ & [2+2] Macrocycle .... 69
    4.2.5 NMR of $\{\text{P}_8\text{W}_{48}\}$ & [2+2] Macrocycle .................. 71
    4.2.6 ESI-TOF-MS of $\{\text{P}_8\text{W}_{48}\}$ & [2+2] Macrocycle .......... 73
  4.3 Conclusions and Outlook ............................................................... 75

REFERENCES ...................................................................................... 76
Chapter 1

Introduction

1.1 Supramolecular Chemistry- Beyond the Molecular Frontier

Supramolecular chemistry or chemistry beyond the molecule is the branch of chemistry that focuses on the study of complex molecular systems formed from several discrete chemical components. In contrast to molecular chemistry, supramolecular chemistry is the “non-covalent” bond formation resulted by the association of two or more building units. Surprisingly, although these complex packed systems seem to be formed by strong covalent interactions, they have been bonded together by an intricate range of weaker, non-covalent interactions such as intermolecular hydrogen bonding, electrostatic interactions, dipole-dipole interactions, hydrophobic forces, van der Waals forces, and pi-pi interactions which exist extensively in numerous vital biological processes. There is plenty of remarkable phenomena that echo the sound of supramolecular chemistry such as host-guest chemistry, molecular self-assembly, and molecular recognition. These supramolecular assemblies have been explored by different areas including molecular machines, gas absorption, catalysis, and drug delivery. It is a cross-discipline of organic chemistry, coordination chemistry, physical chemistry, polymer chemistry, material science, and biological science. Supramolecular chemistry, therefore, attracted not only chemists but biologists, environmental scientists, physicists, biochemists, and crystallographers.[1]
1.2 Host-Guest Chemistry

Engineering of supramolecular and coordination driven assemblies for encapsulation of a myriad of molecular guests has recently dominated scientific literature as a consequence of the direct applicability of such systems in catalysis, drug delivery, and energy storage. Ever since Cram’s description of the “Molecular Containers” bearing interior cavities that allow intercalating guest molecules,[3] thousands of examples have been communicated, and this progress is mainly concentrated upon organic macrocycles such as cyclodextrins, cucurbiturils, calixarenes, and the newly emerged pillararenes (Figure.1).[4] Hybrid host matrices involving metal-organic frameworks[5] and coordination cages,[6] have also been actively studied as models for gas storage and energy-intensive separations. By stark contrast, inorganic host-guest chemistry has been trailing behind as this realm differs noticeably from its organic counterpart primarily because of the dissimilar notions of bonding and synthesis.[7] Till 1991, a particular subset of inorganic supramolecular chemistry, namely, “Metal-Oxo Cluster within Cluster” mode, was first proposed by Müller and co-workers.[8] Such assemblies, being termed polyoxometalates (POMs),[9] enable stabilization of reactive and transient metal-oxo fragments that are otherwise hard to capture.
Figure 1. Examples of Organic macrocycles. a) Cyclodextrins; b) Cucurbiturils; c) Calixarenes; d) Pillararenes
1.3 Polyoxometalates

Polyoxometalates (POMs) represent a unique class of discrete anionic metal oxide nanoclusters constructed mainly by early transition metals of group 5 and 6, most notably V\(^V\), Mo\(^VI\), and W\(^VI\) in their highest oxidation states (d\(^0\) configuration). POMs envelope a diverse range of molecular clusters with supreme physical and chemical properties and structural topologies together with the ability to construct dynamic structures ranging in size from the nano- to the micrometer scale.\[^{10}\] Due to their fascinating properties such as redox behavior, oxidative stability, tunable acidity and impressive sensitivity to electricity, POMs are found to be divergent in use involving medicine, material science, magnetism, electro/photochemistry, and most notably catalysis.\[^{11}\]

1.3.1 Historical Background

The history of the POM discipline has been brightened by the outstanding generation of researchers since the mid-18\(^{th}\) century, and it continues to charm young promising scientists all over the world. The outset step was pioneered by J.J Berzelius, who has always credited with the first example of POMs that was reported in his 1826 paper when he observed the formation of a yellow precipitate, which is now known to be ammonium 12-phosphomolybdate, (NH\(_4\))\(_3\)[P\(^V\)Mo\(^VI\)\(_{12}\)O\(_{40}\)].aq., formed after mixing an excess amount of orthophosphoric acid with ammonium molybdate.\[^{12}\] From then onwards, attempts to further understand the structure and composition of these materials, were led by several scientists. Amongst them L. Pauling in 1929, applied the principles based upon Werner’s coordination theory and Miolati-Rosenheim’s structural hypothesis together to explain
and express the structures of 12:1 heteropolyanion species.\textsuperscript{[13]} Pauling was then able to further elucidate and develop the structure for the 12-heteropolyacids of molybdenum and tungsten based compounds when he suggested corner-sharing octahedra based on ionic radii.\textsuperscript{[14]} It was yet required a full elucidation of the final structure, which we call it now, crystal structure, determined by X-ray diffraction methods, discovered first by Laue in 1912\textsuperscript{[15]} and pioneered by Brag who set the basis for the determination of crystal structure.\textsuperscript{[16]} Moving on, in 1933, it was Keggin who first used the X-ray diffraction in POM chemistry reported the real solved structure of \([\text{H}_3\text{P}^{\text{V}}\text{W}^{\text{VI}}_12\text{O}_{40}]\cdot5\text{H}_2\text{O}\) by means of a powder X-ray diffraction study, which is often referred to “Keggin” type structure.\textsuperscript{[17]}

Figure 2. Data taken from SciFinder Scholar, illustrating the exponential increase in the number of publications containing “polyoxometalate” as a keyword over the last two centuries
After that, the roads for POM structures have been widened as in 1948, Evans determined the Anderson-Evans heteropolyanion (1:6) \([\text{Te}^{VI}\text{Mo}^{VI}6\text{O}_{24}]^{6−}\) by single crystal X-ray analysis.\[^{18}\] Followed by the Wells-Dawson (2:18) \([\text{P}^{V2}\text{W}^{VI}18\text{O}_{62}]^{6−}\) structure, that was reported in 1953 by Dawson.\[^{19}\] Noteworthy, X-ray diffraction methods were a critical juncture in POM chemistry. Over the last few decades, research in POMs was unstoppable, hundreds of structures have been reported, knocking the door of various scientists in the world and bringing POMs in the front face of inorganic chemistry. (Figure 2).

### 1.3.2 Composition and Classification

The typical POMs structures are composed of a metal-oxygen bond, practically, metals bridged by oxygen atoms. The metals are mainly restricted to group V and VI (such as Mo and W and less frequently V, Nb, and Ta) in their high oxidation state, \(d^0\) or \(d^1\) electronic configurations. In \(\text{MO}_n\) units, POMs composed basically, where ‘n’ indicates the coordination number of M (n= 4, 5, 6 or 7). The most common building blocks are \([\text{MO}_6]\) octahedra. The great accomplishments of many chemists have resulted in a broad expansion of POM clusters with endless shapes and sizes. Therefore, it was crucial to conceptualize and grasp these numerous structures. According to their chemical composition, POMs could be classified into two main subsets: I) isopolyanions (IPAs) with the general formula: \(([\text{M}_m\text{O}_y]^z)\), in which all metal atoms are the same. II) Heteropolyanions (HPAs) with the general formula: \(([\text{X}_z\text{M}_m\text{O}_y]^z)\), where M is the metallic element that acts as an addenda atom and X is the heteroatom and commonly inhabits the center. The embodiment of heteroanions such as \([\text{SO}_4]^{2−}\), \([\text{AsO}_4]^{3−}\), \([\text{SiO}_4]^{4−}\),
and most commonly $[\text{PO}_4]^{3-}$, provides stability to the structure as well as introduce negative charges.$^{[10]}$ Various examples of HPAs have been brought to lights, most frequently, Keggin$^{[17]}$ ($[\text{XM}_{12}\text{O}_{40}]^{n-}$), Wells-Dawson,$^{[19]}$ ($[\text{X}_2\text{M}_{18}\text{O}_{62}]^{n-}$), and Anderson-Evans,$^{[18]}$ ($[\text{XM}_6\text{O}_{24}]^{n-}$) structural motifs. Waugh (1:9)$^{[20]}$ and Silverton (1:12)$^{[21]}$ topologies were also perceived in sequence. IPAs are less stable than HPAs and few species have been reported. Lindqvist IPA$^{[22]}$ ($[\text{M}_6\text{O}_{19}]^{n-}$) represents the smallest POM cluster so far. Since then, six classical structural modes of POMs have been established. (Figure 3).

![Figure 3. Classical structural types of POMs: (a) Keggin, (b) Wells-Dawson, (c) Anderson-Evans, (d) Waugh, (e) Silverton, and (f) Lindqvist. Color code, balls: X (green); polyhedra: \{MO$_6$\} (red) (M, addenda atom; X, hetero atom).](image-url)
1.3.3 Proposed Formation Mechanism

Although theoretical research in POM chemistry has been widely developed during past decades, the mechanism of synthesis remains incomprehensible and commonly describes as self-assembly. It seems likely that the formation of a POM structure occurs through linking of polyhedral MOₙ units (n = 4, 5, 6, or 7). The self-assembly of polyhedral occurs after acidification of the aqueous solution of monomeric o xoanions. The acidification will cause the metal coordination shell of the starting materials to expand from 4 (tetrahedral) to 6 (octahedral) followed by the condensation between MO₆ fragments into larger clusters via edge- and/or corner- and/or rarely face-sharing fashion (Figure 4). The formation of such “lego kits” are greatly dependent upon a combination of reaction conditions (e.g., pH, solvent system, ionic strength, temperature, and counter cations).[10] POMs are primarily characterized by MO₆ octahedra with “terminal” M=O bonds are essentially formed because of the empty d orbitals (highest oxidation state) of the metal. As a consequence, a strong metal oxide π bond is formed in addition to the basic coordination bond between the metal and the ligand. Hence, this “terminal” M=O bond will limit the polymerization growth of metal-oxide structures and favor the formation of discrete finite clusters.[23]

![Diagram](Corner-sharing Edge-sharing Face-sharing)

Figure 4. Polyhedral representation of the three connection models of MO₆ units
1.3.4 Typical Structural Types

Since the development of numerous POM structures and after the classification of POMs, six typical structures of POMs have been represented. These structures speak for the most explored collections so far with great emphasis on 1) the HPA Keggin \([\text{XM}_{12}\text{O}_{40}]^{n-}\) (where \(\text{M} = \text{W}^{VI}\) or \(\text{Mo}^{VI}\); \(X\) is a tetrahedral group, such as \([\text{PO}_{4}]^{3-}\)), is formed by assembly of four corner-shared \(\text{M}_3\text{O}_{13}\) triads. Every triad is composed of three edge-connected \([\text{MO}_6]\) octahedra, and every \(\{\text{M}_3\}\) fragment are corner-linked and fused around the central heteroanion by coordinating to one of the \([\text{XO}_4]^n\) oxygen ligands. (Figure 5a). Keggin structure is the most known structural form for heteropoly acids. \[17\][24]

2) Wells-Dawson structure or simply the Dawson anion, \([\text{X}_2\text{M}_{18}\text{O}_{62}]^{n-}\) (where \(\text{M} = \text{W}^{VI}\) or \(\text{Mo}^{VI}\); \(X\) is a tetrahedral group, such as \([\text{PO}_4]^{3-}\)) was suggested by A. F. Wells in 1945,\[30\] then confirmed by Dawson in 1953 by using single crystal X-ray diffraction. Since then, this type of structure is now referred as the Wells-Dawson structure. Wells-Dawson is a derivative of the Keggin structure, formed from the combination of two Keggin-type structures of the \([\alpha\text{-A-XW}_{9}\text{O}_{34}]^{n-}\) type. This eighteen metal-containing polyanion is composed of two central belts connected through three corner-sharing \([\text{M}_2\text{O}_{10}]\) dioctahedra, each belt clasps a central heteroanion \([\text{XO}_4]^n\) coordinating to the oxygens of the three \([\text{M}_2\text{O}_{10}]\) in an X-O-M bond and thus, supporting the \([\text{M}_2\text{O}_{10}]\) fragment. It also consists of two \([\text{M}_3\text{O}_{13}]\) triad caps positioned at the top and bottom of the two belts linked to the cluster by six corner-sharing oxygens and interacting with the central heteroanion \([\text{XO}_4]^n\) via one X-O-M coordination bond. (Figure 5b). \[19\][25][26][27]

3) Anderson-Evans structure, \([\text{XM}_6\text{O}_{24}]^{n-}\) (where \(\text{M} = \text{W}^{VI}\) or \(\text{Mo}^{VI}\); \(X\) is an octahedral
group, such as \([\text{TeO}_6]^{6-}\) was proposed by Anderson in 1937\(^{29}\) and confirmed by Evans in 1948 by using single crystal X-ray diffraction. Since then, this type of structure is now referred as Anderson-Evans structure. This HPA is formed by the assembly of six edge-connected octahedral \(\text{MO}_6\), and all metal ions interact with the tellurium heteroatom at the center via two X-O-M coordination bonds. (Figure 5c)\(^{18}\) 4) Lindqvist IPA, \(((\text{M}_6\text{O}_{19})^{n-}\) (where M = Mo\(^{VI}\), W\(^{VI}\), V\(^{V}\), Nb\(^{V}\) or Ta\(^{V}\)), is the smallest POM cluster so far. This polyanion consists of six octahedral \(\text{MO}_6\), assembled together by edge-sharing of each \(\text{MO}_6\) with the neighboring octahedra. (Figure 5d)\(^{22}\)\(^{24}\) 5) Waugh-type cluster, \([\text{XM}_9\text{O}_{32}]^{n-}\) (where M = W\(^{VI}\) or Mo\(^{VI}\); X is an octahedral group) which consists of a central octahedra heteroatom connecting with nine distorted \(\text{MO}_6\) octahedra through edge-sharing. The Waugh-type cluster \([\text{MnMo}_9\text{O}_{32}]^{6-}\) was first isolated with only a single type of heteroatom Mn\(^{IV}\) and reported in 1954.\(^{20}\)\(^{28}\) 6) Silverton-type HPA, \([\text{XMO}_{12}\text{O}_{42}]^{n-}\) (where M = W\(^{VI}\) or Mo\(^{VI}\); X is a polyhedral group), formed by assembly of six face-connected \(\text{M}_2\text{O}_9\) octahedral, each \(\text{M}_2\text{O}_9\) unit share corners with the adjacent \(\text{M}_2\text{O}_9\) unit, and the central heteroatom is coordinated in an icosahedral geometry to the oxygen atoms of the six \(\text{M}_2\text{O}_9\) units.\(^{21}\)

\textbf{a) Keggin }\(\alpha\)-\(\text{XM}^{12}\text{O}_{40}\)\(^{n-}\)
b) Wells–Dawson $X_2M_{18}O_{62}^{n-}$

c) Anderson–Evans $XM_6O_{24}^{n-}$
Figure 5. Polyhedral and ball-and-stick representations of HPAs (A, B, and C) and IPA (D) Black spheres are metal centers, red ones are oxygens. Blue polyhedra are heteroatoms.

### 1.3.5 Lacunary Wells-Dawson Derivatives

There is an occasion where one or more of the addenda atoms, along with the oxygen are being missed from the structure upon the treatment of a base, and thus causing a defect in the polyanion structure. Such structures are called lacunary polyanions. Parenthetically, the famous Wells-Dawson anion $\alpha$-[X$_2$M$_{18}$O$_{62}$]$^{12-}$ is formed as a result of a combination of two lacunary keggin fragments [$\alpha$-XMo$_9$O$_{34}$], through six corner-sharing modes. [19][25][26][27] (Figure 6).
Figure 6. Polyhedral representation of the formation of the Wells–Dawson structure X$_2$M$_{18}$ by removing 3 corner-sharing octahedral from the α-XM$_{12}$ Keggin anion. Assembly of the two lacunary Keggin anions will form the Dawson structure.

Particularly, if a solution of polyoxotungstate is treated with an acid of below pH = 2 with an excess amount of phosphate, two isomers of a Wells-Dawson [P$_2$W$_{18}$O$_{62}$]$^{6-}$ HPA will take place instead of the Keggin structure. Since the addition of an acid is putting these metal oxides together, accordingly, the basicity will fall them apart to form lacunary species. In this regard, the basification of a Wells-Dawson solution will result in the formation of several lacunary species of the Wells-Dawson anion. A hydrolytic cleavage of the M-O bonds is happening behind the scenes upon controlled increase of the pH to levels higher than pH = 6. And subsequently, generating monovacant [P$_2$W$_{17}$O$_{61}$]$^{10-}$ lacunary species. However, two isomers of this structure are recognized and it is contingent on the position of the vacancy. When the loss of the “M=O” fragment is from the apical triad that caps the cluster, the [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ isomer is formed. However, if the loss of the “M=O” fragment is from the central six-membered built, an [α$_1$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ isomer is formed. The formation of the second isomer is a complicated procedure as it requires re-assembly of the cluster. Consequently, [α$_1$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ anion is unstable and willingly undergoes isomerization to the [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$. In other cases,
where the cleavage of the M-O bonds is happening upon controlled increase of the pH to 10, one of the triad caps will be removed and a trilacunary anion $[P_2W_{15}O_{56}]^{12-}$ is formed. (Figure 7).

Figure 7. Polyhedral representation of $[\alpha_2-P_2W_{17}O_{61}]^{10-}$ and $[P_2W_{15}O_{56}]^{12-}$.

The Wells–Dawson octadecatungstodiphosphate HPA has also another lacunary species, which is the hexavacant tungstophosphate $[H_2P_2W_{12}O_{48}]^{12-}$. Amongst all Wells–Dawson HPA lacunary species, it has the highest vacancy as it has six vacancies and so-called “hexalacunary”. It was first isolated by Contant,[32] lacking one addenda metal from each of $[M_3O_{13}]$ triad caps and four from the equatorial region of the cluster (Figure 8). From the $\alpha-[X_2M_{18}O_{62}]^{3+}$ anion, four lacunary Wells–Dawson tungstophosphate species have been derived, which have been mentioned in this section.
Figure 8. Polyhedral and ball-and-stick representations of the hexavanant tungstophosphate $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$.
A polarographic investigation was reported by Contant,[32] describing the three steps alkaline degradation of the symmetrical parent HPA $\alpha$-[P$_2$W$_{18}$O$_{62}$]$^6^-$, all the way until the formation of [H$_2$P$_2$W$_{12}$O$_{48}$]$^{12^-}$. Starting with the formation of the lacunary [P$_2$W$_{17}$O$_{61}$]$^{10^-}$ first, followed by the reversible formation of [$\alpha$-P$_2$W$_{17}$O$_{61}$]$^{10^-}$ upon addition of sodium ions. Lastly, [H$_2$P$_2$W$_{12}$O$_{48}$]$^{12^-}$ is formed irreversibly. Upon acidification, [H$_2$P$_2$W$_{12}$O$_{48}$]$^{12^-}$ take its reversible way back to [P$_2$W$_{17}$O$_{61}$]$^{10^-}$, which in turn takes its way reversibly back to the parent $\alpha$-[P$_2$W$_{18}$O$_{62}$]$^6^-$. (Scheme 1).

Scheme 1. Polarographic representation of the alkaline degradation of $\alpha$-18-tungsto-2-phosphate in solution.

The stability of these lacunary fragments has paved the way to 1) complexation of transition metal cations, since the exposed vacancies of high negatively oxygen-donor ligands can be filled with electrophilic counterparts and thus, altering the properties of the lacunary cluster such as providing molecular magnetism.[33] 2) formation of giant inorganic aggregates by the assembly of multiple lacunary building units, which can be
called superlacunary polyanions and thus making these supramolecular inorganic clusters a point of interest to many chemists and scientists. \[34\][35][36][37][38]

### 1.3.6 Wheel Cluster \{P_8W_{48}\}

Keggin and Wells-Dawson are two iconic structures in the family of HPA. More specifically, heteropolytungstates or tungsten-based structures are the most robust and rigid, which have been invested to develop lacunary derivatives.\[10f\] One of the most famous structures developed from Keggin and Wells-Dawson lacunary derivatives to form superlacunary structures are called crown HPAs. One example of this family is the Preyssler anion \([\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}\)[39] which was a byproduct from the preparation of \([\text{P}_2\text{W}_{18}\text{O}_{62}]^6-\)[40] (Figure 9). It was the largest polyoxotungstate until 1985, when Contant and Tézé first reported the crown-type or wheel-type polyanion \([\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}\) as a mixed potassium/lithium salt, \(\text{K}_{28}\text{Li}_5\text{H}_7[\text{P}_8\text{W}_{48}\text{O}_{184}] \cdot 92\text{H}_2\text{O}\).[34]

![Figure 9. Polyhedral representation of the Preyssler anion \([\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}\)](image-url)
Interestingly, the hexadecavacant \([\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}\) (hereafter referred to as \{\text{P}_8\text{W}_{48}\}) is formed by corner-sharing end to end linkage of four units of the \([\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}\) solid precursor.\[^{34}\] Re-dissolving the solid precursor \{\text{P}_2\text{W}_{12}\} in a lithium acetate buffer with an addition of exclusively potassium ions, will result in \(\text{K}_{28}\text{Li}_{5}\text{H}_7[\text{P}_8\text{W}_{48}\text{O}_{184}]{\cdot}92\text{H}_2\text{O}\) crystals to give the cyclic polyanion \([\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}\) with approximate \(D_{4h}\) symmetry. (Figure 12).\[^{34}\] Within its 1 nm sized cavity, reside eight potassium cations from inner oxygen atoms. These potassium ions play a key role in decreasing the repulsion between the negative charges of the nucleophilic oxygen surface in the inner cavity. Therefore, providing stability to the crown cluster. It is solution stable over a large range pH (1-8).\[^{34}\][41][42][43] (Figure 11 & 11).

Figure 10. Ball-and-stick representation of \([\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}\).
Figure 11. Polyhedral representation of \([\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}\).

Figure 12. Polyhedral representation of the formation of the cyclic polyanion \(\{\text{P}_8\text{W}_{48}\}\) by removing 6 corner-sharing octahedra from the \(\{\text{P}_2\text{W}_{18}\}\) Wells-Dawson anion. Assembly of the four lacunary Dawson anions will form the final cyclic structure.
1.3.7 Transition Metal-Incorporated POMs

As have been mentioned in section 1.4. Multi-vacant lacunary derivatives have the affinity to incorporate paramagnetic transitions metal electrophiles for the design and construction of transitions metal incorporated POMs (TMIPs). The first example of TMIPs was reported by Simmons in 1962, wherein one tungsten atom of the Keggin structure is replaced by a Co$^{2+}$ ion to give a structure of (11-tungstosilicate), which was determined in 1966.$^{[44]}$[45] This discovery was a major breakthrough in the field of polyoxotungstate family, hence paving the way to POM chemists to develop more novel TMIP-based materials. Subsequently, this field has undergone a great deal of investigation, and since then, a large library of TMIPs has been reported.$^{[46]}

1.3.8 Applications

The unique and applicable physicochemical properties of POMs have mainly relied on the diversity of their size, shape, molecular composition, solubility, charge density, and redox potential.$^{[47]}$ It has been shown that the incorporation of transition metals within POMs has introduced properties to the clusters and thus broadening the functionality of such materials with different sizes, shapes, composition, solubility, magnetism, catalysis and redox potential.$^{[11]}$ Specifically the giant wheel-type $\{P_8W_{48}\}$ with D$_{4h}$ symmetry, has attracted increased attention in recent years because of its 1) remarkable stability over a large pH range (1-8). 2) Rich oxygen content on the outer surface of the superlacunary cluster and inside its nano-sized cavity which gives access to remarkable electrochemistry and electrocatalytic activity.$^{[46]}$[47][48] A variety of clusters have been
isolated by the nucleation of different electrophiles inside its cavity, which made the versatileness of the \( \{P_8W_{48}\} \) wheel becoming clear. Different TM-containing \( \{P_8W_{48}\} \) has been prepared by fine-tuning the selection of TM cations and reaction conditions.\(^{49}\) The fully oxidized (d\(^0\)) tungsten metal atoms of the bulky diamagnetic \( \{P_8W_{48}\} \) cluster, with its 16 donor oxygens inside its cavity, can induce multiple paramagnetic metal centers, leading to interesting intramolecular spin exchange phenomena, including ferro/antiferromagnetism and single-molecule magnetic (SMM) behavior.\(^{50}\) as the \( \{P_8W_{48}\} \) wheel contain fully oxidized (d\(^0\)) metal atoms, it is resistant to oxidative decomposition, in addition to its redox nature that evolved from the bulky negative charges that allow bearing and releasing of electrons, all along with tunable acidity are making this cyclic polyanion a robust catalyst for oxidation reactions.\(^{51}\) For TM-containing \( \{P_8W_{48}\} \) wheel, it has been reported that TM cations are promoting the catalytic activity of the wheel catalyst.\(^{52}\) With TM-substituted POMs, catalytic active sites can be designed with tailored acidic and redox properties.\(^{53}\)

1.4 Objectives

The target structure of this thesis was the wheel-type heteropolytungstate, \( K_{28}Li_5H_7[P_8W_{48}O_{184}] \cdot 92\text{H}_2\text{O} \).

In Chapter 3, we plan to introduce the main group IIIA elements into the wheel-type heteropolytungstate, \( K_{28}Li_5H_7[P_8W_{48}O_{184}] \cdot 92\text{H}_2\text{O} \). As compared to transition metals, main group IIIA metal ions within \( \{P_8W_{48}\} \) have been rather underexplored. In particular, we chose to incorporate Ga\(^{\text{III}}\) and In\(^{\text{III}}\) metals as their complexes have interesting catalytic properties, especially combine with POM framework. What is
challenging is that the main group IIIA elements would like to go through strong hydrolysis in reactions. So, at the end of the project we hope to answer 1 question, will we be able to isolate Ga\textsuperscript{III} and In\textsuperscript{III} Lewis acids within the \{P\textsubscript{8}W\textsubscript{48}\} wheel? The work has been extended towards testing the catalysis of the previously isolated \{Al\textsubscript{16}-P\textsubscript{8}W\textsubscript{48}\} in the oxidation of thioether reaction.

In Chapter 4, we will examine the assembly of the inorganic-organic hydrophilic hybrids in aqueous solutions. At the end of the project, we hope to answer two questions. 1) Will the combination of the giant wheel-type heteropolytungstate, K\textsubscript{28}Li\textsubscript{5}H\textsubscript{7}[P\textsubscript{8}W\textsubscript{48}O\textsubscript{184}] \cdot 92H\textsubscript{2}O macroions and the relative small [2+2] organic macrocycle, be able to form “blackberries” in aqueous solutions? 2) if not, what kind of connection between the prospective hybrids has happened, or do we have any?
Chapter 2

Experimentation

2.1 Materials

All reagents were purchased from commercial sources and used without further purification. Sodium tungstate dihydrate (ACS reagent, ≥99%, SIGMA-ALDRICH), orthophosphoric acid (85% aq. Soln., Alfa Aesar), nitric acid (68-70%, VWR chemicals), ammonium chloride (99.99%, SIGMA-ALDRICH), potassium chloride (ACS reagent, 99-100%, SIGMA-ALDRICH), tris (hydroxymethyl-)aminomethane (ACS reagent, ≥99.8%), potassium carbonate (99.99%, SIGMA-ALDRICH), acetic acid, glacial (≥99.7% Fisher chemical), lithium hydroxide monohydrate (ACS reagent, ≥98%, SIGMA-ALDRICH), ethanol (96%, VWR chemicals), gallium (III) nitrate hydrate (crystalline, 99.9% trace metals basis, SIGMA-ALDRICH), aluminum nitrate nonahydrate, (Crystals, 98%, Alfa Aesar), methanol (ACS reagent, ≥99.8%, Fisher Scientific), triethylamine (≥99%, SIGMA-ALDRICH), sodium borohydride (99%, SIGMA-ALDRICH), acetonitrile (anhydrous, 99.8%, SIGMA-ALDRICH). Dimethyl sulfoxide (CHROMASOLV, 99.7%, SIGMA-ALDRICH), dichloromethane (ACS, Stabilized with ethanol 0.1%, VWR chemicals), hydrogen peroxide solution (30 wt. % in H₂O, ACS reagent, SIGMA-ALDRICH), 2, 6-Pyridinedicarboxaldehyde (97%, SIGMA-ALDRICH), (1R, 2R)- (−)-1, 2-Diamino- cyclohexane (98%, SIGMA-ALDRICH).
2.2 Characterization Techniques

2.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

The FT-IR spectra were recorded on KBr disk using a Nicolet-Avatar 370 spectrometer between 400 and 4000 cm$^{-1}$.

2.2.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

All solid-state MAS NMR spectra were recorded using a Bruker 400 MHz AVANACIII NMR spectrometer equipped with a 4 mm Bruker MAS probe (BrukerBioSpin, Rheinstetten, Germany). The sample was packed evenly into 4mm zirconia rotor and sealed at the open end with a Vespel cap. The $^{31}$P NMR spectrum was measured under 14 kHz spinning rate using onepulse program with 30 degrees tilted angle recycle delay time of 15s. The $^{71}$Ga NMR spectrum was measured under 14 kHz spinning rate using onepulse program with 2s recycle delay. Topspin 3.5pl7 software (Bruker BioSpin, Rheinstetten, Germany) was used for spectral measurements and for data analysis. For solution NMR, the 1D $^1$H NMR spectra were recorded using a Bruker 500 MHz AVANACIII NMR spectrometer equipped with CryoProbe (BrukerBioSpin, Rheinstetten, Germany). Bruker Topspin 3.5 pl7 software (Bruker BioSpin, Rheinstetten, Germany) was used to collect and analyze the data. The 2D NOESY NMR spectra were recorded using a Bruker 600 MHz AVANACIII NMR spectrometer equipped with Bruker BBOF probe.
2.2.3 Single Crystal X-ray Diffraction (SXRD)

Crystal data for the structure of the compound was collected at 150 K on a Bruker D8 VENTURE single-crystal diffractometer equipped with a sealed Mo tube and a graphite monochromator ($\lambda = 0.71073 \text{ Å}$). The crystal was mounted in a Hampton cryoloop with light oil to prevent water loss. The SHELX software package (Bruker) was used to solve and refine the structure.$^{[54]}$ An empirical absorption correction was applied using the SADABS program.$^{[55]}$ The structure was solved by direct methods and refined by the full-matrix least-squares method ($\Sigma w(|F_o|^2 - |F_c|^2)^2$) with anisotropic thermal parameters for all heavy atoms included in the model.

2.2.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL min$^{-1}$ flow of nitrogen; the temperature was ramped from 20 °C to 800 °C at a rate of 5 °C min$^{-1}$.

2.2.5 Gas Chromatography-Mass Spectrometry (GC-MS)

Angilent 7890A GC system with Agilent 5975 inert XL EI/CI MS detector, and Agilent 7693 autosampler have been used throughout our study.

2.2.6 Dynamic Light Scattering (DLS)

Dynamic light scattering and Zeta-potential were measured by a Zetasizer instrument (NanoZS, Malvern, UK). The precipitate has been shaken. 1 mL of the shaked solution has been transferred to a SQUARE cell and a folded capillary cell for DLS
measurements. Zetasizer software has been used to run the sample at 25°C with water as a dispersant and 90º scattering angle.

2.2.7 Transmission Electron Microscopy (TEM)

The morphology of the structures was observed by TEM images that have been collected in a transmission electron microscope (Tecnai T12, FEI, US) instrument. Microscope operated at 120 kV.

2.2.8 Electrospray Ionization Time-of-Flight Mass Spectrometry (ESI-TOF-MS)

The accurate mass determination of the samples were acquired in the positive ion mode using Bruker Daltonics Micro-TOF Mass Spectrometer equipped with heated ESI ion source.

2.2.9 Elemental Analyses (Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) and (C, H, N))

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C elemental analyzer. ICP-OES was carried out on a PerkinElmer Optima 8300.

2.2.10 UV-vis Spectroscopy

The UV-vis spectrum was recorded in 1 cm quartz cuvettes on a SHIMADZU UV-2600 UV-vis spectrophotometer in the range of 200 – 800 nm.
2.3. Synthetic Procedures

2.3.1 Synthesis of $\text{K}_{28}\text{Li}_5[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]\cdot 92\text{H}_2\text{O}$ salt

The precursor $\text{K}_{28}\text{Li}_5[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]\cdot 92\text{H}_2\text{O}$ was synthesized according to the published procedure of Contant. The salt was prepared in three steps:

Step 1: Synthesis of potassium octadecatungstodiphosphate: $\text{K}_6[\alpha-/\beta-\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot 14\text{H}_2\text{O}$:

In a 1 L beaker, a sample of 125 g (0.38 mol) of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ was dissolved in 250 mL of water and 105 mL (1.545 mol) of orthophosphoric acid (85%) was added. The solution is heated at reflux for 4 h. The greenish coloration can be removed by addition of a few drops of nitric acid to the hot solution. After cooling, 50 g of ammonium chloride was added, and the solution was stirred for 10 min. The pale-yellow salt was removed by filtering, redissolved in 50 mL of water, and precipitated again with 13 g of ammonium chloride. After stirring for 10 min, filtration through a coarse frit, and suction, the precipitate was redissolved in 125 mL of warm water (-45 °C). Potassium chloride (20 g) was added to the cold solution, the potassium salt was removed by filtration and then dissolved in 125 mL of hot water (80 °C). On slow cooling to 15 °C, the by-product of white needles of triacontatungstopentaphosphate was removed by filtration. The filtrate was treated directly with 15 g of potassium chloride. The precipitate was filtered again and dried for 1 day. Yield: 82 g (80%).

Step 2: Synthesis of potassium $\alpha$-dodecatungstodiphosphate, $\text{K}_{12}[\alpha-\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]\cdot 24\text{H}_2\text{O}$:
In a 1 L beaker, a sample of 4 g (8.5 x 10^{-3} mol) of K_6[\alpha-/\beta-P_2W_{18}O_{62}]\cdot 14H_2O was dissolved in 150 mL of water, and a solution of 48.4 g (0.2 mol) of tris(hydroxymethyl) aminomethane in 100 mL of water was added. The solution was left at room temperature for 30 min and then 40 g of potassium chloride was added. After complete dissolution, a solution of 27.7 g (0.4 mol) of potassium carbonate in 100 mL of water was added. The solution was vigorously stirred for 15 min, and the white precipitate that appears after a few minutes was filtered on a coarse sintered glass frit, dried under suction for 20 min, washed with 50 mL of ethanol for 2 to 3 min and air-dried under suction, washed again with ethanol and dried under suction, and finally, air dried for 1 day. Yield: 60 g (89%).

Step 3: Synthesis of potassium lithium octatetraacontatungstooctaphosphate, K_{28}Li_5[H_7P_8W_{48}O_{184}]\cdot 92H_2O:

In 950 mL of water were dissolved, successively, 60 g (1 mole) of glacial acetic acid, 21 g (0.5 mol) of lithium hydroxide, 21 g (0.5 mol) of lithium chloride, and 28 g (7 x 10^{-2} mol) of K_{12}[\alpha-H_2P_2W_{12}O_{48}]\cdot 24H_2O. The solution was left in a closed flask. After 1 day, white needles appear and crystallization continues for several days. When a week has passed, the crystals were collected by suction filtration on a coarse frit and air dried. Yield 9 g (34%).

2.3.2 Synthesis of K_{11}Li_9(NH_4)_4[Ga_{16}(OH)_{32}(P_8W_{48}O_{184})]\cdot 112H_2O

A sample of Ga(NO_3)_3 (0.3 mmol, 76.8 mg) was dissolved in LiCH_3COO/CH_3COOH buffer (2 M, 9 ml) at pH 5. Then a sample of K_{28}Li_5[H_7P_8W_{48}O_{184}]\cdot 92H_2O (6 \mu mol, 90 mg) was added to the above solution. The mixture was vigorously stirred at 80 °C for 60
hours. After cooling to room temperature, the filtrate was layered with NH₄Cl (1M, 10 drops) solution. Slow evaporation in an open vial at room temperature resulted in rod-shaped, colorless crystals after about four weeks, which were then collected by filtration, washed with cold water and air dried. Yield: 0.026 g (27% based on \{P₈W₄₈\}).

2.3.3 Synthesis of [2+2] Macrocycle

In a 100 mL double neck round flask, (1R,2R)-(-)-1,2-Diamino- cyclohexane ( 0.2 g, 1.75×10⁻³ mol) was dissolved in 20 mL MeOH. 2,6-Pyridinedicarboxaldehyde was then added (0.235 g, 1.75×10⁻³ mol) to the mixture and 0.609 mL of triethylamine was added dropwise. After the whole mixture was stirred overnight at room temperature, in an ice bath, 200 mg of sodium borohydride was slowly added and stirred for 4 hours. After that, the mixture was rotatory evaporated and washed with acetonitrile several times and finally vacuum dried to get a white colored product. Yield: 52% ¹H NMR (500 MHz, DMSO-d₆) δ 8.5 (s, 2H, CHar), 7.31 (q, 6H, CHar), 6.65 (s, 1H), 4.25 (dd, 4H, methylene), 3.88 (dd, 4H, methylene), 2.27 (d, 4H, H-N), 1.75 (d, 4H, CH-N), 1.22 – 1.11 (m, 8H). (Figure 13).

2.3.4. Synthesis of \{P₈W₄₈\} & [2+2] Macrocycle

We prepared the mixture in two different concentrations that will be written separately. 1) In a vial, [2+2] macrocycle (20 mg, 0.046 mmol) was dissolved in 5 mL of H₂O. After complete dissolution, K₂₈Li₅[H₇P₈W₄₈O₁₈₄] ·92H₂O crystals (30 mg, 0.0021 mmol) in LiCl (3 mL, 1M), was added drop wise to form a white precipitate (solution concentration (2.63×10⁻⁴ mmol/mL). ¹H NMR (500 MHz, DMSO-d₆) δ 8.41 (s), 8.17 (s), 7.50-6.85
2) In a vial, [2+2] macrocycle (20 mg, 0.046 mmol) was dissolved in 50 mL of H$_2$O. After complete dissolution, K$_{28}$Li$_5$[H$_7$P$_8$W$_{48}$O$_{184}$] ·92H$_2$O crystals (30 mg, 0.0021 mmol) in LiCl (3 mL, 1M), was added drop wise to form a white precipitate (Solution Concentration (3.96×10$^{-5}$ mmol/mL). $^1$H NMR (500 MHz, DMSO-d$_6$) δ 8.46 (s), 7.40 (s, 1H), 8.13 (s), 7.56-6.91 (m), 5.76 (s), 4.60-3.76 (m), 2.25-2.01 (m), 1.84-1.60 (m), 1.38-0.80 (m).

Figure 13. Synthesis of [2+2] macrocycle.
Chapter 3

Group IIIAGuest in \{P_8W_{48}\} Archetypal Polyoxotungstate Host: Catalytic Prospects via Metal-Oxo Cluster within Cluster Assemblies

3.1 Introduction and Literature Review

POMs represent a unique class of discrete anionic metal oxide nanoclusters,\textsuperscript{[10]} with fascinating properties such as redox behavior, oxidative stability, tunable acidity and impressive sensitivity to electricity and therefore, found to be divergent in use of medicine, material science, magnetism, electro/photochemistry, and most notably catalysis.\textsuperscript{[11]} Amongst all POMs, the superlacunary cyclic 48-tungsto-8- phosphate, \([P_8W_{48}O_{184}]^{40-}\) is of particular interest, bearing attractive features such as a) stability over a large range pH (1-8), which has been reported as one of the most attractive and stable POMs to date. b) its internal central cavity of diameter of 1 nm size with 16 donor oxygens that has been reported as the most reactive sites of \{P_8W_{48}\}.\textsuperscript{[48]} All of these have resulted in an inorganic molecular container that allows for encapsulation of a variety of guest metal-oxo clusters, of which the number of metallic centers could be larger than 10. Although this compound was known over many years in 1985, only in 2005, the first example of transition metal incorporated \{P_8W_{48}\} was isolated by Kortz and co-workers.\textsuperscript{[57]} The reason behind why the cluster \{P_8W_{48}\} has been neglected all over the years was largely attributed to the conclusion that Contant and Tézé came with, in 1985 which says that the \([P_8W_{48}O_{184}]^{40-}\) “does not give complexes with divalent or trivalent transition metal ions”.\textsuperscript{[34]} Twenty years later, in 2005, this conclusion has been faded away when Kortz et al. reported the first TM-substituted \{P_8W_{48}\} structure, incorporating
a 20-copper-hydroxo cluster in the cavity of \{P_8W_{48}\} to give the final cluster of 
[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-} and therefore, proving that this cyclic super-
lacunary polyanion can be used as a precursor, by a simple one-pot reaction with Cu^{2+} ions in an aqueous lithium acetate buffer.[^57] (Figure 14a). Since this discovery, several derivatives of the wheel-shaped \{P_8W_{48}\} has been explored over the years including the azido derivative of the Cu-containing \{P_8W_{48}\} reported by Mialane and coworkers in 2007, with a structure of [P_8W_{48}O_{184}Cu_{20}(N_3)_{16}(OH)_{18}]^{24+}, where the presence of a large excess of N_3^- is providing remarkable stability to the cluster.[^58] (Figure 14b). In the same year, the introduction of early lanthanides to the wheel-shaped \{P_8W_{48}\} has been reported by Pope et al, with a structure of \{Ln_4(H_2O)_{28}[K⊂P_8W_{48}O_{184}(H_4WO_{12})_2Ln_2(H_2O)_{10}]^{13-}\}_{x} (Ln = La, Ce, Pr, Nd).[^59] (Figure 14c). Also the generation of magnetically interesting mixed valence vanadium species [K_8{P_8W_{48}O_{184}}{V^V\cdot V^IV_2(OH)_{2}}_{2}]^{24-} was successfully synthesized by Müller and Pope.[^60] (Figure 14d). In the same year, Kortz et al. reported the first organometallic derivative \{[[K(H_2O)]_3{Ru(p-cymene)(H_2O)}]_4P_8W_{49}O_{186}-(H_2O)_2\}^{27-} with the catalytically active ruthenium metal.[^61] (Figure 14e). In 2008, The Fe_{16}-containing [P_8W_{48}O_{184} Fe_{16}(OH)_{28}(H_2O)_4]^{20-} has been synthesized by Kortz, Müller and co-workers. Which is different from the other TM-containing \{P_8W_{48}\} in a way that it still has a central cavity that could be interestingly filled with additional metal centers and thus leading to interesting magnetic and catalytic properties.[^62] (Figure 14f). In 2009, the first \{P_8W_{48}\} based-frameworks was introduced by Cronin et al., by careful control of the reaction conditions, Cronin was able to obtain his Co(II)-substituted \{P_8W_{48}\}, decorated with Co(II) inside the cavity and most
importantly on the outer surface and thus linking the \{P_8W_{48}\} units into 1D chains and 3D frameworks.\cite{63} (Figure 14g).

Figure 14. Polyhedral representation of different TMSP. a) Cu$_{20}$-P$_8$W$_{48}$. b) Cu$_{20}$-azido-P$_8$W$_{48}$. c) Lanthanide-P$_8$W$_{48}$. d) Mixed valence vanadium-P$_8$W$_{48}$. e) Ru($\mu$-cyrene)-P$_8$W$_{48}$. f) Fe$_{16}$-P$_8$W$_{48}$. g) Co-P$_8$W$_{48}$.

However, besides $d$ and $f$ block elements, the reactivity of group IIIA metals towards \{P$_8$W$_{48}$\} is still unexplored. Specifically, Al$^{\text{III}}$, Ga$^{\text{III}}$, and In$^{\text{III}}$ metal ions have been widely used in catalysis for many organic transformation reactions.\cite{64} Notably, compared with $d$ and $f$ block elements, only a limited number of Al$^{\text{III}}$,\cite{65} Ga$^{\text{III}}$\cite{66} and In$^{\text{III}}$\cite{67} containing POMs have been synthesized and structurally characterized, this might be attributed to the strong hydrolysis of Al$^{\text{III}}$, Ga$^{\text{III}}$, and In$^{\text{III}}$ ions, resulting in a pronounced influence on the reaction pH, which will, in turn, complicates the pH-dependent POM systems. In addition, with highly positive charge and small ionic radius, Al$^{\text{III}}$ and Ga$^{\text{III}}$ ions may prefer to stay as external counter cations rather than react with POM directly. It is worth to mention that, by far, most of the reported Al$^{\text{III}}$, Ga$^{\text{III}}$ and In$^{\text{III}}$ containing POMs display
space-limited, sandwich-type structural modes that restrict the number of incorporated $\text{Al}^{\text{III}}$, $\text{Ga}^{\text{III}}$, and $\text{In}^{\text{III}}$ ions to form large $\text{Al}^{\text{III}}$, $\text{Ga}^{\text{III}}$ and $\text{In}^{\text{III}}$ oxo clusters. To overcome these, we think that the super-vacant, wheel-shaped phosphotungstate $[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]^{33-}$ \{P$_8$W$_{48}$\} would be a good candidate for the previously mentioned reasons, 1) solution stable within an unusual large pH window from 1 to 8; 2) an inherent central cavity (diameter of ca. 1 nm) with available space for chemical modification; 3) rigid backbone with size in the nanometer regime) and up to now, the reactivity of group IIIA metals toward \{P$_8$W$_{48}$\} is still unexplored, where the growth of “Metal-Oxo Cluster within Cluster” aggregates could be envisioned. The first $\text{Al}^{\text{III}}$ containing-\{P$_8$W$_{48}$\} has been successfully isolated by Dr. Peng Yang, which comprises the largest $\text{Al}^{\text{III}}$ containing-POM with 16 $\text{Al}^{\text{III}}$ centers inside the cavity of the \{P$_8$W$_{48}$\} container. In this work, we aim to test the reactivity of $\text{Ga}^{\text{III}}$ and $\text{In}^{\text{III}}$ metals toward \{P$_8$W$_{48}$\}. The work has been extended toward testing the catalysis of the previously isolated \{Al$_{16}$-P$_8$W$_{48}$\} in an oxidation of thioether reaction. Since Aluminum is cheaper, and the industrialized catalysts should be cost-effective. Will be discussed in section 3.3.

3.2 Results and Discussion

3.2.1 \{P$_8$W$_{48}$\}

The precursor $\text{K}_{28}\text{Li}_5[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]\cdot 92\text{H}_2\text{O}$ was synthesized according to the published procedure of Contant as mentioned in section 2.3.1, and the structural information has been provided by FT-IR, and Mass Spectrometry. Figure 15 represents the FT-IR spectrum as transmittance (%) as a function of wavenumber (cm$^{-1}$).
Figure 15. FT-IR spectrum of \{\text{P}_8\text{W}_{48}\}. a) \text{K}_6[\text{P}_2\text{W}_{18}\text{O}_{62}].14\text{H}_2\text{O}. b) \text{K}_{12}[\alpha-\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}].24\text{H}_2\text{O}. c) \text{K}_{28}\text{Li}_5[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}] \cdot 92\text{H}_2\text{O}

3.2.1.1 ESI-TOF-MS of \{\text{P}_8\text{W}_{48}\}

ESI-TOF-MS has been performed to confirm the atomic mass unit of the sample. From Figure 16, you can see the mass spectrum as mass to charge ratio as a function of intensity, which represents the simulated mass of \text{K}_{28}\text{Li}_5[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}] \cdot 92\text{H}_2\text{O} to be 12163.9304 a.m.u. but from Figure 17, the actual mass cannot be found, this might be attributed to the solubility issue of the compound as it dissolves in \text{Li}^+\text{-containing aqueous solution only and may be unstable during the ionization process.}
Figure 16. Simulated ESI-TOF-MS of \{P_{8}W_{48}\}

Figure 17. ESI-TOF-MS of \{P_{8}W_{48}\}
3.2.2 \( \{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\} \)

\( \{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\} \) has been prepared as mentioned in section 2.3.2. Crystal obtained has been characterized with different techniques as will be discussed in the following sections. The colorless, rod-shaped crystals can be easily seen and they blur beautifully upon applying light as shown in (Figure 18a). (Figure 18b) is a microscopic image of the obtained crystal, it shows a flower-like pattern.

![Figure 18](image)

Figure 18. \( \{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\} \) crystals. a) Pictures of crystals without and with light; b) Microscopic image of the latter crystal.

3.2.3 SXRD of \( \{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\} \)

Single crystal XRD revealed that the inner rim of \( \{\text{P}_8\text{W}_{48}\} \) has been decorated with a cationic nanoscale Ga\textsuperscript{III}-oxo-cluster built up by 16 GaO\textsubscript{6} units, leading to a pseudo-\( D_{4h} \) symmetry. Figure 19 and Figure 20. The incorporated “Ga\textsubscript{16} ring” is composed of eight pairs of structurally equivalent, edge-shared GaO\textsubscript{6} octahedra that are interconnected via corners. Each of the 16 Ga\textsuperscript{III} centers is bound to \( \{\text{P}_8\text{W}_{48}\} \) by a Ga–O(W) and a Ga–O(P)
bond, resulting in a tight anchoring of the 16-Ga\textsuperscript{III}-32-oxo core. The bond distances of Ga–O fall in the range of 1.896(5) – 2.068(5) Å and the corresponding Ga–O–Ga angles are in the range of 96.4(2)° – 143.9(3)°. The H atoms of the crystal waters were not located. It was not possible to localize all cations by X-ray diffraction studies probably due to the severe crystallographic disorder, which is a common problem in POM crystallography. Therefore, the exact number of counter cations and crystal water contents in the formulas were determined by elemental analysis.

Figure 19. Ball-and stick-representation of [Ga\textsubscript{16}(OH)\textsubscript{32}(P\textsubscript{8}W\textsubscript{48}O\textsubscript{184})]\textsuperscript{24−}. Color code: W, black.; P, blue; Ga, green; O, red; OH, pink.
Figure 20. Polyhedral representation of \([\text{Ga}_{16}(\text{OH})_{32}(\text{P}_5\text{W}_{48}\text{O}_{184})]\)\(^{24-}\). Color code: WO\(_6\), red octahedra; PO\(_4\), blue tetrahedra; Ga, green; O, red; OH, pink.
Table 1. Crystal data and structure refinement for Ga\textsubscript{16}-P\textsubscript{8}W\textsubscript{48}.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>$K_{11}Li_{9}Ga_{16}P_{8}W_{48}H_{272}N_{4}O_{328}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight, g/mole</td>
<td>16258.84</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>15.5558(12)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>19.8832(16)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>21.2896(17)</td>
</tr>
<tr>
<td>$\alpha$, °</td>
<td>98.369(3)</td>
</tr>
<tr>
<td>$\beta$, °</td>
<td>99.707(3)</td>
</tr>
<tr>
<td>$\gamma$, °</td>
<td>91.050(3)</td>
</tr>
<tr>
<td>Volume, Å\textsuperscript{3}</td>
<td>6415.3(9)</td>
</tr>
<tr>
<td>$Z$</td>
<td>1</td>
</tr>
<tr>
<td>$D_{calc}$, g/cm\textsuperscript{3}</td>
<td>4.208</td>
</tr>
<tr>
<td>Absorption coefficient, mm\textsuperscript{-1}</td>
<td>23.447</td>
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<tr>
<td>$F(000)$</td>
<td>7328</td>
</tr>
<tr>
<td>Theta range for data collection, °</td>
<td>2.155 to 28.314</td>
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<td>Completeness to $\Theta_{max}$</td>
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<tr>
<td>Index ranges</td>
<td>$-20\leq h \leq 20$, $-26\leq k \leq 26$, $-28\leq l \leq 28$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>403735</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>31857</td>
</tr>
<tr>
<td>$R$(int)</td>
<td>0.0360</td>
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<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>31857 / 0 / 1489</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.021</td>
</tr>
<tr>
<td>$R_1$, [a] $wR_2$ [b] ($I &gt; 2\sigma(I)$)</td>
<td>$R_1 = 0.0300$, $wR_2 = 0.0906$</td>
</tr>
<tr>
<td>$R_1$, [a] $wR_2$ [b] (all data)</td>
<td>$R_1 = 0.0331$, $wR_2 = 0.0936$</td>
</tr>
<tr>
<td>Largest diff. peak and hole, e/Å\textsuperscript{3}</td>
<td>5.541 and -2.359</td>
</tr>
</tbody>
</table>

[a] $R_1 = \Sigma||F_o|| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. 
Figure 21. Perspective views of the crystal packing mode of \{Ga_{16}-P_8W_{48}\}

3.2.4 Bond Valence Sum of \{Ga_{16}-P_8W_{48}\}

Bond valence sum (BVS) calculations have confirmed that, most of Ga–O–Ga bridges are monoprotonated, yielding a \{Ga_{16}(OH)_{32}\}^{16+} oxo-cluster (Table 2 Figure 22 and).\textsuperscript{[68]}

Table 2. Bond valence sum values for different structural types of oxygen atoms in the 16-Ga\textsuperscript{III}-32-oxo clusters.

<table>
<thead>
<tr>
<th>16-Ga\textsuperscript{III}-32-oxo cluster</th>
<th>(\mu_2)-O (Ga–O–Ga)</th>
<th>BVS value</th>
<th>(\mu_2)-O (Ga–O–Ga)</th>
<th>BVS value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2G1</td>
<td>0.959</td>
<td>O2G4</td>
<td>0.944</td>
<td></td>
</tr>
<tr>
<td>O3G1</td>
<td>1.157</td>
<td>O3G4</td>
<td>1.143</td>
<td></td>
</tr>
<tr>
<td>O4G1</td>
<td>1.268</td>
<td>O2G5</td>
<td>1.280</td>
<td></td>
</tr>
<tr>
<td>O5G1</td>
<td>1.168</td>
<td>O3G5</td>
<td>1.159</td>
<td></td>
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<tr>
<td>O2G2</td>
<td>1.251</td>
<td>O2G6</td>
<td>1.260</td>
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<td>O2G3</td>
<td>1.141</td>
<td>O1G7</td>
<td>1.159</td>
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</tr>
<tr>
<td>O3G3</td>
<td>0.969</td>
<td>O3G7</td>
<td>0.950</td>
<td></td>
</tr>
<tr>
<td>O4G3</td>
<td>1.145</td>
<td>O4G7</td>
<td>1.135</td>
<td></td>
</tr>
</tbody>
</table>
3.2.5 $^{31}$P and $^{71}$Ga NMR of $\{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\}$

Due to the poor aqueous solubility of $\{\text{Ga}_{16}-\text{P}_8\text{W}_{48}\}$ compound, the multinuclear solid-state MAS NMR ($^{31}$P and $^{71}$Ga) measurements have been applied to provide further structural information. The $^{31}$P MAS NMR spectrum exhibits a single peak at $-5.1$ ppm. (Figure 23a). As expected, $^{71}$Ga MAS NMR spectrum shows a singlet centered at 18.5
ppm. (Figure 23b). The slightly asymmetrical distribution of the peak could be assigned to the distorted hexa-coordination environment of the Ga\textsuperscript{III} ions. As outlined above, NMR results are in full agreement with their solid-state structures seen by single crystal XRD.

![Figure 23](image)

Figure 23. \textsuperscript{31}P (a) and \textsuperscript{71}Ga (b) MAS NMR spectra of \{Ga\textsubscript{16}-P\textsubscript{8}W\textsubscript{48}\}

### 3.2.6 FTIR Spectroscopy of \{Ga\textsubscript{16}-P\textsubscript{8}W\textsubscript{48}\}

The identity of \{Ga\textsubscript{16}-P\textsubscript{8}W\textsubscript{48}\} has been confirmed by FT-IR (2% KBr pellet, v/cm\textsuperscript{-1}): 1628 (s), 1404 (s), 1211 (w), 1072 (s), 1022 (w), 930 (m), 833 (m), 760 (s), 650 (s), 463 (w). It clearly shows a different fingerprint from the parent \{P\textsubscript{8}W\textsubscript{48}\} (Figure 24). Figure 25 shows a closer insight into the fingerprint area.
Figure 24. FT-IR spectra of Ga\textsubscript{16}-P\textsubscript{8}W\textsubscript{48}. a) K\textsubscript{11}Li\textsubscript{9}(NH\textsubscript{4})\textsubscript{4}[Ga\textsubscript{16}(OH)\textsubscript{32}(P\textsubscript{8}W\textsubscript{48}O\textsubscript{184})]\cdot 112H\textsubscript{2}O. b) K\textsubscript{28}Li\textsubscript{5}[H\textsubscript{7}P\textsubscript{8}W\textsubscript{48}O\textsubscript{184}]\cdot 92H\textsubscript{2}O

Figure 25. FT-IR spectrum of \{Ga\textsubscript{16}-P\textsubscript{8}W\textsubscript{48}\}
3.2.7 Elemental Analyses of \{Ga_{16}-P_{8}W_{48}\}

The Elemental analysis (%) of K\textsubscript{11}Li\textsubscript{9}(NH\textsubscript{4})\textsubscript{4}[Ga\textsubscript{16}(OH)\textsubscript{32}(P\textsubscript{8}W\textsubscript{48}O\textsubscript{184})]\cdot 112\textsubscript{2}O is N 0.27, K 2.51, Li 0.43, Ga 6.87, P 1.57, W 54.36. which is in a good agreement with the calculated Elemental analysis (%): N 0.34, K 2.65, Li 0.38, Ga 6.86, P 1.52, W 54.28.

3.2.8 UV Spectrum of \{Ga_{16}-P_{8}W_{48}\}

![UV spectrum](image)

Figure 26. UV-vis spectrum of \{Ga_{16}-P_{8}W_{48}\}

In 1 M LiCl solution (sample concentration of 3.0 \times 10^{-6} M). The absorption band at 210 nm could be attributed to the p\pi-d\pi charge-transfer transitions of the O\rightarrow W band, and the peaks centered at 275 nm could be assigned to the overlap of p\pi-d\pi charge-transfer
transitions of the $O_{b,c} \rightarrow W$ bands and the electronic transition between HOMO and LUMO of the oligomeric Ga$^{III}$-oxo species. (Figure 26)[69]

3.2.9 TGA of $\{Ga_{16}-P_8W_{48}\}$

Figure 27. Thermogram of $\{Ga_{16}-P_8W_{48}\}$ from 20 to 800 °C under N2 atmosphere.

Figure 27 shows TGA thermogram which indicates the weight loss as a function of temperature. The temperature was ramped from 20 °C to 800 °C at a rate of 5 °C min$^{-1}$. At 205°C, the crystal water decomposes which indicates the presence of water crystals.
within our cluster. At 565°C, the organic constituents decompose, which matches with the existence of NH$_4^+$ counterparts.

### 3.3 Catalysis of \{Al$_{16}$-P$_8$W$_{48}$\}

#### 3.3.1 Thioether Oxidation Reaction

A mixture of K$_8$Na$_3$Li$_5$\{[Na(NO$_3$)(H$_2$O)$_4$][Al$_{16}$(OH)$_{24}$(H$_2$O)$_8$(P$_8$W$_{48}$O$_{184}$)]\}·66H$_2$O (50 mg, 3.33 µmole), Hydrogen peroxide (1.02 mL, 0.01 mol) and dimethyl sulfide (0.73 mL, 0.01 mol) has been stirred in dichloromethane (10 mL) at 30 ºC for 6 hrs. The product was monitored by GC-MS and $^1$H NMR.

![Figure 28. Proposed catalytic reaction](image)

#### 3.3.2 Catalytic Results

We tracked the product every 30 minutes using GC-MS. According to GC-MS, the reaction seemed to be completed at 30 minutes. GC-MS give only two signals, which belong to DCM and Methylsulfonylmethane ((CH$_3$)$_2$SO$_2$) or DMSO$_2$, without any DMS, as shown in (Figure 29). However, NMR results at the same time (30 min), has indicated the presence of DMS as shown in (Figure 30). NMR results seem to be more accurate, thus we continue to monitor all the reactions using NMR.
Figure 29. GC-Mass spectra of a) Dichloromethane and b) methylsulfonylmethane

Figure 30. NMR spectrum of the product. Red: DMS; Green: DMSO2
The following $^1$H NMR spectra in (Figure 31a-d) are representing the monitored reaction product starting from 10 minutes until 2 hours. Figure 31 (a) shows NMR spectrum of the reaction product at 10 minutes: $^1$H NMR (500 MHz, Chloroform-$d$) δ 5.31 (s), 2.99 (s, 6H), 2.13 (s, 6H). With increasing time until 30 minutes, the signal of (DMSO$_2$) is getting stronger and stronger until 2 hours and the signal of DMS is getting weaker and we can observe the existence of dimethyl sulfoxide (DMSO) with a very weak signal at δ 2.85. Figure 31 (b, c, and d).

Figure 31. NMR spectrums of the reaction product after a) 10 min; b)30 min; c) 1 hour; d) 2 hours. Red: DMS; Green: DMSO$_2$

The next step was to run the same reaction without using our catalyst $\{Al_{16}-P_8W_{48}\}$, with using only $H_2O_2$ as an oxidant, in order to test the oxidation ability of our catalyst.
Figure 32. Catalytic reaction without \{Al_{16}-P_{8}W_{48}\} catalyst.

\[
\begin{align*}
\text{H}_3\text{C} & \xleftarrow{1. \text{H}_2\text{O}_2}\text{CH}_3 \\
 & \text{DCM, 30\degree C, 6 hrs} \\
\text{H}_3\text{C} & \xrightarrow{} \text{CH}_3
\end{align*}
\]

Figure 33. NMR spectrums of the reaction product without \{Al_{16}-P_{8}W_{48}\} catalyst. Reaction after a) 30 min; b) 1 hour; c) 2 hours; d) 5 hours; e) 6 hours. Red: DMS; blue: DMSO
As we did for the first reaction, we monitored the reaction product by $^1$H NMR. The following NMR spectrums are representing the monitored reaction product starting from 30 minutes until 6 hours. Figure 33 (a-e). Figure 33 (a) shows the NMR spectrum of the reaction product after 30 minutes: $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 5.31 (s), 2.60 (s,6H), 2.10 (s, 6H). We can observe that without using our catalyst $\{\text{Al}_{16}\text{P}_8\text{W}_{48}\}$, the product is only DMSO, and the signal is getting stronger with time until 6 hours as the signal of DMS is getting weaker. Figure 33 (b-e).

### 3.4 Conclusions and Outlook

For section 3.2, we have successfully isolated $\text{K}_{11}\text{Li}_9(\text{NH}_4)_4[\text{Ga}_{16}(\text{OH})_{32}(\text{P}_8\text{W}_{48}\text{O}_{184})] \cdot 112\text{H}_2\text{O}$ and confirmed its structure using various techniques. The as-made POM represents the discrete assembly containing the largest number of Ga$^{\text{III}}$ ions yet found in POM chemistry. Besides, it contains an interesting cavity of the diameter of 0.6 nm, which could pave the way for host-guest chemistry to incorporate other metal cations inside the cavity, such work is underway in our lab.

For section 3.3, we concluded the following: 1) our catalyst $\{\text{Al}_{16}\text{P}_8\text{W}_{48}\}$ has a strong oxidant ability based on our observation that it could directly oxidize DMS to DMSO$_2$ at low temperature. So we can push it for other oxidation reactions like oxidation of alcohols to give formaldehyde or carboxylic acid. 2) We need to increase the reaction temperature and see if we could get better results. 3) H$_2$O$_2$ is expensive and we might replace it with O$_2$. 
Chapter 4

Inorganic-Organic Hybrid Hydrophilic Assemblies in Aqueous Solutions: Investigate the Assembly of the Wheel-Type \{P_8W_{48}\} Macroion with Organic Macrocycle

4.1 Introduction and Literature Review

For inorganic solutes in dilute solutions, it is usually a very quick process to reach the thermodynamic equilibrium state. The simplest example is the quick disappear of NaCl crystals in water, NaCl solution then takes no more than seconds to reach the equilibrium. For larger systems like organic macromolecules, considering their size they expectedly take a little bit longer, but usually no more than hours.[70] One example is the micellization of block polymers in solution.[71] On the other hand, it is unusual to take months to reach the thermodynamic equilibrium state in dilute solutions. This phenomenon has been first observed in 2001 by Achim Müller et al for soluble inorganic ions like Mo_{154} blue POMs in aqueous solutions.[72] These supramolecular structures have been proved as hollow, spherical, “blackberry”-like vesicles in solution, via using dynamic and static light scattering techniques (DLS and SLS) by Tianbo Liu in 2002.[73] The slow process of the blackberry formation is mainly attributed to the high energy barrier needed for the transformation from single macroions to blackberries.[74] The absences of the hydrophobic region which is responsible for the formation of surfactant vesicles, has resulted in the formation of blackberries (hydrophilic inorganic macroions fully covered with water ligands).[75] The electrostatic interaction has been reported as the major driving force for the blackberry formation, which is attributed to the disparity in
Ionic size and charge density between small cations and large macroanions.\textsuperscript{[76]} Beside {Mo\textsubscript{154}}, other types of POMs have been also reported with the same solution behavior like {Mo\textsubscript{132}},\textsuperscript{[76]} {Mo\textsubscript{72}Fe\textsubscript{30}},\textsuperscript{[77]} {Mo\textsubscript{72}V\textsubscript{30}},\textsuperscript{[78]} {Mo\textsubscript{72}Cr\textsubscript{30}},\textsuperscript{[79]} {P\textsubscript{8}W\textsubscript{48}Cu\textsubscript{20}},\textsuperscript{[80]} {Mo\textsubscript{368}}\textsuperscript{[81]} and {P\textsubscript{4}Y\textsubscript{8}W\textsubscript{43}}.\textsuperscript{[82]} This phenomena has not been restricted to POMs only, since other types of macroions besides POMs have been reported with a similar phenomenon, like metal-organic hybrid nanocages,\textsuperscript{[83]} carboxylic acid-functionalized hydrophilic fullerene,\textsuperscript{[84]} γ-cyclodextrin\textsuperscript{[85]} and poly(propyleneimine) dendrimers.\textsuperscript{[86]} Hybrid structures have been also reported to form blackberries under conditional design in which POMs are the dominant part in the structure, otherwise, the hydrophobic interaction will take place and form surfactants.\textsuperscript{[87][88]} In this work, we assume that the combination of the large negative inorganic wheel {P\textsubscript{8}W\textsubscript{48}} and the small organic cation in solution would be interesting. Considering that they are both hydrophilic and there is a disparity in size between the two moieties, it is possible that they would form blackberries like the represented design. (Figure 34).

Figure 34. Illustration of the anticipated blackberry structure
4.2 Results and Discussion

4.2.1 \( P_8W_{48} \& [2+2] \) Macrocycle

The latter material has been synthesized as mentioned in experimental chapter section 2.2.3, with two different concentrations \((2.63 \times 10^{-4} \text{ mmol/mL} \) and \(3.96 \times 10^{-5} \text{ mmol/mL}\), a white precipitate has formed from both concentrations. (Figure 35).

![Figure 35. Precipitate formation. a) 2.63×10^{-4} mmol/mL. b) 3.96×10^{-5} mmol/mL](image)

**4.2.2 DLS of \( \{P_8W_{48}\} \&[2+2] \) Macrocycle**

The latter precipitate has been shaken. 1 mL of the shaken solution has been transferred to a SQUARE cell and a folded capillary cell for DLS measurements. Zetasizer software has been used to run the sample at 25°C with water as a dispersant and 90° scattering
angle. Figure 36 represents DLS results for the first concentration $2.63 \times 10^{-4}$ mmol/mL. Size in (nm) on the left, zeta potential on the right as a function of time.

At different times from 10 min until overnight, size and zeta potential has been measured respectively as the following: 2000±394.3 nm, -13.4±3.39 at 10min; 2053±483.9 nm, -16.4±2.98 at 20min; 2113±509 nm, -11.5±2.68 at 30min; 1692±529 nm, -14.9±2.63 after 1 hour; 1958±614.4 nm, -13.3±3.06 after 2 hours; 1728±513.7 nm, -15±2.95 after 6 hours and 2042±556.6 nm, -11.6±2.56 after overnight. The following graphs are the sizes and zeta potential of the starting materials. (Figure 37).
Figure 37. a) Zeta potential for starting materials. Red bar: \{P_8W_{48}\}; blue bar: [2+2] Macrocycle. b) Size of \{P_8W_{48}\}. c) Size of [2+2] Macrocycle

Figure 38 represents DLS results for the second concentration $3.96 \times 10^{-5}$ mmol/mL. With different times from 10 min until overnight, size and zeta potential has been measured respectively as the following: 2617±870.3 nm, -20.4±3.16 at 10min; 2487±621.9 nm, -19±3.46 at 20min; 2510±740.1 nm, -20.1±3.09 at 30min; 2313±674.8 nm, -22.1±3.34 after 1 hour; 2123±544 nm, -21.4±3.07 after 2 hours; 2455±786.2 nm, -22±3.25 after 6 hours and 2283±502.8 nm, -25.8±3.56 after overnight. (Figure 38).
Figure 38. DLS measurements for \( \text{P}_8\text{W}_{48} \) & [2+2] Macrocycle (3.96×10^{-5} mmol/mL).

Blackberry structures have their size in the nanometer region. However, DLS results have shown a size range in the micrometer, which indicates the formation of particles other than blackberry assemblies.

**4.2.3 TEM of \( \text{P}_8\text{W}_{48} \) & [2+2] Macrocycle**

The morphology of the products of both concentrations (2.63×10^{-4} mmol/mL and 3.96×10^{-5} mmol/mL) were observed by TEM images that have been collected in a transmission electron microscope.
Figure 39. TEM images of the product. (2.63×10^-4 mmol/mL).

Figure 40. TEM images of the product. (3.96×10^-5 mmol/mL).
From Figure 39, TEM images show no specific morphology that indicates no blackberry formation. Even when the mixture solution is diluted to $3.96 \times 10^{-5}$ mmol/mL, the morphology of the structure is still indefinable (Figure 40). From TEM results we can confirm that our system didn’t form a blackberry structure. Figure 41 represents TEM images of the starting materials.

### 4.2.4 FTIR Spectroscopy of $\{P_8W_{48}\}$ & [2+2] Macrocycle

The C-H stretching and bending of the macrocycle is present in the spectrum, FT-IR (2% KBr pellet, v/cm$^{-1}$): 2933 (w), 2856 (w), 1448 (m), 1376 (w), 1343 (w); and the N-H stretching and bending as well, FT-IR (2% KBr pellet, v/cm$^{-1}$): 3194 (w), 1595 (m). Also
the O-H scissorring vibration of the \( \{P_8W_{48}\} \) (1656 (m)) is present in the product spectrum, that’s why we have a broad band at (1595-1656 (m), also the C=C stretching of the macrocycle is present within this range). The =C-H stretching and bending of the macrocycle is present in the product spectrum, (FT-IR (2% KBr pellet, \( \nu/cm^{-1} \)): 3054 (w), 687 (s). From the fingerprint area of the product spectrum, it seems that we have a mixture of the starting materials. (Figure 42).

Figure 42. FT-IR spectrum. a) Reaction product. b) \( \{P_8W_{48}\} \). C) [2+2] Macrocyle.
4.2.5 NMR of \{P_8W_{48}\} & [2+2] Macrocycle

From the NMR results, the broad multiplet signal at δ 1.22 – 1.11 (m, 8H,) in (a) spectrum, is becoming broader and broader in spectrum b and c. The doublet signal at δ 1.75 (d, 4H, CH-N) is becoming broader and weaker signal in spectrum b and c. The signal with δ 2.27 (d, 4H, H-N) in spectrum (a) is becoming stronger in both b and c spectrums. The methylene signals 4.25 (dd, 4H, methylene), 3.88 (dd, 4H, methylene) in spectrum (a) are becoming weaker and broader with one doublet in spectrum c and very weak and broad signal in spectrum b. Both b and c spectrums showed two new signals at (b: 8.13 (s), 5.76 (s)) and (c: 8.17 (s) 5.76 (s)). Signal δ 7.31 (q, 6H, CH_ar) in spectrum (a) is becoming broader in both b and c spectrums. Signal at δ 8.5 (s, 2H, CH_ar) in spectrum (a), is becoming broader and weaker in both b and c spectrums. (Figure 43).

Figure 43. NMR spectrum. a) [2+2] Macrocycle. b) 3.96×10⁻⁵ mmol/mL. c) 2.63×10⁻⁴ mmol/mL
NMR results showing a trend of signals broadening of the [2+2] Macrocycle spectrum. The broadening of signals might be coming from the H-bonding. We think that 1D NMR results alone couldn’t give us a clear picture of what is going in between the organic macrocycle and \{P_8W_{48}\}.

The following spectrum is representing 2D $^1$H NMR of the reaction product.

![2D NOISY $^1$H NMR spectrum of the reaction product.](image)

From 2D $^1$H NMR, we think that we’re just providing structural confirmation of the organic macrocycle. All the signals are in correlation with each other to confirm the structure of the organic macrocycle. To confirm that, we ran 2D $^1$H NMR for the [2+2] macrocycle and indeed we can see the macrocycle only. (Figure. 45).
4.2.6 ESI-TOF-MS of \{P_8W_{48}\} & [2+2] Macrocycle

The mass spectrum in (Figure 46) is a plot of relative abundance of the fragments (radical cations) and their m/z (molecular weight). From ESI-TOF-MS spectrum, the dominant signals are for the organic macrocycle and we can observe some fragments with range of 950 m/z that we think it might be fragments from the decomposition of \{P_8W_{48}\}. These results are in a good agreement with NMR and elemental analysis.
Figure 46. ESI-TOF-Mass spectrum of the product.

Figure 47. ESI-TOF-Mass spectrums. Zoomed in signals.
4.3 Conclusions and Outlook

Dynamic light scattering (DLS) and transmission electron microscope (TEM) do not indicate any blackberry formation, as the size of blackberries have been reported to be in the range of 10-100 nm and they have a spherical morphology under TEM and SEM. FT-IR, NMR, and ESI-TOF-MS, all indicate the presence of [2+2] Macrocycle as the dominant particle and showing no sign of combination between [2+2] Macrocycle and \{P_8W_{48}\}.
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