“Polynuclear Transition Metal-Oxo Complexes Stabilized by Heteropolytungstates”

by

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Abstract

This dissertation describes the incorporation of multinuclear transition metal complexes in polyoxometalate (POM) frameworks. In the course of this work we were able to develop a novel, simple and one-pot synthetic strategy for the preparation of high-nuclearity, magnetic transition metal-containing POMs.

This dissertation comprises five chapters. Chapter 1 is a comprehensive introduction to the class of POMs, whereas Chapter 2 describes the most common analytical techniques used in POM synthesis, as well as the synthesis procedures of many different POM precursors. Chapter 3 discusses the eight novel compounds 1-8, which were synthesized and characterized in detail during the course of my doctoral work. The Mn$^{II}$-containing polyanions $[\text{Mn}_{19}(\text{OH})_{12}(\text{SiW}_{10}\text{O}_{37})_{6}]^{34^-}$ (1), $[[\text{Mn} (\text{H}_2\text{O})_3]_2\{\text{Mn}_2(\alpha\text{-GeW}_{10}\text{O}_{38})\}_3]^{20^-}$ (2), and $[[\text{Mn}_3(B-\beta\text{-PW}_{9}\text{O}_{33}(\text{OH})) (B-\beta\text{-PW}_{8}\text{O}_{29}(\text{OH})_2)]_2]^{22^-}$ (3) are hexameric, trimeric, and dimeric structures, respectively. The planar Mn$_{19}$ magnetic core in 1 is unprecedented in POM chemistry, and also represents the highest nuclearity manganese-containing POM to date. The trimeric polyanion 2 is composed of three $\{\alpha\text{-Mn}_2\text{GeW}_{10}\text{O}_{38}\}$ Keggin fragments and two central capping manganese(II) ions. Polyanion 3 is a sandwich-type structure composed of two nonequivalent Keggin subunits, $(B-\beta\text{-PW}_{9}\text{O}_{34})$ and $(B-\beta\text{-PW}_{8}\text{O}_{31})$, as well as three encapsulated Mn$^{II}$ ions. The 16-Co$^{II}$-containing $[[\text{Co}_4(\text{OH})_3\text{PO}_4]_4(A-\alpha\text{-PW}_{9}\text{O}_{34})_4]^{28^-}$ (8) represents the largest cobalt aggregate in polyoxotungstate chemistry, and the first example of a POM-based cobalt-core possessing single molecule magnetic behavior. Polyanion 8 comprises a central $\{\text{Co}_6\text{O}_4\}$ cubane unit which is capped by four tri-Co$^{II}$ substituted Keggin...
fragments \([\text{(Co(OH)}]_3(A-\alpha-PW_9O_{34})\]^{6-}\) and four phosphate linkers, resulting in an assembly with idealized \(T_d\) symmetry.

The tetrameric \(14\text{-Ni}^{II}\)-containing \([(\text{Ni}_{14}(\text{H}_2\text{O})_{10}(\text{OH})_6(\text{PO}_3(\text{OH}))_3(\alpha-\text{P}_2\text{W}_{15}\text{O}_{56})_3)]^{34-}\) (5) is composed of four Wells-Dawson type \{Ni_3P_2W_15\} fragments encapsulating a central dinickel-oxo unit and four capping phosphate groups. Polyon 5 represents the largest nickel aggregate in polyoxotungstate chemistry. The \(5\text{-Ni}^{II}\)-containing \([\text{Ni}_5(\text{H}_2\text{O})_4(\text{OH})_4(\beta-\text{GeW}_9\text{O}_{34})(\beta-\text{GeW}_8\text{O}_{31})]\)\(^{14-}\) (6) is composed of two asymmetric Keggin units, \{β-Ni_3GeW_9O_{34}\} and \{β-Ni_2GeW_8O_{31}\}, whereas the dimeric, sandwich-type polyon \([(\text{NaOH})_2\text{Ni}_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{18-}\) (7) contains a tetranuclear, rhombic core of two central Ni\(^{II}\) ions and two sodium ions. The \(15\text{-Cu}^{II}\)-containing \([(A-\alpha-\text{SiW}_9\text{O}_{34})_3\text{Cu}_{15}\text{O}_4(\text{OH})_8\text{Cl}]^{27-}\) (8) represents the polyon with the second largest copper-oxo-hydroxo core. The magnetic core is stabilized by four capping \{A-α-SiW_9O_{34}\}\(^{10^+}\) units and a chloride ion. The \(Y^{III}\)-containing polyions \([\{\text{Y}(\text{H}_2\text{O})(\text{B-}\alpha-\text{H}_2\text{SbW}_9\text{O}_{33})\}_3(\text{CH}_3\text{COO})_3(\text{WO}_4)]^{17-}\) (9a) and \([\{\text{Y}(\text{H}_2\text{O})_3\}_8(\text{As}_2\text{W}_{19}\text{O}_{68})_3(\text{As}_2\text{W}_{19}\text{O}_{68})(\text{W}_2\text{O}_6)_2(\text{WO}_6)]^{43-}\) (10) have also been synthesized and structurally characterized. Polyon 9a is composed of three \{α-SbW_9O_{33}\} units linked by three Y\(^{III}\) atoms and a central, tetrahedral \(\text{WO}_4\) unit, resulting in a structure with \(C_{3v}\) symmetry. On the other hand, the giant polyon 13 is composed of four \{As_2W_{19}\} units, two ditungsten fragments, one monotungsten unit, and eight yttrium(III) ions.

Chapter 4 describes the reactivity of the monocationic, trinuclear \([\text{Ru}_3\text{O(OOCCH}_3)_6(\text{CH}_3\text{OH})_3]^+\) with Keggin and Wells-Dawson type polyions, resulting in reactions with Keggin and Wells-Dawson type polyions, resulting in

\[ \text{K}_2\text{Na}[\text{Ru}_3\text{O(OOCCH}_3)_6(\text{H}_2\text{O})_3][\alpha-\text{GeW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \quad (\text{Ru}_3\text{-11}), \]

\[ \text{K}_3[\text{Ru}_3\text{O(OOCCH}_3)_6(\text{H}_2\text{O})_3][\alpha-\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \quad (\text{Ru}_3\text{-12}), \quad \text{K}_3[\text{Ru}_3\text{O(OOCCH}_3)_6(\text{H}_2\text{O})_3][\alpha-\text{SiMo}_{12}\text{O}_{40}] \cdot 7\text{H}_2\text{O} \quad (\text{Ru}_3\text{-13}), \quad \text{and} \quad \text{K}_2\text{Na}[\text{Ru}_3\text{O(OOCCH}_3)_6(\text{H}_2\text{O})_3][\alpha-\text{P}_2\text{W}_{18}\text{O}_{62}] \cdot 26\text{H}_2\text{O} \quad (\text{Ru}_3-\text{IV}) \]
14). These solid-state frameworks, composed of cocrystallized trinuclear ruthenium cations and polyanions exhibit nanosized voids filled with crystal waters. These water molecules can be removed reversibly upon heating under a vacuum, and powder XRD measurements demonstrated that the crystallinity of the compound was preserved. Sorption studies on ethanol and methanol were also performed.

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<td>Na$<em>{34}$[Mn$</em>{19}$(OH)$<em>{12}$(SiW$</em>{10}$O$_{37}$)$_6$]·115H$_2$O</td>
<td>Na-1</td>
</tr>
<tr>
<td>K$_{18}$Mn[Mn$_2$(H$_2$O)$_6$]$<em>3$[Mn$<em>2$(GeW$</em>{10}$O$</em>{38}$)]$_3$·20H$_2$O</td>
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<tr>
<td>Cs$<em>{10}$Na$</em>{12}$[Mn$_3$(B-$\beta$-PW$<em>9$O$</em>{33}$)(OH))(B-$\beta$-PW$<em>8$O$</em>{29}$)(OH)$_2$]$_2$·45H$_2$O</td>
<td>CsNa-3</td>
</tr>
<tr>
<td>Na$_{22}$Rb$_6$[[Co$_4$(OH)$_3$PO$_4$]$_4$(A-$\alpha$-W$<em>9$O$</em>{34}$)]$_4$·76H$_2$O</td>
<td>NaRb-4</td>
</tr>
<tr>
<td>Na$_{26}$Rb$<em>6$[(Ni$</em>{14}$(H$<em>2$O)$</em>{10}$(OH)$_3$(PO$_3$(OH))$<em>4$(A-$\alpha$-P$<em>2$W$</em>{15}$O$</em>{56}$)$_4$]$_4$·96H$_2$O</td>
<td>NaRb-5</td>
</tr>
<tr>
<td>K$_{14}$[Ni$_5$(H$_2$O)$_6$(OH)$_3$(GeW$<em>9$O$</em>{34}$)]$_3$(GeW$<em>8$O$</em>{31}$)]·29H$_2$O</td>
<td>K-6</td>
</tr>
<tr>
<td>Na$_{14}$[(NaOH)$_2$]$_2$Ni$_2$<a href="OH">P$<em>2$W$</em>{15}$O$_{56}$</a>$_2$]$_2$·43H$_2$O</td>
<td>Na-7</td>
</tr>
<tr>
<td>Na$<em>3$K$</em>{24}$[(A-$\alpha$-SiW$<em>9$O$</em>{34}$)$<em>4$Cu$</em>{15}$O$_4$(OH)$_3$Cl]·50H$_2$O</td>
<td>KNa-8</td>
</tr>
<tr>
<td>Na$_{16}$(NH$_4$)[{Y(\alpha-ShW$<em>9$O$</em>{31}$(OH)$_2$(CH$_3$COO))(H$_2$O)}$_3$(WO$_4$)]·48H$_2$O</td>
<td>NaNH$_4$-9a</td>
</tr>
<tr>
<td>Cs$<em>7$Na$</em>{35}$[Y(H$_2$O)$_3$]$<em>8$(As$<em>2$W$</em>{19}$O$</em>{68}$)$<em>3$(As$<em>2$W$</em>{19}$O$</em>{66}$)(W$_2$O$_6$)$_2$(WO$_6$)]·230H$_2$O</td>
<td>CsNa-10</td>
</tr>
<tr>
<td>K$_2$Na[Ru$_3$O(OOCCH$_3$)$_6$(H$<em>2$O)$<em>3$][\alpha-GeW$</em>{12}$O$</em>{40}$]·10H$_2$O</td>
<td>Ru$_3$-11</td>
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<tr>
<td>K$_3$[Ru$_3$O(OOCCH$_3$)$_6$(H$<em>2$O)$<em>3$][\alpha-SiW$</em>{12}$O$</em>{40}$]·18H$_2$O</td>
<td>Ru$_3$-12</td>
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<tr>
<td>K$_3$[Ru$_3$O(OOCCH$_3$)$_6$(H$<em>2$O)$<em>3$][\alpha-SiMo$</em>{12}$O$</em>{40}$]·7H$_2$O</td>
<td>Ru$_3$-13</td>
</tr>
<tr>
<td>K$_2$Na[Ru$_3$O(OOCCH$_3$)$_6$(H$_2$O)$<em>3$][\alpha-P$<em>2$W$</em>{18}$O$</em>{62}$]·26H$_2$O</td>
<td>Ru$_3$-14</td>
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</table>
Chapter 1

Introduction

Polyoxometalates (POMs), represent a class of inorganic metal-oxo anions which are formed in solution (usually aqueous) through condensation of metolate groups in acidic medium. The framework of many POMs consists of d⁰, d¹ M atoms (most frequently M=Mo, W, V and Nb) bound to oxo (O²⁻) ligands. Polyoxometalates have recently acquired a remarkable place in the field inorganic chemistry due to their enormous structural diversity and applicability in various fields such as catalysis, analytical chemistry, magnetism, nanotechnology, and medicine.¹

1.1 Historical Background

If we look at the history of polyoxometalates, the very first report that we can find is by Berzelius in 1826. He was the one who observed the formation of yellow (heretopolyanion) products as a result of the reaction of molybdate with phosphate or arsenate.² Then the first heteropolytungstates were discovered and characterized by Marignac in 1862.³ Polyoxometalates were thoroughly investigated within next 70 years and hundreds of such compounds were described.⁴ These compounds presented significant conceptual and experimental challenges to Werner, Pauling and to many other investigators. Pauling in 1929 made a remarkable progress by proposing a structure made of a central XO₄ unit surrounded by twelve corner shared MO₆ octahedra.⁵ However in 1933 Keggin determined the real structure of heteropolyanions, [H₃PW₁₂O₄₀]·5H₂O, by powder X-ray diffraction. and
confirmed the presence of four edge shared triads, W$_3$O$_{13}$ units, connected to each other via corner sharing. Thus such types of polyanions are referred to as Keggin ions.$^6$ Later on in 1948 Evans solved the structure of [TeMo$_6$O$_{24}$]$^6^-$ by single-crystal X-ray analysis. This type of assembly is now called as Anderson-Evans structure.$^7$ Another famous heteropoly anion, [P$_2$W$_{18}$O$_{62}$]$^6^-$, now known as Wells-Dawson ion, was reported in 1953 by Dawson.$^8$

The field of POM chemistry has undergone a revolution during last few decades due to the developments of some experimental techniques such as single crystal XRD and multinuclear NMR. Particularly X-ray crystallographic hardware and software have changed the situation greatly, hence the number of reported POM compounds is being increasing tremendously. There are over 500 POM based papers (not including patents) published each year, and this number is rapidly increasing.$^1$

1.2 Synthetic Strategies

Heteropoly- and isopolyanions have been formed and isolated generally from aqueous solution. The route to produce POM based clusters are simple, involving small number of steps or even just one step (one-pot syntheses). Mostly, in the “one-pot” process, acidification of the precursor metal salts such as sodium tungstate in aqueous solutions, in the presence or absence hetero-elements, counterions etc. allow the linking of polyhedral units. These small building blocks, which are formed by the edge- and corner-sharing of {MO$_x$} units (where M = Mo, W; $x = 4–7$), then self-assemble to form various polyanions depending on the reaction conditions, such as pH, ionic strength, reaction time, temperature, counterions, concentration of starting materials etc. Still some fundamental aspects regarding the limits to composition, size, metal incorporation, mechanism of synthesis and reactivity are not fully understood.
One of the most important steps, in synthetic procedures of POMs, is the isolation of crystals so that their structure can be determined. The formed polyanions are precipitated or crystallized by adding suitable countercations (alkali metals, organic cations like TBA, etc.) and subsequently separated through filtration.

\[
12[\text{WO}_4]^2^- + [\text{HPO}_4]^{2^-} + 23\text{H}^+ \rightarrow [\text{PW}_{12}\text{O}_{40}]^{3^-} + 12\text{H}_2\text{O}
\]

\[
7[\text{MoO}_4]^2^- + 8\text{H}^+ \rightarrow [\text{Mo}_7\text{O}_{24}]^{6^-} + 4\text{H}_2\text{O}
\]

*Figure 1.1* Scheme highlighting the fact that discrete metal-oxo fragments (POMs) are in between [MO₄]ⁿ⁺ and mono extended solid oxide. The controlled acidification of a solution of [MO₄]ⁿ⁺ leads to the formation of discrete structures (POMs).
Usually the solid state structure of polyoxometalates is preserved in solution. For solution study if the original salt is not soluble enough then an appropriate choice of the counterion allows the redissolution of a polyoxoanion in aqueous, organic or mixed aqueous/organic solvents. The structure of polyoxoanions is determined by single-crystal X-ray diffraction and the diamagnetic nature enables the use of multinuclear NMR, which is the most powerful technique for studying the structure in solutions. POMs are hydrolytically and thermally stable so can be prepared and stored under normal bench conditions.¹

### 1.3 Structural Principles of Polyoxometalates

The framework of a polyoxoanion is mainly composed of addenda atoms, typically W, Mo, V, and oxo ligands and a central hetero atom labeled as X. Only, strictly speaking, those atoms can act as addenda atoms which have ability to increase coordination number with oxygen from 4 to 6 as they polymerize in solution upon acidification. Ionic radius and high positive charge of the addenda atoms are also mandatory for the formation of octahedral packing with oxygen ligands. Another criterion for a metal to be an addenda atom is its ability to form double bonds with unshared oxygens of MO₆ octahedra, by pπ–dp interaction.⁹ There is no such limitation on the heteroatom. So far more than 70 elements from all groups of the Periodic Table, except rare gases, have been reported. Examples of various coordination numbers around the hetero-atom are known.¹

- 3 coordinate, with lone pair (trigonal pyramid) in [XW₉O₃₃]⁹⁻ (X = As³⁺, Sb³⁺, Bi³⁺).
- 3 coordinate (trigonal planar) in [BW₁₂O₄₀]⁵⁻, including its lacunary derivatives.
- 4 coordinate (tetrahedral) in Keggin and wells-Dawson (e.g. PV⁴O₄, Si⁴VO₄, Ge⁴VO₄, As⁵VO₄)
- 6 coordinate (octahedral) in Anderson structure (e.g. $[\text{Te}^{VI}_6\text{W}_6\text{O}_{24}]^6$).

Figure 1.2 Common coordination geometries of the heteroatoms in polyoxometalates.

Figure 1.3 Possible linking modes of $\text{MO}_6$ octahedra in POMs. (left) corner-sharing, (middle) edge-sharing and (right) face-sharing.
POMs are composed of MO\textsubscript{n} units, where ‘n’ indicates the coordination number of M (n = 4, 5, 6 or 7). Polyoxometalate framework is constructed by the union of these smallest building units by sharing corners, edges or faces (which is not very common) (see Figure 1.3). The most common unit for polyoxometalate is the octahedral MO\textsubscript{6} unit, which is a distorted octahedron where the M atom moves off center due to polarizability and the short M-O $\pi$ bonding. Consequently the strong polarizability and double bond characteristic of the terminal oxygens make them less basic and hence obstruct protonation, preventing further polymerization thus lead to the formation of the discrete structures. Regarding the number of terminal oxygen, Lipscomb\textsuperscript{10} rule states that no MO\textsubscript{6} octahedra in a POM have more than two unshared oxygens. While Pope\textsuperscript{1a} classified polyanion on the basis of terminal oxygen as type I (mono-oxo) and type II (cis-dioxo), where the number of terminal oxygen atoms per addenda atom is one for type I and two in cis position for type II.

1.4 Structural Types in Polyoxometalates

The class of POMs can be subdivided in isopolyanions and heteropolyanions\textsuperscript{1} the former are composed of only addenda atoms (e.g. W, Mo, V) and oxygen ligands. A well-known example is the so called hexametallate or Lindqvist ion, [M\textsubscript{6}O\textsubscript{19}]\textsuperscript{2-} (M = W, Mo) (see Figure 1.4). This ion is composed of six edge-shared MO\textsubscript{6} octahedra, resulting in an overall octahedral assembly i.e. [M\textsubscript{6}O\textsubscript{19}]\textsuperscript{2-}, [W\textsubscript{6}O\textsubscript{19}]\textsuperscript{2-}, [Ta\textsubscript{6}O\textsubscript{19}]\textsuperscript{8-}, [V\textsubscript{6}O\textsubscript{19}]\textsuperscript{8-}.\textsuperscript{14} On the other hand, heteropolyanions contain an additional hetero element which can either be from the main groups or the d-block. A common example of a heteropolyanion is the highly symmetrical Keggin ion, e.g. [SiW\textsubscript{12}O\textsubscript{40}]\textsuperscript{4-}, [PMo\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-}) (see Figure. 1.4). This species is composed of a central, tetrahedral XO\textsubscript{4} hetero group surrounded by 12 MO\textsubscript{6} octahedra. The latter are arranged in four corner-shared M\textsubscript{3}O\textsubscript{13} triads with each triad being composed of three
edge-shared MO$_6$ octahedra. Another, slightly larger relative of the Keggin ion is the Wells-Dawson species, e.g. \([P_2W_{18}O_{62}]^{6-}\) (see Figure. 1.4). This species contains two XO$_4$ hetero groups and a total of 18 addenda atoms. Heteropolyanions with an octahedral hetero group are also known, e.g., the Anderson-Evans ion \([IMo_6O_{24}]^{5-}\) (see Figure. 1.4). It is also possible that in a POM more than one type of addenda atom is present (e.g. \([P_2W_{15}Mo_2VO_{62}]^{7-}\)) and such species are called mixed-addenda polyanions.

![Lindqvist Ion \([M_{n}O_{19}]^{n-}\)](image)

![Anderson-Evans Ion \([XM_{n}O_{24}]^{n-}\)](image)

![Keggin Ion \([XM_{12}O_{40}]^{n-}\)](image)

![Wells-Dawson Ion \([X_{2}W_{18}O_{62}]^{n-}\)](image)

**Figure 1.4** Some common iso- and heteropolyanions.
1.5 Structural Isomerism

This section deals with the possible isomerization of the two most common POM structures, Keggin ion and Wells-Dawson ion. The Keggin structure, \([\text{XM}_12\text{O}_{40}]^n\) is composed of a tetrahedral heteroatom (\(\text{XO}_4\)), and each corner of this tetrahedron is associated with a 3-fold \(\text{M}_3\text{O}_{13}\) unit or triad. Each triad is composed of three edge-shared \(\text{Mo}_6\) octahedra. The Four triads are connected to each other via corner sharing. The Keggin ion has an overall \(T_d\) symmetry. The kegging ion is an ideal example of type 1 ion, as mentioned before, due to the presence of only one terminal oxygen on each \(\text{Mo}_6\) octahedra. The most common and studied heteroatoms are \(\text{Si(IV)}, \text{Ge(IV)}, \text{P(V)}, \text{and As(V)}\). Theoretical studies on POM structures have revealed that the basicity increases with the net charge of the \(\text{XO}_4\) species due to the addition of polarization on the \(\text{M}_{12}\text{O}_{36}\) neutral sphere.\(^{20}\)

Baker and Figgis suggested that the Keggin ion can have up to five structural isomers (see Figure 1.5). The parent isomer, with four equivalent triads, is termed as \(\alpha\)-Keggin and the other isomers namely \(\beta, \gamma, \delta,\) and \(\varepsilon\) are obtained by 60° rotation of 1, 2, 3, and 4 triads respectively.\(^{21}\) The \(\gamma, \delta,\) and \(\varepsilon\) isomers are less stable than the \(\alpha\) and \(\beta\) isomers. There are two, three and six edge shared octahedra in gamma, delta and epsilon isomers respectively. The increased coulombic repulsion in the rotated triads and the resultant less favorable \(p\pi - d\pi\) interactions make all these isomers less stable than the parent alpha Keggin ion.\(^{22}\)
Figure 1.5 The five Baker-Figgis isomers of the Keggin polyanion. Rotated \( \{M_{13}O_{13}\} \) triads are represented in red polyhedra.
Another well studied ion is Wells-Dawson ion with heteroatoms P(V) and As(V). This ion can be viewed as two fused units of $[A-\alpha-XW_9O_{34}]$ or two $[A-\beta-XW_9O_{34}]$. Alpha isomer forms when two $A-\alpha$ units are combined together through all six oxygens of lacunary sites, (Figure 1.6), whereas fusion of one $A-\alpha$ and one $A-\beta$ generates the $\beta$ isomer and finally linking of two $A-\beta$ produces the $\gamma$ isomer.\textsuperscript{23}

### 1.6 Lacunary Species Derived from Keggin Ion and Wells-Dawson Ion

Hydrolytic cleavage of the M-O bond under basic conditions results in the formation of the so-called lacunary or defect species.

*Figure 1.6* Polyhedral representation of parent polyanions. (left) Keggin ion.
1.6.1 Lacunary Derivatives of Keggin Ion

Lacunary polyanions of the respective Baker-Figgis isomers (\(\alpha, \beta, \gamma\)) of \([XM_{12}O_{40}]^{\text{n}}\) can be produced by elimination of various number of octahedral. For example plenary ion, \([XM_{12}O_{40}]^{\text{n}}\) give mono- and trilacunary ions by removal of one and three octahedral units. In the case of trilacunary species, no matter whether they derived from an alpha- or beta isomer, there are two types of structures namely A-type and B-type. The A-type trilacunary anion is formed when corner shared octahedra are removed and B-type generates when an edge shared triad is eliminated. \(^{24}\) There are six and seven strong basic oxygen located on the vacant sites of A-type and B-type structures respectively. A lacunary Keggin structure in which two adjacent octahedra have been removed has not been reported for the \(\alpha\), and \(\beta\) isomers, but observed only for the \(\gamma\) isomer. The dilacunary \([\gamma-XW_{10}O_{36}]^{\text{n}}\) is obtained by removal of one octahedron from each \(\{\text{W}_3\text{O}_{13}\}\) rotated triads. \(^{25}\) Three lacunary species namely \(\beta_1\), \(\beta_2\), \(\beta_3\) are originated from the parent beta isomer (\(C_{3v}\) symmetry). In \(\beta_1\), the octahedron is removed from a triad which is located opposite to the rotated one. In \(\beta_2\) the vacant site located in the belt, while \(\beta_3\) type is formed when the remove octahedron is part of the rotated triad \(^{24}\) (see Figure 1.7).

However heteropolyanions, which contain a heterogroup with a trigonal pyramid (e.g. As\(^{\text{III}}\)O\(_3\), Sb\(^{\text{III}}\)O\(_3\)), such as \([XW_9O_{33}]^{9}\) (\(X = \text{As}^{\text{III}}, \text{Sb}^{\text{III}}, \text{Bi}^{\text{III}}\)), exist exclusively in the \(B\)-type. Due to the presence of the lone pair, the closed Keggin unit cannot be formed, and hence ‘unconventional’ structures may be obtained. \(^{26}\)
Figure 1.7 The three monolacunary species derived from the \([\beta\text{-XM}_{12}\text{O}_{40}]^{n-}\) Keggin heteropolyanion.
Figure 1.8 The A- and B-type trilacunary species derived from the \([\alpha\cdot{XM_{12}O_{40}}]^n\) Keggin heteropolyanion.
1.6.2 Lacunary Derivatives of Wells-Dawson Ion

\[ \text{[P}_2\text{W}_{18}\text{O}_{62}]^{6-} \]

\[ \text{[α}_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-} \]
\[ \text{[α-P}_2\text{W}_{15}\text{O}_{56}]^{12-} \]
\[ \text{[α-H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-} \]

*Figure 1.9* Polyhedral representation of parent Wells-Dawson ion and its mono-, tri- and hexalacunary derivatives.
Regarding Wells-Dawson ion, only the alpha isomer produces the stable lacunary species. The two monolacunary, \([\alpha_1-X_2W_{17}O_{61}]^{10-}\) and \([\alpha_2-X_2W_{17}O_{61}]^{10-}\) are obtained when one octahedron is lost from the belt or from the cap respectively. Trilacunary \([P_2W_{15}O_{56}]^{12-}\) and hexalacunary \([H_2P_2W_{12}O_{48}]^{12-}\) can also be produced by using bases of different strengths\(^{27}\) (see Figure 1.9).

### 1.7 General Properties

Polyoxometalate chemistry is no doubt one of the rapidly growing fields in inorganic chemistry because of their versatile nature in terms of structure, size, redox chemistry, photochemistry, and charge distribution. Typically polyanions are water- and air stable. They are often more stable in acidic media, nevertheless, depending on the type of polyanion involved, the pH range (pH ~ 1-14) at which they preserve their structures is quite large. Another significant general property of polyoxometalates is their solubility (in the presence of appropriate counterions) in solvents ranging in polarity from dimethyl sulfoxide to benzene. This property of polyoxometalates extends their chemistry to include the reactions of organometallic species. The polyanion salts and acids are highly hydrated, with ~up to 50 water molecules per anion. Polyoxometalates are extremely thermally robust species which usually start to decompose at 400°C. They are of large size (6-25 Å) and having high ionic masses (ca. 1000 to10,000 g/mol.).\(^1\) Since majority of POMs have been synthesized and studied in aqueous solution it is appropriate to consider formation and solution properties together. Different studies, on the solution containing starting material (as discussed in section 1.2), have shown that there might be several species in equilibrium depending on the pH. Hence the compound isolated in the form of crystals may not necessarily be the one with the highest abundance.\(^1\) In addition, POMs exhibit interesting thermochromic behavior or
electrochemical properties that are related to the electron-transfer reactions within the clusters. All the type I POMs, (according to the classification of Pope, are those POMs that have a single terminal oxygen for each MO$_6$ octahedron), have the ability to accept and release specific number of electrons reversibly without bringing any major change in the structure of anion. While type II polyoxometalates are reduced irreversibly and with more difficulty.$^{28}$ The heteropolymolybdates have greater tendency to get reduced than heteropolytungstates. The extent of reduction also depends on the acidity or pH of the medium and charge of the polyanion. In order to retain electro neutrality, the additional negative charge will be balanced by protonation from the solvent.$^{20}$

The Keggin structures, which are mainly constructed from the type I octahedra, are therefore easily reduced to mixed-valence species which are deeply colored and termed as “heteropolyblues.” The heteropolyblues show paramagnetic behavior with one electron reduction and ESR spectroscopy revealed the rapid intramolecular electron transfer among all addenda centers at room temperature. On the other hand 2 electrons reduced species are ESR silent, showing diamagnetic nature.$^{29}$

Herteropolyacids (HPAs, heteropolyanions having H$^+$ as the only counter cation) are strong Brønsted acid and most of them are stronger in acidity than the usual inorganic acids (HCl, H$_2$SO$_4$, HNO$_3$, HBr), even stronger than HClO$_4$. This is of fundamental importance for POM application in acid catalysis. The strong acidity of HPAs as compared to the typical inorganic acid is probably due to the larger size and higher negative charges density of the former one. Therefore the strength of bonding between the proton and heteropoly anions should be lower, which results in lower dissociation constants compared to the usual acids. Among the HPAs, the acid strength depends upon the kind of addenda atom and as well as heteroatom,
tungstate are stronger than molybdates and $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ is considered to be the strongest in the Keggin type series.$^{1b,30,31}$

### 1.8 Applications

The applications of polyoxometalates are mainly based on their previously discussed properties, including size, mass, electron- and proton-transfer/storage abilities, thermal stability and high Brønsted acidity of the polyoxometalates. In this section some of the interesting applications will be discussed.

#### 1.8.1 POM-Based Materials with Magnetic and Conducting Properties

Lacunary polytungstate enriched with oxo ligands can act as ligands and stabilizing agents toward 3$d$-transition metal ions leads to the encapsulation of a variety of magnetic clusters with different spin ground states that can exhibit ferromagnetic and/or antiferromagnetic exchange interactions.$^{32}$

The well insulated magnetic clusters serve as model systems for understanding of the magnetic exchange interactions and in the meantime also provide a base to study the magnetic theories. Interestingly on the other hand some of the POM based magnetic materials show single molecule magnet behavior.$^{33}$ Single-molecule magnets (SMMs) are molecules that are magnetized in a magnetic field and show slow relaxation when the magnetic field is removed.$^{34}$ SMMs have great potential applications in many fields such as information processing, data storage, quantum computing and biomedical applications (like MRI contrast agents).$^{35,36}$
1.8.2 Catalysis

One of the most important applications of POMs is their use in the field of catalysis. In particular heteropoly compounds have significant importance in the field of catalysis because of their multifunctionality and structural mobility. Furthermore, HPAs have a very strong Brønsted acidity. Also polyoxometalates are effective oxidant and as a rigid electron reservoir they exhibit rapid reversible multielectron redox transformation under mild conditions. Notably, many polyoxometalates have a very high thermal stability in the solid state which is of great importance in the field of heterogeneous catalysis. Being anionic in nature, it is possible to exchange their countercations by metathesis reactions. Therefore both inorganic and organic salts are allowed to form. Selection of countercation can make the POM soluble in either water or organic phases typically tetrabutylammonium (TBA) is chosen as the counteraction for organic phase reactions, and alkali metal cations like Na\(^+\) or K\(^+\) are selected for aqueous phase reactions. The catalytic reactions can be carried out in homogeneous as well as in heterogeneous (gas–solid, liquid–solid or biphasic liquid–liquid) systems. Heteropolyacids and their salts have even found their way to industrial large scale acid and oxidation catalyzed processes. The basic reversible redox reactions involved in substrate oxidations are shown in Equations (a) and (b), where [HPA]\(_{ox}\) and [HPA]\(_{red}\) symbolize the oxidized and reduced forms of a heteropolyanion. Such catalysts can be used, in the formation of carboxylic acids from the corresponding aldehydes, as well as in the dehydrogenation of alcohols, aldehydes, and carboxylic acids to form C=C and C=O bonds.

\[
[HPA]_{ox} + \text{substrate} + n \, H^+ \quad \leftrightarrow \quad H_n[HPA]_{red} + \text{oxidized substrate} \quad (a)
\]

\[
H_n[HPA]_{red} + n/4 \, O_2 \quad \leftrightarrow \quad [HPA]_{ox} + n/2 \, H_2O \quad (b)
\]
The above general equations indicate that the substrate is first oxidized by the POM which is then regenerated by the oxidant that is often oxygen to form water. Oxidation of the substrate is often accompanied by proton transfer to the consequently reduced catalyst. Regarding acid catalysis, heteropolyacids can be used instead of mineral acids as acid catalyst. Although heteropoly acids are more expensive than mineral acids like sulfuric and hydrochloric acid, they have the advantages of being nonvolatile, odorless, and thermally stable. They can be used in homogeneous acid catalysis as well as in heterogeneous catalysis using supports like silica gel or activated charcoal at temperatures of approximately 300 °C. For example, tungstophosphoric acid is used as a catalyst in the industrial production of 2-propanol, 2-butanol, and tert-butanol by liquid-phase hydration of the corresponding olefins. 1,37,38, 39

1.8.3 Medicine

Considering the number of POMs already synthesized and characterized chemically, their application to medicine is relatively in its initial stages. Many polyoxometalate salts have been shown to be biologically active due to their stability at physiological pH, size, shape and electron acceptor properties. One of the most important features of POMs is that despite very large size, they still can penetrate cell membranes and localize within the cells.1 Perhaps the most significant general medical property of POMs is their antiviral activity. The antiviral activity of POMs was first noted by Raynaud et al. in 1971 in France.40 They used tungstosilicate anoin, in vitro, for the inhibition of murine leukemia sarcoma virus (MLSV). Later on in vitro studies conducted by various groups showed the efficacy of these POMs against several other viruses like vesicular stomatitis (VSV), polio, rubella, rauscher leukemia (RLV), rabies (RV), rhabdovirus, and epstein-barr (EBV). The first POM which was administered to human was (NH₄)₁₇Na[NaSb₉W₂₁O₆₆], the French drug historically called
HPA-23, however it was one of the most toxic POMs examined to date, which unfortunately retarded investigation of all biological research on POMs. So far antiviral effectiveness of over 200 POMs has been reported in vitro, and less than 20 reports are found for efficacy in vivo. Nevertheless the anticancer activity of POMs in vivo is very limited.\textsuperscript{41} Mukherjee was the first who administrated a POM based drug PTMC (which contains H\textsubscript{3}[PW\textsubscript{12}O\textsubscript{40}], H\textsubscript{3}[PMO\textsubscript{12}O\textsubscript{40}] and caffeine) to a patient with intestinal tract carcinoma. The drug PTMC remarkably either shrunk the tumors or killed it completely.\textsuperscript{42} There are some reports where [Mo\textsubscript{7}O\textsubscript{23}(OH)]\textsuperscript{6-} and [Mo\textsubscript{7}O\textsubscript{24}]\textsuperscript{6-} were used in vivo as anticancer agents.\textsuperscript{41,43}
1.9 References


(4) *Gmelin Handbuch der Anorganischen Chemie*, Verlag Chemie, Berlin; System- No. 53 (Molybdän) 1935; System-No. 54 (Wolfram) 1933.


(13) A. Thiele, J. Fuchs, *Private Communication* **1979**.


Chapter 1

Introduction


Chapter 2

Experimental Details

2.1 Instrumentation

All of the synthesized compounds, which will be discussed in the next section, were isolated in the form of crystals. FT-IR spectroscopy is the very first technique to analyse the nature of the prepared compounds. FT-IR is a very useful technique which provide information about the characteristic region (~1000-400 cm\(^{-1}\)) of a polyanion in the spectrum, \(^1\) this region is known as “finger print” where absorptions due to metal–oxygen stretching vibrations occur. The obtained spectra are then compared with the existing spectra of the precursor used and with the relative spectra of the local data base or the one given in literature, if possible. Difference of spectral bands position, shapes and relative intensities for the two complexes strongly show the presence of different structures. After being investigated by FT-IR the next extremely important technique is single crystal XRD which determine the structure and provide detailed information about almost every atom present in the compound, about the bond length and bond angle Thermogravimetric analysis are performed between 25 and 900 °C under a nitrogen atmosphere to determine the amount of crystal water present in the polyanion.

At this point it is important to mention that all the formulae are based on three different analytical methods namely single crystal XRD, elemental analysis and TGA and the
combined results from these methods are taken into account to determine the molecular composition of any compound.

2.1.1 Fourier Transform Infrared Spectroscopy

Infrared spectra were recorded on a Nicolet Avatar 370 FT-IR spectrophotometer as KBr pellet samples. The following abbreviation was used to assign the peak intensities: w: weak; m: medium; s: strong; vs: very strong; b: broad; sh: shoulder.

2.1.2 Single Crystal X-Ray Diffraction

All crystals were mounted in Hampton cryoloops using light oil for data collection at 173 K. Indexing and data collection were performed using a Bruker X8 APEX II CCD diffractometer with κ geometry and Mo Kα radiation (λ=0.71073 Å). Data integration and routine processing were performed using the SAINT software suite. Further data processing, including multiscan absorption corrections, was performed using SADABS. Direct method (SHELXS97) solutions successfully located the W atoms, and successive Fourier syntheses (SHELXL97) revealed the remaining atoms. Refinements were full-matrix least-squares against F2 using all data. All nondisordered heavy atoms were refined anisotropically, while the O atoms and disordered countercations were refined with fractional occupancies. No H or Li atoms were included in the models.

The degree of refinement is commonly expressed by the R factor, which is a measure of the degree of deviation of the predicted model (calculated) from the scattering amplitudes (observed): 

$$R = \sum \frac{\| F(\text{obs}) \| - \| F(\text{calc}) \|}{\sum \| F(\text{obs}) \|}$$
2.1.3 Thermogravimetry

Thermogravimetric analyses were performed on a Q 600 device from TA Instruments with 10-30 mg samples in 100 μL alumina pans, under a 100 mL/min. N₂ flow with a heating rate of 5 °C/min.

2.1.4 Nuclear Magnetic Resonance Spectroscopy

The \(^1\)H and \(^{13}\)C NMR spectra were recorded using 5 mm tubes, whereas the \(^{183}\)W and \(^{89}\)Y NMR spectra were recorded in 10 mm tubes. The respective resonance frequencies were 16.69 MHz (\(^{183}\)W), 19.63 MHz (\(^{89}\)Y), 399.78 MHz (\(^1\)H), and 100.53 MHz (\(^{13}\)C). The chemical shifts are reported with respect to the references Na₂WO₄ (\(^{183}\)W), Y(NO₃)₃ (\(^{89}\)Y), and TMS (\(^1\)H and \(^{13}\)C).

2.2 Synthesis of Precursors

All the involved precursors were synthesized according to the published procedures and characterized by IR spectroscopy.

2.2.1 Synthesis of Wells-Dawson Polyanions

2.2.1.1 (NH₄)₆\([\alpha-P_2W_{18}O_{62}]\)·14H₂O

This product was synthesized as the reported one but with slight modification: 125 g of Na₂WO₄·2H₂O was dissolved in 250 mL of distilled H₂O. Then 105 mL of 85% H₃PO₄ was added slowly to the former solution. The resultant mixture was refluxed for 4 hours at 126 °C. After being refluxed solution was cooled to room temperature and then added 50 g of
NH₄Cl. The precipitate was collected in a Büchner funnel. This precipitate was dissolved in NH₄Cl solution (12.5 g NH₄Cl in 50 mL of water), again collected the precipitate and air dried for 4 days.4

2.2.1.2 Na₁₂[α-P₂W₁₅O₅₆]·24H₂O

In a 600 mL beaker a sample of 38.5 g of K₆[α-P₂W₁₈O₆₂]·14H₂O is dissolved in 125 mL of water, and 35 g of NaClO₄·H₂O are added. After vigorous stirring for 20 minutes, the mixture is cooled on an ice bath, and the potassium perchlorate is removed by filtering after approx. 3 hrs. A solution of 10.6 g of Na₂CO₃ in 100 mL of water is added to the filtrate. A fine white precipitate appears almost instantaneously and is decanted and then filtered on a medium porosity sintered glass frit and dried under suction for ~ 3 hrs. The precipitate is then washed for 1 to 2 minutes with a solution of 4 g of NaCl in 25 mL of water, dried under suction for approx. 3 hours, washed for 2 to 3 min. with 25 mL of ethanol, and air dried under suction for 3 hrs., washed again with EtOH and dried under suction, and finally air dried for 3 days (yield: 22 g, 62%).5

2.2.2 Synthesis of Lacunary Keggin Polyanions

2.2.2.1 K₆Na₂[α-GeW₁₁O₃₉]·13H₂O

3.5 g of germanium dioxide was dissolved in 7.5 mL of 1M NaOH solution. An aqueous solution containing 121 g of sodium tungstate dihydrate in 200 mL of water was added to the solution. The mixture was stirred and heated. Then 400 mL of 4M HCl was added drop wise to the hot solution under vigorous stirring. The solution was boiled for about one hour and cooled to room temperature. White precipitate appeared upon addition of 100 g of solid potassium chloride. The precipitate was filtered through Büchner funnel and then dissolved in
adequate volume of hot water. Filtered again through filter paper and kept the solution in open
air for crystallization.⁶

2.2.2.2 \( \text{K}_8[\beta_2-\text{GeW}_{11}\text{O}_{39}]\cdot14\text{H}_2\text{O} \)

Germanium dioxide (5.4 g) was dissolved in 100 mL of water (solution A). Then, 182 g of
sodium tungstate was dissolved in 300 mL of water in a separate beaker (solution B). To this
solution, 165 mL of 4 M HCl was added with vigorous stirring in small portions over 15 min.
Then, solution A was poured into the tungstate solution (solution B), and the pH adjusted to
between 5.2 and 5.8 by addition of 4 M HCl solution (40 mL). This pH was maintained for
100 min by addition of the HCl solution. Then, 90 g of solid KCl was added with gentle
stirring. After 15 min, the precipitate (yield: 112.1 g, 68%) was collected by
filtration on a sintered glass filter.⁷

2.2.2.3 \( \text{K}_8[\alpha-\text{SiW}_{11}\text{O}_{39}]\cdot13\text{H}_2\text{O} \)

Solution A: 11 g of sodium metasilicate are dissolved in 100 mL of distilled water at room
temperature. Undissolved material is filtered off. Solution B: 182 g of \( \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \) are
dissolved in 300 mL of water in a 1 liter beaker. To the boiling Solution B, 165 mL of 4M
HCl are added dropwise in approx. 30 min. with vigorous stirring to dissolve the local
precipitate of tungstic acid. Solution A is then added and, quickly, 50 mL of 4M HCl are also
added, whereas the pH is at this point between 5 and 6. The solution is kept boiling for 1 hr.
After cooling to room temperature, the solution is filtered if it is not completely clear. 150 g
of KCl are added to the solution under stirring. The white solid product is collected on a
sintered glass funnel of medium porosity, washed with two 50-mL portions of 1M KCl
solution and then washed with 50mL of cold water. The desired phase is air dried giving an approx. 90% yield (145 g).

2.2.2.4 $K_8[\gamma$-GeW$_{10}$O$_{36}]\cdot6$H$_2$O

15.2 g of $K_8[\beta_2$-GeW$_{11}$O$_{39}]\cdot14$H$_2$O (synthetic procedure of this monolacunary polyanion is described earlier in this chapter) were dissolved in 150 mL of water. A small amount of insoluble material was removed by rapid filtration on a fine frit or through Celite®. The pH of the solution was quickly adjusted to 8.7-8.9 by addition of a 2 M aqueous solution of K$_2$CO$_3$. The pH was kept at this value by addition of the K$_2$CO$_3$ solution for exactly 16 min. The product was then precipitated by addition of solid KCl (40 g). During the precipitation (10 min), the pH was maintained at 8.8 by addition of small amounts of the K$_2$CO$_3$ solution or dilute HCl as needed. Then, the solid (yield: 12.4 g, 92%) was filtered off and air-dried.

2.2.2.5 $Na_{10}[A$-$\alpha$-SiW$_9$O$_{34}]$

11 g (50 mmol) of sodium metasilicate and (182 g, 0.55 mol) sodium tungstate are dissolved in 200 mL of hot water at 80-100°C upon stirring. 130 mL of HCl (6 M) are added dropwise, to the solution, in ~ 30 min with vigorous stirring. The solution was then boiled until the volume is ~ 300 mL. Unreacted silica is removed by filtration through a fine frit. A second solution was prepared by dissolving 50 g of Na$_2$CO$_3$ in 150 mL of water. This solution is slowly added to first solution with gentle stirring. A precipitate, which forms slowly, is removed by filtration through a fine frit after 1 hour. This solid is then stirred with 1 L of NaCl (4 M) solution and filtered again. Then it is washed twice with 100-mL portions of ethanol and once with 100 mL of diethyl ether, and dried under vacuum.
2.2.2.6 $K_{10}[\alpha$-$SiW_9O_{34}]\cdot24H_2O$

$K_8[\alpha$-$SiW_{11}O_{39}]\cdot13H_2O$ (synthetic procedure of this monolacunary polyanion is described earlier in this chapter) (10 g, 3.12 mmol) was dissolved in 100 mL of water at 50 °C upon stirring. The solution was cooled to room temperature (solution A). A second solution was prepared by dissolving $K_2CO_3$ (2.58 g, 18.72 mmol) in 22 mL of water at room temperature. The solution of potassium carbonate was slowly added to the solution A. Then, the pH was ~9.4. After being stirred for 20 min, the solution was filtered if it was not completely clear (solution B). $K_2CO_3$ (8 g, 0.058 mol) was added to the solution B. The mixture was gently stirred for 2 h, and a white precipitate appeared slowly. The solid was collected by filtration through a fine frit, washed with a saturated KCl solution (6 mL), and dried in air. Yield: 6.6 g (73%).

2.2.2.7 $Na_9[\alpha$-$PW_9O_{34}]\cdot7H_2O$

120 g of Na$_2$WO$_4\cdot2H_2O$ were dissolved in 150 g of distilled water, 4 mL H$_3$PO$_4$ (85%) was added dropwise with stirring. Afterwards, the pH of the solution was measured to be 8.9. Glacial CH$_3$COOH was added slowly with vigorous stirring. Large quantities of white precipitate were formed during the addition. The final pH of the solution was 7.8. The solution was stirred at least for an hour and the precipitate was collected on a medium frit. Heating of the crude product at 120 °C induces a solid state isomerization from $A$-type to $B$-type.
2.2.3 Synthesis Lone Pair Containing POM Precursors

2.2.3.1 Synthesis of Na$_9$[B-$\alpha$-AsW$_9$O$_{33}$]·27H$_2$O

This precursor was prepared by adding 11 g As$_2$O$_3$ to a hot solution of 330 g Na$_2$WO$_4$·H$_2$O in 350 mL water. After the addition of 83 mL 11M HCl with vigorous stirring over 2 min., the solution was heated at 95°C for 10 min. and filtrate was left in an open beaker. The product crystallized overnight with a good yield of approx. 90% (280 g).$^9$

2.2.3.2 Synthesis of Na$_9$[B-$\alpha$-SbW$_9$O$_{33}$]·27H$_2$O

Solution A: 1.96 g of Sb$_2$O$_3$ was dissolved in 10 mL conc. HCl. Solution. B: 40 g of Na$_2$WO$_4$·2H$_2$O was dissolved in 80 mL of distilled water (~90 °C). Solution A was transferred into the beaker containing Solution B including the non dissolved Sb$_2$O$_3$ drop wise and then, the whole reaction mixture was refluxed for approximately an hour. The solution was cooled and filtered, crystals start forming immediately. Solution was left open until it reached the level of crystals.$^{10}$
2.3 References


(2) G. M. Sheldrick, SADABS; University of Göttingen: Göttingen, Germany, 1996.

(3) G. M. Sheldrick, SHELXS-97; University of Göttingen: Göttingen, Germany, 1997.


Chapter 3

Results: Synthesis and Characterization of Transition Metal-Containing Polyoxotungstates

The key focus of this dissertation is incorporation of multinuclear-transition metal complexes in polyoxometalate frameworks. This chapter summarizes the research work conducted in that particular field, during which we were able to develop a new synthetic route in high nuclearity transition metal-containing polyoxometalate (POM) chemistry. Following an introductory section which provides some insight into TM-containing POMs, sections (3.1-3.4) describes the 8 novel multi transition metal-containing polyanions.

Introduction

Transition metal substituted polyoxometalates (POMs) are a rapidly growing field because of their potential applications in areas as diverse as magnetochemistry, catalysis, medicinal chemistry, material science and nanotechnology.\(^1\) POMs are ideal candidates for the encapsulation of multinuclear magnetic transition metal clusters. This is essentially due to the isolation of a large number of vacant, stable polytungstate precursors through controlled base hydrolysis. The removal of one or more metal centers in them allow the formation of lacunary POMs which own extra terminal and basic oxygen atoms that can coordinate to electrophilic centers. Therefore, lacunary POMs are usually considered as diamagnetic, inorganic multidentate ligands that can also encapsulate metal-oxo clusters, especially paramagnetic
Variety of lacunary heteropolytungstate precursors e.g. \([\text{SiW}_{11}\text{O}_{39}]^{8-}\), \([\gamma-\text{SiW}_{10}\text{O}_{36}]^{8-}\), \([\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}\), \([\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}\) and \([\text{H}_8\text{P}_8\text{W}_{48}\text{O}_{184}]^{32-}\) etc. having voids of 1, 2, 3, 6 and 20 respectively are being used extensively for encapsulation of a large number of spin-coupled magnetic centers (d- or f-block), usually bridged via \(\mu_2\)-oxo/hydroxo/aqua groups. Various O- or N-containing organic ligands such as carboxylate, and alkoxide are involved for the rational formation of majority of the ploynuclear transition metal clusters. Inorganic lacunary POM ligands also not only assist in stabilizing and bridging of metal ions, but also impart a major role towards the engineering of high nuclearity complexes. Furthermore, due to diamagnetic tungsten-oxo capping fragments the magnetic clusters are well isolated and usually embedded in the POM frameworks. Different shapes, sizes, and types of magnetic core can be formed as a result dimeric, trimeric or tetrameric assemblies. Examples of such kind of magnetically interesting polyoxometalates are: \(\{\text{W}_{19}\text{Ni}_7,\text{W}_{18}\text{Ni}_6\}\), \(\{\text{W}_{32}\text{Cu}_{14},\text{W}_{34}\text{Cu}_{10}\text{Ni}_3\}\), \(\{\text{W}_{27}\text{Co}_9\}\), \(\{\text{W}_{27}\text{Ni}_9\}\), \(\{\text{Mo}_{72}\text{Fe}_{30}\}\), \(\{\text{W}_{36}\text{Cu}_{14}\}\), \(\{\text{W}_{48}\text{Cu}_{20}\}\), \(\{\text{W}_{12}\text{Fe}_9,\text{W}_{48}\text{Fe}_{28}\}\), \(\{\text{W}_{13}\text{Fe}_6\}\), \(\{\text{W}_{24}\text{Co}_9\}\), \(\{\text{W}_{18}\text{Mn}_6/\text{Cu}_6\}\), \(\{\text{W}_{48}\text{V}_6\}\), \(\{\text{W}_{60}\text{Fe}_{12}\}\), \(\{\text{W}_{36}\text{Fe}_{13}\}\), \(\{\text{W}_{48}\text{Cu}_{20}\text{Ni}_3\}\), \(\{\text{W}_{48}\text{Fe}_{16}\}\), \(\{\text{W}_{18}\text{Mn}_6\}\), \(\{\text{W}_{18}/\text{Ni}_8/\text{Ni}_9\}\), \(\{\text{W}_{16}\text{Mn}_6\}\), \(\{\text{W}_{90}\text{Mn}_6\}\), \(\{\text{W}_{48}\text{Cu}_{20}\text{X}\}\), \(\{\text{W}_{34}\text{Ni}_{20}\}\), \(\{\text{W}_{36}\text{Mn}_{14}\}\), \(\{\text{Ni}_{12}\text{W}_{35}\}\).

Transition metal-substituted POMs, which constitute the largest subclass of polyanions, have been intensively investigated and a significant numbers of structures have been reported. The paramagnetic clusters with large-spin ground states may behave as single-molecule magnets (SMMs). The observation of slow relaxation of magnetization in such metal clusters is of great interest, due to their potential applications in high-density information storage and quantum computation at the molecular level. During the past decade the high-nuclearity coordination complexes of transition metal cations have become one of the most active research areas due to their interesting electronic and magnetic properties.
was the synthesis of $[\text{Mn}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}]$ ($\text{Mn}_{12}$) by Lis in 1980, and only thirteen years later Gatteschi’s group showed this molecule to exhibit single molecule magnet (SMM) behavior.

3.1 Multi-Manganese(II)-Containing Polyoxotungstates

In this section the synthesis, characterization, and crystal structures of three novel polyoxotungstate complexes of $\text{Mn}^{II}$, $\text{Mn}_{19}$-containing $\text{Na}_{34}[\text{Mn}_{19}(\text{OH})_{12}(\text{SiW}_{10}\text{O}_{37})_6]\cdot 115\text{H}_2\text{O}$ ($\text{Na-1}$), $\text{Mn}_8$-containing of $K_{20}[\{\text{Mn}(\text{H}_2\text{O})_3\}_2\{\text{Mn}_2(\text{GeW}_{10}\text{O}_{38})\}_3]$, 20 $\text{H}_2\text{O}$ ($\text{K-2}$) and $\text{Mn}_3$-containing $\text{Cs}_{10}\text{Na}_{12}[\{\text{Mn}_3(\text{B-β-PW}_9\text{O}_{33}(\text{OH}))\}^\text{+}(\text{B-β-PW}_8\text{O}_{29}(\text{OH})_2)]^\text{2-}45\text{H}_2\text{O}$ ($\text{CsNa-3}$). will be discussed. These polyanions were synthesized in simple one-pot reactions in aqueous basic media, as result of interaction of $\text{Mn}^{II}$ centers and the polyoxotungstate ligands, $[A-\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, $[\gamma\text{-GeW}_{10}\text{O}_{36}]^{8-}$ and $[A-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ respectively and structurally characterized in the solid state by single-crystal X-ray diffraction, FT-IR, and TGA.

3.1.1 $\text{Na}_{34}[\text{Mn}_{19}(\text{OH})_{12}(\text{SiW}_{10}\text{O}_{37})_6]\cdot 115\text{H}_2\text{O}$ ($\text{Na-1}$)

**Synthesis:** $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.13 g, 0.63 mmol) was dissolved in 20 mL $\text{H}_2\text{O}$. Then solid $\text{Na}_{10}[A-\alpha\text{-SiW}_9\text{O}_{34}]$ 31 (0.50 g, 0.20 mmol) was added and stirred until a clear yellow solution was obtained. The pH value of the resulting mixture was adjusted to 8.0 with 4 M NaOH. The turbid solution was stirred for 30 minutes at room temperature. Then solid $\text{Na}_3\text{PO}_4$ (0.50 g, 3.0 mmol) was added to this solution in small portions, while maintaining the pH at 8 with $\text{HCl}_{aq}$. The mixture was heated to 70 °C for 1 hour, allowed to cool to room temperature, and then filtered. The filtrate was allowed to evaporate in an open vial at room temperature. After two weeks a brown crystalline product started to appear. Evaporation was allowed to continue
until the solution level had approached the solid product, which was then collected by filtration and air dried. Yield 40 mg (6.5%).

IR (2% KBr pellet, v/cm\(^{-1}\)): 988 (w), 945 (m), 890 (s), 790 (s), 707 (m), 650 (m), 535 (m), see Fig. 3.1. Elemental analysis for Na-1, calc (found): Na 4.1% (4.2%), Si 0.89% (0.86%), Mn 5.54% (5.61%), W 58.5% (59.1%).
**Figure 3.1.** Infra red spectra of the POM precursor \( \text{SiW}_9 \) and the product \( \text{Na-1} \).

**Figure 3.2.** TGA curve of \( \text{Na-1} \) from room temperature to 1000 °C.
3.1.1.1 Single Crystal X-Ray Diffraction

**Na-1** crystallizes in the triclinic space group *P*-1. Crystallographic data are detailed in Table 3.1.

**Table 3.1 Crystal data for Na-1.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Na-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Na$<em>{34}$[Mn$</em>{19}$(OH)$<em>{12}$(SiW$</em>{10}$O$<em>{37}$)$</em>{6}$]·115H$_2$O</td>
</tr>
<tr>
<td>Formula weight, g/mol</td>
<td>18853.00</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td><em>P</em>-1</td>
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<tr>
<td>$a$, Å</td>
<td>16.1359(6)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>23.5734(10)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>24.7172(17)</td>
</tr>
<tr>
<td>$\alpha$, °</td>
<td>112.039(3)</td>
</tr>
<tr>
<td>$\beta$, °</td>
<td>100.018(3)</td>
</tr>
<tr>
<td>$\gamma$, °</td>
<td>107.583(2)</td>
</tr>
<tr>
<td>Volume, Å$^3$</td>
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</tr>
<tr>
<td>$Z$</td>
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</tr>
<tr>
<td>$D_{\text{calc}}$, g/cm$^3$</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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</tr>
<tr>
<td>$R$(int)</td>
<td>0.1052</td>
</tr>
<tr>
<td>Observed ($I &gt; 2\sigma(I)$)</td>
<td>13005</td>
</tr>
<tr>
<td>$R_1$($I &gt; 2\sigma(I)$)$^{[a]}$</td>
<td>0.0643</td>
</tr>
<tr>
<td>wR$_2$ (all data)$^{[b]}$</td>
<td>0.2148</td>
</tr>
</tbody>
</table>

$^{[a]} R = \Sigma ||F_o|| - |F_c||/\Sigma |F_o|$.  $^{[b]} R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.  

40
3.1.1.2 Results and Discussion

The polyanion 1 was synthesized in a simple one-pot reaction of MnCl$_2$ with Na$_{10}[A-\alpha$-SiW$_9$O$_{34}]$ in aqueous medium at pH 8 and then isolated as a hydrated sodium salt, Na$_{34}[\text{Mn}_{19}(\text{OH})_{12}(\text{SiW}_{10}\text{O}_{37})_6]\cdot115\text{H}_2\text{O} (\text{Na-1}).$

Polyanion 1 consists of a cationic \{Mn$_{19}$(OH)$_{12}$\}\textsuperscript{26+} (Mn$_{19}$) assembly stabilized by six dilacunary \[\alpha\text{-SiW}_{10}\text{O}_{37}\]\textsuperscript{10-} units resulting in a structure with $S_6$ point group symmetry (see Figure 3.3). To the best of our knowledge, 1 represents the highest nuclearity manganese-containing POM known to date. All 19 Mn$^{II}$ ions lie in the same plane forming a hexagonal structure based on edge-shared MnO$_6$ octahedra. The Mn$^{II}$ ions in Mn$_{19}$ are connected in total via twelve $\mu_3$-hydroxo bridges, as based on bond valence sum (BVS) calculations.$^{32}$ The discrete Mn$_{19}$ nanosheet (see Figure 3.5) is held in place by six dilacunary \[\alpha\text{-SiW}_{10}\text{O}_{37}\]\textsuperscript{10-} units via $\mu_4$, $\mu_3$, and $\mu_2$-oxo bridges. The central Mn$^{II}$ ion in Mn$_{19}$ is hexa-coordinated in a regular octahedral fashion with average Mn-O bond lengths of 2.21(4) Å. This unique Mn$^{II}$ ion is bridged to the six surrounding Mn$^{II}$ ions via six hydroxo bridges, resulting in a compact Mn$_7$ core-fragment resembling the Anderson-Evans structure type.$^{33}$ Interestingly, all these six outer Mn$^{II}$ ions are seven-coordinated, each with four ‘normal’ Mn-O bonds (ca 2.1-2.2 Å) and three long Mn-O bonds (ca 2.4-2.6 Å). BVS calculations reveal a combined contribution of ca. 1.5 bond valences from the four shorter bonds and 0.5 from the three longer ones, resulting in the expected total bond valence of 2.0 for each of the six Mn$^{II}$. Seven-coordination for Mn$^{II}$ is not unusual, and has in fact been observed previously in coordination chemistry.$^{34}$ The Mn$_7$ core itself is surrounded by a ring of 12 Mn$^{II}$ ions, which are all hexa-coordinated in a distorted octahedral fashion with Mn-O bond lengths ranging from 2.02(3)
Figure 3.3 Combined polyhedral/ball-and-stick representation of 1 Protonated oxygens are shown in pink. Color code: WO$_6$ green octahedra, SiO$_4$ blue tetrahedra, Mn yellow balls, O red balls.

Figure 3.4 Ball-and-stick representation of the Mn$_{19}$-oxo-hydroxo core in 1.
to 2.37(2) Å. These 12 outer Mn\textsuperscript{II} ions are arranged in six edge-shared pairs, each filling the lacunary sites of the six \([\alpha\text{-SiW}_{10}O_{37}]^{10}\) units.

Polyanion \textbf{1} crystallized as a hydrated sodium salt (Na-\textbf{1}) in the triclinic space group \textit{P}-\textit{1}. Thermogravimetric analysis (TGA) was performed on Na-\textbf{1} and resulted in 115 water crystal waters (see Figure. 3.2).

A number of synthetic factors play a significant role in the formation of polyanion \textbf{1}, such as the type of reactant salt, ratio of reactants, pH, temperature, and solvent. The synthesis of polyanion \textbf{1} is only successful when starting with the sodium salt of the trilacunary precursor \([A-\alpha\text{-SiW}_9O_{34}]^{10}\) and if no other counter cations are present in solution during the reaction. An extra tungsten center is inserted into \([A-\alpha\text{-SiW}_9O_{34}]^{10}\) in-situ, most likely as a result of partial decomposition of some of the lacunary POM precursor in solution. Interestingly, addition of one equivalent of sodium tungstate at any point during the reaction did not result in \textbf{1}.

The synthetic procedure of \textbf{1} consists of two steps. The first step involves reaction of Mn\textsuperscript{II} ions with the trilacunary precursor \([A-\alpha\text{-SiW}_9O_{34}]^{10}\) at room temperature and pH 8 for about 30 minutes, and the second step involves addition of sodium phosphate and adjustment to pH 8, followed by moderate heating for around one hour. These two steps appear to be crucial for the successful synthesis of polyanion \textbf{1}. If the reaction is performed directly in phosphate buffer, \textbf{1} is not formed. The pH of formation is also critical, as pH <7 or >9 does not lead to the formation of \textbf{1}. The temperature of step 2 is also crucial, as the yield improves with increasing temperature, but above 70 °C an unidentified black-brown side-product is formed. Also, step 2 seems to work only in sodium phosphate buffer. Efforts to reproduce polyanion \textbf{1} by addition of sodium acetate, sodium carbonate or NaCl instead of Na\textsubscript{3}PO\textsubscript{4} to the reaction
Figure 3.5 Polyhedral and ball-and-stick representations of the basic building blocks of 1.
mixture, while keeping the pH at 8, were all unsuccessful. All this reflects the difficulty of rationalizing the mechanistic pathways of POM formation.

Another \( \text{Mn}_{19} \) compact cluster has been reported by Westin et al through reaction of elemental potassium with the anhydrous MnCl\(_2\) salt in methanol to give the methoxyethoxide-stabilized [Mn\(_{19}\)O\(_{12}\)(moe)\(_{14}\)(moeH)\(_{10}\)] \((\text{Mn}_{19}\text{org})\).\(^{35}\) The structure of \( \text{Mn}_{19}\text{org} \) reveals considerable differences with that of \( \text{Mn}_{19} \) in polyanion 1. All the manganese centers in \( \text{Mn}_{19}\text{org} \) are hexacoordinated and the twelve outer manganese cations are edge shared amongst each other and not arranged in pairs like in \( \text{Mn}_{19} \).

### 3.1.1.3 Conclusions

In summary, we have prepared the novel and unexpected, discrete polyanion 1, comprising a planar \( \text{Mn}_{19}(\text{OH})_{12}\)^{26+} assembly incorporated in a 60-tungsto-6-silicate by reaction of Mn\(^{II}\) ions with [\( \text{A-}\alpha\text{-SiW}_{9}\text{O}_{34}\)]\(^{10}\) in aqueous solution at room temperature and pH 8. The planar Mn\(_{19}\) magnetic cluster in 1 is unprecedented in POM chemistry, and in fact 1 contains more manganese ions than any other polyanion reported to date. For more information regarding magnetic studies, please see chapter five section (5.1.1). The manuscript for this result has been accepted in Angewandte Chemie.
3.1.2 $K_{18}Mn[Mn_2(H_2O)_6\{Mn_2(GeW_{10}O_{38})\}]_3 \cdot 20H_2O \ (KMn-2)$

**Synthesis:** 0.24 g (0.83 mmol) of Mn(NO$_3$)$_2$ were dissolved in 20 mL of distilled water, then 0.58 g (0.20 mmol) of $K_8[\gamma-GeW_{10}O_{36}] \cdot 6H_2O$ were added. Using 2M K$_2$CO$_3$, pH of the resulting clear yellow solution was adjusted to 8 and it was left to stir at room temperature for 1 hour. The resultant turbid solution was left untouched in order to allow the precipitate to settle down and then filtered. The filtrate was left to evaporate slowly leading to the formation of yellow crystals. It should be noted that $KMn-2$ crystals have to be collected early enough (after one week) before $\{Mn_4(Ge_2W_{18})\}$ starts to appear as a by-product. The two types of products are distinguishable by shape and color, the desired product is in the form of pale yellow big crystals while the side product is yellowish brown crystalline product. Yield 100 mg (47%).

IR (2% KBr pellet, v/cm$^{-1}$): 923 (m), 876 (m), 773 (s), 738 (w), 511 (w), 444 (m), see Fig. 3.6
Figure 3.6 Infra-red spectra of the POM precursor \{\text{GeW}_{10}\} in black, and the product \text{KMn-2} in blue.

Figure 3.7 TGA curve of \text{KMn-2} from room temperature to 800 °C.
3.1.2.1 Single Crystal X-Ray Diffraction

Polyanion 2 crystallized as a hydrated potassium salt (KMn-2) in the monoclinic space group $P2_1/n$. Crystallographic data are detailed in Table 3.2.

Table 3.2 Crystal data for KMn-2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>KMn-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
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</tr>
<tr>
<td>Formula weight, g/mol</td>
<td>3140.26</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/n$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>13.4079(10)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>35.009(3)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>32.162(3)</td>
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<tr>
<td>$\alpha$,°</td>
<td>90.00</td>
</tr>
<tr>
<td>$\beta$,°</td>
<td>95.132(3)</td>
</tr>
<tr>
<td>$\gamma$,°</td>
<td>90.00</td>
</tr>
<tr>
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</tr>
<tr>
<td>$Z$</td>
<td>8</td>
</tr>
<tr>
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<tr>
<td>Independent reflections</td>
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</tr>
<tr>
<td>$R$(int)</td>
<td>0.1016</td>
</tr>
<tr>
<td>Observed (I &gt; 2σ(I))</td>
<td>14361</td>
</tr>
<tr>
<td>$R_I[</td>
<td>I &gt; 2\sigma(I)]^{[a]}$</td>
</tr>
<tr>
<td>wR$_2$ (all data)$^{[b]}$</td>
<td>0.2657</td>
</tr>
</tbody>
</table>

$^{[a]} R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^{[b]} R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. 

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3.1.2.2 Results and Discussion

Interaction of Mn$^{II}$ ions with $[\gamma$-GeW$_{10}$O$_{36}]^{8-}$ in a ratio of 4:1, in aqueous medium (pH adjusted to 8) resulted in the novel, trimeric $[\text{Mn}_2(\text{H}_2\text{O})_6\{\text{Mn}_2(\alpha$-GeW$_{10}$O$_{38})\}]^{20-}$ (2), see Fig.3.8. The core of polyanion 2 is composed of six Mn$^{II}$ ions that are encapsulated by three ($\alpha$-GeW$_{10}$O$_{38}$) and two capping manganese centers. Polyanion 2 is composed of three $\{\alpha$-Mn$_2$GeW$_{10}$O$_{38}\}$ Keggin fragments that are linked via Mn-O-W bridges leading to a trimeric assembly. Each of the Mn$^{II}$ ions are six-coordinated with six oxygen atoms adopting distorted octahedral geometries.

*Figure 3.8* Combined polyhedral/ball-and-stick representation of 2. Color code: GeO$_4$ violet tetrahedra, Mn yellow balls, O red balls.
Figure 3.9 Ball and stick presentation of 2. Color code: W (green), Mn (yellow), Ge (violet), and O (red).

Figure 3.10 Ball-and-stick representation of the Mn₈ core of 2.
Each Mn ion in the \{\alpha-\text{Mn}_2\text{GeW}_{10}\text{O}_{38}\} Keggin units occupies the vacant position of a \([\alpha-\text{GeW}_{10}\text{O}_{38}]^{12-}\) fragment through bonding to six oxygen atoms, three from WO$_6$ octahedra of the host Keggin unit, one from the central GeO$_4$ tetrahedron group, one from WO$_6$ octahedra of the neighbouring kegging unit and one from $\mu_3$-oxygen atoms of one of the central capping Mn$^{II}$.

According to IUPAC the Keggin type monomeric units should be formulated as \([\alpha-(1,4)\text{-}\text{Mn}_2\text{GeW}_{10}\text{O}_{38}]^8\) for 2.$^{37}$ The dilacunary polyanion \([\alpha(1,4)\text{-}\text{GeW}_{10}\text{O}_{38}]^{12-}\) is derived from a saturated Keggin unit \([\alpha\text{-}\text{GeW}_{12}\text{O}_{40}]^{4-}\) by removal of two W=O groups in the 1 and 4 positions, respectively, as defined by Pope and Scully.$^{38}$

Unlike \([\gamma\text{-}\text{XW}_{10}\text{O}_{36}]^{8-}\) (X= Ge, Si) the corresponding beta- and alpha-isomers \([\beta\text{-}\text{XW}_{10}\text{O}_{37}]^{10-}\) and \([\alpha\text{-}\text{XW}_{10}\text{O}_{38}]^{12-}\) could not be isolated yet by themselves, but only in the form of transition metal containing polyanions. The dilacunary polyanion \([\gamma\text{-}\text{XW}_{10}\text{O}_{36}]^{8-}\) can isomerize easily in aqueous solution to corresponding $\alpha$- and $\beta$-isomers. The three Keggin fragments are of the $\alpha$-type in polyanion 2, which is rare and the first structurally characterized compound containing such a dilacunary tungstogermanate fragment was the dimeric Ln-POMs which consist of two \([\text{Ln}_2(\alpha(1,4)\text{-}\text{GeW}_{10}\text{O}_{38})(\text{H}_2\text{O})_3])^{6-}\) (Ln = Dy, Er) moieties. Four lanthanide ions were located in the central belt between two \([\alpha(1,4)\text{-}\text{GeW}_{10}\text{O}_{38}]^{12-}\) units.$^{39}$ Therefore 2 is the second example composed of a $\alpha$–decatungstogermanate Keggin fragments and it represents the first trimeric derivative.

The formation of the \{\alpha-\text{XW}_{10}\text{O}_{38}\} unit is quite unusual, due to a strong tendency of the dilacunary $\alpha$-Keggin fragments to either form the plenary Keggin ion \([\alpha\text{-}\text{XW}_{12}\text{O}_{40}]^{4+}\) by uptake of two additional W$^{VI}$ centers (which can form in solution by partial decomposition of
the POM precursor) or the trilacunary derivative \([\alpha-XW_{9}O_{34}]^{10-}\) by loss of a tungsten atom.

Regarding silicotungstate, polyanions containing \(\{\alpha-SiW_{10}O_{38}\}\) have also been reported, such as \([Fe_{4}(OH)_{4}(\alpha-SiW_{10}O_{37})_{2}]^{12-}\) and \([\alpha-SiW_{10}Pt^{IV}_{2}O_{40}]^{8-}\). 40

The first in situ formation of beta isomer from \([\gamma-GeW_{10}O_{36}]^{8-}\) was observed by our group in \([K(H_{2}O)(\beta-Fe_{2}GeW_{10}O_{37}(OH))(\gamma-GeW_{10}O_{36})]^{12-}\) and \([\{\beta-Fe_{2}GeW_{10}O_{37}(OH)\}_{2}]^{12-}\). 41 On the other hand the \(\{\beta-SiW_{10}O_{37}\}\) units were found in \([\{\beta-Si_{2}W_{10}O_{37}(OH)_{2}(H_{2}O)\}_{2}]^{12-}\), \([\{\beta-Ti_{2}SiW_{10}O_{39}\}_{4}]^{24-}\), \([Zr_{4}O_{2}(OH)_{2}(H_{2}O)_{4}(\beta-SiW_{10}O_{37})_{2}]^{10-}\), and \([Zr_{6}O_{2}(OH)_{4}(H_{2}O)_{3}(\beta-SiW_{10}O_{37})_{3}]^{14-}\). 42

Bond valence sum calculations (BVS)\(^{32}\) indicate that 2 is not protonated and therefore its charge must be -20. Thermogravimetric analysis of \(KMn-2\) was performed between 25 and 800 °C under a nitrogen atmosphere to determine the amount of crystal water present in the polyanion (see Figure. 3.7). We observed a weight loss of approximately 10.5 % between 25 – 350 °C which can be assigned to the loss of 20 crystal waters

Polyanion 2 was initially obtained as a side product, such that few crystals of the title polyanion were found embedded in the precipitate of reported compound \([M_{4}(H_{2}O)_{2}(GeW_{9}O_{34})_{2}]^{12-}\) \(\{Mn_{4}\}\). 43 The heating temperature, concentration of the starting materials, source of Mn\(^{II}\) ions and nature of base used, affects the formation of polyanion 2 in terms of yield and side-product \(\{Mn_{4}\}\). The yield of 2 improves when going from higher temperature to room temperature conditions. Different bases i.e. NaOH, KOH, Na\(_{2}\)CO\(_{3}\) and K\(_{2}\)CO\(_{3}\) were used for pH adjustment purposes, among them 2M K\(_{2}\)CO\(_{3}\) found to give best results regarding yield and purity. Another important factor that played a very crucial role was the ratio of metal to ligand, addition of excess of metal ions than required resulted in longer
time gap to collect the desired compound, hence in good yield, before appearance of \(\text{[Mn}_4\text{]}\).

In addition, different manganese salts like Mn(CH\(_3\text{COO})_2\cdot4\text{H}_2\text{O}, \text{Mn(Cl)}_2\cdot2\text{H}_2\text{O}\) and Mn(NO\(_3\))\(_2\) were used as metal ion source, however XRD quality crystals were obtained with interaction of Mn(NO\(_3\))\(_2\).

### 3.1.2.3 Conclusions

In summary we have synthesized a novel Mn\(^{\text{II}}\)-containing tungstogerminate(IV) \([\text{Mn}_2(\text{H}_2\text{O})_6\{\text{Mn}_2(\alpha-\text{GeW}_{10}\text{O}_{38})\}_3]^{20-}\) (2) using a simple, one-pot procedure by reacting the dilacunary POM precursor \([\gamma-\text{GeW}_{10}\text{O}_{38}]^{8-}\) with the Mn\(^{\text{II}}\) ions in aqueous basic medium (pH 8), and structurally characterized in the solid state by single-crystal X-ray diffraction, FT-IR, and TGA. Polyanion 2 has an open, trimeric structure and is composed of six Mn\(^{\text{II}}\) ions that are encapsulated by three \((\alpha-\text{GeW}_{10}\text{O}_{38})\) and two central capping manganese cations in up and below fashion. Considering that 2 was prepared using the dilacunary gamma-Keggin isomer \([\gamma-\text{GeW}_{10}\text{O}_{36}]^{8-}\) it is obvious that this precursor must have isomerized in-situ to yield \([\alpha-\text{GeW}_{10}\text{O}_{38}]^{12-}\) fragments in 2 which encapsulate two manganese centers in vacant site. In addition, there are synthetic conditions that could affect the experimental results; those are reaction temperature, pH, concentration and nature of the starting material.
3.1.3 \( \text{Cs}_{10}\text{Na}_{12} \{[\text{Mn}_3(\text{B-\(\beta\)-PW}_9\text{O}_{33}(\text{OH})) (\text{B-\(\beta\)-PW}_8\text{O}_{29}(\text{OH})_2)]_2 \}\text{H}_2\text{O} \) (CsNa-3)

**Synthesis:** (0.125 g, 0.63 mmol) of \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) was dissolved in \( \text{H}_2\text{O} \) (20 mL). Solid \( \text{Na}_9[\text{A-\(\alpha\)-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O} \) (0.58 g, 0.20 mmol) was then added and stirred till a clear yellow solution is obtained. The pH value of the resulting mixture was adjusted to 8.0 with 6 M \( \text{NaOH} \). The resulting turbid solution was stirred for 30 minutes at room temperature. Solid \( \text{Na}_3\text{PO}_4 \) (0.5 g, 3.0 mmol) was then added to this solution in small portions while maintaining the pH at 8 with \( \text{HCl} \). The solution was stirred for one hour at room temperature. The mixture was allowed to stand at room temperature until the entire light brown precipitate settled down at the bottom of the beaker and then filtered. 1 mL of a 1 M \( \text{CsCl} \) solution was added to the filtrate, and the solution was allowed to evaporate at room temperature. After two week an orange crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the half of the original solution. The product was then collected by filtration and air dried.

**IR (2\% KBr pellet, \( \text{v/cm}^{-1} \)):** 3431 (s), 1617 (s), 1090 (w), 1031 (s), 957 (w), 932 (m), 877 (s), 781 (w), 726(s), 514 (w), 478 (w).
Chapter 3

Results: Transition Metal-Containing POMs

Figure 3.11 Infra-red spectra of the POM precursor {PW₉} (black) and the product CsNa-3 (blue).

Figure 3.12 TGA curve of CsNa-3 from room temperature to 1000 °C.

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3.1.3.1 Single Crystal X-Ray Diffraction

Polyanion 3 crystallized as a cesium sodium salt (CsNa-3) in the monoclinic space group $P2_1/n$. Data collected at room temperature is insufficient for a complete refinement and creation of cif file. Data collection at -100 °C temperature is hence necessary for satisfactory refinement and is desired to be performed later.

3.1.3.2 Results and Discussion

Reaction of Mn$^{II}$ ions with $[A-\alpha$-PW$_9$O$_{34}]^{9-}$ in a ratio of 3:1 in phosphate buffer medium (pH 8) at room temperature resulted in the asymmetric dimeric sandwich assembly $[\{\text{Mn}_3(B-\beta$-PW$_9$O$_{33}(OH))(B-\beta$-PW$_8$O$_{29}(OH)_2)\}_2]^{22-}$ (3) (see Figure 3.11).

![Figure 3.13](image1)

*Figure 3.13* (Left) Polyhedral presentation of 3. (Right) Mn$_3$ core of 3. Color code: rotated WO$_6$ (lime), MnO$_6$ (brown) and PO$_4$ (yellow).
This polyanion is composed of two non-equivalent Keggin fragments, \((B-\beta\text{-PW}_9\text{O}_{34})\) and \((B-\beta\text{-PW}_9\text{O}_{34})\), which are held together by three Mn\(^{II}\) ions, resulting in an asymmetric \((C_1\text{symmetry})\) sandwich structure.

This type of assembly has been observed by our group in \([\text{Co}_3(\text{H}_2\text{O})(B-\beta\text{-SiW}_9\text{O}_{33}(\text{OH}))B-\beta\text{-SiW}_9\text{O}_{29}(\text{OH})_2]\)\(^{11-}\) \(^{45a}\) and \([\text{Mn}(\text{H}_2\text{O})_2\{\text{Mn}_3(\text{H}_2\text{O})(B-\beta\text{-GeW}_9\text{O}_{33}(\text{OH}))B-\beta\text{-GeW}_9\text{O}_{30}(\text{OH})\}_2]\)\(^{22-}\) \(^{45b}\). The Mn atoms are linked to each of the lacunary units via two Mn-O-W bonds. The two outer Mn atoms are also linked to an oxygen atom of each PO\(_4\) hetero group, while the “inner” Mn atom completes its octahedral coordination sphere by an oxygen atom of the PO\(_4\) hetero group of the \((B-\beta\text{-PW}_9\text{O}_{34})\) fragment and a terminal water ligand. We assume that \((B-\beta\text{-PW}_9\text{O}_{34})\) fragment in 3 is formed by isomerization followed by the loss of one edge-shared WO\(_6\) octahedra from the rotated triad. Such transformation has been previously found in tungstosilicate and tungstogermanate chemistry namely, for \([\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}\) and \([\gamma\text{-GeW}_{10}\text{O}_{36}]^{8-}\) (mentioned before). \(^{45}\) Thus, 3 is the only polyanion to date containing \((B-\beta\text{-PW}_9\text{O}_{34})\) and \((B-\beta\text{-PW}_9\text{O}_{34})\) units generated by isomerization/decomposition from the \(A-\alpha\text{-nonatungstophosphate}\). It should also be noted that unlike \([\text{Co}_3(\text{H}_2\text{O})(B-\beta\text{-SiW}_9\text{O}_{33}(\text{OH}))B-\beta\text{-SiW}_9\text{O}_{29}(\text{OH})_2]\)\(^{11-}\) \(^{45a}\) and \([\text{Mn}(\text{H}_2\text{O})_2\{\text{Mn}_3(\text{H}_2\text{O})(B-\beta\text{-GeW}_9\text{O}_{33}(\text{OH}))B-\beta\text{-GeW}_9\text{O}_{30}(\text{OH})\}_2]\)\(^{22-}\) \(^{45b}\) polyanion 3 is formed under basic conditions (pH 8).

### 3.1.3.3 Conclusions

The manganese-containing phosphotungstate sandwich dimer \([\{\text{Mn}_3(B-\beta\text{-PW}_9\text{O}_{33}(\text{OH}))B-\beta\text{-PW}_9\text{O}_{29}(\text{OH})_2\}_2]\)\(^{22-}\) (3) has been synthesized in a simple, one-pot reaction in phosphate buffer medium (pH 8). Polyanion 3 is a sandwich type structure composed of two nonequivalent Keggin subunits, \((B-\beta\text{-PW}_9\text{O}_{34})\), \((B-\beta\text{-PW}_9\text{O}_{34})\) and three encapsulated Mn\(^{II}\) ions. These two fragments are linked via two Mn-O-W bridges resulting in the dimeric polyanion assembly.
The compound has been structurally characterized in the solid state by single-crystal X-ray diffraction, FT-IR, and TGA.
3.2 16-Cobalt(II)-Containing, 36-Tungsto-8-Phosphate

\[
[\{\text{Co}_4(\text{OH})_3\text{PO}_4\}_4(\text{PW}_9\text{O}_{34})_4]^{28-}
\]

3.2.1 Na$_{22}$Rb$_6[\{\text{Co}_4(\text{OH})_3\text{PO}_4\}_4(\text{A-}\alpha-\text{PW}_9\text{O}_{34})_4] \cdot 76\text{H}_2\text{O} (\text{NaRb-4})$

**Synthesis:** 0.39 g (1.63 mmol) of CoCl$_2$·6H$_2$O was dissolved in 20 mL H$_2$O. Then 0.58 g (0.20 mmol) Na$_9[\text{A-}\alpha-\text{PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ was added and stirred until a clear, purple solution was obtained. Then 0.50 g (3.0 mmol) Na$_3\text{PO}_4$ was added in small portions while maintaining the pH at 8 with HCl$_{aq}$. The resulting turbid solution was stirred for one hour at room temperature. Then the solution was allowed to stand at room temperature until the entire purple precipitate had settled at the bottom of the beaker and was then filtered off. Addition of 5-8 drops of 1.0 M RbCl solution to the filtrate resulted in a precipitate. The reaction mixture was kept at 30 °C for 10 minutes, and then filtered. The clear, dark purple filtrate was kept in an open vial at room temperature for slow evaporation. After one week a dark purple crystalline product started to appear. Evaporation was allowed to continue until about half the solvent had evaporated. The solid product was then collected by filtration and air-dried. Yield 100 mg (15 %).

IR (2% KBr pellet, v/cm$^{-1}$): 3468 (s), 1630 (s), 1088 (w), 1068 (m), 1026 (m), 940 (s), 884 (w), 816 (m), 703 (.w), 679 (w), 611 (w).

Elemental analysis for Na$_{22}$Rb$_6[\{\text{Co}_4(\text{OH})_3\text{PO}_4\}_4(\text{A-}\alpha-\text{PW}_9\text{O}_{34})_4] \cdot 76\text{H}_2\text{O}$ (NaRb-4), calc (found): Na 3.87% (3.16%), P 1.90% (1.95%), Co 7.22% (7.15%), W 50.71% (51.30%).
Figure 3.14 FT-IR spectra of \{PW_9\} precursor (black) and NaRb-4 (blue).

Figure 3.15 TGA curve of NaRb-4 from room temperature to 900 °C.
3.2.1.1 Single Crystal X-Ray Diffraction

Polyanion 4 crystallized as a hydrated sodium rubidium salt (NaRb-4) in the cubic space group Fd-3. Crystallographic data are detailed in Table 3.3.

Table 3.3 Crystal data for NaRb-4.

<table>
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<th>Compound</th>
<th>NaRb-4</th>
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<tbody>
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<td>Formula</td>
<td>Na_{22}Rb_{6}[{Co_{4}(OH)<em>{3}PO</em>{4}}<em>{4}(A-\alpha-PW</em>{9}O_{34})<em>{4}]76H</em>{2}O</td>
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<tr>
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<td>D_{calc}, g/cm³</td>
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<td>Crystal size, mm</td>
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<td>R(int)</td>
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<tr>
<td>Observed (I &gt; 2σ(I))</td>
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<tr>
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<tr>
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<tr>
<td>R_{1}[I &gt; 2σ(I)]^{[a]}</td>
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<tr>
<td>wR_{2} (all data)^{[b]}</td>
<td>0.2472</td>
</tr>
</tbody>
</table>

[a] \( R = \Sigma||F_o|| - |F_c||/\Sigma|F_o| \). 
[b] \( R_w = \left[ \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2 \right]^{1/2} \).
3.2.1.2 Results and Discussion

The Polyanion 4 was synthesized in a simple one-pot reaction of CoCl$_2$·6H$_2$O with Na$_9$[A-α-PW$_9$O$_{34}$]·7H$_2$O in aqueous medium at pH 8. The title polyanion crystallized as a hydrated sodium rubidium salt, Na$_{22}$Rb$_6$[{(Co$_4$(OH)$_3$)(A-α-PW$_9$O$_{34}$))$_4$]·76H$_2$O (NaRb-4) in the cubic space group Fd-3. Single-crystal XRD analysis on NaRb-4 revealed that 4 comprises a central {Co$_4$O$_4$} cubane unit which is capped by four tri-Co$^{II}$ substituted Keggin fragments [(Co(OH))$_3$(A-α-PW$_9$O$_{34}$)]$^6^-$ and four phosphate linkers, resulting in an assembly with idealized $T_d$ symmetry (see Figure 3.16).

Alternatively, the structure of polyanion 4 can be viewed as a tetrahedral {Co$_4$(PO$_4$)$_4$}$_4^+$ core capped by four [(Co(OH))$_3$(A-α-PW$_9$O$_{34}$)]$^6^-$ via the vertices. The four Co$^{II}$ ions in the cubane unit are coordinated by three $\mu_3$-OH groups of the [(Co(OH))$_3$(A-α-PW$_9$O$_{34}$)]$^6^-$ units and three $\mu_4$-O atoms of three PO$_4$ linkers. The three ‘outer’ oxygens of each phosphate group link three [(Co(OH))$_3$(A-α-PW$_9$O$_{34}$)]$^6^-$ fragments via three P-O(Co) bonds. All 16 Co$^{II}$ ions in 4 exhibit a distorted octahedral geometry with Co-O bond lengths in the range 2.053(19)-2.364(19) Å. Interestingly the magnetic {Co$_{16}$(OH)$_{12}$(PO$_4$)$_4$}$_{8^+}$ core exhibits single-molecule magnetic behavior. Polyoxometalates with enriched nucleophilic oxo ligands possess great potential tendency to stabilize and synthesize polynuclear metal aggregates with desirable SMM behaviors. Such type of polyoxometalate based SMMs have been reported recently.$^{47}$ Protonated oxygens were identified by bond valence sum (BVS) calculations.$^{32}$ All 12 $\mu_3$-
Figure 3.16 Representations of the various building blocks comprising 8 (upper left) 8, (upper middle) \{Co_2(PO_4)_4\}^{8-}, (upper right) polyanion 8, (middle left) \{Co_{16}(OH)_{12}(PO_4)_4\}^{14+} (middle right) Platonic picture. Color code: Co violet octahedra, PO_4 yellow tetrahedra, Co violet balls. Protonated oxygens are shown in rose.
oxygens bridging Co ions in 4 are monoprotonated, whereas all the phosphate oxygens are non-protonated, supporting the polyanion formula \([\{\text{Co}_4(\text{OH})_3\text{PO}_4\}_4(\text{A}-\alpha-\text{PW}_9\text{O}_{34})_4]\)\(^{28}\). The total charge of 4 is therefore 28- which is balanced in the solid state by 22 sodium and six rubidium countercations. The reported formula is based on three different analytical methods namely single-crystal XRD, elemental analysis and thermogravimetric analysis (TGA). The latter technique indicated the presence of 76 crystal waters in NaRb-4 (see Figure 3.15).

Transition metal-substituted POMs constitute the largest subclass of polyanions, and compare to the rest of transition metals, Co\(^{II}\)-containing heteropolyoxometalates have been intensively investigated and quite a large number of structures have been reported. So far from two to sixteen Co\(^{II}\) containing polyoxometalates have been reported. The class of cobalt-containing POMs was pioneered by Baker and Pope.\(^{48a,b}\) Meanwhile a large number of dimeric, sandwich-type polyanions of the Weakley-type with 4 Co\(^{II}\) centers have been reported.\(^{48c-g}\)

Very recently it was shown that \([\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]\)\(^{10}\) is a hydrolytically and oxidatively stable homogeneous water oxidation catalyst.\(^{48g}\) The penta-cobalt-containing \([\text{Co}_3(\text{H}_2\text{O})_2(\text{CoW}_9\text{O}_{34})_2]\)\(^{12-}\),\(^{49a}\) the hexanuclear \([((\text{COOH})_2\text{Co}_2\text{PW}_9\text{O}_{34})_2(\text{PW}_6\text{O}_{26})]\)\(^{17-}\),\(^{49b}\) and the heptanuclear \([\text{Co}_7(\text{H}_2\text{O})_2(\text{OH})_2\text{P}_2\text{W}_{25}\text{O}_{94}]\)\(^{16-}\),\(^{49c}\) have also been reported. The octanuclear \([(\text{A}-\alpha-\text{SiW}_9\text{O}_{34})_2\text{Co}_8(\text{OH})_6(\text{H}_2\text{O})_2(\text{CO}_3)_3]\)\(^{16-}\) is also known.\(^{49d}\) The nonanuclear \([\text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_6\text{O}_{34})]\)\(^{16}\) was first identified as a by-product by Weakley,\(^{50a}\) and later reinvestigated by Coronado including magnetic studies.\(^{50b}\) Our group has reported the nonanuclear \([\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_9(\beta-\text{SiW}_8\text{O}_{31})_3]\)\(^{17-}\) which in addition contains six antenna-like, capping Co\(^{II}\) ions in the solid state.
3.2.1.3 Conclusions

It is a challenge to encapsulate high nuclearity magnetic cores in diamagnetic POM shells, in particular by using conventional, soft synthesis methods. However we were able to prepare the 16 cobalt(II)-containing, tetrameric 36-tungsto-8-phosphate \([\{\text{Co}_4\text{(OH)}_3\text{PO}_4\}_4\text{(PW} _9\text{O}_{34})_4\}^{28-}\) (4) via a simple, one-pot synthetic procedure. The magnetic \(\{\text{Co}_{16}\text{(OH)}_{12}\text{(PO}_4)_4\}^{8+}\) core exhibits single-molecule magnetic behavior and represents the largest cobalt aggregate in polyoxotungstate chemistry. For more information regarding magnetic studies, please see chapter five section (5.1.2).
3.3 Multi-Nickel(II)-Containing Polyoxometalates

In this section the synthesis, characterization and crystal structures of the tetradeca-Ni\(^{II}\) containing tetrameric \([(\text{Ni}_{14}(\text{H}_2\text{O})_{10}(\text{OH})_{6}(\text{PO}_3\text{(OH)})_4(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_4)^{-34}\) \(5\), penta- Ni\(^{II}\)-substituted asymmetric dimeric \([\text{Ni}_5(\text{H}_2\text{O})_4(\text{OH})_4(\beta\text{-GeW}_9\text{O}_{34})(\beta\text{-GeW}_8\text{O}_{31})]^{14}\) \(6\) and di- Ni\(^{II}\)-substituted symmetric dimeric \([\text{NaOH}_2\text{Ni}_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^ {18}\) \(7\) will be discussed.

3.3.1 \(\text{Na}_{26}\text{Rb}_8[(\text{Ni}_{14}(\text{H}_2\text{O})_{10}(\text{OH})_6(\text{PO}_3\text{(OH)})_4(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_4)^{-96}\text{H}_2\text{O}\) (NaRb-5)

**Synthesis:** \(\text{NiCl}_2\cdot6\text{H}_2\text{O}\) (0.15 g, 0.63 mmol) was dissolved in 20 mL \(\text{H}_2\text{O}\). Then solid \(\text{Na}_{12}[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]\cdot24\text{H}_2\text{O}\) (0.88 g, 0.20 mmol) was added and stirred until a clear green solution was obtained. The pH value of the resulting mixture was adjusted to 8.0 with 4 M \(\text{NaOH}\) and was stirred for 10 minutes at room temperature. Then solid \(\text{Na}_3\text{PO}_4\) (0.50 g, 3.0 mmol) was added to this solution in small portions, while maintaining the pH at 8 with \(\text{HCl}_\text{aq}\). The mixture was stirred at room temperature for 1 hour, allowed to settle down the precipitate, and then filtered. The filtrate was allowed to evaporate in an open vial at room temperature. After one week a green crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the solid product, which was then collected by filtration and air dried. Yield 400 mg (42 %).

**IR (2% KBr pellet, v/cm\(^{-1}\)):** \(1085\) (s), \(1051\) (m), \(1011\) (w), \(938\) (m), \(912\) (w), \(880\) (w), \(813\) (s), \(728\) (s), \(599\) (w), \(562\) (w) \(520\) (s), \(458\) (w). see Figure 3.17.
Figure 3.17 Infra-red spectra of the POM precursor \( \{P_2W_{15}\} \) (black) and the product \textbf{NaRb-5} (blue).

Figure 3.18 TGA curve of \textbf{NaRb-5} from room temperature to 1000 °C.
3.3.1.1 Single Crystal X-Ray Diffraction

Polyanion 5 crystallized as a hydrated sodium rubidium salt (NaRb-5) in the triclinic space group $P\overline{1}$.

Because of having continuous problem with low temperature device, data collection at -100K temperature was performed by Prof. G.B. Jamesom from Institute of Fundamental Sciences, Massey University, New Zealand. Crystal data and structure refinement details for 5 therefore will be provided later.

3.3.1.2 Results and Discussion

The reaction of trilacunary polyanion $[\alpha-P_2W_{15}O_{56}]^{12-}$ with NiCl$_2\cdot$6H$_2$O in phosphate buffer (pH 8) at normal conditions gives a novel tetrameric polyoxotungstate 5, having the molecular formula Na$_{26}$Rb$_8$[(Ni$_{14}$(H$_2$O)$_{10}$(OH)$_6$(PO$_3$(OH))$_4$]$\{\alpha$-P$_2W_{15}O_{56}\}$_4$]96H$_2$O. The compound was well characterized by IR, TGA studies and single crystal XRD analysis. The 14 Ni$^{II}$ containing $[(A-\alpha-P_2W_{15}O_{56})_4(Ni_{14}(H_2O)_{10}(OH)_6(PO_3)_{4})_4]^{38-}$ is composed of four Wells-Dawson type $\{Ni_3P_2W_{15}\}$ fragments encapsulating a central di-nickel-oxo unit and four capping phosphate groups. The resulting structure contains a central $\{Ni_{14}P_4\}$ core, consisting of four groups of three edge-shared, corner-linked NiO$_6$ octahedra. The four Ni$_{3}$-capped Dawson units are arranged in a tetrahedral fashion around the central $\{Ni_2P_4\}$ templating unit, see Figure 3.19, which in turn links up the four Wells-Dawson units.

One of two Ni$^{II}$ ions in the $\{Ni_2P_4\}$ unit are coordinated by two $\mu_3$-OH groups of the $\{(Ni_{III}O_2(OH))(\alpha-P_2W_{15}O_{56})\}$ units and four $\mu_2$-O atoms of two capping PO$_4$ units, while the second Ni$^{III}$ center in the $\{Ni_2P_4\}$ unit are coordinated by two $\mu_3$-OH groups of the
Figure 3.19 Combined polyhedral/ball-and-stick representation, (upper left) the basic building blocks of 5, (upper right) 5 (bottom right) polyanion (5), (bottom left) $\{\text{Ni}_{14}\}$ core. Color code: PO$_4$ yellow tetrahedra, Ni bright green balls, O red.
\(\{(\text{Ni}^\text{II}O_2(OH))(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})\}\) units and two \(\mu_2\)-O atoms of two capping \(\text{PO}_4\) units and the remaining two coordination sphere is filled by the two aqua ligands. The two oxygens of each phosphate group link two \(\{(\text{Ni}^\text{II}O_2(OH))(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})\}\) fragments via two P-O(Ni) bonds. All fourteen Ni\(^{\text{II}}\) ions in 5 exhibit a distorted octahedral geometry with Ni-O bond lengths in the range 2.00-2.35 Å. Protonated oxygens were identified by bond valence sum (BVS) calculations.\(^{32}\) The total charge of 5 is therefore 34-, which is balanced by 28 sodium and 8 rubidium counter cations in the solid state. Thermogravimetric analysis (TGA) indicated the presence of 96 crystal waters in \(\text{NaRb-5}\) (see Fig 3.18).

Polyanion 5 represents to date the largest nickel aggregate in polyoxotungstate chemistry, though an organic–inorganic hybrid polytungstate containing 20-Ni-substituted \([\text{H}_2\text{Ni}_{20}\text{P}_4\text{W}_{34}(\text{OH})_4\text{O}_{136}(\text{enMe})_8(\text{H}_2\text{O})_6]\)\(^{6-}\) ion with three \([\text{Ni}(\text{enMe})_2]^{2+}\) complexes as countercations has recently been reported.\(^{25}\) Unlike our polyanion 5, the reported \(\{\text{Ni}_{20}\}\) was synthesized under hydrothermal conditions and is composed of two \([\text{Ni}_6\text{O}_3(\text{OH})_2(\text{H}_2\text{O})(\text{enMe})_2(\text{PW}_6\text{O}_{26})(\text{PW}_9\text{O}_{34})]\) moieties \(\{\text{Ni}_6\text{P}_2\text{W}_{15}\}\), linked by a central \(\{\text{Ni}_8\text{W}_4\text{O}_{26}(\text{H}_2\text{O})_4(\text{enMe})_4\}\) segment \(\{\text{Ni}_8\text{W}_4\}\).

### 3.3.1.3 Conclusions

In summary, we have synthesized the 14-Ni\(^{\text{II}}\)-containing 60-tungsto-12-phosphate \(\{(\text{Ni}_{14}(\text{H}_2\text{O})_{10}(\text{OH})_6(\text{PO}_3(\text{OH}))_4(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_4\}_4\text{NaRb-5}\) using a simple, one-pot procedure by reacting the trilacunary 15-tungstophosphate precursor \([\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}\) with Ni\(^{\text{II}}\) ions in phosphate buffer. Polyanion 5 was isolated as a hydrated sodium rubidium salt \(\text{Na}_{26}\text{Rb}_8[(\text{Ni}_{14}(\text{H}_2\text{O})_{10}(\text{OH})_6(\text{PO}_3(\text{OH}))_4(\alpha\text{-P}_2\text{W}_{15}\text{O}_{56})_4\}_4\text{NaRb-5}]\cdot76\text{H}_2\text{O}\) (\(\text{NaRb-5}\)), which was investigated in the solid state by single-crystal XRD, FT-IR spectroscopy and thermogravimetric analysis, as well. The novel polyanion 5 represents the largest nickel
aggregate in polyoxotungstate chemistry. We plan to perform magnetic studies on the title polyanion.
3.3.2 $K_{14}[Ni_5(H_2O)_4(OH)_4(\beta-GeW_9O_{34})(\beta-GeW_8O_{31})] \cdot 29H_2O$ (K-6)

**Synthesis:** 0.15 g (0.63 mmol) of NiCl$_2$·6H$_2$O were dissolved in 20 mL of distilled water, then 0.58 g (0.20 mmol) of $K_8[\gamma-GeW_{10}O_{36}] \cdot 6H_2O$ were added. Using 2M K$_2$CO$_3$, pH of the resulting clear green solution was adjusted to 8 and it was left to stir at room temperature for 1 hour. The resultant turbid solution was left untouched in order to allow the precipitate to settle down and then filtered. After addition of 3-5 drops of 1.0 M KCl the filtrate was left to evaporate slowly leading to the formation of green crystals. Yield 50 mg (8 %).

IR (2% KBr pellet, $\nu$/cm$^{-1}$): 936 (s), 871 (m), 791 (s), 694 (.m), 550 (w), 458 (s) see Figure. 3.20.
Figure 3.20 Infra-red spectra of the precursor \([\text{GeW}_{10}]\) (black) and the product \(\text{K-6}\) (blue).

Figure 3.21 TGA curve of \(\text{K-6}\) from room temperature to 1000 °C.
3.3.2.1 Single Crystal X-Ray Diffraction

Polyanion 6 crystallized as a hydrated potassium salt (K-6) in the triclinic space group *P*-1. Crystallographic data are detailed in Table 3.4.

**Table 3.4 Crystal data for K-6.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>K-6.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>$K_{14}[\text{Ni}<em>5(\text{H}<em>2\text{O})<em>9(\text{OH})<em>d(\beta-\text{GeW}</em>{9}\text{O}</em>{34})(\beta-\text{GeW}</em>{8}\text{O}</em>{31})] \cdot 29\text{H}_2\text{O}$</td>
</tr>
<tr>
<td><strong>Formula weight, g/mol</strong></td>
<td>6277.99</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td><em>P</em>-1</td>
</tr>
<tr>
<td><strong>a</strong>, Å</td>
<td>18.4924(4)</td>
</tr>
<tr>
<td><strong>b</strong>, Å</td>
<td>21.8208(4)</td>
</tr>
<tr>
<td><strong>c</strong>, Å</td>
<td>25.2971(6)</td>
</tr>
<tr>
<td><strong>α</strong>, °</td>
<td>81.7470(10)</td>
</tr>
<tr>
<td><strong>β</strong>, °</td>
<td>73.8930(10)</td>
</tr>
<tr>
<td><strong>γ</strong>, °</td>
<td>85.1010(10)</td>
</tr>
<tr>
<td><strong>Volume, Å(^3)</strong></td>
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</tr>
<tr>
<td><strong>Z</strong></td>
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</tr>
<tr>
<td><strong>Absorption coefficient</strong></td>
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</tr>
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<td><strong>Reflections collected</strong></td>
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</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>39077</td>
</tr>
<tr>
<td><strong>R(int)</strong></td>
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</tr>
<tr>
<td><strong>Observed (I &gt; 2σ(I))</strong></td>
<td>27241</td>
</tr>
<tr>
<td><strong>R(_1)[I &gt; 2σ(I)](^{[a]})</strong></td>
<td>0.0529</td>
</tr>
<tr>
<td><strong>wR(_2) (all data)(^{[b]})</strong></td>
<td>0.1566</td>
</tr>
</tbody>
</table>

\[ [a] \ R = \Sigma |F_o| - |F_c|/\Sigma |F_o|. \ [b] \ wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}. \]

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3.3.2.2 Results and Discussion

Interaction of Ni$^{II}$ ions with [$\gamma$-GeW$_{10}$O$_{36}$]$^{8-}$ in a ratio of 3:1, in aqueous medium (pH adjusted to 8) resulted in the nonequivalent, dimeric polyanion [Ni$_3$(H$_2$O)$_4$(OH)$_4$(β-GeW$_9$O$_{34}$)(β-GeW$_8$O$_{31}$)]$^{14-}$ (6), see Figure 3.22. Single crystal XRD reveals that polyanion 6 is composed of two asymmetric Keggin units, [β-GeW$_9$O$_{34}$]$^{10-}$ and [β-GeW$_8$O$_{31}$]$^{10-}$ which are connected via a penta-Ni-cluster. The polyanion can also be described as a dimer consisting of the tri-Ni$^{II}$-substituted β-Keggin-type polyoxoanions {β-Ni$_3$GeW$_{9}$O$_{34}$} and the di-Ni$^{II}$-substituted β-structure {β-Ni$_2$GeW$_{8}$O$_{31}$} linked by three $\mu_3$-OH groups. All the Ni$^{II}$ centers are hexa coordinated with distorted octahedral geometry.

Figure 3.22 Combined polyhedral/ball-and-stick representation, (left) 6, (right) {Ni$_6$} core. Color code: rotated WO$_6$ lime, GeO$_4$ purple tetrahedra.
To the best of our knowledge, this type assembly was first reported for the silicotungstate by Enbo Wang in 2007. So far only a few examples of the asymmetric dimeric structure have been reported, which has been discussed in detail in previous section (3.1.3.2).

Bond-valence calculations confirmed that the terminal oxygen atoms are all deprotonated and all $\mu_2$-oxo linking the nickel ions are monoprotonated. The total charge of 6 is therefore 14-, which is balanced by 14 potassium counter cations in the solid state Thermogravimetric analysis (TGA) was performed on K-6 in order to estimate the number of crystal water molecules per formula units, and was calculated to be ca 29 water molecules (see Figure. 3.21).

### 3.3.2.3 Conclusions

In summary, we have successfully synthesized a rare penta-Ni$^{II}$-substituted dimeric assembly $[\text{Ni}_5(\text{H}_2\text{O})_4(\text{OH})(\beta\text{-GeW}_9\text{O}_{34})(\beta\text{-GeW}_8\text{O}_{31})]^{14-}$ (6), made up of two nonequivalent Keggin units, $\{\beta\text{-Ni}_3\text{GeW}_9\text{O}_{34}\}$ and $\{\beta\text{-Ni}_2\text{GeW}_8\text{O}_{31}\}$ and was structurally characterized in the solid state by single-crystal X-ray diffraction, FT-IR, and TGA. The magnetic studies will be carried out by our collaborators.
3.3.3 \( \text{Na}_{14}[(\text{NaOH}_2)_2\text{Ni}_2\{\text{P}_2\text{W}_{15}\text{O}_{54}(\text{OH})_2\}]_2\cdot 43\text{H}_2\text{O} \) (Na-7)

**Synthesis:** \( \text{NiCl}_2 \cdot 6\text{H}_2\text{O} \) (0.15 g, 0.63 mmol) was dissolved in 20 mL \( \text{H}_2\text{O} \). Then solid \( \text{Na}_{12}[^{\alpha}-\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 24\text{H}_2\text{O} \) (0.88 g, 0.20 mmol) was added and stirred until a clear green solution was obtained. Solid 3.57 g of \( \text{Na}_2\text{C}_2\text{O}_4 \) was added to the reaction mixture which raised the pH of the solution to 8. The mixture was stirred at room temperature for 1 hour, allowed to settle down the precipitate, and then filtered. The filtrate was allowed to evaporate in an open vial at room temperature. After one week a green crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the solid product, which was then collected by filtration and air dried.

IR (2\% KBr pellet, \( \text{v/cm}^{-1} \)): 1085 (s), 1048 (w), 1030 (w), 1017 (m), 932 (m), 881 (m), 801 (m), 742 (s), 601 (.w), 524 (m) see Figure 3.23.
Figure 3.23 Infra-red spectra of the POM precursor \{P_2W_{15}\} (black) and the product \textbf{Na-7} (blue).

Figure 3.24 TGA curve of \textbf{K-6} from room temperature to 1000 °C.
3.3.3.1 Single Crystal X-Ray Diffraction Data

Polyanion 7 crystallized as a hydrated sodium salt (Na-7) in the triclinic space group P-1. Crystallographic data are detailed in Table 3.5.

Table 3.5 Crystal data for Na-7.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Na-7.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Na_{14}[(\text{NaOH}_2)_2\text{Ni}<em>2{(\text{P}<em>2\text{W}</em>{15}\text{O}</em>{44}(\text{OH})_2)}_2]\cdot43\text{H}_2\text{O}</td>
</tr>
<tr>
<td>Formula weight, g/mol</td>
<td>8727.36</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>(a), Å</td>
<td>13.243(4)</td>
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<tr>
<td>(b), Å</td>
<td>13.892(4)</td>
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<tr>
<td>(c), Å</td>
<td>23.614(8)</td>
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<td>(\alpha),°</td>
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<td>(\beta),°</td>
<td>78.234(9)</td>
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<tr>
<td>(\gamma),°</td>
<td>65.512(8)</td>
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<tr>
<td>Volume, Å(^3)</td>
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<td>(Z)</td>
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<td>(D_{\text{calc}}), g/cm(^3)</td>
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<td>Independent reflections</td>
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<tr>
<td>Observed (I &gt; 2(\sigma(I)))</td>
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<tr>
<td>(R_I[I &gt; 2\sigma(I)])(^{[a]})</td>
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<tr>
<td>(wR_2) (all data)(^{[b]})</td>
<td>0.1724</td>
</tr>
</tbody>
</table>

\(^{[a]} R = \Sigma|F_o| - |F_c|/\Sigma|F_o|. \)\(^{[b]} R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}. \)
3.3.3.2 Results and Discussion

The polyanion [(NaOH$_2$)$_2$Ni$_2$(P$_2$W$_{15}$O$_{56}$)$_2$]$^{18-}$ was synthesized in a simple one-pot reaction of NiCl$_2$ with Na$_{12}$$[\alpha$-$P_2$W$_{15}$O$_{56}]$$\cdot$24H$_2$O in aqueous medium at pH 8 in the presence of excess of sodium oxalate and then isolated as a hydrated sodium salt, Na$_{18}$$[(NaOH)$_2$Ni$_2$(P$_2$W$_{15}$O$_{56}$)$_2$]$$\cdot$43H$_2$O (Na-7). It seems that the presence of high concentration of Na$^+$ ions is essential for the formation of disubstituted sandwich-type polyoxoanion 7, which consists of two trilacunary $[\alpha$-$P_2$W$_{15}$O$_{56}]$$^{12-}$Wells-Dawson moieties linked via two Ni$^{II}$ ions and two sodium ions resulting in a sandwich-type structure of C$_{2h}$ symmetry (see Figure 3.25).

*Figure 3.25* Combined polyhedral/ball-and-stick representation, (left) 7, (right) {Na$_2$Ni$_2$} core. Color code: PO$_4$ yellow tetrahedra, Ni bright green balls, sodium grey balls.
This structure is similar to that of the tetranuclear Weakly type species \{\text{shortly } M_4P_4W_{30}\}, where the two “external” transition metals has been replaced by two weakly bound seven-coordinated Na\(^+\) ions; this substitution maintains the \(C_2h\) symmetry of the \{\text{M}_4\text{P}_4\text{W}_{30}\} framework.\(^{54}\) Each sodium ion is coordinated to six \(\mu_3\)-oxygen oxygen atoms of two trivacant \([\text{a-P}_2\text{W}_{15}\text{O}_{56}]^{12-}\) units and a weakly bound terminal water molecule. Such coordination geometry for Na\(^+\) ions in hydrated solids are not unusual. In POM chemistry such kind of non-octahedral coordination geometry has been also observed.\(^{55}\) The two Ni\(^{II}\) centers are chemically equivalent and octahedrally coordinated. Each of the four edge-sharing polyhedral units in the central unit (two internal NiO\(_6\) octahedra and two external distorted NaO\(_7\) heptahedra) shares corners with a pair of corner shared WO\(_6\) octahedra at the belt position of the trivacant \{\text{P}_2\text{W}_{15}\} unit.

Our polyanion \([(\text{NaOH}_2)_2\text{Ni}_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2]^{18-}\) is an analogue of Wells-Dawson derivatives containing two transition metals in the central belt \([(\text{NaOH}_2)_2\text{M}_2(\text{X}_2\text{W}_{15}\text{O}_{56})_2]^n^-\) \((X = \text{P}^V, M = \text{Fe}^{II}, \text{Cu}^{II}; X = \text{As}^V, M=\text{Fe}^{III})\) which was reported by the Hill group.\(^{56}\) Also Ruhlmann and Thouvenot’s group reported the Co\(^{II}\) analogue whose structure was confirmed by IR, elemental analysis, and \(^{31}\)P NMR spectroscopy.\(^{57}\) Moreover, diuranium and dineptunium containing POMs have also been obtained based on an A-type trivacant Keggin unit, including \([\text{M}_2(\text{UO}_2)_2(\text{A-XW}_9\text{O}_{34})_2]^n^-\) \((X = \text{P}^V, M = \text{K}, \text{Na}, \text{NH}_4; X = \text{Ge}^{IV}, \text{Si}^{IV})\), \([\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{XW}_9\text{O}_{33})_2]^n^-\) \((X = \text{Sb}^{III}, \text{Te}^{IV})\), and \([\text{Na}_2(\text{NpO}_2)_2(\text{A-PW}_9\text{O}_{34})_2]^{14-}\). Very recently Hill group reported on complexes, \([\text{M'}_2\text{M}_2(\text{PW}_9\text{O}_{34})_2]^{12-}\) \((M' = \text{Na or Li, } M = \text{Mn}^{II}, \text{Co}^{II}, \text{Ni}^{II} \text{ and } \text{Zn}^{II})\) which contain two transition metals and two alkali metal centers sandwiched between two \([B-\text{a-PW}_9\text{O}_{34}]^\nu\) Keggin fragments.\(^{59}\)
3.3.3.3 Conclusions

We have prepared a sandwich-type polytungstophosphate in which two different types of metals are sandwiched between two \([\alpha-P_{2}W_{15}O_{56}]^{12-}\) units. The high concentration of sodium ions stabilizes lacunary, sandwich-type species The core of 7 is composed of two Ni\(^{II}\) ions, located in the two internal positions, and two sodium caions, which occupy the two external positions. These external loosely bound Na\(^{+}\) ions can be replaced by a variety of transition. Such products might have different magnetic and catalytic properties. The polyanion has been characterized by FTIR and single crystal X-ray diffraction.
3.4 15-Copper(II)-Containing 36-Tungsto-4-Silicate [(A-α-SiW<sub>9</sub>O<sub>34</sub>)<sub>4</sub>Cu<sub>15</sub>O<sub>4</sub>(OH)<sub>8</sub>Cl]<sup>27-</sup>

3.4.1 Na<sub>3</sub>K<sub>24</sub>[(A-α-SiW<sub>9</sub>O<sub>34</sub>)<sub>4</sub>Cu<sub>15</sub>O<sub>4</sub>(OH)<sub>8</sub>Cl]<sup>·</sup>50H<sub>2</sub>O (KNa-8)

**Synthesis:** (0.11 g, 0.63 mmol) of CuCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in 20 mL of distilled water. Solid K<sub>10</sub>[A-α-SiW<sub>9</sub>O<sub>34</sub>]·24H<sub>2</sub>O<sup>60</sup>(0.52 g, 0.20 mmol) was then added and stirred till a clear green solution is obtained. The pH of the solution was raised from 4.3 to 8 by 6 M NaOH. The resulting solution was stirred for one hour at room temperature. The mixture was allowed to stand at room temperature until the entire green precipitate settled down at the bottom of the beaker and then filtered. The clear green solution thus obtained was filtered and kept open at room temperature for slow evaporation in a vial. Next day a dark green crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the half of the original solution. The product was then collected by filtration and air dried. Yield 420 mg (70 %).

IR (2% KBr pellet, ν/cm<sup>-1</sup>): 1005 (s), 942 (w), 909 (s), 802 (m), 752 (s), 665 (s), 526 (s). (see Figure. 3.26).

Elemental analysis for KNa-8, calc (found): Na 0.57% (0.62%), K 7.82% (7.04%) Si 0.94% (0.90%), Cl 0.30% (0.20%), Cu 7.94% (7.89%), W 55.14% (55.2%).
Figure 3.26 Infra-red spectra of the precursor $\{\text{SiW}_9\}$ (black), and the product $\text{KNa-8}$ (blue).

Figure 3.27 TGA curve of $\text{KNa-8}$ from room temperature to 900 °C.
3.4.1.1 Single Crystal X-ray Diffraction

Polyanion 8 crystallized as a hydrated potassium sodium salt (KNa-8) in the triclinic space group P-1. Crystallographic data are detailed in Table 3.6.

Table 3.6 Crystal data for KNa-8.

<table>
<thead>
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<th>Compound</th>
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<tr>
<td>Formula</td>
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<tr>
<td>Formula weight, g/mol</td>
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<td>Crystal system</td>
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<tr>
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<td>P-1</td>
</tr>
<tr>
<td>a, Å</td>
<td>19.2429(6)</td>
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<td>b, Å</td>
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<td>c, Å</td>
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<td>α, °</td>
<td>106.8890(10)</td>
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<tr>
<td>β, °</td>
<td>101.894(2)</td>
</tr>
<tr>
<td>γ, °</td>
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<tr>
<td>Volume, Å³</td>
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<td>R₁(I &gt; 2σ(I))[a]</td>
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</tr>
<tr>
<td>wR₂ (all data)[b]</td>
<td>0.2452</td>
</tr>
</tbody>
</table>

[a] \( R = \sum||F_o| - |F_c||/\sum|F_o| \). [b] \( R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2} \).
3.4.1.2 Results and Discussion

**KNa-4** was synthesized in good yield by the reaction of K$_{10}$[A-$\alpha$-SiW$_9$O$_{34}$]·24H$_2$O and CuCl$_2$·2H$_2$O in aqueous basic media at room temperature and was structurally characterized in the solid state by FTIR, TGA, elemental analysis and single-crystal XRD. Synthesis of polyanion 4 proceeds only when starting with the potassium salt of the trilcaunary precursor [A-$\alpha$-SiW$_9$O$_{34}$]$^{10-}$. While on the other hand if the sodium salt of the precursor is used, target product is obtained in very low yield embedded in the precipitate of unidentified compound. The difference between the reactivity of the sodium versus the potassium salt of [A-$\alpha$-SiW$_9$O$_{34}$]$^{10-}$ has been previously observed.$^{60,61}$

Single-crystal X-ray diffraction analyses reveals that polyanion 4 is composed of two tricopper substituted Keggin units, $\{(\text{SiW}_9\text{O}_{34})(\text{Cu}_3\text{O}_2\text{(OH)})\}$, $\{(\text{SiW}_9\text{O}_{34})(\text{Cu}_3\text{O}(\text{OH})_2)\}$ (denoted \{Cu$_3$\}) and two four copper substituted Keggin units, $\{(\text{SiW}_9\text{O}_{34})(\text{Cu}_4\text{O}(\text{OH})_3)\}$, $\{(\text{SiW}_9\text{O}_{34})(\text{Cu}_4\text{O}(\text{OH})_2)\}$ (denoted \{Cu$_4$\} and an encapsulated chloride ion (see Figure 3.28). Each subunit contains two Cu$^{II}$ center in a square pyramidal environment, the remaining Cu$^{II}$ centers are in a distorted octahedral geometry. The whole structure is constructed by the union of subunits via two $\mu_3$-oxo/ $\mu_3$-hydroxo bridges involving the neighboring hexa coordinated Cu$^{II}$ ions and one $\mu_3$-oxo bridges involving penta coordinated Cu$^{II}$ centers. Moreover the central encapsulated Cu$^{II}$ cation also combine these four units through three $\mu_3$-oxo and two $\mu_4$-oxo bridges. Further, a Cl anion is also enclose in the center of the cluster,
**Figure 3.28** Combined polyhedral/ball-and-stick representation, (upper) the basic building blocks of 4, (middle) \( \{\text{Cu}_{15}\} \) core, (bottom) (4). Color code: SiO₄ blue tetrahedra, Cu turquoise balls, Cl brown ball, O red balls Protonated oxygens are shown in pink.
surrounded by two \( \text{Cu}^{II} \) cations with long \( \text{Cu}-\text{Cl} \) distances (\( d_{\text{Cu-Cl}}=2.780-2.793 \) Å). Two \{Cu4\} units linked to the central halide.

The protonated oxo bridges were localized by valence bound summations \(^{32}\). The total charge of 4 is therefore 27-, which is balanced by 24 potassium and 3 sodium counter cations in the solid state. Thermogravimetric analysis (TGA) was performed on KNa-4 in order to estimate the number of crystal water molecules per formula units, and was calculated to be ca 50 water molecules (see Figure 3.27).

Efforts to prepare the Br-derivative of 4 were unsuccessful. The target product could not be achieved even on reaction of CuBr with potassium salt of \([A-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}\) (in this case the precursor was not washed with saturated KCl in order to avoid the presence of any chloride ion).

In 2003 Mialane and Dolbecq reported the 14 copper-containing complex \([\{(\text{SiW}_9\text{O}_{34})\}^{-}\{\text{SiW}_9\text{O}_{33}(\text{OH})\}^{6}\text{Cu}\}_2X]^\otimes\) (X=Cl, Br), \{Cu14\} which was synthesized from an azido complex of general formula H\(_3\)K\(_6\)[(SiW\(_9\)O\(_{37}\))Cu\(_3\)N\(_3\)]·19H\(_2\)O as precursor. The aforementioned azido complex when dissolved in molar NaCl or NaBr aqueous media gave \{Cu14\}. \(^9\)

### 3.4.1.3 Conclusions

Polyanion 4 represents to date the second highest nuclearity copper-containing POM, and is synthesized under conventional conditions in basic aqueous solution and crystallizes as sodium salt KNa-4 in the triclinic space group \( P-1 \). The fifteen copper cluster is stabilized by four capping \([A-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}\) units and a encapsulated chloride ion. The polyanion 4 was
structurally characterized in the solid state as potassium sodium salt by FTIR, TGA, elemental analysis and single-crystal XRD.

3.5 Yttrium(III)-Containing Polyoxotungstates

This section deals with the interaction of Y\textsuperscript{III} ions and lone pair containing poyanions. As discussed before in section 1.4 heteropolyanions, in contrast to isopolyanions, contain a heterogroup X which is often tetrahedrally coordinated (e.g. PO\textsubscript{4}, SiO\textsubscript{4}) or exhibits a trigonal pyramid (e.g. As\textsuperscript{III}O\textsubscript{4}, Sb\textsuperscript{III}O\textsubscript{3}). Due to the presence of the lone pair, the closed Keggin unit cannot be formed, and hence ‘unconventional’ structures may be obtained, such as [NH\textsubscript{4}As\textsubscript{4}W\textsubscript{140}O\textsubscript{524}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{23-}, [As\textsubscript{4}W\textsubscript{20}O\textsubscript{72}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{12-}, [H\textsubscript{2}AsW\textsubscript{18}O\textsubscript{60}]\textsuperscript{7-} or [As\textsubscript{8}W\textsubscript{36}O\textsubscript{32}AsO\textsubscript{6}]\textsuperscript{7-} \textsuperscript{62-64}. Lone pair-containing, trilacunary polyanions are also known to act as multidentate ligands of lanthanide\textsuperscript{65-69} and transition metal ions.\textsuperscript{70}

Lanthanide (Ln) and yttrium(III) ions are of special interest due to their oxophilicity and large coordination numbers (CN = 8–12).\textsuperscript{71} They can link two or more polyanion units to form very large structures, such as Pope’s [As\textsubscript{12}Ce\textsubscript{16}(H\textsubscript{2}O)\textsubscript{38}W\textsubscript{148}O\textsubscript{524}]\textsuperscript{76-65}. Further more POMs achieve certain functionalities, specially photoluminescence, in the presence of lanthanide ions.\textsuperscript{72} The reactivity of lanthanide ions with lacunary polytungstate precursors has been investigated predominantly by the groups of Pope, Yamase, Francesconi, Krebs and Ozeki.\textsuperscript{65-69} The groups of Gouzerh, Boskovic and Patzke have also synthesized high-nuclearity lanthanide-containing polyoxotungstates.\textsuperscript{73-75} Our group has also reported several examples of such species.\textsuperscript{76}

In 1971 Peacock and Weakley were the first to describe the yttrium(III)- and lanthanide(III)-containing sandwich-type decatungstate.\textsuperscript{77} In 2000 these salts were used as catalysts with H\textsubscript{2}O\textsubscript{2} for alcohol oxidations and alkene epoxidations.\textsuperscript{78} In 2008 our group reported on the
synthesis and solid state structure of the yttrium-derivative \([YW_{10}O_{36}]^{9-}\), as well as its solution properties by \(^{183}\)W and \(^{89}\)Y NMR.\(^{79}\) This polyanion consists of two monolacunary Lindqvist based \([W_{5}O_{18}]^{6-}\) fragments encapsulating a central \(Y^{III}\) ion, exhibiting a square-antiprismatic coordination. In 2009 we reported another class of yttrium(III)- and lanthanide(III)-containing isopolytungstates, \([M_2(H_2O)_{10}W_{22}O_{72}(OH)_2]^{9+}\) (\(M^{3+} = Y, La, Ce, Tb, Dy, Ho, Er, Tm, Yb, Lu\)).\(^{76e}\) These isostructural polyanions are composed of the 22-tungsten isopolyanion unit \(\{W_{22}\}^\) which is coordinated to two \(Y(III)/Ln(III)\) ions. Very recently the \(Y\)-containing, acetate-bridged, dimeric undecatungstate \([Y(CH_3COO)XW_{11}O_{39}(H_2O)]^{6-}\) (\(X=Si^{IV}\) and Ge\(^{IV}\)) was reported.\(^{80}\) Very recently our group prepared a family of yttrium(III)- and lanthanide(III)-encapsulated heteropolydiallates, \([X^{III}Pd^{II}_{12}(AsPh)_8O_{32}]^{6-}\) (\(X = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu\)). These cuboid-shaped polyanions consist of a cage of twelve \(Pd^{2+}\) ions with eight capping phenylarsonate heterogroups and a central guest ion \(X\).\(^{81}\) Francesconi’s group reported on the \(Y\)-containing tungstophosphate \([(PY_2W_{10}O_{38})_4(W_3O_{14})]^{30-}\) which is composed of four \([PW_9O_{34}]^{9-}\) units connected via a central \([Y_8W_7O_{30}]^{6+}\) assembly.\(^{67}\) Solution studies demonstrated that this polyanion self-assembles to single-layer vesicle-like supramolecular blackberry structures in dilute aqueous solutions.\(^{82}\) Hill and co-workers reported on two sandwich-type structures which were dependent on the presence of the carbonate dianion in the reaction mixture.\(^{83}\) In the polyanion \([(YOH_2)_3(CO_3)(A-\alpha-PW_9O_{34})_2]^{11-}\) three \(Y^{III}\) ions are sandwiched between two \([A-\alpha-PW_9O_{34}]^{9-}\) moieties encapsulating a central carbonate ion. However, the Wells–Dawson based \(Y\)-containing polyanion \([(Y_4(\mu_3-OH)_{4}(H_2O)_{8})(\alpha-P_2W_{15}O_{56})_2]^{16-}\) does not contain a carbonate ion.\(^{84}\) One-dimensional solid state structures constructed by \(Y^{III}\) and \([GeW_{11}O_{39}]^{8-}\) have also been reported.\(^{85}\) The \(Y^{III}\) containing 40-tungsto-4-arsenate(III)
[Y(H_2O)_3{Ni(H_2O)}_2As_4W_40O_{140}]^{21-} is composed of the known polyanion [As_4W_{40}O_{140}]^{28-} with Y^{III} in the central S1 site and two Ni^{2+} in the S2 sites.\(^{86}\)

We decided to further investigate the reactivity of yttrium(III) ions with lone-pair containing, trilacunary heteropolytungstates. Herein the synthesis and structural characterization of two novel yttrium^{III}-containing polyanion will be discussed.

3.5.1 Na\(_{16}\)(NH\(_4\))\([\{Y(\alpha-SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)\} \cdot 48H_2O\) (NaNH\(_4\)-9a)

**Synthesis:** 2.153 g (0.750 mmol) Na\(_9[\alpha-SbW_9O_{33}]\cdot 19.5H_2O^{87}\) and 0.228 g (0.750 mmol) YCl\(_3\) were added to 20 mL of 1 M LiOAc/AcOH buffer at pH 5.3. To the reaction mixture 82.45 mg (0.250 mmol) of Na\(_2WO_4\) were added. The solution was heated to 80 °C for 60 minutes and filtered when it was still hot. Then 0.5 mL of 1.0 M NH\(_4\)Cl solution was added to the yellow filtrate, which was then allowed to evaporate in an open beaker at room temperature. After two weeks a yellow crystalline product appeared, which was collected by filtration and air dried. Yield: 1.56 g (23 %). IR (2% KBr pellet, v/cm\(^{-1}\)): 1629(s), 1541(s), 1460(w), 1348(sh), 934(m), 896(sh), 836(m), 784(m), 683(sh), (505)w, 437(m). Elemental analysis (%) calcd for Na\(_{16}\)(NH\(_4\))\([\{Y(\alpha-SbW_9O_{31}(OH)_2)(CH_3COO)(H_2O)\}_3(WO_4)\} \cdot 48H_2O\) (NaNH\(_4\)-9a): Na 4.13, W 57.74, Sb 4.12, Y 2.99, C 0.81, H 1.32, N 0.16; found: Na 4.39, W 57.60, Sb 4.21, Y 3.12, C 1.08, H 1.21, N 0.20; Product recrystallized from NMR tube: Na\(_{14}\)(NH\(_4\))\([\{Y(\alpha-SbW_9O_{31}(OH)_2)\}_3(CH_3COO)(H_2O)\}_7(WO_4)\} \cdot 48H_2O\) (NaNH\(_4\)-9b): C 0.27, H 1.41, N 0.16; found: C 0.32, H 1.20, N 0.23.
Figure 3.29 Infra-red spectra of the POM precursor \([\text{SbW}_9]\) (black), \(\text{NaNH}_4\cdot9\text{b}\) (pink) and the product \(\text{NaNH}_4\cdot9\text{a}\) (blue).

Figure 3.30 FT-IR spectra of \(\text{NaNH}_4\cdot9\text{a}\) at room temperature, and after heating to 500 °C.
Figure 3.31 TGA curves of $\text{NaNH}_4$-$9a$ (black), $\text{NaNH}_4$-$9b$ (green) from room temperature to 900 °C and $\text{NaNH}_4$-$9a$ from room temperature to 500 °C (red), all under N$_2$ atmosphere.
3.5.1.1 Single Crystal X-ray Diffraction

Polynionate 9a crystallized as a hydrated sodium ammonium salt (NaNH₄-9a) in the Orthorhombic space group Pnma. Crystallographic data are detailed in Table 3.7.

**Table 3.7 Crystal data for (NaNH₄-9a).**

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<th>Compound</th>
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<tr>
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</tr>
</tbody>
</table>

[a] R = Σ||F₀| – |Fᵣ||/Σ|F₀|,  [b] R<sub>ω</sub> = [Σw(F₀² – Fᵣ²)²/Σw(F₀²)²]<sup>1/2</sup>.
3.5.1.2 Results and Discussion

We have synthesized the yttrium(III)-containing tungstoantimonate(III) \( \{\text{Y}(\alpha-\text{SbW}_9\text{O}_{33})(\text{OH})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})\}_3(\text{WO}_4)\}^{17} \) (9a) in a simple one-pot reaction of \( \text{Y}^{\text{III}} \) ions with \([\alpha-\text{SbW}_9\text{O}_{33}]^{9-}\) and \( \text{WO}_4^{2-}\) in a 3:3:1 molar ratio in 1 M LiOAc/AcOH buffer at pH 5.3. The hydrated sodium-ammonium salt \( \text{Na}_{16}(\text{NH}_4)[\{\text{Y}(\alpha-\text{SbW}_9\text{O}_{33})(\text{OH})_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})\}_3(\text{WO}_4)\}]^{48}\text{H}_2\text{O} \) (NaNH₄·9a) was characterized in the solid state by IR spectroscopy, thermogravimetric (TGA) and elemental analyses. Single crystal XRD on NaNH₄·9a revealed that the triangular title polyanion 9a is composed of three \( (\alpha-\text{SbW}_9\text{O}_{33}) \) units linked by three 8-coordinated yttrium(III) ions and a capping, tetrahedral tungstate group leading to a structure with idealized \( C_{3v} \) point group symmetry (see Figure 3.32).

![Figure 3.32 Top view of 9a along the 3-fold axis. Color code: Sb (rose), Y (orange), unique tetrahedral W (red), O (red), O₉ (light blue), C (black), and H (grey).](image-url)
Each $Y^{III}$ ion bridges two Keggin units via four $Y$-$O$(W) bonds, two from each $\{\text{SbW}_9\}$ subunit involving corner-shared WO$_6$ octahedra. Such type of assembly is also found in our previously reported tin-containing, trimeric assembly $[(\text{Sn(CH}_3)_2\text{(H}_2\text{O})_2\text{Sn(CH}_3)_2\text{As}_3(\alpha\text{-AsW}_9\text{O}_{33}))^4]^{21-}$, which is capped by a formally neutral $\{\text{As}_3(\alpha\text{-AsW}_9\text{O}_{33})\}$ fragment.\(^88\) However, the three tin centers have a different coordination number (six and seven) than the yttrium ions (eight) in 9a. Furthermore, the capping tungstate unit in polyanion 9a appears to be more strongly bound than the tungstoarsenate cap in our organotin species.

\textbf{Figure 3.33} View of the capping tungstate group in 9a and the coordination spheres of the three yttrium ions. The color code is the same as in Fig. 3.32, except O of unique W is brown here.

Each of the three $Y^{III}$ ions in 9a is also coordinated by an external, terminal acetate group, bound in a bidentate fashion via the carboxylate function (see Figure 3.33). The two remaining coordination sites of the yttrium(III) ions are filled by an aqua ligand from one side and a $Y$-$O$(W) bridge to the capping, tetrahedral WO$_4^{2-}$ unit from the other side. The
coordination geometry of each Y\textsuperscript{III} ion can be considered as distorted square-antiprismatic with Y-O bond distances in the range 2.24(5) – 2.45(4) Å. The presence of the tetrahedral, capping tungstate group in 9a is interesting and surprising, as tungsten is usually 6-coordinated in polyanions and no extra tungstate was added in the initial reactions. A possible source could be minor tungstate impurities in the starting POM precursor salt, or \textit{in situ} generation of WO\textsubscript{4}\textsuperscript{2-} due to partial decomposition of [\alpha-SbW\textsubscript{9}O\textsubscript{33}]\textsuperscript{9-} during the reaction. We discovered that the yield of 9a can be increased when adding one equivalent of tungstate during the reaction. Hence, the tetrahedral WO\textsubscript{4}\textsuperscript{2-} group appears to play an important templating role during the formation of 9a. Three oxygen atoms of the \{WO\textsubscript{4}\} moiety coordinate each to an Y\textsuperscript{III} ion, whereas the fourth oxygen is terminal, being situated on the three-fold axis of the title polyanion. The capping tungstate group has idealized tetrahedral symmetry with W-O bond lengths in the range 1.68(5)-1.80(5) Å and O-W-O angles in the range 106.9(12)-112.6(17) °. The template effect of small anions in POM chemistry is well known and several examples have been reported.\textsuperscript{7,23,89} Very recently, Wang’s group reported a nickel-containing tungstophosphate containing an encapsulated, tetrahedral tungstate group with W-O bond lengths in the range 1.716(17)-1.821(17) Å and O-W-O angles in the range 106.8(9)-111.6(8).\textsuperscript{27}

We also performed bond valence sum (BVS) calculations on 9a to identify possible protonation sites on the oxygens of the polyanion.\textsuperscript{32} The BVS values for the terminal oxygens of the yttrium ions (0.43 - 0.48) suggest that these oxygen atoms are diprotonated, corresponding to aqua ligands. Also, the two terminal oxygens at the lacunary site of each (\alpha-SbW\textsubscript{9}O\textsubscript{33}) unit have a BVS range of 1.19 - 1.38, indicating monoprotonation. The total charge of 9a is therefore 17-, which is balanced by an ammonium and 16 sodium counter cations in
the solid state. The number of counter cations was determined by elemental analysis, whereas the number of water molecules was determined by TGA. Only 6 Na counter cations and 14 crystal waters could be determined by single-crystal XRD due to disorder, which is a common feature in POM (in particular polyoxotungstate) crystallography. As expected, the ammonium counter cation could also not be located by single-crystal XRD, but its presence was identified by elemental analysis.

**IR Spectroscopy**

Figure 3.29 shows the IR spectra of precursor \{SbW\}_9, NaNH\(_4\)-9a, and NaNH\(_4\)-9b which was obtained in the NMR tube when a solution of redissolved NaNH\(_4\)-9a for NMR measurements was left open for slow evaporation of the solvent. Both FT-IR spectra of NaNH\(_4\)-9a and NaNH\(_4\)-9b display a fingerprint region that is characteristic for POMs,\(^90\) and an additional band appearing at around 836 cm\(^{-1}\) belongs to vibrations of Y-O(W) bonds. The very intense peaks related to acetate carboxylate groups are observed only in NaNH\(_4\)-9a. The bands at 1541, 1460, and 1409 cm\(^{-1}\) are attributed to stretching bands of the acetate carboxylate groups. The bands belonging to rocking vibrations of these carboxylate groups are observed at 620 and 505 cm\(^{-1}\). The peaks at 1348 and 1230 cm\(^{-1}\) are attributed to bending and rocking vibrations of the acetate methyl groups in NaNH\(_4\)-9a.\(^91\) While the IR spectrum of NaNH\(_4\)-9b shows acetate bands with much reduced intensity, the structure of polyanion 9a remains essentially unchanged, suggesting loss of some acetate groups. This indicates that the title polyanion 9b has lost some acetate groups. These observations are consistent with elemental and thermogravimetric analyses of NaNH\(_4\)-9b (see Figure 3.31). The IR spectrum of NaNH\(_4\)-9a after this salt had been heated to 500 °C shows no characteristic stretching bands associated with the acetate groups, indicating that they have
decomposed at this temperature (see Figure 3.30). The broad peak at 3432 cm\(^{-1}\) and a strong peak at 1629 cm\(^{-1}\) correspond to stretching and bending vibrations of crystal waters, respectively.

**Thermogravimetric Analysis**

Thermogravimetric analysis of NaNH\(_4\)-9a was performed between 25 and 900 °C under a nitrogen atmosphere to determine the amount of crystal water present in the polyanion (see Figure 3.31). We observed a weight loss of approximately 10.5 % between 25–270 °C which can be assigned to the loss of 48 crystal waters and the 3 coordinated aqua ligands per formula unit (calcld 11.4 %). In addition, there is a weight loss of approximately 2.2 % from 271 to 490 °C corresponding to the decomposition of the three acetate ligands and the ammonium counter cation in NaNH\(_4\)-9a This hypothesis was confirmed by heating a solid sample of NaNH\(_4\)-9a to 500 °C, and a subsequent FT-IR measurement did not show anymore the characteristic stretching frequencies of acetate (see Figure. 3.30). Thermogravimetric analysis was also carried out on NaNH\(_4\)-9b which was recrystallized from an NMR tube (see Figure. 3.31). An obvious change in the thermogram can be observed in the region where acetate decomposes. This observation is consistent with FT-IR and elemental analysis of NaNH\(_4\)-9b indicating that two of the originally three coordinated acetate ligands have been replaced by a total of 4 water ligands.

**Multinuclear NMR Spectroscopy**

We also performed multinuclear NMR studies on NaNH\(_4\)-9a redissolved in H\(_2\)O/D\(_2\)O, in order to study the solution stability of the title polyanion. The \(^{183}\text{W}\) NMR spectrum consists of six singlets at -20.0, -74.6, -93.7, -143.7, -166.0, and -209.5 ppm with relative intensities
Figure 3.34 Solution $^{183}$W NMR spectrum (at RT) of a freshly prepared solution of NaNH$_4$-9a redissolved in H$_2$O/D$_2$O.

Figure 3.35 Solution $^{89}$Y NMR spectrum (at RT) of a freshly prepared solution of NaNH$_4$-9a redissolved in H$_2$O/D$_2$O.
6:6:6:6:3:1 (see Figure 3.34). These results are fully consistent with the $C_{3v}$ symmetry of 9a observed in the solid-state. The four downfield signals of largest intensity (-20.0, -74.6, -93.7, and -143.7 ppm) can be assigned to the three pairs of belt and one pair of cap tungstens in each of the three Keggin units. The signal of medium intensity (-166.0 ppm) can be assigned to the unique cap tungstens in each of the three Keggin units. Finally, the most upfield signal (-209.5 ppm) of lowest intensity can be assigned to the unique, tetrahedral capping tungsten atom. The $^{89}$Y NMR spectrum showed the expected singlet at $\delta$ 47.2 ppm (see Figure 3.35).

The $^{13}$C spectrum showed singlets at 23.5 ppm and 181.6 ppm, which also corresponds to the chemical shifts of free acetate (see Figure 3.36). Addition of solid sodium acetate to the solution did not result in the appearance of any new signals, indicating that the three acetate groups bound to 9a in the solid state are labile in solution, and are most likely replaced by aqua ligands. This hypothesis is reinforced by IR spectroscopy, thermogravimetric analysis and elemental analysis of the crystalline solid Na$_{16}$(NH$_4$)$_4$[Y($\alpha$-
SbW$_9$O$_{31}$(OH)$_2$(CH$_3$COO)(H$_2$O)$_3$(WO$_4$)]$_3$48H$_2$O (NaNH$_4$-9b). This material could be crystallized in the NMR tube when the solution of NaNH$_4$-9a was kept (after the NMR measurements) in an open vial allowing for slow evaporation of the solvent. The IR spectrum of NaNH$_4$-9b showed acetate bands with reduced intensity, but the structure of polyanion 9a remained unchanged. Elemental analysis for NaNH$_4$-9b is consistent with the loss of two (of the three) acetate ligands, which were replaced by 4 water molecules from the solvent. Efforts to perform single-crystal XRD measurements on NaNH$_4$-9b were unsuccessful due to insufficient quality of the crystals.

### 3.5.1.3 Conclusions

In summary we have synthesized the yttrium(III)-containing tungstoantimonate(III) [{Y(α-SbW$_9$O$_{33}$)]$_9$} using a simple, one-pot procedure by reacting the trilacunary POM precursor [α-SbW$_9$O$_{33}$]$^{9-}$ with Y(III) ions in the presence of free WO$_4^{2-}$ ions. Polyanion 9a has an open, trimeric structure and is capped by a tetrahedral tungstate group. It is likely that derivatives of 9a may be formed with the acetate ligands replaced by other carboxylic acids or carboxylate containing functionalities. We have discovered that the presence of WO$_4^{2-}$ ions in the reaction mixture is the key factor for the formation of 9a. Multinuclear NMR studies are consistent with the solution stability of the title polyanion.
3.5.2 \( \text{Cs}_7\text{Na}_{35}\left\{\text{Y(H_2O)_3}\right\}_8(\text{As}_2\text{W}_{19}\text{O}_{68})_3(\text{As}_2\text{W}_{19}\text{O}_{66})(\text{W}_2\text{O}_6)_2(\text{WO}_6)\} \cdot 230\text{H}_2\text{O} \) (CsNa-10)

**Synthesis:** 50 g (0.20 mmol) \( \text{Na}_9[\text{B-}\alpha-\text{AsW}_9\text{O}_{33}]\cdot27\text{H}_2\text{O} \) and 0.182 g (0.60 mmol) \( \text{YCl}_3 \) were added to 16 mL of 1 M \( \text{NaOAc/AcOH} \) buffer at pH 4.8. The solution was heated to 80 °C for 60 minutes and filtered after cooling to room temperature. Addition of five drops of 1.0 M \( \text{CsCl} \) solution to the filtrate resulted in a precipitate. The reaction mixture was kept at 30 °C for 5 minutes, and then filtered. The clear colorless filtrate was kept in an open vial at room temperature for slow evaporation. After one week a colorless crystalline product started to appear. Evaporation was allowed to continue until about half the solvent had evaporated. The solid product was then collected by filtration and air-dried. Yield: 250 mg (38 %).

IR (2% KBr pellet, \( \text{v/cm}^{-1} \)): 1623(s), 949 (m), 864(s), 788(m), 707(m), (454)w.

Elemental analysis for **CsNa-10**, calc (found): Na 3.02% (2.72%), As 2.25% (2.09%), Y 2.67% (2.87%), W 54.48% (55.2%).
Figure 3.37 Infra red spectra of the precursor \( \{\text{AsW}_9\} \) (black) and the product \( \text{CsNa-10} \) (blue).

Figure 3.38 TGA curve of \( \text{CsNa-10} \) from room temperature to 1000 °C.
3.5.2.1 Single Crystal X-Ray Diffraction

Polyanion 10 crystallized as a hydrated cesium sodium salt (CsNa-10) in the triclinic space group P-1.

3.5.2.2 Results and Discussion

The octanuclear yttrium-containing tungstoarsenate(III), \([\{Y(H_2O)_3\}_8(As_2W_{19}O_{68})(As_2W_{19}O_{66})(W_2O_6)_2(WO_6)\}]^{43-}\) with 81 tungsten centers was synthesized in a one-pot reaction from Na9[AsW9O33] and Y(III) in a 1:3 molar ratio in 1 M NaOAc/AcOH buffer at pH 4.7. The polyanion 10 is composed of four \{As2W19O67(H2O)\} units, two \{W2O10\} fragments, one \{WO6\} unit and eight yttrium ions (see Figure 3.40). These units are likely formed from fragmentation of some of the [AsW9O33]9− lacunary polytungstate precursors during the course of the reaction, as has been observed previously for other complex POM architectures.92 The \{As2W19O68\} fragment, which is formed in situ, is consist of two \{AsW9O33\} units connected to each other by an octahedral \{WO2\} unit via the corner-sharing mode. Two such \{As2W19\} units are further linked by edge-shared \{W2O6\} via corner-sharing. The polyanion 10 can be described as a dimer of two dimers \{(Y2As2W19W)2\} which are linked through unique W14 and Y-O-W bridges in an asymmetric way. Each of the \{As2W19\} contains two YIII centers. The yttrium ions are all eight-coordinate with distorted square antiprismatic geometries and Y–O bond distances in the range of 2.298–2.478 Å. The coordination of each YIII center is composed of bridging oxo and terminal aqua ligands. To the best of our knowledge 10 has the largest number of yttrium ions (octa nuclear) which was also observed in another kind of POM assembly \([\{PY_2W_{10}O_{38}\}_4(W_3O_{14})\}]^{30-}\) reported by Francesconi’s group.67
Figure 3.39 Combined polyhedral/ball-and-stick representation of 10. Color code: WO$_6$ green octahedra, AsO$_3$ pink balls, Y orange balls, O$_{qua}$ turquoise balls.
Figure 3.40 Combined polyhedral/ball-and-stick representation of the basic building blocks of 10.
3.5.2.3 Conclusions

In conclusion, we have successfully synthesized the yttrium(III)-containing tungstoarsenate(III) \([\{Y(H_2O)_3\} _8(As_2W_{19}O_{68})_3(As_2W_{19}O_{66})(W_2O_6)_2(WO_6)\}]^{43-}\) (10) using a simple, one-pot procedure by reacting the trilacunary POM precursor \([\alpha-AsW_{9}O_{33}]^9-\) with \(Y^{III}\) ions in a 1:3 molar ratio in 1 M NaOAc/AcOH buffer at pH 4.7. Polyanion 10 was characterized in the solid state by IR spectroscopy, Single crystal XRD and thermogravimetric analysis. The giant polyanion also demonstrated that yttrium due to its capability to acquire large coordination number can act as highly efficient linkers to form large POM architectures.
3.6 References


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Chapter 4

Results: Keggin and Wells-Dawson Salts of $[\text{Ru}_3\text{O(OOCCCH}_3)_6(\text{CH}_3\text{OH})_3]^+$

The objective of this initial research project was to construct inorganic or inorganic/organic hybrid nanostructured compounds which possess molecule sized spaces in their lattice. Such zeolite type materials can give rise to unique selectivity in sorption, ion exchange, and catalysis. This chapter contains a brief overview of the relevant field and also discusses the syntheses and solid state characterizations of four novel ionic crystalline materials based on trinuclear ruthenium (III)-acetato cations and Keggin or Wells-Dawson anions.

Introduction

POMs are also suitable building blocks for crystalline, microstructured materials with unique physical and chemical properties.\(^1\) The construction of inorganic or hybrid organic/inorganic nanostructured compounds with well-defined pores can exhibit shape- and/or size-selective sorption of small organic molecules leading to applications in separation science and catalytic processes.\(^2\)

Recently, Mizuno and coworkers published a series of papers on the synthesis, structure and selective sorption/catalysis properties of solid state materials resulting from interaction of the oxo-centered chromium trimer cation $[\text{Cr}_3\text{O(OOCH)}_6(\text{H}_2\text{O})_3]^+$ with Keggin polyanions.\(^3\) Due
to the interesting redox, electrochemical and catalytic properties of ruthenium, we decided to study the formation of ionic crystals made up of polyanions and the trinuclear, oxo-centered ruthenium(III) cation \([\text{Ru}_3\text{O(OOCCH}_3\text{)}_6(\text{CH}_3\text{OH})_3]^+\) which was synthesized using the reported procedure of Meyer.\(^4\) Previous studies on \([\text{Ru}_3\text{O(OOCCH}_3\text{)}_6(\text{CH}_3\text{OH})_3]^+\) indicate that it is an efficient catalyst for the selective oxidation of primary and secondary alcohols to aldehydes and ketones, using molecular oxygen as the oxidant.\(^5\) Transition-metal cluster complexes showing multi-electron redox behavior are rare and usually not stable over wide ranges of oxidation states. On the other hand, complexes of the type \([\text{Ru}^\text{III}_3\text{O(CO}_2\text{R})_6\text{L}_3]^+\) provide a unique opportunity to construct stable multi-metal/multi-electron/multi-step redox systems. This behavior is important in the sense that it can be used as an artificial model in understanding the mechanisms of biological metalloenzymes.\(^4,6\)

Four solid state materials based on the trinuclear ruthenium-monocation and Keggin or Wells-Dawson type polyanions were isolated:

\[
\text{K}_2\text{Na}[\text{Ru}_3\text{O(OOCCH}_3\text{)}_6(\text{H}_2\text{O})_3][\alpha-\text{GeW}_{12}\text{O}_{40}]\cdot10\text{H}_2\text{O (Ru}_3\text{-11)}
\]

\[
\text{K}_3[\text{Ru}_3\text{O(OOCCH}_3\text{)}_6(\text{H}_2\text{O})_3][\alpha-\text{SiW}_{12}\text{O}_{40}]\cdot18\text{H}_2\text{O (Ru}_3\text{-12)}
\]

\[
\text{K}_3[\text{Ru}_3\text{O(OOCCH}_3\text{)}_6(\text{H}_2\text{O})_3][\alpha-\text{SiMo}_{12}\text{O}_{40}]\cdot7\text{H}_2\text{O (Ru}_3\text{-13)}
\]

\[
\text{K}_2\text{Na}[\text{Ru}_3\text{O(OOCCH}_3\text{)}_6(\text{H}_2\text{O})_3][\alpha-\text{P}_2\text{W}_{18}\text{O}_{62}]\cdot26\text{H}_2\text{O (Ru}_3\text{-14)}
\]
4.1.1 Synthetic Procedures

The precursor polyanions \([\alpha-\text{GeW}_{11}\text{O}_{39}]^8\), \([\alpha-\text{SiW}_{11}\text{O}_{39}]^8\), \([\alpha-\text{SiMo}_{12}\text{O}_{40}]^4\), and \([\alpha-\text{P}_2\text{W}_{18}\text{O}_{62}]^6\) were all synthesized according to published procedures and their purity was checked with IR spectroscopy.\(^7\)

\[
\text{K}_3\text{Na}[\text{Ru}_3\text{O}(\text{OOCCH}_3)_{6}(\text{H}_2\text{O})_3][\alpha-\text{GeW}_{12}\text{O}_{40}]\cdot\text{10H}_2\text{O (Ru}_3\text{-11)}
\]

**Synthesis:** To 20 mL of distilled water 2.5 mL (0.100 mmol) of \([\text{Ru}_3\text{O}(\text{OOCCH}_3)_{6}(\text{CH}_3\text{OH})_3]\) were added. After complete dissolution, 0.323 g (0.100 mmol) of \(\text{K}_6\text{Na}_2[\alpha-\text{GeW}_{11}\text{O}_{39}]\cdot\text{13H}_2\text{O}\) were added. Then, the pH was adjusted to 2.0 by dropwise addition of 1M HCl\(_{aq}\). The solution was then stirred for 30 minutes at 50 °C, cooled to room temperature and filtered. Slow evaporation of the solvent in an open vial at room temperature resulted in dark green crystals of \text{Ru}_3\text{-11}. (yield 0.061 g, 14%) after ~2 weeks.

IR data for \text{Ru}_3\text{-11} in cm\(^{-1}\): 1619(w), 1427(m), 1353(w), 975(s), 890(s), 828(w), 779(s), 687(w), 617(w), 532(w), 463(m). Elem. Anal. Calc. (Found) for \text{Ru}_3\text{-11}: K 2.0 (3.2), Na 0.6 (0.88), Ge 1.9 (1.4), Ru 7.7 (7.6), W 56.2 (57.4).

\[
\text{K}_3[\text{Ru}_3\text{O}(\text{OOCCH}_3)_{6}(\text{H}_2\text{O})_3][\alpha-\text{SiW}_{12}\text{O}_{40}]\cdot\text{18H}_2\text{O (Ru}_3\text{-12)}
\]

**Synthesis:** The synthetic procedure for compound \text{Ru}_3\text{-12} was identical to that of \text{Ru}_3\text{-11}, but 0.322 g (0.100 mmol) \(\text{K}_8[\alpha-\text{SiW}_{11}\text{O}_{39}]\cdot\text{13H}_2\text{O}\) was used. Dark green crystals of \text{Ru}_3\text{-12} (yield 0.044 g, 11%) were obtained after ~2 weeks.
IR data for Ru\textsubscript{3}-12 in cm\textsuperscript{-1}: 1625(m), 1420(m), 1353(w), 1018(w), 976(m), 923(s), 880(sh), 796(s), 686(w), 660(sh), 650(w), 531(w). Elem. Anal. Calc. (Found) for Ru\textsubscript{3}-12: K 2.9 (2.6), Si 0.7 (1.5), Ru 7.5 (6.9), W 54.6 (55.4).

K\textsubscript{3}[Ru\textsubscript{3}O(OOCC\textsubscript{3})\textsubscript{6}(H\textsubscript{2}O)\textsubscript{3}][α-SiMo\textsubscript{12}O\textsubscript{40}]·7H\textsubscript{2}O (Ru\textsubscript{3}-13)

**Synthesis:** The synthetic procedure for compound Ru\textsubscript{3}-13 was also identical to that of Ru\textsubscript{3}-11, but 0.203 g K\textsubscript{4}[α-SiMo\textsubscript{12}O\textsubscript{40}]·3H\textsubscript{2}O was used. Dark green crystals of Ru\textsubscript{3}-13 (yield 0.100 g, 35%), were obtained after ~2 weeks.

IR data for Ru\textsubscript{3}-13 in cm\textsuperscript{-1}: 1617(w), 1424(m), 1353(w), 958(w), 907(s), 791(s), 686(w), 617(w), 534(w). Elem. Anal. Calc. (Found) for Ru\textsubscript{3}-13: K 4.2 (5.1), Si 1.0 (1.9), Ru 10.9 (11.5), Mo 41.3 (41.5).

K\textsubscript{2}Na[Ru\textsubscript{3}O(OOCC\textsubscript{3})\textsubscript{6}(H\textsubscript{2}O)\textsubscript{3}][α-P\textsubscript{2}W\textsubscript{18}O\textsubscript{62}]·26H\textsubscript{2}O (Ru\textsubscript{3}-14).

**Synthesis:** Compound Ru\textsubscript{3}-14 was synthesized by dissolving 7.5 mL (ca. 0.300 mmol) [Ru\textsubscript{3}O(OOCC\textsubscript{3})\textsubscript{6}(CH\textsubscript{3}OH)\textsubscript{3}](OOCC\textsubscript{3}) in 20 mL 0.01 M HNO\textsubscript{3}(aq) followed by 1.0 g (0.210 mmol) (NH\textsubscript{4})\textsubscript{6}[α-P\textsubscript{2}W\textsubscript{18}O\textsubscript{62}]·14H\textsubscript{2}O. The solution was stirred at 50 °C for 30 minutes, cooled to room temperature and then filtered. The filtrate was layered with a few drops of 1M KCl. Slow evaporation of the solvent in an open vial at room temperature resulted in dark green crystals of Ru\textsubscript{3}-14 (yield 0.094 g, 13%) after ~2 weeks. Compound Ru\textsubscript{3}-14 contains one sodium ion, although no such ions were explicitly used during the synthesis. Hence it appears that the impurity results from residual sodium ions in the POM precursor.
IR data for Ru-14 in cm⁻¹: 1638(w), 1617(w), 1427(s), 1353(w), 1092(s), 960(s), 910(m), 795(s), 687(w), 619(w), 474(w) cm⁻¹. Elem. Anal. Calc. (Found) for Ru-14: K 1.1 (1.0), Na 0.3 (0.31), P 0.9 (0.8), Ru 12.8 (11.0), W 46.5 (47.6).
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Results: Keggin and Wells-Dawson Salts of $[\text{Ru}_3\text{O(OOCCH}_3\text{)}_6\text{(CH}_3\text{OH)}_3]^+$

**Figure 4.1** Infra-red spectra of the $\text{Ru}_3\text{-11}$ (pink), $\text{Ru}_3\text{-12}$ (blue), $\text{Ru}_3\text{-13}$ (black), $\text{Ru}_3\text{-14}$ (turquoise).

**Figure 4.2** TGA overlay of compounds $\text{Ru}_3\text{-11}$ (green), $\text{Ru}_3\text{-12}$ (red) $\text{Ru}_3\text{-13}$ (purple) $\text{Ru}_3\text{-14}$ (blue).
4.1.1.1 Single Crystal X-Ray Diffraction

The crystallographic data for compounds Ru$_3$-11, Ru$_3$-12, Ru$_3$-13 and Ru$_3$-14, are summarized in Table 4.1.

**Table 4.1** Crystal data for compounds Ru$_3$-11, Ru$_3$-12, Ru$_3$-13 and Ru$_3$-14.

<table>
<thead>
<tr>
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<th>Ru$_3$-11</th>
<th>Ru$_3$-12</th>
<th>Ru$_3$-13</th>
<th>Ru$_3$-14</th>
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<tr>
<td>emp formula</td>
<td>C$<em>{12}$H$</em>{84}$GeK$<em>2$NaO$</em>{86}$Ru$<em>3$W$</em>{12}$</td>
<td>C$<em>{12}$H$</em>{62}$K$<em>2$O$</em>{75}$Ru$<em>3$W$</em>{12}$</td>
<td>C$<em>{36}$H$</em>{125.4}$K$<em>{1.5}$Na$</em>{0.25}$O$_{136}$</td>
<td>C$<em>{12}$H$</em>{84}$GeK$<em>2$NaO$</em>{86}$Ru$<em>3$W$</em>{12}$</td>
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<td>b (Å)</td>
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<td>0.150</td>
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$^aR = \sum |F_o| - |F_c|/\sum |F_o|$. $^bR_w = \left[\sum w(F_o^2 - F_c^2)^2/\sum (F_o^2)^2\right]^{1/2}$. 

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Figure 4.3 Top: Ball-and-stick/polyhedral presentation of Ru₃-11. The color code is as follows: GeO₄ (blue), RuO₆ (dark red), carbon (black) and hydrogen (brown). Bottom: view of the solid state packing of Ru₃-11.
Figure 4.4 Top: Ball-and-stick/polyhedral presentation of Ru$_3$-14. Bottom: view of the solid state packing of Ru$_3$-14 along the b axis showing the hexagonal channels.
4.1.1.2 Results and Discussion

Compound \( \text{Ru}_3\text{-11} \) was synthesized in aqueous, acidic medium using a simple, one pot procedure. The synthetic procedures for compounds \( \text{Ru}_3\text{-12}, \text{Ru}_3\text{-13}, \) and \( \text{Ru}_3\text{-14} \) were similar to that of \( \text{Ru}_3\text{-11} \), except that different polyanion precursors were used. All compounds were characterized by single-crystal X-ray diffraction, FTIR spectroscopy, thermogravimetric and elemental analysis, while compound \( \text{Ru}_3\text{-11} \) was also investigated by powder X-ray diffraction. Unlike compounds \( \text{Ru}_3\text{-13} \) and \( \text{Ru}_3\text{-14} \), which were synthesized using the plenary Keggin (\( [\alpha-\text{SiMo}_{12}\text{O}_{40}]^{\text{4+}} \)) or Wells-Dawson (\( [\alpha-\text{P}_2\text{W}_{18}\text{O}_{62}]^{\text{3-}} \)) polyanions, compounds \( \text{Ru}_3\text{-11} \) and \( \text{Ru}_3\text{-12} \) were prepared using the monolacunary undecatungstogermanate (\( [\alpha-\text{GeW}_{11}\text{O}_{39}]^{\text{8-}} \)) or -silicate (\( [\alpha-\text{SiW}_{11}\text{O}_{39}]^{\text{8-}} \)) polyanion precursors. It is evident that the rather low reaction pH of 2.0 resulted in the transformation of the lacunary \{XW\text{11}\} to the plenary \{XW\text{12}\} Keggin species. Compounds \( \text{Ru}_3\text{-11-Ru}_3\text{-13} \) are isostructural and they all crystallize in the monoclinic space group \( P2_1/n \) either as a mixed potassium/sodium/ \( \text{Ru}_3 \) salt (\( \text{Ru}_3\text{-11} \)) or as a potassium/ \( \text{Ru}_3 \) salt (\( \text{Ru}_3\text{-12, Ru}_3\text{-13} \)). Figure 4.3 shows the arrangement of the anionic \{GeW\text{12O}_{40}\} units and the cationic \( [\text{Ru}_3\text{O(OOCCH}_3)_6\text{(OH}_2)_3]^+ \) (\( \text{Ru}_3 \)) in the solid state. The crystal packing of \( \text{Ru}_3\text{-11} \) reveals hexagonal channels along the b axis of the unit cell. These hexagonal channels are formed from parallel, alternating polyanion/ \( \text{Ru}_3 \) rows, arranged so that at each corner of the hexagonal channel there are also alternating polyanion/ \( \text{Ru}_3 \) positions. Therefore, each ‘section’ of the hexagonal channels contains alternatingly three polyanion and three \( \text{Ru}_3 \) molecules (see Figure 4.3).

The idealized symmetry of the channels reveals regular hexagons with an edge length of about 13 Å. Structural data show a channel diameter of ca. 15 Å. Interestingly, these channels are occupied with crystal waters most of which are weakly-coordinated to the \( \text{K}^+/\text{Na}^+ \) counter.
cations, which in turn are coordinated to oxygens of the polyanions and Ru$_3$ in the vicinity of the channels (close to the hexagonal edges). Keeping this in mind, removal of the water molecules by heating might result in “empty channels” which can offer potential sorption properties. The absence of counter cations inside the channels reinforces such possibilities.

This is why we treated compound Ru$_3$-11 under different outgassing conditions (100 ℃ and 150 ℃ under vacuum), then allowing the samples to cool down to room temperature under inert gas (N$_2$), followed by thermogravimetric analysis (TGA). All these results are compared with the non-pretreated sample Ru$_3$-11.

Compound Ru$_3$-14 crystallizes as a mixed sodium-potassium-Ru$_3$ salt in the monoclinic space group $P2_1/n$. In the solid state structure of Ru$_3$-14 each $[\alpha-P_2W_{18}O_{62}]^6-$ polyanion is surrounded by three Ru$_3$ units, resulting in a macrocation/macroanion assembly with a total charge of -3, in complete analogy with Ru$_3$-11 - Ru$_3$-13. The crystal packing of Ru$_3$-14 along the b axis also involves hexagonal arrangements of two main types of columns which we identify as A and B. Column A corresponds to Ru$_3$ units, whereas column B corresponds to alternating $[\alpha-P_2W_{18}O_{62}]^6$/Ru$_3$ units. The third column C, also corresponding to alternating $[\alpha-P_2W_{18}O_{62}]^6$/Ru$_3$ units but reversed with respect to column B, is centered with respect to each hexagonal arrangement of columns A and B (see Figure. 4.4 for more details).

The IR spectra (Figures 4.1) of compounds Ru$_3$-11 - Ru$_3$-14 all show two separate ranges of bands. The fingerprint region for the respective Keggin and Wells-Dawson polyanions is observed between 400 and 1200 cm$^{-1}$, whereas the bands for Ru$_3$ can be identified in the range 1300 to 1650 cm$^{-1}$. The fact that the IR spectra of Ru$_3$-11 - Ru$_3$-14 are essentially the sum of the spectra of the two components (polyanion + trinuclear cation) reflects the absence of covalent intermolecular interactions. It appears that electrostatic and packing forces mainly
hold together the polyanions and Ru3 cations in our products Ru3-11 - Ru3-14. Such intermolecular interaction reduces the charge of the macrocation/macroanion assemblies to -3 for all materials Ru3-11 - Ru3-14. This remaining charge is balanced in the solid state by potassium and/or sodium counter cations which are located in the interstices. It is not surprising that the larger Wells-Dawson ion, compared to the Keggin ion, is surrounded by three rather than one Ru3.

Thermogravimetric analyses (TGA) for Ru3-11- Ru3-14 indicated very similar behavior for all four compounds (see Figure 4.2). The thermogravimetric profiles show the occurrence of dehydration followed by decomposition in two main steps. The dehydration process involves the release of crystal waters. The TGA weight loss of ~5% up to 200 °C for compound Ru3-11 can be assigned to ~10 H2O, which corresponds exactly to the formula unit of Ru3-11 (vide supra). The weight loss occurs in two steps, with the first step up to 100 °C corresponding to ~3% (~6 H2O, loosely bound water) and the second step between 100 °C and 200 °C corresponding to ~2% (~4 H2O, tightly bound water). A sharp weight loss around ~300-350 °C is observed due to decomposition of the macrocation Ru3. The thermograms of Ru3-12 - Ru3-14 are similar to that of Ru3-11, exhibiting loss of crystal water up to ca. 200 °C followed by decomposition starting at ca. 300 °C.

**Sorption Studies.** Due to the particularly interesting solid state structure of Ru3-11 exhibiting large channels filled with crystal waters, we decided to perform sorption studies on this compound. These studies involved outgassing samples under vacuum at different temperatures and checking for water content by TGA. Powder XRD measurements were also performed on the outgassed samples and compared with those of the hydrated ones. As TGA
for compound Ru$_3$-11 showed two water loss steps, we decided to test if the loosely and tightly bound waters could be selectively outgassed.

Figure 4.5 Thermogram of Ru$_3$-11 without any pre-treatment (blue), outgassed under vacuum at 150 °C (purple), outgassed under vacuum at 100 °C (red), and exposed to air for 48 h after outgassing at 150 °C (green).
Figure 4.6 Powder XRD pattern of compound Ru$_3$-11 outgassed at 150 °C under vacuum (red) and without any pre-treatment (black).
Figure 4.7 Powder XRD pattern of compound Ru$_3$-11 exposed to air for 48 hr after outgassing at 150 °C under vacuum (red) and without any pre-treatment (black).
If compound Ru$_3$-11 is initially outgassed at 150 °C followed by TGA on this sample, no water loss was observed indicating that it had disappeared already (see Figure 4.5). However, if the outgassing on Ru$_3$-11 is performed at 100 °C under vacuum followed by TGA on this sample, then a weight loss of ~2% (~4 H$_2$O) was observed (see Figure 4.5). This indicates total lattice water removal at 150 °C without vacuum versus selective removal of only the loosely bound crystal waters at 100 °C under vacuum. Powder XRD measurements on a sample of Ru$_3$-11 which had been outgassed at 150 °C showed essentially the same peak pattern as for the hydrated form, but with a slight shift towards lower angles reflecting a small change in the unit cell dimensions (see Figure 4.6). This indicates that dehydration of
compound \( \text{Ru}_3 \text{-11} \) does not affect its crystalline nature and essentially does not alters its solid-state packing arrangement.

Interestingly, if compound \( \text{Ru}_3 \text{-11} \) is outgassed at 150 °C under vacuum and then exposed to ambient air for 48 hours, its TGA changes and becomes virtually identical with that of the hydrated form (see Figure 4.5). Furthermore, XRD measurements showed that the air-exposed sample had the same powder pattern as that of the original sample (see Figure. 4.7). Therefore, compound \( \text{Ru}_3 \text{-11} \) can lose and regain its crystal water molecules without changing crystalline order. Our preliminary outgassing studies on \( \text{Ru}_3 \text{-12} \) indicate that this material has a very similar behaviour as \( \text{Ru}_3 \text{-11} \). We expect the same for \( \text{Ru}_3 \text{-11} \), due to the isostructural nature of \( \text{Ru}_3 \text{-11} \text{- Ru}_3 \text{-11} \). On the other hand, the solid state structure of \( \text{Ru}_3 \text{-14} \) is completely different from that of \( \text{Ru}_3 \text{-11} \text{- Ru}_3 \text{-11} \) as the former does not exhibit any channels in the solid state (see Figure. 4.4). Our preliminary thermal, powder XRD and outgassing studies on \( \text{Ru}_3 \text{-14} \) have shown that this material does not undergo reversible loss of crystal waters. In fact, the crystallinity of \( \text{Ru}_3 \text{-14} \) is completely lost upon heating to 150 °C.

We also decided to investigate the sorption properties of compound \( \text{Ru}_3 \text{-11} \) with different short chain alcohols, namely methanol and ethanol. Compound \( \text{Ru}_3 \text{-11} \) was pretreated under vacuum at 150 °C to remove all crystal water molecules and was then immersed in 1 mL of methanol or ethanol and kept in an open vial until complete evaporation of the liquid. Afterwards, TGA measurements were performed on the remaining solids (see Figure. 4.8). The TGA graph for the ethanol-treated sample showed less weight loss than that of methanol, indicating less sorption of ethanol than methanol. Furthermore, the methanol-treated sample showed a sharper slope for the first weight loss step which may reflect the lower boiling point
of methanol as compared to ethanol. Next, we immersed a pretreated sample of Ru₃-11 in 1 mL of a 1:1 mixture of ethanol and methanol. TGA measurements showed a graph with intermediate weight loss and slope compared to ethanol and methanol alone.

Finally, we performed powder XRD measurements on all samples of Ru₃-11 after alcohol adsorption, which however showed loss of crystallinity as identified by the absence of any distinguishable peaks. Then the same samples were outgassed at 150 °C and investigated by powder XRD. However, the results showed that the powders were not crystalline and different from the original outgassed material. We conclude that the alcohol sorption with Ru₃-11 is irreversible and may in fact lead to a change in the solid state packing of the material.

4.1.1.3 Conclusions

We have investigated for the first time the interaction of the trinuclear, oxo-centered ruthenium(III) cation \([\text{Ru}_3\text{O(OOCCH}_3)_6(\text{H}_2\text{O})_3]^+\) with Keggin and Wells-Dawson polyanions in aqueous solution. All the resulted compounds were fully characterized in the solid state by single-crystal XRD, FTIR, TGA and elemental analysis. The Keggin based systems exhibit hexagonal channels in the solid state lattices which are filled with crystal waters, indicating a potential for interesting sorption properties. Sorption/desorption studies on Ru₃-11 for water indicated reversible behavior as seen by powder-XRD and TGA. On the other hand, the same studies on Ru₃-11 for methanol and ethanol as well as for mixtures of the two alcohols indicated irreversibility due to decomposition of Ru₃-11. The solid state structure of Ru₃-14 does not exhibit any channels in the solid state and as expected our preliminary thermal, powder XRD and outgassing studies showed that this material does not undergo reversible loss of crystal waters.
4.3 References


Chapter 4 Results: Keggin and Wells-Dawson Salts of $[\text{Ru}_3\text{O(OOCCH}_3)_6\text{(CH}_3\text{OH)}_3]^+$


Chapter 5

Collaborative Work

5.1 Magnetic Studies

The magnetic studies on polyanion 1 were performed by the group of Prof. N. S. Dalal from the Department of Chemistry and Biochemistry, Florida State University and National High Magnetic Field Laboratory and Center for Interdisciplinary Magnetic Resonance, Tallahassee, Florida 32306, USA. The Magnetic studies on polyanion 4 were performed by the group of Prof. A. K. Powell from the Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstr, 15 Geb, 30.45.

5.1.1 Magnetic Studies of [Mn_{19}(OH)_{12}(SiW_{10}O_{37})_6]^{34-} (1)

The Mn_{19} core in polyanion 1 is of obvious interest for its magnetic properties, as this structure presents an intermediate between an infinite 2-dimensional triangular lattice and a small molecular complex with a well-defined spin ground state. Spin-frustrated triangular lattices show a variety of phase transitions and magnetic structures. As mentioned earlier in results and discussion part of Na-1, the magnetic properties of Westin’s organic-capped coordination complex complex [Mn_{19}O_{12}(moe)_{14}(moeH)_{10}] ([Mn_{19}org]), have been investigated, but the EPR measurements were reported to be somewhat problematic due to saturation effects. Extensive Monte Carlo simulations of the magnetic susceptibility showed
that the magnetic properties of \{\text{Mn}_{19}\text{org}\} are dominated by strong antiferromagnetic interactions \((J = -24 \text{ K})\) between the 7 central Mn\textsuperscript{II} ions, with a ground state of \(S = 5/2\). The role of the other, peripheral 12 Mn\textsuperscript{II} ions was found to be minor.

So the motivation here was to examine the magnetic and EPR properties of the Mn\textsubscript{19} assembly in polyanion 1, and to compare them with those observed for \{\text{Mn}_{19}\text{org}\}. Such studies could possibly allow identifying if the organic vs. inorganic capping groups exhibit different effects on the magnetic properties of the Mn\textsubscript{19} cluster. The planar Mn\textsubscript{19} magnetic cluster in 1 is unprecedented in POM chemistry, and in fact 1 contains more manganese ions than any other polyanion reported to date. The magnetic susceptibility and magnetization data for 1 are significantly different from those of \{\text{Mn}_{19}\text{org}\}. The simple analysis procedure for the magnetic susceptibility of 1 was also performed, and the same ground state \((S = 5/2)\) was obtained, compare to those derived from the earlier Monte Carlo results on \{\text{Mn}_{19}\text{org}\}, even though the \{\text{Mn}_{19}\text{inorg}\} data show that the peripheral Mn\textsuperscript{II} ions also interact significantly with the central core of 7 Mn\textsuperscript{II} ions. Moreover, there was no particular difficulty in carrying out detailed EPR measurements, in contrast to \{\text{Mn}_{19}\text{org}\}.
Figure 5.1 Plot of $\chi_m T$ for a polycrystalline sample of I measured in an applied magnetic field of 0.02 T. Inset: $1/\chi_m$ as a function of temperature with a fit of the Curie-Weiss law based on the data of 50-300 K (red solid line).

Figure 5.2 Spin topology of the Mn$_{19}$ core in polyanion I.
5.1.2 Magnetic Studies of \([\{\text{Co}_4(\text{OH})_3\text{PO}_4\}_4(A-\alpha-\text{PW}_9\text{O}_{34})_4]^{28-}\) (4)

The magnetic measurements on a polycrystalline sample of \textbf{NaRb-4} gave an experimental \(\chi T\) value (47.28 cm\(^3\) K mol\(^{-1}\)) which is much higher than the expected value (30.0 cm\(^3\) K mol\(^{-1}\)) for sixteen spin-only high-spin (HS) Co\(^{II}\) ions \((S = 3/2)\). The \(\chi T\) value declines gradually with decreasing temperature and reaches a round minimum of 40.38 cm\(^3\) K mol\(^{-1}\) at 45 K. Upon further cooling, the \(\chi T\) value increases rapidly, reaching a maximum of 48.24 cm\(^3\) K mol\(^{-1}\) at 5 K, and then falling sharply to 45.97 cm\(^3\) K mol\(^{-1}\) at 1.8 K. The decrease of \(\chi T\) above 45 K is apparently due to the spin-orbital coupling of the Co\(^{II}\) ions, while the behavior below 45 K indicates overall ferromagnetic coupling between the Co\(^{II}\) ions. The final decrease of \(\chi T\) below 5 K is likely to be associated with intermolecular antiferromagnetic interactions and/or magnetic anisotropy. The field dependence of the magnetization at low temperatures for \textbf{NaRb-4} shows that the magnetization increases rapidly to reach \textit{ca.} 15 \(\mu_B\) up to 10 kOe, which is consistent with the presence of ferromagnetic interactions. Above 10 kOe, the magnetization curve increases in a linear fashion to reach 19.3 \(\mu_B\) with a lack of saturation even at 70 kOe (see Figure 5.3, inset). This is indicative of the possible presence of magnetic anisotropy. The experimental \((\chi T)_{max}\) of 48.24 cm\(^3\) K mol\(^{-1}\) at 5 K suggests a \(g\) factor of 2.3, if it is considered that all sixteen Co\(^{II}\) ions are ferromagnetically coupled, and thus the total spin of this compound would be \(1/2 \times 16 = 8\). This result is qualitatively supported by the field dependence of the magnetization at low temperatures (see above), in which the magnetization reaches 19.3 \(\mu_B\) which is almost consistent with sixteen HS Co\(^{II}\) ions with an effective spin 1/2 for each Co\(^{II}\) center and a \(g\) factor of 2.4, further indicating the presence of magnetic anisotropy of the Co\(^{II}\) ions.
The dynamic properties of NaRb-4 were also investigated using temperature and frequency dependent ac susceptibility measurements. The frequency dependence of both in-phase and out-of-phase components can be observed in zero dc field below 6 K, indicating slow relaxation of the magnetization (see Figures 5.4a, b). In addition, frequency sweeping ac susceptibilities were measured at different temperatures (see Figure 5.4c, d) and the shape and frequency dependence both indicate that this compound is a single molecule magnet (SMM).

Figure 5.3 Temperature dependence of the $\chi T$ product for compounds NaRb-4 at 1000 Oe (with $\chi$ being the molar susceptibility defined as $M/H$). Inset: Field dependence of magnetization of NaRb-4 at indicated temperatures.
Figure 5.4 Temperature dependence of the in-phase (a) and out-of-phase (b) components of the ac magnetic susceptibility at different frequencies and frequency dependence of the in-phase (c) and the out-of-phase (d) components of the ac susceptibility at different temperatures for \textit{NaRb-4} under zero dc field.
5.2 References


Curriculum Vitae

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1997 University of Punjab, Lahore, Pakistan
MSc (Chemistry)

1992 University of Balochistan, Quetta, Pakistan
BSc (Chemistry, Botany, Zoology)

1990 Government Girls Science College, Quetta, Pakistan
HSSC/Intermediate (Chemistry, Physics, Botany, Zoology)
EMPLOYMENT/ EXPERIENCE

2000- Present  Lecturer  Chemistry Department, Balochistan University, Quetta, Pakistan.

1997-1998  Research Associate  Pakistan Science Foundation, Balochistan University, Quetta, Pakistan.

2009-2010  Teaching Assistant  General and Advanced Inorganic Chemistry Courses at Jacobs University Bremen, Germany.

ANALYTICAL SKILLS

Experienced in handling different essential analytical tools (single crystal XRD, UV-vis spectroscopy, infrared spectroscopy, cyclic voltammetry, multi nuclear NMR spectroscopy, thermal techniques (TG-DTA)) required for characterization of polyoxoanions.

AWARDS AND SCHOLARSHIPS

1. Recipient of DAAD Scholarship for the Ph.D. program.
2. Recipient of Indigenous Scholarship for the local Ph.D. program from Higher Education of Pakistan (HEC).

MEMBERSHIPS AND AFFILIATIONS

1. Life member, Chemical Society of Pakistan.
2. Member Balochistan Foundation for Development.
**PUBLICATIONS**

- *Large Cation-Anion Materials Based on Trinuclear Ruthenium(III) Salts of Keggin and Wells-Dawson Anions Having Water-Filled Channels.*
  

- *The Wheel-Shaped Cu20-Tungstophosphate [Cu_{20}X(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-} Ion (X = Cl, Br, I) and the Role of the Halide Guest.*
  

- *Cobalt, Manganese, Nickel, and Vanadium Derivatives of the Cyclic 48-Tungsto-8-Phosphate [H_7P_8W_{48}O_{184}]^{33-}.*
  

- *Yttrium(III)-containing tungstoantimonate(III) stabilized by capping, tetrahedral WO_4^{2-} unit, [[Y(a-SbW_9O_{31}(OH)_{2})(CH_3COO)(H_2O)]_3(WO_4)^{17-}.*
  
- **Planar \( [\text{Mn}_{19}(OH)_{12}]^{26+} \) Assembly Incorporated in 60-Tungsto-6-Silicate Polyanion**

- **Hexadeca-Cobalt(II) Containing Polyoxometalate-Based Single-Molecule Magnet**
CONFERENCES AND MEETINGS

- Oral presentation at the 11th Northen-German Doctoral Student Colloquium of Inorganic Chemistry in Burg Warberg, Germany, 25.-26.09.2008. The oral presentation was entitled “Interaction of Trinuclear Oxo-Centered Ruthenium(III) cation[Ru₃O(OOCCH₃)₆(H₂O)₃]⁺ with Keggin and Wells-Dawson polyanions.”

- Poster presentation at the Meeting of DAAD Scholarship Holders in the Field of Chemistry in Cooperation with BASF Chemical Company: Science Meets Industry–Catalysis in Fundamental Research and Industrial Application, in Heidelberg, Germany, 16.–19.11.2008. Title “Large Cation-Anion Materials Based on Trinuclear Ruthenium(III) Salts of Keggin and Wells-Dawson Anions Having Water-Filled Channels.”

- Poster presentation at the International Polyoxometalate Symposium, in Jacobs University, Bremen, Germany, 28 July-01 August, 2009. Title “Large Cation-Anion Materials Based on Trinuclear Ruthenium(III) Salts of Keggin and Wells-Dawson Anions Having Water-Filled Channels.”

- Poster presentation at the 3rd EuCheMS Chemistry Congress, Nürnberg, Germany, August 29-September 2, 2010. Title “Cobalt, Manganese, Nickel, and Vanadium Derivatives of the Cyclic 48-Tungsto-8-Phosphate [H₇P₈W₄O₁₈₄]^{33-}.”
• Oral presentation at the **13th Northen-German Doctoral Student Colloquium of Inorganic Chemistry**, Greifswald, Germany, 24-25.09.2010. Title “Polyoxoanion stabilized by tetrahedral tungsten centre: A novel yttrium containing trimeric tungstoantimonate (III),\([\{Y(H_2O)(\alpha-H_2SbW_9O_{33})\}_3(CH_3COO)_3(WO_4)\}]^{7-}\)”

• Poster presentation at the **Workshop on Functional Materials and Nanomolecular Science**, Clausthal-Zellerfeld, 12-14 January, 2011. Title “High Nuclearity Transition Metal containing Polyoxometalates”
Appendix

Published Articles

• *Large Cation-Anion Materials Based on Trinuclear Ruthenium(III) Salts of Keggin and Wells-Dawson Anions Having Water-Filled Channels.*

• *The Wheel-Shaped Cu20-Tungstophosphate [Cu_{20}X(OH)_{34}(H_{2}O)_{12}(P_{8}W_{48}O_{184})]^{25-} Ion (X = Cl, Br, I) and the Role of the Halide Guest.*

• *Cobalt, Manganese, Nickel, and Vanadium Derivatives of the Cyclic 48-Tungsto-8-Phosphate [H_{7}P_{8}W_{48}O_{184}]^{33-}.*

• *Yttrium(III)-containing tungstoantimonate(III) stabilized by capping, tetrahedral WO_{4}^{2-} unit, [[Y(a-SbW_{6}O_{21}(OH)_{2})(CH_{3}COO)(H_{2}O)]_{3}(WO_{4})]^{17-}.*

- **Planar \( \{\text{Mn}_{19}(\text{OH})_{12}\}^{26+} \) Assembly Incorporated in 60-Tungsto-6-Silicate Polyanion**

- **Hexadeca-Cobalt(II) Containing Polyoxometalate-Based Single-Molecule Magnet**