Synthesis of Chromium-Containing and Some Other Heteropolytungstates and Study of Their Magnetic, Electrochemical, and Biological Properties

by

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ABSTRACT

Discrete metal-oxides, also known as polyoxometalates (POMs), possess a large structural and compositional variety, and a unique range of associated physicochemical properties, leading to applications in many different areas such as catalysis, materials science, and medicine. Transition metal-substituted POMs are an important subclass, and many derivatives of 3d metal ions are known, but to date only a handful of Cr-containing POMs has been reported.

In the course of this work a novel synthetic strategy has been developed which has led to the discovery of six novel Cr\textsuperscript{III}-containing POMs 1a – 6a. The two polyanions [Cr\textsuperscript{III}(HX\textsuperscript{V}W\textsubscript{7}O\textsubscript{28})\textsubscript{2}]\textsuperscript{13\textsuperscript{-}} (X = P (1a), As (2a)) are the first examples of mononuclear Cr-containing heteropolytungstates, and they exhibit an exceptionally large magnetic anisotropy. Systematic evolution of this structural family by heteroatom substitution has resulted in the two di-Cr\textsuperscript{III}-containing heteropolytungstates, [Cr\textsuperscript{III}\textsubscript{2}(B-β-SiW\textsubscript{8}O\textsubscript{31})\textsubscript{2}]\textsuperscript{14\textsuperscript{-}} (3a) and [Cr\textsuperscript{III}\textsubscript{2}(B-β-GeW\textsubscript{8}O\textsubscript{31})\textsubscript{2}]\textsuperscript{14\textsuperscript{-}} (4a). Polyanions 3a and 4a represent the first examples of sandwich-type POMs comprising two \{XW\textsubscript{8}O\textsubscript{31}\} (X = Si, Ge) units, and they are stable in solution from pH 1 – 7. Biological studies on 3a and 4a demonstrated interesting antidiabetic and anticancer activity. The polyanion [Cr\textsuperscript{III}\textsubscript{2}(As\textsuperscript{III}W\textsubscript{6}O\textsubscript{23})\textsubscript{2}(As\textsuperscript{III}O\textsubscript{3})\textsubscript{2}]\textsuperscript{14\textsuperscript{-}} (5a) exhibits the first example of a di-Cr\textsuperscript{III}-containing tungstoarsenate(III) and comprises two \{(AsW\textsubscript{6}O\textsubscript{21})(AsO\textsubscript{3})\textsubscript{2}\} units linked by two Cr\textsuperscript{III} centers. The preparation of 1a - 5a demonstrates a remarkable heteroatom template effect in the formation of new POM archetypes. The Cr\textsuperscript{III}-containing hexatungstate [H\textsubscript{3}Cr\textsuperscript{III}W\textsubscript{6}O\textsubscript{24}]\textsuperscript{6\textsuperscript{-}} (6a) reveals the first chromium derivative of this large Anderson-Evans-type structural heteropolytungstate family.
Following the newly developed synthetic strategy it was possible to isolate another 14 novel polyanions 7a – 20a comprising hexa-, hepta-, and octa-heteropolytungstates, which are all described in Chapter 4. For example, the iron(III)-containing [Fe<sup>III</sup>(HPW<sub>7</sub>O<sub>28</sub>)<sub>2</sub>]<sup>13-</sup> (7a) and the high-valent manganese(III)-containing [Mn<sup>III</sup>(HPW<sub>7</sub>O<sub>28</sub>)<sub>2</sub>]<sup>13-</sup> (8a) were prepared, and shown to possess interesting magnetic properties. The di-manganese(II)-containing [H<sub>3</sub>Mn<sup>II</sup><sub>2</sub>(As<sup>III</sup>W<sub>6</sub>O<sub>21</sub>)<sub>2</sub>(As<sup>III</sup>O<sub>3</sub>)<sub>4</sub>]<sup>11-</sup> (14a) is composed of two equivalent {[(AsW<sub>6</sub>O<sub>21</sub>)(AsO<sub>3</sub>)<sub>2</sub>] units with four terminal arsenate groups. By a slightly modified synthetic procedure the nickel(II)- and manganese(II)-containing polyanions [{Na(H<sub>2</sub>O)M<sup>II</sup>(P<sub>4</sub>W<sub>6</sub>O<sub>34</sub>)}<sub>2</sub>]<sup>18-</sup> (M = Ni<sup>II</sup> (19a), Mn<sup>II</sup> (20a)) could be prepared, which have a sandwich-type structure capped by three phosphate groups on either side.
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<tr>
<td>Na(<em>{13})[Cr(</em>{III})(HP(_V)W(<em>7)O(</em>{28}))(_2)]\cdot47(\text{H}_2)O</td>
<td>1</td>
</tr>
<tr>
<td>Na(<em>{13})[Cr(</em>{III})(HAs(_V)W(<em>7)O(</em>{28}))(_2)]\cdot52(\text{H}_2)O</td>
<td>2</td>
</tr>
<tr>
<td>Na(<em>{14})[Cr(</em>{III})(<em>2)(B-(\beta)-Si(</em>{IV})W(<em>8)O(</em>{31}))(_2)]\cdot45(\text{H}_2)O</td>
<td>3</td>
</tr>
<tr>
<td>Na(<em>{14})[Cr(</em>{III})(<em>2)(B-(\beta)-Ge(</em>{IV})W(<em>8)O(</em>{31}))(_2)]\cdot50(\text{H}_2)O</td>
<td>4</td>
</tr>
<tr>
<td>Na(_{11})[H(<em>3)Cr(</em>{II})(AsW(<em>6)O(</em>{23}))(_2)(AsO(_3))(_2)]\cdot45(\text{H}_2)O</td>
<td>5</td>
</tr>
<tr>
<td>Na(_6)[H(<em>3)Cr(</em>{II})W(<em>6)O(</em>{24})]\cdot22(\text{H}_2)O</td>
<td>6</td>
</tr>
<tr>
<td>Na(<em>{13})[Fe(</em>{III})(HP(_V)W(<em>7)O(</em>{28}))(_2)]\cdot42(\text{H}_2)O</td>
<td>7</td>
</tr>
<tr>
<td>Na(<em>{13})[Mn(</em>{III})(HP(_V)W(<em>7)O(</em>{28}))(_2)]\cdot43(\text{H}_2)O</td>
<td>8</td>
</tr>
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<td>Na(<em>{13})[Ga(</em>{III})(HP(_V)W(<em>7)O(</em>{28}))(_2)]\cdot48(\text{H}_2)O</td>
<td>9</td>
</tr>
<tr>
<td>Na(<em>{13})[In(</em>{III})(HP(_V)W(<em>7)O(</em>{28}))(_2)]\cdot44(\text{H}_2)O</td>
<td>10</td>
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<tr>
<td>Na(<em>{14})[Mg(</em>{II})(HP(_V)W(<em>7)O(</em>{28}))(_2)]\cdot44(\text{H}_2)O</td>
<td>11</td>
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<tr>
<td>Na(<em>{14})[Ga(</em>{III})(<em>2)(B-(\beta)-Ge(</em>{IV})W(<em>8)O(</em>{31}))(_2)]\cdot56(\text{H}_2)O</td>
<td>12</td>
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<tr>
<td>Na(<em>{14})[In(</em>{III})(<em>2)(B-(\beta)-Ge(</em>{IV})W(<em>8)O(</em>{31}))(_2)]\cdot56(\text{H}_2)O</td>
<td>13</td>
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<tr>
<td>Na(<em>{11})[H(<em>3)Mn(</em>{II})(As(</em>{III})W(<em>6)O(</em>{21}))(<em>2)(As(</em>{III})O(_3))(_4)]\cdot44(\text{H}_2)O</td>
<td>14</td>
</tr>
<tr>
<td>Na(_{12})[H(<em>2)Fe(</em>{III})(_2)(AsW(<em>6)O(</em>{23}))(<em>2)(As(</em>{III})O(_3))(_2)]\cdot48(\text{H}_2)O</td>
<td>15</td>
</tr>
<tr>
<td>Na(_{12})[H(<em>2)Sc(</em>{III})(<em>2)(As(</em>{III})W(<em>6)O(</em>{23}))(<em>2)(As(</em>{III})O(_3))(_2)]\cdot39(\text{H}_2)O</td>
<td>16</td>
</tr>
<tr>
<td>Na(_{12})[H(<em>2)In(</em>{III})(_2)(AsW(<em>6)O(</em>{23}))(<em>2)(As(</em>{III})O(_3))(_2)]\cdot49(\text{H}_2)O</td>
<td>17</td>
</tr>
<tr>
<td>Na(<em>{11})[HT(</em>{II})(As(_{III})W(<em>6)O(</em>{23}))(<em>2)(As(</em>{III})O(_3))(_2)]\cdot41(\text{H}_2)O</td>
<td>18</td>
</tr>
<tr>
<td>Na(_{14})[H(<em>4){Na(H(<em>2)O)Ni(</em>{II})(P(</em>{IV})W(<em>6)O(</em>{34}))}_2]\cdot30(\text{H}_2)O</td>
<td>19</td>
</tr>
<tr>
<td>Na(_{14})[H(<em>4){Na(H(<em>2)O)Mn(</em>{II})(P(</em>{IV})W(<em>6)O(</em>{34}))}_2]\cdot30(\text{H}_2)O</td>
<td>20</td>
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1. General Introduction

Polyoxometalates (abbreviated POMs), as its name suggests, represent a class of multi-metal oxyanions usually formed by early transition metals pertaining a d⁰ or d¹ electron configuration (e.g. V⁵⁺, Mo⁵⁺, Nb⁵⁺, Ta⁵⁺, Mo⁶⁺, W⁶⁺). POM chemistry has developed exponentially due to the modern instrumentation and novel synthetic approaches, starting from the 1991 review.[1] The development of single crystal XRD technique has allowed collecting the diffraction data to obtain the structure much easier than the initial structure solution. POMs, structurally well-defined molecular species, are not only aesthetically beautiful but also of importance for different aspects, such as analytical and clinical chemistry,[2] biology,[3, 4] materials,[5] catalysis[6-9] and magnetism.[10]

1.1 Structural Principles of Polyoxometalates

POMs are composed of aggregates of the metal-oxygen unit MOₙ, where M can be visualized as the central metal of a polyhedron, and O can be regarded as the vertices of that polyhedron, the n indicates the coordination number (n = 4, 5, 6, 7). These MOₙ polyhedra can be connected to each other via corner- or edge-sharing modes (face sharing is rarely seen), see Fig.1.1. These structural building blocks may be used to prepare or conceptualize the primary, secondary, and tertiary structures of the POM clusters.[11] Therefore, the different structural POM assemblies can be formed by the linking or aggregation of these polyhedra via a self-assembly process.[12] Usually POM clusters can be investigated in solution chemistry due to the fact that they are normally
anionic. Therefore, the structures of POMs can be broken down into either isopolyanions or heteropolyanions depending on the inexistence or existence of an internal heteroatom (X).

![Diagram of corner- and edge-sharing polyhedra](image.png)

**Fig.1.1** A representation of corner- and edge-sharing polyhedra found in POMs clusters, the metal ions are positioned in the center of the polyhedra and the oxygen ligands are at the vertices. Color code: MO₆ octahedra (blue).

### 1.1.1 Isopolyanions

This class of compounds is composed of only one kind of addenda atoms (e.g. Nb, W, Mo, V) together with oxygen atoms, but without the internal heteroatom. According to this definition, we can use a general formula \([M_mO_y]^{p^-}\) to describe them. The most representative example is the Lindqvist ion,[13-15] \([M_6O_{19}]^{2-}\) (M = W, Mo, Ta, V), as shown in Fig.1.2, which is a compact arrangement of six edge-sharing MO₆ octahedra with idealized \(O_h\) symmetry.
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Other examples include the dodecatungstates [H\textsubscript{2}W\textsubscript{12}O\textsubscript{40}]\textsuperscript{6-} (metatungstate, \textit{Td} symmetry, Fig.1.3)[16] [H\textsubscript{2}W\textsubscript{12}O\textsubscript{42}]\textsuperscript{10-} (paratungstate, \textit{C\textsubscript{2h}} symmetry, Fig.1.4)[17, 18] as well as the heptatungstate [W\textsubscript{7}O\textsubscript{24}]\textsuperscript{6-}, which act as isolated units or as components of high molecular aggregates. Brüdgam \textit{et al.} also reported a large isopolyoxotungstate [W\textsubscript{24}O\textsubscript{84}]\textsuperscript{24+}, which has a \{W\textsubscript{24}\} ring based around a six-fold axis (Fig.1.5).[19] Interestingly, it is made up of WO\textsubscript{6} octahedra as well as the rarely seen WO\textsubscript{5} units. In this structure, six corner-shared WO\textsubscript{6} octahedra form an inner ring which is connected to six \{W\textsubscript{3}O\textsubscript{13}\} groups via corner-sharing at the WO\textsubscript{6} octahedra vertices. These \{W\textsubscript{3}O\textsubscript{13}\} groups are made of two corner-shared WO\textsubscript{6} octahedra and one pyramidal WO\textsubscript{5}. 


Fig.1.3 Polyhedral representation of the metatungstate \([\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}\). Color code: WO₆ octahedra (blue). [16]

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The largest isopolyoxotungstate \([H_{12}W_{36}O_{120}]^{11-}\) to date was reported by employing enormous organic cations (Fig.1.6).[20] This anion comprises three \{W\(_{11}\)\} cluster subunits linked by three \{W\(_1\)\} bridges with an apparent \(C_{3v}\) symmetry. The \{W\(_{11}\)\} cluster comprises six basal \{WO\(_6\)\} positions as a ring, an additional \{WO\(_6\)\} positioned in the center of this ring, and four apical \{WO\(_6\)\} positions. In general, isopolyanions can thus be used as building blocks since they usually have strongly basic oxygen surfaces.
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1.1.2 Heteropolyanions

This subfamily of compounds is comprised of metal oxides including heteroanions. According to the definition, we can use a general formula $[X_\text{x}M_\text{m}O_\text{y}]^{q-}$ to describe these seemingly endless number of structures, where “$X$” is the heteroatom located in the center of the polyanion, usually $x \leq m$. The most common and widely studied heteropolyanion structures are:

a) The Anderson-Evans $[X\text{M}_6\text{O}_{24}]^{q-}$ is a planar arrangement of six MO$_6$ octahedra with a central heteroatom XO$_6$ octahedron, resulting in an overall $D_{3h}$-symmetric shape (Fig. 1.7).[21-23]

b) The Keggin $[X\text{M}_{12}\text{O}_{40}]^{q-}$ is composed of a central XO$_4$ tetrahedron surrounded by four corner-shared $\{\text{M}_3\text{O}_{13}\}$ groups with each triad being composed of three edge-shared MO$_6$ octahedra, resulting in an overall $T_d$-symmetry (Fig.1.8).[24]

c) The Wells-Dawson $[(\text{XO}_4)\text{M}_{18}\text{O}_{54}]^{q-}$ is assembled by the fusion of two trilacunary Keggin-type units $[\text{XM}_9\text{O}_{34}]^{q-}$ via corner-sharing at the vacant sites. This structure
consists of two unequivalent metal centers, the caps (polar positions) and belts (equatorial regions), where the cap is composed of three edge-shared MO$_6$ octahedra forming a \{M$_3$O$_{13}$\} triad and the belt is formed by alternating corner- and edge-shared MO$_6$ octahedra, as shown in Fig.1.9.[25]

d) The Weakley-Peacock-Yamase structure [X$^{n+}$O$_8$W$_{10}$O$_{28}$]$^{(12-n)^-}$ is composed of two [W$_3$O$_{18}$]$^{6^-}$ units connected by a central XO$_8$ square antiprism, forming a sandwich type structure, as shown in Fig.1.10.[26-28]

e) The Dexter-Silverton structure [XM$_{12}$O$_{42}$]$^{n^-}$ consists of a central XO$_{12}$ icosahedron surrounded by six face-shared \{M$_2$O$_9$\} units connected by corner-sharing, as shown in Fig.1.11.[29, 30]

![Polyhedral representation of the Anderson-Evans anion [XM$_6$O$_{24}$]$^{n^-}$. Color code: MO$_6$ octahedra (blue), XO$_6$ (yellow).][21-23]
Fig. 1.8 Polyhedral representation of Keggin [XM\textsubscript{12}O\textsubscript{40}]\textsuperscript{n−}. Color code: heteroatom (red), each \{M\textsubscript{3}O\textsubscript{13}\} triad is in different color.[24]

Fig. 1.9 Polyhedral representation of Wells-Dawson anion [(XO\textsubscript{4})\textsubscript{2}M\textsubscript{18}O\textsubscript{54}]\textsuperscript{n−}. Color code: XO\textsubscript{4} (yellow), MO\textsubscript{6} octahedra in the cap (blue), MO\textsubscript{6} octahedra in the belt (violet).[25]
Fig. 1.10 Combined polyhedral and ball-and-stick representation of Weakley-Peacock-Yamase structure $[X^{n+}O_6W_{10}O_{28}]^{(12-n)^-}$. Color code: X (violet), WO$_6$ octahedra (blue).[26-28]

Fig. 1.11 Combined polyhedral and ball-and-stick representation of Dexter-Silverton structure $[XM_{12}O_{42}]^{n^+}$. Color code: X (green), MO$_6$ octahedra (blue). [29, 30]
1.2 Baker-Figgis Isomers

Structural isomerism is common in POMs. In the example of the Keggin-type heteropolyanion, five rotational isomers are possible, which are obtained by 60° rotation of one, two, three or four of the triads, see Fig.1.12.[31] Poblet et al. reported the relative stabilities of the five rotational isomers (α, β, γ, δ and ε) by theoretical calculations resulting in the following relative energy trend, $\alpha < \beta < \gamma < \delta < \varepsilon$. The most stable forms ($\alpha$ and $\beta$) with zero and one rotated triads, respectively, do not feature close M–M contacts. In comparison, for $\gamma$, $\delta$ and $\varepsilon$ isomers, with respectively two, three and four rotated triads, an increasing number of M–M contacts are formed and thus have comparable instabilities.[32]

![Fig.1.12 Five rotational Baker-Figgis isomers of the Keggin anion. Color code: XO$_4$ (red), MO$_6$ octahedra (yellow), the rotated {M$_3$O$_{13}$} triads (blue).[31]](image-url)
only XRD can identify isomers but also UV, Infrared, Raman, NMR spectroscopy, and especially polarography.[33-35] From XRD data, the structure can be directly determined, however a single crystal with a good diffraction is needed. Also the difference in the redox behavior between different isomers is of great importance for identifying them, since $\alpha$, $\beta$, $\gamma$, $\delta$ and $\epsilon$ isomers only differ in the way how the $\{W_{5}O_{13}\}$ triads are linked together. [36]

1.3 Applications

The use of polyoxometalate clusters as catalysts is one of the most important application areas due to the variable redox potentials available in the POM family. In the example of a redox-active polyanion $[\{\text{Ru}_4\text{O}_4\text{(OH)}_2\text{(H}_2\text{O})_4\}\{\gamma\text{-SiW}_{10}\text{O}_{36}\}_2]^{10-}$, [37] it was found to catalyze the oxidation of $\text{H}_2\text{O}$ to $\text{O}_2$ in water with chemical oxidants Ce(IV) or with [$\text{Ru(bipy)}_3]^{3+}$ photoactivation, showing efficient catalytic water splitting.[8, 37-39] Recently, Sakai et al. reinvestigated the Anderson-Evans type $[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-}$ and the di-catalyst cores $[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4]^{6-}$, demonstrating that they are active $\text{O}_2$-evolving catalysts in a system combined with [$\text{Ru(bipy)}_3]^{3+}$ and $\text{S}_2\text{O}_8^{2-}$ in aqueous basic media.[40] Kinetic studies demonstrated that the cobalt nuclearity is not a key factor for the $\text{O}_2$ evolution rate. In recent years, many reviews and papers studied POM-catalysis aspects including alkene and alcohol oxidation, and green $\text{H}_2\text{O}_2$-based epoxidation systems.[41-44]

In principle, the redox properties can be modified by incorporating different heteroatoms, different metal ions, or a mixture of more than one type of metal ions. The fact that POMs are electronically rich and redox active is one of the major strengths in magnetic systems. For example, a series of compounds with Lindqvist-type structure
pertaining a \{\text{V}^\text{III}\text{V}^\text{IV}_5\text{O}_{19}\} core showed ferromagnetic \text{V}^\text{IV}\cdots\text{V}^\text{III} interactions.\cite{45} The reported heterometallic sandwich-based POM compound \([\text{CrFe(AsMo}_7\text{O}_{27})_2]^{12-}\)\cite{46} with \text{Cr(III)} and \text{Fe(III)} as paramagnetic centers showed a significant antiferromagnetic exchange interaction between the metal centers.

Recently, there are a number of studies focusing on employing POMs as anticancer and anti-viral agents. For example, \(\text{[iPrNH}_3\text{]}_6[\text{Mo}_7\text{O}_{24}]\) was found to show activity against human colon, breast, and lung cancer effectively.\cite{47, 48} In biological study, \text{Mo} is required in organometallic cofactors as well as redox enzymes in order to catalyze some critical steps in carbon, nitrogen, and sulfur fixation. Hence \text{N}_2-fixing bacteria enhance the utility of nitrogenase in molybdenum starvation using a special \text{Mo} storage protein prepared by the self- and protein-driven assembly processes with \([\text{Mo}_8\text{O}_{26}]^{4+}\) clusters allowing for storage of more than 100 \text{Mo} atoms.\cite{49}
2. State of the art

The application of polyoxometalates (POMs) towards molecular magnetism has been one of the most attractive research areas because magnetic materials show promising prospects in integrated information storage, quantum computing devices, biochemistry, and molecule-based magnets.[43, 50-54] The implication of different magnetic centers such as transition metals, lanthanides, mixed 3d-4f clusters, or polynuclear transition metal clusters has resulted in a plethora of structures with variable magnetic behaviors.[55-57] In a broad domain of POM chemistry, the magnetic properties of POMs incorporating paramagnetic 3d metals like manganese, iron, cobalt, nickel, and copper have been widely studied. In contrast, chromium-containing POMs are, by and large, less well-explored, mainly due to the kinetic inertness of hexa-aqua Cr\textsuperscript{III} ions towards ligand exchange in solution.[58, 59]

However, the challenge of preparing new Cr-containing POMs remains a highly rewarding research area due to the following reasons: (i) the paramagnetic nature of Cr\textsuperscript{III} can provide a platform for studying magnetic properties at atomic or molecular levels; (ii) Many of the earlier EPR studies have been on complexes where Cr\textsuperscript{III} is used as a dopant ion in lattices such as ruby,[60] CaO,[61] and MgWO\textsubscript{4},[62] for probing phase transitions in ferroelectric lattices;[63, 64] (iii) Developing Cr\textsuperscript{III} complexes with large magnetic anisotropy since they can serve as building blocks for novel molecular magnets such as single molecule magnets that can find applications in high-density information storage, quantum computing and spintronics.[65-67] Long and coworkers
[68] have made significant progress in this regard, showing that by adding ligands with large spin-orbit coupling to Cr$^{\text{III}}$ ions and causing large structural distortion to their octahedral coordination could lead to large $D$, as much as 2.3 cm$^{-1}$. Goswami and Misra [69] have carried out theoretical analyses in support of this approach, emphasizing that the experimental determination of the sign of the $D$ value is an important parameter in understanding the electronic structure of such molecules. Therefore, precise information on the spin state and the magnetic parameters, including their signs, is of fundamental theoretical importance. This factor provided an impetus for studying Cr-containing POMs.

Preliminary investigations upon the reaction of lacunary POMs with paramagnetic chromium ions were performed by the groups of Lunk [70-72] and Mialane [73]. These attempts successfully managed in obtaining the initial results of characterizable POM compounds with chromium ions. In this section the development of this research area along with compounds obtained and characterized will be discussed. A list of structural types of chromium polyoxometalates reported to date is shown in Table 2.1.

Table 2.1 A summary of a number of Cr-Polyoxometalates published.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Metal core</th>
<th>Magnetic behavior</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cr-polyoxotungstates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[$A$-$\alpha$-SiW$<em>9$O$</em>{34}$Cr$_3$(OH)$_3$(H$_2$O)$_3$]$^{1+}$</td>
<td>Cr$_3$</td>
<td>___</td>
<td>[70]</td>
</tr>
<tr>
<td>[${A$-$\alpha$-SiW$<em>9$O$</em>{34}$Cr$_3$(OH)$_3}$_2$(OH)$_3$]$^{11-}$</td>
<td>2Cr$_3$</td>
<td>Antiferromagnetic</td>
<td>[71]</td>
</tr>
<tr>
<td>[$\gamma$-SiW$<em>{10}$O$</em>{36}$Cr$_2$(OH)(OOCCH$_3$)$_2$(H$_2$O)$_3$]$^{5+}$</td>
<td>Cr$_2$</td>
<td>Antiferromagnetic</td>
<td>[72]</td>
</tr>
<tr>
<td>[(</td>
<td>$\gamma$-SiW$<em>{10}$O$</em>{36}$)$_2$(Cr(OH)(H$_2$O))$_3$]$^{10-}$</td>
<td>Cr$_3$</td>
<td>Antiferromagnetic</td>
</tr>
<tr>
<td>[(</td>
<td>$\gamma$-SiW$<em>{10}$O$</em>{36}$)$_2$(Cr(OH)(H$_2$O))$_3$(La(H$_2$O)$_7$)$_2$]$^{5-}$</td>
<td>Cr$_3$</td>
<td>___</td>
</tr>
<tr>
<td><strong>Cr-polyoxomolybdate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(OH)$_6$Mo$<em>9$O$</em>{18}$]$^{3-}$</td>
<td>Cr</td>
<td>Antiferromagnetic</td>
<td>[74-76]</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>Cation</td>
<td>Magnetic Property</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------------------------------------</td>
<td>--------</td>
<td>-------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>([\text{Cr(OH)}_6\text{Mo}<em>6\text{O}</em>{18}{\text{Cu(phen)}(\text{H}_2\text{O})_2}_2])</td>
<td>Cr</td>
<td>Antiferromagnetic</td>
<td>[77]</td>
</tr>
<tr>
<td>([\text{Cr(OH)}_6\text{Mo}<em>6\text{O}</em>{18}{\text{Cu(phen)}\text{Cl}}_2])</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Cr}_2(\text{AsMo}<em>7\text{O}</em>{27})_2]^{12-})</td>
<td>(\text{Cr}_2)</td>
<td>Antiferromagnetic</td>
<td>[78]</td>
</tr>
<tr>
<td>([\text{CrFe}(\text{AsMo}<em>7\text{O}</em>{27})_2]^{12-})</td>
<td>(\text{CrFe})</td>
<td>Antiferromagnetic</td>
<td>[46]</td>
</tr>
<tr>
<td>([\text{Cr}^{\text{III}}\text{Cl}]_6\text{O}{\text{MeC}(\text{CH}_2\text{O})_3}_4]^{2-})</td>
<td>6Cr</td>
<td>Antiferromagnetic</td>
<td>[79]</td>
</tr>
</tbody>
</table>

**Cr-isopolyanion**

Fig.2.1 Combined polyhedral and ball-and-stick representation of \([A-\alpha-\text{SiW}_9\text{O}_{34}\text{Cr}_3(\text{OH})_3(\text{H}_2\text{O})_3]^+\). Color code: SiO₄ tetrahedron (orange), WO₆ octahedra (blue), Cr (green), O (red/pink).[70]

### 2.1 Chromium-Containing Heteropolytungstates

The structure of the first chromium(III)-containing polyoxotungstate, \([A-\alpha-\text{SiW}_9\text{O}_{34}\text{Cr}_3(\text{OH})_3(\text{H}_2\text{O})_3]^+\).[70] was reported by Lunk et al. in 1994 (Fig.2.1), previously synthesized by Peng et al. however without X-ray analysis.[36] The potassium salt of this compound was obtained by adding Cr(III) and \([A-\alpha-\text{SiW}_9\text{O}_{34}]^{10-}\) with the same ratio in H₂O at pH = 4, and then adding an excess of KCl solid to this
solution. After a few days, the recrystallized potassium salt yielded green crystals. This complex can be seen as three Cr$^{III}$ centers are bridged by three hydroxo groups which are fixed on the trivacant tungsten sites in $[A\alpha\text{-SiW}_{9}\text{O}_{34}]^{10-}$.

Fig.2.2 Combined polyhedral and ball-and-stick representation of $\{[A\alpha\text{-SiW}_{9}\text{O}_{34}\text{Cr}_{3}\text{(OH)}_{3}]_{2}\text{(OH)}_{3}\}^{11-}$. Color code: SiO$_4$ tetrahedron (orange), WO$_6$ octahedra (blue), Cr (green), O (red).[71]

In the year 1995, the same group report on the chromium (III) derivative $\{[A\alpha\text{-SiW}_{9}\text{O}_{34}\text{Cr}_{3}\text{(OH)}_{3}]_{2}\text{(OH)}_{3}\}^{11-}$, which represented the first example of a Keggin dimer substituted by paramagnetic transition metal ions (Fig.2.2).[71] This complex is composed of two trilacunary Keggin anions $\{\text{Cr}_3\text{SiW}_{9}\text{O}_{34}\text{(OH)}_3\}$ linked via three hydroxo groups, obtained by the condensation of the first compound in aqueous solution. Nevertheless, the synthesis procedure is very complex by adding $\text{K}_4[A\alpha\text{-SiW}_{9}\text{O}_{34}\text{Cr}_{3}\text{(OH)}_3(\text{H}_2\text{O})_3]\cdot13\text{H}_2\text{O}$ in a strong acid proton cation exchange, and then with gradual addition of 1M NaOH and gradual refluxing, then recrystallized from
warm water by addition of NH₄Cl solid. ESR spectra exhibit exchange interactions between the Cr(III) centers, which coincides with its structure.

Fig.2.3 Combined polyhedral and ball-and-stick representation of \([\gamma^{-}\text{SiW}_{10}\text{O}_{36}\text{Cr}_2\text{(OH)}(\text{OOCCH}_3)_2(\text{H}_2\text{O})_2]^5^-\). Color code: SiO₄ tetrahedron (orange), WO₆ octahedra (blue), Cr (green), O (red), C (black). [72]

In 1996, the same group studied the reaction of Cr(III) with the potassium-salt of \([\gamma^{-}\text{SiW}_{10}\text{O}_{36}]^8^-\) which gave \([\gamma^{-}\text{SiW}_{10}\text{O}_{36}\text{Cr}_2\text{(OH)}(\text{OOCCH}_3)_2(\text{H}_2\text{O})_2]^5^-\), Fig.2.3.[72] This was obtained by mixing 2 equivalents of Cr(III) per equivalent of K₈[\(\gamma^{-}\text{SiW}_{10}\text{O}_{36}]\cdot12\text{H}_2\text{O}\) in a potassium acetate buffer at pH = 4.8 and heated the solution to 80°C. After cooling to room temperature, the addition of CsCl gave a white precipitate. Recrystallization from warm water gave blue-green crystals of di-chromium substituted \([\gamma^{-}\text{SiW}_{10}\text{O}_{36}]^8^-\). In this structure, the chromium centers in the two corner-linked CrO₆ octahedra are bridged by two acetate ligands, which occupy the vacant sites of the \{\gamma^{-}
SiW$_{10}$} unit. The recorded ESR spectra give evidence for antiferromagnetic coupling between the Cr(III) centers.

Fig.2.4 Combined polyhedral and ball-and-stick representation of [(γ-SiW$_{10}$O$_{36}$)$_2$(Cr(OH)(H$_2$O)$_3$)$_3$]$^{10-}$. Color code: SiO$_4$ tetrahedron (orange), WO$_6$ octahedra (blue), Cr (green), O (red). [73]

In a more recent study, the group of Mialane has presented their first Cr(III) polyoxometalate complex [(γ-SiW$_{10}$O$_{36}$)$_2$(Cr(OH)(H$_2$O)$_3$)$_3$]$^{10-}$, Fig.2.4.[73] The synthesis procedure is very similar to the above dinuclear compound, however was prepared by using the trinuclear chromium(III) acetate hydroxide [Cr$_3$(CH$_3$COO)$_7$(OH)$_2$] as the Cr(III) source instead of the mononuclear Cr(NO$_3$)$_3$ salt as well as a water-mediated solution instead of sodium acetate. In this structure, a triangular {Cr$_{III}$$_3$} core where the
Paramagnetic centers are connected by three hydroxo groups is connected at the vacant site of two \(\{\gamma\text{-SiW}_{10}\}\) units. Electronic absorption spectroscopy and electrochemical experiments were studied to support the stable nature of this compound as well as its inertness when heated under reflux. The magnetic curves exhibit a continuous decrease from room temperature to 13K, the expected \(\chi_M T\) for three uncoupled \(S = 3/2\) centers at room temperature is higher than the obtained value, indicating an antiferromagnetic coupling between the Cr(III) centers.

The inert and stable nature of this chromium-containing polyanion was proven by its interaction in hot water with excess La(III) resulting in a 3d-4f complex \([(\gamma\text{-SiW}_{10}O_{36})_2(Cr(OH)(H_2O))_3(La(H_2O)\gamma)_2]^5-\) with an intact structure of the polyanion. Each La center connects two adjacent complexes \([(\gamma\text{-SiW}_{10}O_{36})_2(Cr(OH)(H_2O))_3]^10-\) via W=O⋯La bonds leading to infinite \{La(\gamma\text{-SiW}_{10}O_{36})_2(Cr(OH)(H_2O))_3\}_\infty linear chains in the solid state.[73]

### 2.2 Chromium-Containing Heteropolymolybdates

In 1970, an anion \([Cr(OH)_6Mo_6O_{18}]^{3-}\) with an Anderson-Evans type structure was reported (Fig.2.5).[74] The central chromium ion is coordinated to six OH groups. There are three kinds of Mo–O bond lengths, the shortest ones are those connecting only one Mo atom to oxygen, intermediate ones are those connecting oxygen to two Mo atoms, and the longest ones are those coordinating oxygen to the Cr and two Mo atoms.
Fig.2.5 Polyhedral representation of $[\text{Cr(OH)}_6\text{Mo}_6\text{O}_{18}]^{3-}$. Color code: CrO$_6$ octahedron (green), MoO$_6$ octahedra (blue). [74]

The fact that this Anderson-Evans polyanion possesses OH groups that might favor the intermolecular interactions through hydrogen bonding and can thus play the role of reacting ligands, thus several new structures based on this structure have been reported.[75, 76] An anhydrous salt was reported, Na$_3[\text{Cr(OH)}_6\text{Mo}_6\text{O}_{18}]\cdot6(\text{CH}_3)_2\text{SO}$, which consists of the same Anderson-Evans polyanion where DMSO molecules substitute water molecules.[80] In the same paper, two decamethylferrocenium salts of this polyanion, $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]_2[\text{Cr(OH)}_6\text{Mo}_6\text{O}_{18}]\cdot20\text{H}_2\text{O}$ and Na$[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_5)_2]_2[\text{Cr(OH)}_6\text{Mo}_6\text{O}_{18}]\cdot3\text{H}_2\text{O}$, where organometallic cations substitute the sodium cations, were also reported. The ESR spectra for the octahedral Cr(III)-containing compounds (3d$^3$, 4F, L = 3, S = 3/2), might reveal a zero field splitting.

The first compound where a transition metal is coordinated to the “discrete” Anderson-Evans type polyanion was reported in 2005, $[\text{Cr(OH)}_6\text{Mo}_6\text{O}_{18}\{\text{Cu(phen)}(\text{H}_2\text{O})_2\}_2][\text{Cr(OH)}_6\text{Mo}_6\text{O}_{18}\{\text{Cu(phen)Cl}\}_2]$, and can be seen as an anion-cation adduct of $[\text{Cr(OH)}_6\text{Mo}_6\text{O}_{18}\{\text{Cu(phen)}(\text{H}_2\text{O})_2\}_2]^{1+}$ and
[Cr(OH)$_6$Mo$_6$O$_{18}$\{Cu(phen)Cl\}_2]$^{1^-}$, as shown in Fig.2.6.[77] This compound was synthesized in a simple one-pot aqueous strategy involving the reaction of Cr$^{III}$ chloride, sodium molybdate, Cu$^{II}$ nitrate and phenanthroline at pH 3, by changing its coordination mode from water to chloride. The ESR spectrum with an anisotropic axial signal ($g_\parallel = 4.3$ and $g_\perp = 1.08$) may reveal a zero-field-splitting of the central Cr(III) ion of the Anderson-Evans structure, with an intense peak of the Cu(II) ion.

In another study,[77] Xue et al. presented two sandwich-type heteropolymolybdates, [Cr$_2$(AsMo$_7$O$_{27}$)$_2$]$^{12^-}$ (Fig.2.7) [78] and [CrFe(AsMo$_7$O$_{27}$)$_2$]$^{12^-}$,[46] both of which are composed of two transition metals sandwiched between two [As$^{III}$(Mo$_7$O$_{27}$)$^9$]$^-$ fragments, where each fragment can be viewed as a mono-capped hexavacant Keggin-type subunit with a central AsO$_3$ group. Their magnetic properties were investigated to give
susceptibility $\chi_M T$ values corresponding to the calculated spin-only value at 300 K, and then showed a continuous decrease upon cooling, indicating antiferromagnetic exchange between the magnetic centers with $J = -6.26 \text{ cm}^{-1}$, 4.09 cm$^{-1}$, respectively.

Fig.2.7 Combined polyhedral and ball-and-stick representation of [Cr$_2$(AsMo$_7$O$_{27}$)$_2$]$^{12-}$. Color code: MoO$_6$ octahedra (violet), As (sky blue), Cr (green), O (red). This figure is also representative of [CrFe(AsMo$_7$O$_{27}$)$_2$]$^{12-}$, where one Cr is replaced by Fe.[78].

2.3 Chromium-Containing Isopolyanions

In 2010, McInnes et al. reported the only chromium-containing isopolyanion known to date which is a chromium(III) hexametalate lindqvist structure
[(Cr\textsuperscript{III}Cl)\textsubscript{6}O\{MeC(CH\textsubscript{2}O)\textsubscript{3}\}\textsubscript{4}](Hpy)\textsubscript{2} and its vanadium and iron analogues by solvothermal reaction at 200°C.\textsuperscript{[79]} This complex crystallizes in the cubic \textit{P}4\textsubscript{3}2\textsubscript{n} space group (Fig.2.8). The cluster anion \[[\text{Cr}^{\text{III}}\text{Cl}]\textsubscript{6}O\{\text{MeC(CH}_{2}O)\textsubscript{3}\}\textsubscript{4}\]\textsuperscript{2-} has crystallographic \textit{C}\textsubscript{3v} symmetry but approximating very close to \textit{T}d. A superoctahedron of six Cr\textsuperscript{III} ions (each with a \{CrCl\textsubscript{6}\} coordination sphere) is centered at a central \(\mu_6\)-oxide, with alternate faces of the octahedron capped by four MeC(CH\textsubscript{2}O)\textsubscript{3}\textsuperscript{3-} ligands. The magnetic properties of this high-symmetry spin cluster are consistent with antiferromagnetic exchange with two exchange interaction \(J_{\text{trans}} = -3.3, J_{\text{cis}} = -2.5 \text{ cm}^{-1} (g = 1.98)\).

**Fig.2.8** Combined polyhedral and ball-and-stick representation of \[[\text{Cr}^{\text{III}}\text{Cl}]\textsubscript{6}O\{\text{MeC(CH}_{2}O)\textsubscript{3}\}\textsubscript{4}\]\textsuperscript{2-}. Color code: Cr\textsubscript{ClO\textsubscript{5}} octahedra (green), Cl (yellow), O (red), C (black).\textsuperscript{[79]}

### 2.4 Cationic Cr\textsubscript{3}-based Polyoxometalate Salts

Beside chromium coordination chemistry, Mizuno \textit{et al.} reported that saturated Keggin ions and Wells-Dawson ions can form ionic crystals with oxo-centered
chromium trimer [Cr₃O(OOCR)₆(H₂O)₃]⁺ (R = H, CH₃). These materials showed interesting guest sorption properties.[81] So far, they have reported the following compounds:

A: K₃[Cr₃O(OOCH)₆(H₂O)₃][α-SiW₁₂O₄₀]·16H₂O [82]
B: Na₂[Cr₃O(OOCH)₆(H₂O)₃][α-PW₁₂O₄₀]·16H₂O [83]
C: Rb₄[Cr₃O(OOCH)₆(H₂O)₃][α-BW₁₂O₄₀]·16H₂O [83]
D: K₃[Cr₃O(OOCH)₆(H₂O)₃][α-PV₁₁O₄₀]·16H₂O [84]
E: Cs₅[Cr₃O(OOCH)₆(H₂O)₃][α-CoW₁₂O₄₀]·7.5H₂O [85]
F: (NH₄)₄[Cr₃O(OOCH)₆(H₂O)₃][α-P₂W₁₆O₄₀]·15H₂O [86]
G: (NH₄)₅[Cr₃O(OOCH)₆(H₂O)₃]₂[α₂-P₂W₁₇V₃O₆₂]·15H₂O [86]
H: (NH₄)₇[Cr₃O(OOCH)₆(H₂O)₃]₂[α₂-P₂W₁₅V₃O₆₂]·15H₂O [86]

These compounds possess a straight channel with water of crystallization. The utilization of the macro cation with a large size and small charge, which reduces the anion-cation interaction, is essential to the formation of these channels. It is easy to desorb water molecules that can form the closely packed guest-free phase under vacuum at room temperature. Water, Methanol and ethanol sorption isotherms show these guest-free phases exhibit unique guest inclusion and catalysis by rationally designed ionic crystals.
3. Results: Synthesis and Characterization of Chromium(III)-containing Heteropolytungstates

3.1 General Methods and Materials

All chemicals were commercially purchased and used in this study without further purification. Compounds were synthesized from sodium acetate solution. Infrared spectra were recorded on a Nicolet Avatar 370 FT-IR spectrophotometer using KBr pellets. The following abbreviations were used to assign the peak intensities: w = weak; m = medium; s = strong; br = broad. Thermogravimetric analyses were carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL/min flow of nitrogen; the temperature was ramped from 20 to 800 °C/1000 °C at a rate of 5 °C/min. Elemental analyses were performed by CNRS, Service Central d’Analyzer, Solaize, France. Temperature-dependent magnetic susceptibility measurements were made using a Quantum Design MPMS-XL-5 SQUID magnetometer over a temperature range of 300 to 1.8 K at a measuring field of 0.01 T. Magnetization measurements at variable temperature and variable field (VTVH) were performed at 1, 3, and 5 T over the temperature range of 300 to 1.8 K. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E500 spectrometer equipped with X and Q-band microwave sources (9.5 and 34.5 GHz, respectively). The frequency was recorded with a built-in digital frequency counter. Variable temperature (4 - 295 K) high-frequency EPR measurements (239.2 GHz) were conducted at the Florida State University National High Magnetic Field Laboratory (FSU-NHMFL) in Tallahassee, FL. The HF-EPR
operates in transmission mode and employs cylindrical waveguides, as described elsewhere.[87-89] The magnetic field was calibrated using a DPPH standard ($g = 2.0036$).

3.2 X-ray Crystallography

Single crystal of each of the compounds, was mounted on a Hampton cryoloop in light oil for data collection at 100 K. Indexing and data collection were measured on a Bruker D8 SMART APEX II CCD diffractometer with kappa geometry (graphite monochromator, $\lambda$ (Mo K\alpha) = 0.71073 Å). Data integration was performed using $SAINT$. Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using $SADABS$. Direct methods ($SHELXS$) successfully located the tungsten atoms, and successive Fourier syntheses ($SHELXL13$) revealed the remaining atoms.[91] Refinements were full-matrix least-squares against $|F|^2$ using all data. The complete X-ray crystallographic data for 1 - 4 (CIF format) is available free of charge via the internet at the FIZ Karlsruhe-Leibniz-Institute http://www.fiz-karlsruhe.de/icsd.html with CSD numbers 427383, 427384, 429021, and 429020, respectively.

3.3 Monochromium-Containing 14-heterotungstates, \[
[Cr^{III}(HX^VW_7O_{28})_2]^{13-} \]
(X = P (1a), X = As (2a))

3.3.1 Experimental Section

\[
Cr^{3+} + 2PO_4^{3-} + 14WO_4^{2-} + 18H^+ \xrightarrow{H_2O} [Cr^{III}O_6H_2(PO_4)_2(W_7O_{21})_2]^{13-} + 8H_2O \text{ (1a)}
\]

\[
Cr^{3+} + 2AsO_4^{3-} + 14WO_4^{2-} + 18H^+ \xrightarrow{H_2O} [Cr^{III}O_6H_2(AsO_4)_2(W_7O_{21})_2]^{13-} + 8H_2O \text{ (2a)}
\]
3.3.1.1 Synthesis of Na$_{13}$[Cr$^{III}$$(H$^V$P$^7$W$_{28}$O$_{28}$)$_2$]$\cdot$47H$_2$O (1)

A sample of Cr(NO$_3$)$_3$$\cdot$9H$_2$O (0.10 g, 0.25 mmol) was first dissolved in 20 mL of sodium acetate solution (1M, pH 6) followed by addition of 85% H$_3$PO$_4$ (53 µL, 0.8 mmol) and Na$_2$WO$_4$$\cdot$2H$_2$O (1.65 g, 5.0 mmol). The mixture was then stirred for 1 h at 80 °C. After cooling to room temperature and filtration, the obtained pH was 8. Slow evaporation of the green solution at room temperature led to the formation of green crystals of 1 within three days (yield 0.12 g, 10% based on Cr). IR (cm$^{-1}$): 1071 (s), 1010 (m), 942 (s), 911 (w), 892 (w), 684 (s, br) 519 (m), 439 (w). Elemental analysis % calc. (found): Na 6.3 (6.5), Cr 1.1 (1.1), P 1.3 (1.4), W 54.4 (53.6). $M = 4731.46$ g/mol.

Fig.3.1 IR spectrum of Na$_{13}$[Cr$^{III}$$(H$^V$P$^7$W$_{28}$O$_{28}$)$_2$]$\cdot$47H$_2$O (1).
3.3.1.2 Synthesis of Na$_{13}$[Cr$^{III}$HAs$^V$W$^V$O$_{28}$]$_2$·52H$_2$O (2)

A sample of Cr(NO$_3$)$_3$·9H$_2$O (0.10 g, 0.25 mmol) was first dissolved in 20 mL of sodium acetate solution (1M, pH 6) followed by the addition of As$_2$O$_5$ (0.08 g, 0.36 mmol) and Na$_2$WO$_4$·2H$_2$O (1.65 g, 5 mmol). The mixture was then stirred for 1 h at 80 °C. After cooling to room temperature and filtration, the obtained pH was 8. Slow evaporation of the green solution at room temperature led to the formation of green crystals of 2 after one week (yield 0.18 g, 15% based on Cr). IR (cm$^{-1}$): 945 (m), 850 (s, br), 679 (s), 519 (m), 427 (w). Elemental analysis % calc. (found): Na 6.1 (6.3), Cr 1.1 (1.3), As 3.1 (3.2), W 52.4 (51.6). $M =$ 4908.50 g/mol.

Fig.3.2 IR spectrum of Na$_{13}$[Cr$^{III}$HAs$^V$W$^V$O$_{28}$]$_2$·52H$_2$O (2).
3.3.2 Results and discussion

3.3.2.1 Synthesis and Structure

The novel polyanions \([\text{Cr}^{III}(\text{HP}^\text{V}\text{W}_7\text{O}_{28})_2]^{13-} (1a)\) and \([\text{Cr}^{III}(\text{HAs}^\text{V}\text{W}_7\text{O}_{28})_2]^{13-} (2a)\) were synthesized in a one-pot procedure under conventional bench conditions, by interaction of the respective hetero group \((\text{H}_3\text{PO}_4/\text{As}_2\text{O}_3)\) with \(\text{Cr(NO}_3\text{)}_3·9\text{H}_2\text{O}\) and \(\text{Na}_2\text{WO}_4·2\text{H}_2\text{O}\) in aqueous NaOAc solution (pH 8) at 80 °C. Polyanions 1a and 2a comprise an octahedrally coordinated Cr\(^{III}\) ion, sandwiched by two \{PW\(_7\)\} or \{AsW\(_7\)\} units. The successful synthesis of 1a and 2a requires several key reaction conditions, such as the final pH value, which is crucial and should be carefully adjusted to 7.5-8.5, starting with a pH 6 solution. With a pH < 7.5, the desired product could not be isolated, whereas pH > 8.5 resulted in the formation of a precipitate. The optimized ratios of \(\text{Cr}^{3+}/\text{XO}_4^{3-}/\text{WO}_4^{2-}\) is 1:2.9:20 for 1a, and 1:3.2:20 for 2a, which is not equivalent to its stoichiometric ratio indicated by the formation equation. In this case, excess of the heteroatom and \(\text{Na}_2\text{WO}_4·2\text{H}_2\text{O}\) is needed to keep the final pH in the range of 7.5 – 8.5. In comparison, less \(\text{Cr}^{3+}\) is needed to avoid the formation of green oily stuff. The formation of 1a and 2a also depends on the reaction temperature, which should be in the range of 75 – 95°C, as lower heating did not lead to the desired products. The choice of solvent is also important, as reaction in plain water under otherwise identical conditions did not provide the title compounds. With respect to the cations present, the corresponding potassium acetate solution resulted in 1 and 2 (as verified by IR and XRD analyses), but with lower yield. The synthetic strategy which we discovered here allowed us to systematic study such structurally type structures which will be used for the following compounds.
Table 3.1 Crystal data for Na$_{13}$[Cr$^{III}$(HP$^V$W$_{7}$O$_{28}$)$_2$]·47H$_2$O (1) and Na$_{13}$[Cr$^{III}$(HAs$^V$W$_{7}$O$_{28}$)$_2$]·52H$_2$O (2).

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<th>Compound</th>
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<tr>
<td>Formula</td>
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<td>Na$<em>{13}$[Cr(HAsW$</em>{7}$O$_{28}$)$_2$]·52H$_2$O</td>
</tr>
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<td>Formula weight, g/mol</td>
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<td>4909.45</td>
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<td>Triclinic</td>
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<td>P$\bar{i}$</td>
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<tr>
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<tr>
<td>$\gamma$, °</td>
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<td>67.134(4)</td>
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<td>2239</td>
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<td>0.15 x 0.12 x 0.02</td>
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<tr>
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<td>10929</td>
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<td>R$_{1}$[I &gt; 2σ(I)]$^{[a]}$</td>
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<tr>
<td>wR$_{2}$ (all data)$^{[b]}$</td>
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<td>0.0772</td>
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</table>

$^{[a]} R = \Sigma||F_o|| - |F_c||/\Sigma|F_o|.$ $^{[b]} R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}.$
Fig. 3.3 Ployhedral (a) and ball-and-stick (b) representations of polyanions 1a and 2a. Color code: X = P, As (yellow), W (blue), Cr (green), O (red).

Crystallographic structural analysis revealed that 1 and 2 are isomorphous, both crystallizing in the triclinic space group Pī (see Table 3.1). The polyanionic entities $[\text{Cr}^{III}(\text{HX}^\text{V}W_7\text{O}_{28})_2]^{13-}$ (X = P, 1a; As, 2a) consist of two equivalent heptatungstate moieties $[\text{HXW}_7\text{O}_{28}]^{8-}$, which are arranged almost orthogonally to each other and linked via a single Cr$^{III}$ ion through four ‘planar’ Cr–O–W and two ‘axial’ Cr–O–X bridges. Each moiety consists of a $\{\text{W}_3\text{O}_{13}\}$ triad linked to an edge-shared half-ring $\{\text{W}_4\text{O}_{19}\}$ via corner-sharing, with both units stabilized by the central $\{\text{XO}_4\}$ group. This structure results therefore in a $C_{2h}$ point-group symmetry, with the $C_2$ axis passing through the Cr$^{III}$ center (Fig. 3.3). The heptatungstate fragment has been reported before.
by our group in the ruthenium-containing \([\text{Ru(dmso)}_3\text{HPW}_{7}\text{O}_{28}]^{6-}\), which was also studied in solution via multinuclear NMR.[92] Recently, similar transition metal-sandwiched compounds with the same structure \([\text{M(HPW}_{7}\text{O}_{28})_2]^{n-}\) \((n = 13, \text{M} = \text{Fe}^{\text{III}}, \text{Mn}^{\text{III}}; n = 14, \text{M} = \text{Co}^{\text{II}}, \text{Cd}^{\text{II}}, \text{Mn}^{\text{II}})\), were also reported.[93, 94]

Table 3.2 Details of heptatungstate/heptamolybdate published.

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<th>Types</th>
<th>Polyhedron types</th>
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<td>a</td>
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<td></td>
<td>[\text{Cd}^{\text{II}}(\text{HPW}<em>{7}\text{O}</em>{28})_2]^{14-}</td>
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<td>[\text{Mn}^{\text{II}}(\text{HPW}<em>{7}\text{O}</em>{28})_2]^{14-}</td>
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</tr>
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<td>{CoW_7}</td>
<td>c</td>
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<td>[97]</td>
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<tr>
<td>{XMo_7}</td>
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<tr>
<td>{AsMo_7}</td>
<td>c</td>
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<td>[46, 78]</td>
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<tr>
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<td>[\text{Fe}^{\text{III}}\text{Cr}^{\text{III}}(\text{As}^{\text{III}}\text{Mo}<em>7\text{O}</em>{27})_2]^{12-}</td>
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<td>[\text{Fe}^{\text{III}}_2(\text{As}^{\text{III}}\text{Mo}<em>7\text{O}</em>{27})_2]^{12-}</td>
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<tr>
<td>{FeMo_7}</td>
<td>c</td>
<td>[\text{As}^{\text{III}}<em>2\text{Fe}^{\text{III}}<em>6\text{Mo}</em>{22}\text{O}</em>{85}(\text{H}_2\text{O})]^{14-}</td>
<td>[98]</td>
</tr>
</tbody>
</table>
Fig. 3.4 Polyhedron structure of (a) {HPW$_7$O$_{28}$}, (b) {TeW$_7$O$_{28}$}, and (c) {HCoW$_7$O$_{28}$}. Color code: P (yellow), WO$_6$ octahedra (blue), Te (bright green), Co (pink), O (red).

The highly vacant heptametalate subunits are few in POM literature. To the best of our knowledge, only five types of heptatungstate {XW$_7$} (X = P,[92-94] As,[92] V,[95] Te,[96] Co[97]) and two types of heptamolybdate {XMo$_7$} (X = As,[46, 78, 99] Fe[98]) subunits are known (Table 3.2). The {PW$_7$} building block is structurally similar to the {AsW$_7$} and {VW$_7$} fragments, however different from {TeW$_7$} (Fig. 3.4b) and {CoW$_7$} (Fig. 3.4c) found in [Te$_2$W$_{18}$O$_{58}$(OH)$_2$]$^{14-}$, [Te$_2$W$_{18}$O$_{62}$(OH)$_2$]$^{10-}$, and [Co$_7$(H$_2$O)$_2$(OH)$_2$P$_2$W$_{25}$O$_{94}$]$^{16-}$.[96, 97] The [TeW$_7$O$_{28}$]$^{10-}$ fragment can be obtained from the trivacant Keggin [$\beta$-TeW$_9$O$_{33}$]$^{8-}$, by the loss of two WO$_6$ octahedra; whereas {HCoW$_7$O$_{28}$} consists of seven edge-shared WO$_6$ octahedra stabilized by a central CoO$_4$ tetrahedron.[97] The structures of {AsMo$_7$} and {FeMo$_7$} are very similar to {CoW$_7$}, and both can be obtained from the trivacant Keggin [XMO$_{33}$]$^{9-}$ ion by the loss of one {M$_3$O$_{13}$} triad and the insertion of one MO$_6$ octahedron into the cavity between the two triad units.
Fig. 3.5 Representation of polyanion 1a and its surrounding Na⁺ counter cations (large orange balls). Water molecules are shown as small red balls, and the Na⁺···OH₂ interactions as dashed lines.

The central Cr³⁺ ion adopts a distorted octahedral geometry with three different types of μ-oxo bridges: two from four {WO₆} octahedra of the {W₃O₁₃} triads (1: Cr–O, 1.953(5)–1.956(5) Å; 2: Cr–O, 1.953(5)–1.975(5) Å) and one from the hetero group XO₄ (1: Cr–O, 1.996(5) Å; 2: Cr–O, 1.999(5) Å). In comparison, the Fe–O bond lengths in [Fe³⁺(HPW₇O₂₈)²⁻] are relatively longer (1.984(6)–2.039(7) Å), in full agreement with the size difference between Cr³⁺ (r = 0.615 Å) and Fe³⁺ (r = 0.645 Å).[46] Within the {HPW₇O₂₈} subunit, four kinds of W–O bond lengths fall within the anticipated ranges for the different types of oxo ligands with an increasing trend: terminal (1.713(5)–1.746(5) Å), μ₂-bridging (1.883(5)–1.958(5) Å), μ₃-bridging (1.900(5)–2.300(5) Å), and μ₄-bridging (2.335(4)–2.357(4) Å). Moreover, one of four oxygen atoms of the PO₄ tetrahedron in [HPW₇O₂₈]⁸⁻ connects to one Cr³⁺ ion, leading to its
distortion. The three P-µ2-O bond lengths differ slightly (1.515(5)–1.531(5) Å), while the P-µ4-O (the central O of the triad) is expectedly longer (1.580(5) Å). In the case of \{HAsW7O28\}, the As–O bond lengths are in the range of 1.667(5)–1.721(4) Å. Selected bond lengths and angles for 1 and 2 are shown in Table 3.3.

In the solid state, the polyanions are surrounded by sodium countercations, which in turn coordinate to crystal water molecules (Fig. 3.5). X-ray diffraction and elemental analysis confirmed that there are 13 Na\(^+\) ions in total per polyanion. Bond valence sum (BVS) calculations show, for each \{HPW7O28\} subunit in 1, that the bridging oxo O46 is monoprotonated with W–O bond lengths of 2.167(5) and 2.183(5) Å and a BVS of 0.91, which is the value expected for a hydroxo group. This gives a total charge of −13 for 1a, which is stabilized in the solid state by sodium countercations. The same applies for compound 2, with the hydroxo group located at O37 (Table 3.3).
Table 3.3 Selected bond lengths (Å) and angles (°) for 1 and 2.

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<th>Polyanion 1</th>
<th>Polyanion 2</th>
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<td></td>
<td>W(1)–O(1T) 1.716(5) W(1)–O(170) 1.893(4)</td>
<td>W(1)–O(1T) 1.713(5) W(1)–O(170) 1.893(4)</td>
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<td>W(2)–O(2T) 1.727(5) W(1)–O(136) 1.908(5)</td>
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Table 3.4 Bond valence sum values for different structural types of bridging oxygen atoms in Na$_{13}$[Cr$^{III}$(HP$^V$W$_7$O$_{28}$)$_2$].47H$_2$O (1) and Na$_{13}$[Cr$^{III}$(HAs$^V$W$_7$O$_{28}$)$_2$].52H$_2$O (2).

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3.3.2.2 Magnetic Studies

(The magnetic studies were performed by our collaborators Prof. Dr. Naresh S. Dalal, Florida State University, USA.)

Detailed magnetic characterization of 1 and 2 is of high interest because they are rare instances of Cr$^{III}$, a 3d$^3$ ion, in a well-defined geometry with six covalently bonded
oxo ligands. Each Cr$^{\text{III}}$ ion is surrounded by many diamagnetic atoms which magnetically insulate the Cr ions from each other, the nearest neighbour Cr$^{\text{III}}$ ion distance being $\approx 10$ Å. This situation is particularly suitable for characterization by EPR, since the lack of dipolar couplings with the nearest neighbours should lead to narrow EPR peaks and thus higher precision for the measurement of magnetic parameters. Distorted octahedral Cr$^{\text{III}}$ complexes usually show small zero-field splitting since the ground states and excited states are generally well separated. As shown below; however, the zero-field parameters of 1 and 2 are found to be unexpectedly large.

![Graph](image1.png)

Fig.3.6 (a) $\mu_{\text{eff}}$ versus $T$ of compound 2. (b) VTVH magnetization measurements of 2 at 1, 3, and 5 T. The solid lines represent the best fits to the experimental data.

![Graph](image2.png)

Fig.3.7 Left: $\mu_{\text{eff}}$ versus $T$ of compound 1. Right: VTVH magnetization measurements of 1 at 1, 3, and 5 T. The solid lines represent the best fits to the experimental data.[68]
As a start, magnetic susceptibility ($\chi$) measurements were undertaken to establish the electronic spin of the $3d^3$ configuration, which is expected to be $S = \frac{3}{2}$, a spin-quartet. Fig. 3.6 shows the measured temperature dependence of the magnetic moment, $\mu_{\text{eff}}$, of 2 from 1.8 - 300 K. The magnetic moment is 3.90 $\mu_\beta$ at room temperature, which is close to the spin-only value for $S = \frac{3}{2}$ (3.87 for $g = 2$). This value remains nearly constant at high temperature, but sharply decreases to 3.3 $\mu_\beta$ below 20 K. Due to the significant Cr–Cr distance in both compounds it was hypothesized that this decrease was due to magnetic interactions within each molecule (spin-spin and spin-orbit coupling) rather than intermolecular $J$ coupling. Such interactions result in zero-field splitting of the electronic eigenstates. Therefore, the magnetic properties of both compounds were evaluated using the following standard spin Hamiltonian of a system with $S = \frac{3}{2}$.

$$\hat{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \hat{S} + D \left( S_z^2 - \frac{S_z^2}{3} \right) + E \left( S_x^2 - S_y^2 \right) \quad (1)$$

In this Hamiltonian, $\mathbf{g}$ is the Zeeman tensor, $D$ and $E$ are the axial and rhombic second order zero-field splitting parameters, and the other terms pertain their usual meaning.[100] The hyperfine interaction is omitted because the magnetic isotope of Cr (i.e. $^{53}\text{Cr}$, with $I = \frac{3}{2}$) has rather small (~ 9.5 %) natural abundance, thus each peak of the hyperfine quartet would be ~ 2.5% of the main peaks. The temperature dependence of the magnetic susceptibility is derived from diagonalization of the Hamiltonian matrix.[101, 102] The data in Fig.3.6 yielded an acceptable fit using the parameters: $S = \frac{3}{2}$, $g = 2.02$, and $D = 3.6 \text{ cm}^{-1}$ and a small $E/D = 0.04$. These data indicate that $D$ is exceptionally large, since the literature values of Cr$^{\text{III}}$ complexes range from 0.107 to 1.28 cm$^{-1}$,[60-64, 68, 103-110] with the sole exception of $D = 2.3 \text{ cm}^{-1}$ found for the octahedral complex [Cr(dmpe)$_2$(CN)$_2$] 1,2-bis(dimethylphosphino)ethane,[68, 69]
although no EPR is provided for the afformentioned compound and the results herein are thus considered a significant addition to this field. Fitting of variable temperature/variable field (VTVH) magnetization measurements of 2 (Fig.3.6, right) yields similar magnetic parameters of $g = 2.03$ and a slightly lower $D$ ($2.5 \text{ cm}^{-1}$). Similar measurements on 1 are shown in Fig.3.7 and were well fit to the same parameters as 2 except with $E/D = 0.02$. Since $\chi$ is not an accurate method for determining $D$ or $g$, a detailed EPR study was undertaken.
Fig.3.8 (a) X-band (9.4 GHz) EPR experimental computer simulated spectra of 2. The top and bottom portions show the energy level diagrams for the \( H \parallel z \) (principal symmetry axis of the molecule) and the perpendicular \( x, y \) directions. The red numbers in the top figure represent the \( M_s \) quantum numbers in the high-field limit. In the bottom figure; however, they are just a label for an energy level since the field strength was not enough to be in the ‘high-field’ limit. Blue arrows mark the EPR transition assignment.

(b) 239.2 GHz EPR experimental and simulated spectra of 2 at 6 K with the energy level diagrams both parallel and perpendicular to the principal symmetry axes (as marked). Blue arrows show the EPR transition assignments. The red numbers are as described in above.

### 3.3.2.3 EPR Measurements

(The EPR measurements were performed by our collaborators Prof. Dr. Naresh S. Dalal, Florida State University, USA.)

Fig.3.8a shows the room temperature, X-band (9.4 GHz) powder EPR spectrum of 2 (middle segment, green trace). Also shown are the simulated energy level diagrams, obtained using a locally developed computer program, for \( H \parallel z \) and along the perpendicular \( x, y \) directions (top and bottom segment respectively). Two distinct \( g \)-tensor components are seen at \( g_\parallel = 1.975 \) and \( g_\perp = 3.752 \). Such large anisotropy is evidence of significant zero-field splitting, thus the \( g \) values are labeled with prime symbols indicating they are effective values. For \( S = \frac{3}{2} \) with a large \( D \) (i.e. \( D >> \) microwave quantum), the effective and real \( g \) values are related by \( g_\perp = g_\perp '/2 \) and \( g_\parallel = g_\parallel '/[69, 111] \). Therefore, the actual \( g \) values
are $g_{||} = 1.975$ and $g_{\perp} = 1.876$. There is slight splitting in the perpendicular line due to small anisotropy between the $x$ and $y$ directions. This feature is not seen in 1, likely due to even smaller rhombic distortion (Fig.3.9). At Q-band frequency (34 GHz), both materials show clear splitting in the perpendicular peaks (Fig.3.10), suggesting the need for HF-EPR.

![Figure 3.9](image_url)

Fig.3.9 X-band (9.5 GHz) EPR experimental and simulation spectra of 1. The top and bottom portions show the energy level diagrams for the $H \parallel z$ (principal symmetry axis of the molecule) and the perpendicular $x$, $y$ directions. The red numbers in the top figure represent the $M_s$ quantum numbers in the high-field limit. In the bottom figure;
however, they are just a label for an energy level since the field strength was not enough to be in the ‘high-field’ limit. Blue arrows mark the EPR transition assignment.

Furthermore, the absence of 9 peaks expected for a $S = \frac{3}{2}$ ion in a distorted octahedral geometry also suggested that the $D$-value must be much larger than the Q-band microwave quantum (1.1 cm$^{-1}$).[112] Computer simulated spectra (middle segment, blue trace), obtained using a locally-developed program [87-89, 113, 114] were in good agreement with the experimental data, and yielded: $S = \frac{3}{2}$, $g_z = 1.97-2.00$, $g_{x,y} = 1.92-1.94$, $|D| = 2.4-2.8$ cm$^{-1}$, and $E/D = 0.02-0.04$.}

![Fig.3.10 Q-band (34 GHz) EPR experimental and simulation spectra measured at room temperature (a) compound 1 (b) compound 2.](image)

Since $D$ and $E$ are related to $g_{||}$ ($g_z$) and $g_{\perp}$ ($g_{x,y}$) via.[111]

$$D(4T_2) = \frac{\zeta_{Cr}}{6} [g_{xx} - \frac{1}{2}(g_{xx} + g_{yy})]$$

$$E(4T_2) = \frac{\zeta_{Cr}}{12} (g_{xx} - g_{yy})$$

(2)

where $\zeta_{Cr}$ is the spin-orbit coupling constant, $\sim 210$ cm$^{-1}$ for Cr$^{III}$.[106] $D$ and $E$ must be large and positive, which is a surprising result when comparing with the literature data. Since interstitial water solvent might easily have been lost from the powder.
sample, the powder data were confirmed through single-crystal angular dependence Q-band EPR (Fig.3.11). In order to obtain precise values for these parameters, we undertook EPR measurements using frequencies higher than 3 cm\(^{-1}\) i.e. initiated high-frequency EPR (HFEPR).

Fig.3.11 Single-crystal angular dependence Q-band (34 GHz) EPR spectra measured at room temperature. The results are fit to \(g^2 = g_\parallel^2 \cos^2(\theta) + g_\perp^2 \sin^2(\theta)\), which describes the angular dependence of the \(g\) factor for single crystals in an axially symmetric environment (a) compound 1 (b) compound 2.[115]

Fig.3.7b shows the 239.2 GHz experimental spectrum of 2 (middle segment, green trace) and the simulated spectra (middle segment, blue trace). Simulations were performed using the same program and parameters as in Fig.3.7a. Although the spectrum becomes increasingly complicated at such high frequencies, it is seen that there is a fine agreement between the experimental and simulated spectra with minor artifacts due to an imperfectly random distribution of crystallites in the powder sample. The top and bottom portions of the figure once again display the energy level diagrams both parallel and perpendicular to the principal symmetry axis, while the blue arrows indicate the observed EPR transitions. The high frequency experimental spectrum and simulation of 1 are shown in Fig.3.12a. The sign of \(D\) was determined by the
comparison of the relative line intensities in the 20 and 6 K spectra of 2 as well as comparison of best-fit simulations for +D and –D parameters (Fig.3.12b and 3.13). These results clearly suggest that the magnitude and sign of D and E to be, D = 2.4 cm\(^{-1}\), and \(E/D = 0.05\). They also confirm the above conclusion that the zero-field splitting is significantly higher than any seen for Cr\(^{III}\) in the literature.[60-62, 64, 68, 103-106, 108-110, 116] Below we present \textit{ab-initio} DFT model calculations that enable us to understand this unusual finding.
Fig. 3.12 (a) The high-frequency (239.2 GHz) EPR experimental and simulation spectra of 1 at 8 K are shown with the energy level diagram for the principal symmetry axis, $H \parallel z$, and the perpendicular $x, y$ directions. The blue arrows mark the EPR transition assignments. (b) High-frequency (239.2 GHz) experimental EPR spectra of 2 at 20 K and 6 K are shown with the energy level diagram, which was derived from the best simulation of these spectra. The sign of $D$ was determined by comparison of the relative line intensities in the two spectra. Upon cooling from 20 K to 6 K the transitions at ~6 and ~6.8 T, which correspond to the lowest lying energy states, become more intense, while the transitions at ~8.2 and 3.6 T, which correspond to the highest energy transitions become less intense. The results are in excellent agreement with the Boltzmann distribution.

Fig. 3.13 High-frequency (239.2 GHz) experimental EPR spectra of 1 at 6 K (black trace) along with the best fit simulations using positive and negative $D$ (red and blue traces respectively). The red peaks in the experimental spectrum are drawn to emphasize the key similarities between the $+D$ simulation and the experiment. The
dashed lines indicate the fine agreement between the +D simulation with the experiment along with the disagreement between the experiment and −D.

### 3.3.2.4 Theoretical analysis of the origin of the large D.

(The theoretical work was performed by our collaborators Prof. Dr. Frank Neese, Max-Plank Institute, Mülheim a.d.R.)

The d^3 configuration of octahedral Cr^{III} spans a ^4A_2(t^3_2) ground state and ^4T_2, ^4T^a_1 and ^4T^b_1 excited states. Trigonal distortions (D_3 symmetry) cause a splitting of the states T_2 and T_1 terms into A_1, E and A_2, E sublevels, respectively and spin-orbit coupling leads to mixing of the trigonally split ^4T_2 terms bearing first order angular momenta into the ^4A_2 ground state spin sublevels. The combined effect of trigonal symmetry and spin-orbit coupling leads to orbital moments into the ^4A_2 ground state and this is the cause of the zero-field splitting (2D): the splitting of the S = 3/2 spin state into two Kramers doublets with M_s = ±3/2 and M_s = ±1/2. Third order perturbation theory yields eq. (3) for D and E with leading contributions from ^4T_2(t^2_e) [^2T_2(t^3_2)] excited states also contribute to D and E,\textsuperscript{[117]} they were accounted for in the ab initio calculations but for simplicity are not be considered here:

\[
D(^4T_2)=\frac{4}{9}\zeta_{\text{eff}}^2 \frac{E(^4T_2,x0)-E(E(^4T_2,x\pm))}{(10Dq)^2}
\]

\[
E(^4T_2)=\frac{2}{9}\zeta_{\text{eff}}^2 \frac{E(^4T_2,x\pm)-E(E(^4T_2,x\pm))}{(10Dq)^2}
\]

In eq. (3) \(\zeta_{\text{eff}}\) is the effective spin-orbit coupling parameter of Cr^{III} (free ion value 273 cm\(^{-1}\)),\textsuperscript{[118]} and 10 Dq (typical values for CrO_6^{3−} chromophores 16000 cm\(^{-1}\))\textsuperscript{[118]} and \(\Delta E_{\text{trig}}=E(^4T_2,x\pm)-E(^4T_2,x0)\) respectively are the cubic (^4T_2−^4A_2) and trigonal ^4T_2(g) excited states also contribute to D and E,\textsuperscript{[117]} they were accounted for in the ab initio calculations but for simplicity are not be considered here:

\[
D(^4T_2)=\frac{4}{9}\zeta_{\text{eff}}^2 \frac{E(^4T_2,x0)-E(E(^4T_2,x\pm))}{(10Dq)^2}
\]

\[
E(^4T_2)=\frac{2}{9}\zeta_{\text{eff}}^2 \frac{E(^4T_2,x\pm)-E(E(^4T_2,x\pm))}{(10Dq)^2}
\]

Angular overlap model considerations (eq. (4),\textsuperscript{[119]}) allow one
to relate the trigonal splitting $E(^{4}T_{2g},x0) - E(^{4}T_{2g},x\pm)$ with the trigonal distortion 
$[\delta\theta>0(\delta\theta<0)$ – trigonal compression (elongation) of the $O_h$ geometry, $\theta_{Oh} = 54.735/180$] 
and the Cr–O $\sigma$ and $\pi$-bonding parameters $e^\sigma$ and $e^\pi$:

$$\Delta E_{\text{org}} = 3\sqrt{2}(\delta\theta)e^\sigma - 18(e^\sigma,\delta\theta)^2 / 10Dq$$ (4)

While the first term on the right hand site of eq. (4) reflects a splitting of the $t_2$ orbital 
that depends on the sign of $\delta\theta$, the second one is always negative and tends to stabilize 
$^{4}T_{2g}\pm$ below $^{4}T_{2g}0$. If metal-ligand $\pi$ interactions are not exclusively large (as is usually 
the case) this second term, according to eq. (4) will lead to a positive $D$. This is the case 
for the CrO$_6$ cores discussed here in 1 and 2. However, adopting a CrO$_6$ geometry given 
by the X-ray structures of 1 and 2 (very close to $O_h$) eqs. (3) and (4) yield values of $D$ ($\cong$ 
0.05 cm$^{-1}$) much smaller than the experimental ones. Influences due to the second 
coordination sphere of Cr$^{III}$ – the formally highly charged cations W$^{VI}$ and P$^{V}$/As$^{V}$, are 
expected to largely lower the symmetry. With W$^{IV}$ and As$^{V}$/P$^{V}$ involved in bonds with 
O that are stronger than Cr$^{III}$–O one, a large misalignment of the oxygen lone pairs with 
respect to the Cr–O bond direction is expected to occur (Fig.3.14).

![Fig.3.14 Misdirected valence imposed by the next nearest neighbors of Cr$^{III}$ as possible origin for high $D$-values. The misalignment of the oxygen lone pairs defined by the angle between the axis of the W–O and As–O bonds and the corresponding Cr–O bond](image-url)
direction (\(\angle \text{AsOCr} = 124.4^\circ; \angle \text{WOCr} = 141.2, 140.6^\circ\)) are visualized. The centroids of these lone pairs define an angular distortion towards an extreme trigonal-flattening of the octahedron.

The orientation of these lone pairs is governed by the electron density on the O–W\(^{VI}\), and O–P(As)\(^V\) bonds in directions opposite to the lone pairs. Such “misdirected valence” was found to alter the donor properties of O, the Cr–O bond and the ligand field caused by the oxygen ligand resulting in spectacular spectroscopic behavior.[119] Assuming here a hybridization of the oxygen orbitals of \(sp\)-type, one observes e.g. for 2 a larger misalignment with of the O lone pairs with respect to the Cr–O bond axis for the Cr–O–As bridge (55.53\(^\circ\)) than for the Cr–O–W bridges (angles 38.8\(^\circ\) and 39.4\(^\circ\), Fig.3.14). This results in an effectively compressed geometry and affects the signs and magnitude of the ZFS tensor parameters – the positive value of \(D\) and non-vanishing \(E\). Correlated calculations on CrO\(_6^3^−\) model complexes with a variable second coordination sphere of Cr–O (Fig.3.15) show that O donor functions are indeed strongly modified by the nature and geometry of the atoms or groups attached to O. With a linear Cr–O–H geometry (\(sp\)-hybridization, Model 1) both \(\sigma\) and \(\pi\)- oxygen donor character is computed. It induces small trigonal and even a smaller orthorhombic t\(_2\) splitting. A DFT optimized Cr(OH)\(_6^3^−\) complex with an angle Cr–O–H close to 90\(^\circ\), represents a basically p\(^3\)-type O donor, with a smaller \(\sigma\) and a vanishing \(\pi\)-energy. The computed trigonal t\(_2\) splitting is twice larger than in the previous case and correlates with a twice larger \(D\) (Table 3.5). Quite interestingly, switching to a sp O-donor by taking linear Cr–O–H arrangement but not changing the geometry of the CrO\(_6\) leads to a drastic lowering of \(\sigma\), and to a non-zero \(\pi\) (Table 3.5). The resulting lowering of 10 Dq leads to a narrowing the \(^4\text{A}_2^\prime\)–\(^4\text{T}_2\) gap and to an enhanced mixing of the two states via spin-orbit
coupling and trigonal field. Taken together, this leads to an increase of $D$ by a factor of three (Table 3.5). Finally, increasing the formal charge from 1(H, Model 1) to 3 (Cr(OBF)$_6^{3+}$ Model 3) induces a strong trigonal $t_2$ splitting and a value of $D = 2.255$ cm$^{-1}$ which fortuitously matches closely the experimental value reported here (2.4 cm$^{-1}$). The underlying reason for the experimental result is thus a density deformation due to atoms directly attached to O which violates the apparent geometry of the CrO$_6$ core (regular close to $O_h$) in 1 and 2. An inspection of Fig.3.14 shows that this deformation is large and in a direction toward a pseudo-planar hexagon.

Fig.3.15 Model complexes for analysis of the correlation between the zero-field splitting $D$ and the Cr–O bonding; Model 1 (left) Cr(OH)$_6^{3–}$ with linear Cr–O–H bond and a geometry of the CrO$_6$ core identical with that of the X-ray geometry of 2; Model 2 (middle): A BP86 DFT optimized Cr(OH)$_6^{3–}$ with a bent Cr–O–H geometry due to strong Cr–OH···O intra molecular hydrogen bond (O···H distances 2.089–2.096 Å); Model 3 (right) the hypothetical bis (trifluoroboroxine) Cr$^{III}$ complex (Cr(OBF)$_6^{3–}$) with a strongly distorted CrO$_6^{3–}$ core and charge density due to the contra polarizing B$^{3+}$ attached to O.

Table 3.5 Characteristic angles $\angle$Cr–O–X, and $\angle$OCrO (in °), Cr–O angular overlap bonding parameters $e_\sigma$ and $e_\pi$ (in cm$^{-1}$), $t_2$ and $e$ orbitals energies due to the dominating trigonal and smaller orthorhombic ligand fields of CrO$_6^{3–}$ from NEVPT2 calculations.
Bonding parameters from ligand field analysis of the *ab initio* results on model complexes, showing dependence on the nature and geometry of the next nearest neighbors of Cr$^{III}$; angles (in °) and zero-field splitting parameters D and E (in cm$^{-1}$) for the three model compounds; those for the trans CrO$_6$W$_4$As$_2$ core in 2 are listed for comparison.$^a$

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<th>Model 2 Cr(OH)$_6^{3−}$</th>
<th>Model 3 Cr(OBF)$_6^{3−}$</th>
<th>CrO$_6$W$_4$As$_2$ (2)</th>
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<td>67.3</td>
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<td>6409</td>
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$^a$ See figure for a visualization of Model 1, Model 2 and Model 3.

### 3.3.2.5 Thermogravimetric Analysis

The thermal analysis of the sodium-salt 1 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 400 °C and involving loss of 47 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 17.9 (17.3)]. A weight loss for 2 begins at room temperature and is complete at ca. 375 °C, which corresponds to the loss of 52 water molecules per
formula unit based on TGA combined with the elemental analysis results [% calc. (found): 19.1 (19.0)].

Fig. 3.16 Thermogram for 1 from room temperature to 800 °C.

Fig. 3.17 Thermogram for 2 from room temperature to 800 °C.
3.3.3 Conclusions

We have prepared the first examples of mono-Cr\textsuperscript{III}-containing POMs, \([\text{Cr}\textsuperscript{III}(\text{HP}\textsuperscript{V}W\textsubscript{7}O\textsubscript{28})\textsubscript{2}]\textsuperscript{13-} (1a) and \([\text{Cr}\textsuperscript{III}(\text{HAs}\textsuperscript{V}W\textsubscript{7}O\textsubscript{28})\textsubscript{2}]\textsuperscript{13-} (2a), by reaction of the composing elements in pH 8 sodium acetate medium. Both compounds were fully characterized in the solid state by IR spectroscopy, single-crystal XRD, elemental and thermal analyses, SQUID and EPR measurements. Polyanions 1a and 2a comprise an octahedrally coordinated Cr\textsuperscript{III} ion, sandwiched by two \{PW\textsubscript{7}\} or \{AsW\textsubscript{7}\} units. Detailed SQUID and EPR spectroscopic measurements on the hydrated sodium salts of 1a and 2a showed that the axial zero-field splitting parameter \((D)\) is unexpectedly large (2.4 cm\textsuperscript{-1}) for a Cr\textsuperscript{III} ion in an octahedral oxo-coordination. The unusually large value of \(D\) has been rationalized using \textit{ab-initio} calculations and subsequent ligand field analysis. The results show that Cr–O bonding is strongly modified by the polarizing, high-valent ions W\textsuperscript{VI} and As\textsuperscript{V}. These ions cause misaligned lone pairs and charge density deviating from the X-ray geometry of the CrO\textsubscript{6} core. The large distortion in the axial direction as well as in the equatorial plane of the CrO\textsubscript{6} octahedron reduces the gap between the t\textsubscript{2g} and the e\textsubscript{g} orbitals, and imposes a large trigonal splitting of the metal-centered multiplets. This distortion splits the excited orbital triplet state and the splitting reacts back through the spin-orbit coupling to remove the degeneracy of the ground spin states. The large distortion along the z-axis leads to the large \(D\), while the equatorial distortion leads to the non-zero \(E\). Similar second-sphere ligand field effects on oxygen ligator ions have been reported in the d-d absorption spectra and EPR of 3d metals in oxidic solids.\cite{119} In addition to this new theoretical insight, we also note the synthetic potential associated with the discovery of 1a and 2a. Possibly, the \{XW\textsubscript{7}\} fragments present in 1a and 2a can be used as building blocks for other POM structures, and such
work is currently underway. Also, we have already prepared several other, novel Cr-containing POMs, and this work will be presented.

3.4 Dichromium-Containing 16-heterotungstates, \([\text{Cr}^{III}_2(\text{B-}\beta-\text{X}^{IV}\text{W}_8\text{O}_{31})]^{14-}\) (X = Si (3a), Ge (4a))

3.4.1 Experimental Section

\[
2\text{Cr}^{3+} + 2\text{SiO}_4^{4-} + 14\text{WO}_4^{2-} + 20\text{H}^+ + \text{H}_2\text{O} \rightarrow [\text{Cr}^{III}_2\text{O}_6\text{H}_2(\text{SiO}_4)_2\text{W}_{16}\text{O}_{62}]^{14+} + 10\text{H}_2\text{O} (3a)
\]

\[
2\text{Cr}^{3+} + 2\text{GeO}_4^{4-} + 14\text{WO}_4^{2-} + 20\text{H}^+ + \text{H}_2\text{O} \rightarrow [\text{Cr}^{III}_2\text{O}_6\text{H}_2(\text{GeO}_4)_2\text{W}_{16}\text{O}_{62}]^{14+} + 10\text{H}_2\text{O} (4a)
\]

3.4.1.1 Synthesis of Na\textsubscript{14}[Cr\textsuperscript{III}\textsubscript{2}(B-\beta-Si\textsuperscript{IV}\text{W}_8\text{O}_{31})\textsubscript{2}]\cdot45\text{H}_2\text{O} (3)

A sample of \(\text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O} (0.1 \text{ g, 0.25 mmol})\) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of \(\text{Na}_2\text{SiO}_3 (0.07 \text{ g, 0.60 mmol})\) and \(\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O} (1.32 \text{ g, 4 mmol})\). The mixture was later stirred for 1 h at 80°C, then after cooling to room temperature and filtration the obtained pH was 8.7. Slow evaporation of the solution at room temperature led to the formation of green crystals of 3 within three weeks (yield 0.05 g, 8% based on Cr). IR (cm\(^{-1}\)): 981 (w), 935 (m), 866 (s), 809 (m), 751 (s), 671 (w), 530 (m), 438 (w), 404 (w). Elemental analysis % calc. (Found): Na 6.16 (6.14), Si 1.07 (1.17), W 56.28 (55.91), Cr 1.99 (2.11). Mw = 5226.11 g/mol.
3.4.1.2 Synthesis of Na₁₄[Crᵢ₃(₂(B-β-Ge⁴W₈O₃₁)₂)]·50H₂O (4)

A sample of Cr(NO₃)₃·9H₂O (0.1 g, 0.25 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of GeO₂ (0.05 g, 0.50 mmol) and Na₂WO₄·2H₂O (1.32 g, 4 mmol). The mixture was later stirred for 1 h at 60°C, then after cooling to room temperature and filtration the obtained pH was 8.7. 4 was obtained as a pure crystalline phase after evaporation of the solution at room temperature within one week (yield 0.4 g, 59% based on Cr). The crude powder was dissolved in minimal amount of sodium acetate buffer (1M, pH 6) at 50°C. The resulting solution was cooled down to room temperature and then kept in a closed vial in fridge (7°C), dark green crystals of 4 suitable for X-ray diffraction were collected within 48 hours. IR (cm⁻¹): 936 (m), 778 (s), 732 (m), 657 (w), 505 (w), 458 (m), 420 (w). Elemental analysis %
calc. (Found): Na 5.95 (5.79), Ge 2.69 (2.87), W 54.42 (54.15), Cr 1.92 (2.28). Mw = 5405.30 g/mol.

3.4.1.3 Electrochemistry

Pure water was obtained with a Milli-Q Intregral 5 purification set. All reagents were of high-purity grade and were used as purchased without further purification: H₂SO₄ (Sigma Aldrich), CH₃COOH (Glacial, Prolabo Normapur), Li₂SO₄·H₂O (Acros Organics) and LiCH₃COO·2H₂O (Acros Organics). The composition of the various media was as follows: for pH 1.0, 2.0 and 3.0, 0.5 M Li₂SO₄ + H₂SO₄; for pH 4.0, 5.0 and 6.0, 1.0 M LiCH₃COO + CH₃COOH.

The stability of 3 and 4 in solution as a function of the pH and time was studied by monitoring the evolution of their UV-visible spectra at least over 24 h. Such duration is long enough for the electrochemical characterization of the compound and its possible application in electrocatalysis processes. These compounds were found to be stable in media having pH values ranging from 1 and up to 7 at least. The UV-visible spectra were recorded on a Perkin-Elmer 750 spectrophotometer with 10⁻⁴ M solutions of the polyanion. Matched 2,000 mm optical path quartz cuvettes were used.

Electrochemical data were obtained using an EG & G 273 A potentiostat driven by a PC with the M270 software. A one-compartment cell with a standard three-electrode configuration was used for cyclic voltammetry experiments. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode a platinum gauze of large surface area; both electrodes were separated from the bulk electrolyte solution via fritted compartments filled with the same electrolyte. The working electrodes were a 3 mm OD pyrolytic carbon disc or a c.a. 10×10×2 mm³ glassy carbon stick (Le Carbone-
Lorraine, France). The pre-treatment of the first electrode before each experiment is adapted from a method described elsewhere.[120] The stick is polished twice with SiC paper, grit 500 (Struers). After each polishing step, which lasts for about 5 minutes, the stick is rinsed and sonicated twice in Millipore water for a total of 10 minutes. Prior to each experiment, solutions were thoroughly de-aerated for at least 30 min with pure Ar. A positive pressure of this gas was maintained during subsequent work. All cyclic voltammograms were recorded at a scan rate of 10 mV s\(^{-1}\) and potentials are quoted against the saturated calomel electrode (SCE) unless otherwise stated. The polyanion concentration was 2×10\(^{-4}\) M. All experiments were performed at room temperature, which is controlled and fixed for the laboratory at 20°C. Results were very reproducible from one experiment to the other and slight variations observed over successive runs are rather attributed to the uncertainty associated with the detection limit of our equipment (potentiostat, hardware and software) and not to the working electrode pre-treatment nor to possible fluctuations in temperature.

### 3.4.1.4 Biological Materials

All the chemicals were purchased commercially and used as received. \(p\)-Nitrophenyl \(\alpha\)-D-glucopyranoside (\(p\)NPG) and \(\alpha\)-Saccharomyces cerevisiae \(\alpha\)-glucosidase, \(\beta\)-glucosidase from sweet almond, enzyme substrate (D,L-glyceraldehyde and sodium-D-glucoronate), and nicotinamide adenine dinucleotide phosphate (NADPH) as a cofactor were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). Commercially available tissue specific alkaline phosphatase enzyme extracted from calf intestine (CIAP) was obtained from Calbiochem, Germany. Alkaline phosphatase (EC 3.1.3.1 from calf intestine), tissue non-specific alkaline phosphatase
(TNAP) from bovine. Lung carcinoma (H157), (ATCC CRL-5802) and kidney fibroblast (BHK-21), (ATCC CCL-10) cell lines and Leishmania major (ATCC 30012D) were purchased from ATCC and African green monkey kidney normal cell line (Vero), (ATCC CCL-81) was acquired from RIKEN Bio Resource Center, Japan. Tris–HCl, MgCl₂, ZnCl₂, RPMI-1640, fetal bovine serum (FBS; Thermo scientific), (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT), D-MEM/F-12 medium (Gibco BRL), glutamine, penicillin, streptomycin, phosphate buffered saline (PBS) and tissue non-specific alkaline phosphatase (TNAP) were purchased from Sigma-Aldrich, Steinheim, Germany.

**Enzyme Inhibition Assays**

**Glucosidase isoenzyme inhibition assays**

Previously described assay methods of α-glucosidase[121] and β-glucosidase[122] enzymes were followed. Briefly, the solutions of α-glucosidase (2.5 U mL⁻¹) and β-glucosidase enzymes (2.0 U mL⁻¹) and their substrate p-NPG were prepared in 0.07 M phosphate buffer (pH 6.8). The assay was started with pre-incubation of enzyme (10 µL) with a test compound (10 µL) at 37 °C for 5 min. After pre-incubation, 10 µL of p-NPG (10 mM) was added to each well of a 96 well plate and further incubated at 37 °C for 30 min. The reaction was stopped by adding 80 µL of 0.2 M Na₂CO₃ solution. Negative control wells contain 10 µL of distilled water instead of test compounds, and the standard drug acarbose was used as a positive control. The activity of test compounds against α -glucosidase and β -glucosidase was determined by measuring p-nitrophenol at a wavelength of 405 nm. The percent inhibition was calculated using the following equation:

\[
\text{Percent inhibition} \% = [1 - (\text{absorbance of sample} / \text{absorbance of control})] \times 100
\]
Dose–response curves of potential inhibitors ($\geq$50%) were obtained and IC$_{50}$ was determined with the help of the Graph Pad prism 5.0 Software Inc., San Diego, California, USA.

**Activity against Alkaline phosphatase isozymes**

The derivatives were tested against tissue non-specific alkaline phosphatase (TNAP) from bovine and tissue specific alkaline phosphatase enzyme extracted from calf intestine (CIAP) was obtained from Calbiochem, Germany. The compounds were initially tested against these enzymes at 10 µM concentration to further make a dose-response curve of potential inhibitors of ALPs by using previously described method by J. Iqbal.[123] For each enzyme, the solution was made in assay buffer (pH 9.5) comprises of Tris-hydrochloride (50 mM), MgCl$_2$ (5 mM), ZnCl$_2$ (0.1 mM) and glycerol 50% in the solution. The solution of enzyme substrate $p$-nitrophenyl phosphate ($p$-NPP) and test compounds was also prepared in the same buffer without glycerol. The assay was started in 96 wells plate by adding 75 µL of assay buffer, 10 µL of test compound (from 100 µM compound stock solution), 5 µL of optimized enzyme (CIAP 0.025 U/mL and TNAP 0.5 U/mL) and then incubated at 37°C for 10 minutes. To initialize the reaction a 10 µL of substrate (5 mM $p$-NPP) was added into each well and again incubated for additional 30 minutes. The change in absorbance of released $p$-nitrophenolate was monitored at 405 nm, using a 96-well microplate reader (Bio-Tek ELx 800TM, Instruments, Inc. Winooski, VT, USA). The percent inhibition of each compound was calculated by comparing the results with the control wells having no inhibitor at all. The compounds which showed $\geq$50% inhibition were selected for further determination of dose-response curves against ALPs. For this purpose 7-9 serial dilutions of each compound spanning three orders of magnitude were
prepared in enzyme assay buffer and their dose response curves were obtained by adopting the same methods used for initial screening. All experiments were repeated three times in triplicate. The Cheng-Prusoff equation was used to calculate the $K_i$ values from the IC$_{50}$ values, determined by the non-linear curve fitting program PRISM 5.0 (GraphPad, San Diego, California, USA).

**Anticancer activity**

**Cell lines and cell cultures**

Lung carcinoma (H157), (ATCC CRL-5802) and kidney fibroblast (BHK-21), (ATCC CCL-10) cell lines and African green monkey kidney normal cell line (Vero), (ATCC CCL-81) were kept in RPMI-1640 [having heat-inactivated fetal bovine serum (10%), glutamine (2 mM), Pyruvate (1 mM), 100 U/mL penicillin and 100 mg/mL streptomycin] in T-75 cm$^2$ sterile tissue culture flasks in a 5% CO$_2$ incubator at 37 °C. [124] 96-Well plates were used for growing cells by inoculating $10^4$ cells per 100 mL per well. For experiments, all the cell lines were grown in 96-well plates by inoculating $10^4$ and $5\times10^4$ cells/100 mL/well respectively, and plates were incubated at 37 °C in a 5% CO$_2$ incubator. Within 24 h, a uniform monolayer was formed which was used for experiments.

**Cytotoxicity analysis by sulforhodamine B (SRB) assays**

To perform cytotoxicity assay with H157, BHK-21 and Vero cells, a previously described method by Skehan et al.[125] was adopted with some modifications. Briefly, cells were cultured in different 96 well plates for 24 h. The compounds in different concentrations (100, 10, 1 and 0.1 mM) were inoculated in test wells while control and blank wells were also prepared contain standard drug (VCN) and culture media with cells respectively. The plates were then incubated for 48 h. After that cells were fixed
with 50mL of 50% ice cold TCA solution at 4 °C for 1 h. The plates were washed 5 times with PBS and air dried. Fixed cells were further treated with 0.4% w/v sulforhodamine B dye prepared in 1% acetic acid solution and left at room temperature for 30 min. After that the plates were rinsed with 1% acetic acid solution and allowed to dry. In order to solubilize the dye, the dried plates were treated with 10 mM Tris base solution for 10 min at room temperature. Absorbance was measured at 490 nm subtracting the background measurement at 630 nm.[126] IC50 values of potential inhibitors (≥50%) were determined with the help of the Graph Pad prism 5.0 Software Inc., San Diego, California, USA.

Antileishmanial activity

Parasite and culture

Leishmania major promastigotes were cultured at 25±1 °C to logarithmic phase in D-MEM/F-12 medium (Gibco BRL) without phenol red, supplemented by 10% heat inactivated fetal bovine serum (FBS), 100 IU/mL penicillin and 100 mg/mL streptomycin, then washed 3 times with phosphate-buffered saline (PBS) by centrifugation at 1500 rpm for 10 min at room temperature and resuspended at a concentration of 2.5 × 10^6 parasites/mL in medium.

Antileishmanial activity assays (MTT assay)

The antileishmanial activity of the compounds was evaluated in vitro against the promastigote forms of Leishmania major using an MTT (3-(4,5-dimethylthiazol- 2yl)-2,5-diphenyltetrazolium bromide)-based microassay as a marker of cell viability. The MTT assay used was based on that originally described by Mosmann[127] modified by Niks and Otto[128]. A stock solution of MTT (Sigma Chemical Co., St. Louis, Mo.) was prepared by dissolving in phosphate-buffered saline (PBS) at 5 mg/mL and storing
in the dark at 4 °C for up to 2 weeks before use. For the antileishmanial activity assays, 100 mL/well of the culture which contained 2.5 × 10^6 cells/mL promastigotes was seeded in 96-well flatbottom plates. Then, 10mL/well from various concentrations of compounds were added to triplicate wells and plates were incubated for 72 h at 25±1 °C. The first well of 96 wells was as a blank well which only contained of 100 mL culture medium without any compound, drug or parasite. Amphotericin B was used as standard drug. At the end of incubation, 10 mL of MTT was added to each well and plates were incubated for 3 h at 25±1 °C. Reaction was then stopped by the addition of 100 mL of 50% isopropanol and 10% sodium dodecyl sulfate. The plates were incubated for an additional 30 min. under agitation at room temperature. Relative optical density (OD) was then measured at a wavelength of 570 nm using a 96-well microplate reader (Bio-Tek ELx 800TM, Instruments, Inc. Winooski, VT, USA). The background absorbance of plates was measured at 690 nm and subtract from 570nm measurement. The absorbance of the formazan produced by the action of mitochondrial dehydrogenases of metabolically active cells is shown to correlate with the number of viable cells. All experiments were repeated at least three times. Results reported are mean of three independent experiments (±SEM) and expressed as percent inhibitions calculated by the formula;

Percent inhibition (%) = \[100 - (\text{absorbance of sample} / \text{absorbance of control}) \times 100\]

IC\(_{50}\) values of potential inhibitors (≥50%) were determined with the help of the Graph Pad prism 5.0 Software Inc., San Diego, California, USA.
Fig. 3.19 Polyhedral (left) and ball-and-stick (right) representations of polyanions 3a and 4a. Color code: X = Si, Ge (pink), W (blue), Cr (green), O (red).

3.4.2 Results and Discussion

3.4.2.1 Synthesis and Structure

The mononuclear chromium (III)-containing polyanions \([\text{Cr}((\text{H})\text{X}^{1/2}\text{W}_{28}^{13-})]^{13-} (X = \text{P, As})\) were previously synthesized by interaction of the respective heterogroup source (H\(_3\)PO\(_4\)/As\(_2\)O\(_5\)) with Cr(NO\(_3\))\(_3\)·9H\(_2\)O and Na\(_2\)WO\(_4\)·2H\(_2\)O in aqueous NaOAc solution at 80 °C.[129] Although the successful synthesis requires careful control of pH and temperature, the stoichiometry indicated by the formation equation is not strictly necessary, which means that the excess of the chromium salts or heteroatom do not influence the final products. Proceeding with this synthetic strategy, which we discovered to work towards different central hetero element. Not surprisingly, we find
their structure formation and properties was affected by the nature of the heteroatom. Reaction of chromium nitrate, sodium tungstate, and sodium metasilicate for 3 or germanium dioxide for 4 at stoichiometric ratio in a sodium acetate buffer (pH 6.0) at high temperature resulted in the sandwich-type octatungstosilicate and octatungstogermanate, [Cr$^{III}_2$(B-β-Si$^{IV}$W$_8$O$_{31}$)$_2$]·45H$_2$O (3) and [Cr$^{III}_2$(B-β-Ge$^{IV}$W$_8$O$_{31}$)$_2$]·50H$_2$O (4), respectively. Also the formation of the compounds depends on the initial reaction temperature, which should be in the range of 60–95°C, with a milder heating not leading to any products.

Table 3.6 Crystal data for 3 and 4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>Na$_{14}$[Cr$_2$(SiW$<em>8$O$</em>{31}$)$_2$]·45H$_2$O</td>
<td>Na$_{14}$[Cr$_2$(GeW$<em>8$O$</em>{31}$)$_2$]·50H$_2$O</td>
</tr>
<tr>
<td>Formula weight, g/mol</td>
<td>5226.35</td>
<td>5405.30</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P̅ī</td>
<td>P̅ī</td>
</tr>
<tr>
<td>a, Å</td>
<td>11.840(3)</td>
<td>11.7963(9)</td>
</tr>
<tr>
<td>b, Å</td>
<td>13.405(5)</td>
<td>13.3898(10)</td>
</tr>
<tr>
<td>c, Å</td>
<td>16.785(4)</td>
<td>16.8498(13)</td>
</tr>
<tr>
<td>α, °</td>
<td>110.892(19)</td>
<td>110.934(4)</td>
</tr>
<tr>
<td>β, °</td>
<td>93.430(13)</td>
<td>93.251(4)</td>
</tr>
<tr>
<td>γ, °</td>
<td>108.697(10)</td>
<td>108.541(3)</td>
</tr>
<tr>
<td>Volume, Å$^3$</td>
<td>2311.4(12)</td>
<td>2312.7(3)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$D_{calc}$, g/cm$^3$</td>
<td>3.755</td>
<td>3.946</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>20.270</td>
<td>20.751</td>
</tr>
<tr>
<td>F(000)</td>
<td>2360</td>
<td>1374</td>
</tr>
<tr>
<td>Crystal size, mm</td>
<td>0.2 x 0.08 x 0.06</td>
<td>0.15 x 0.10 x 0.04</td>
</tr>
<tr>
<td>Theta range for data</td>
<td>1.324 – 25.200</td>
<td></td>
</tr>
<tr>
<td>collection, °</td>
<td>3.445 – 30.034</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>Reflections collected</td>
<td>108797</td>
<td>239622</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8299</td>
<td>13500</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.0553</td>
<td>0.067</td>
</tr>
<tr>
<td>Observed (I &gt; 2σ(I))</td>
<td>8299</td>
<td>13500</td>
</tr>
<tr>
<td>Goodness-of-fit on F2</td>
<td>1.010</td>
<td>1.013</td>
</tr>
<tr>
<td>R₁[I &gt; 2σ(I)] [a]\</td>
<td>0.0387</td>
<td>0.0443</td>
</tr>
<tr>
<td>wR₂ (all data) [b]\</td>
<td>0.1250</td>
<td>0.1181</td>
</tr>
</tbody>
</table>

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

Crystallographic structural analysis revealed that 3 and 4 are isomorphous, both crystallizing in the triclinic \( P\overline{1} \) space group (see Table 3.6). Polyanions 3a and 4a consist of two equivalent octatungstosilicate \{Si₈W₈\} or \{Ge₈W₈\} moieties linked by two trivalent Cr centers, leading to a sandwich-like structure with \( C_{2h} \) point-group symmetry with a \( C_2 \) axis passing through the two \( \text{Cr}^{\text{III}} \) centers and a perpendicular \( \sigma_h \) mirror plane (Fig. 3.19). Each moiety consists of two \{W₃O₁₃\} triads linked to two edge-shared WO₆ octahedra, with both units are stabilized by the central SiO₄ or GeO₄ hetero group.

The fragment \{B-\( \beta \)-SiW₈O₃₁\} had been suggested for the first time in 2005 by our group in the Co(II)-containing silicotungstate, \[(\text{Co}_6(\text{H}_2\text{O})_5\{\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_6(\text{\( \beta \)-SiW₈O₃₁})\})^5\] \[130\] which forms a satellite-like structure. This polyanion is composed of nine Co^{II} ions that are encapsulated by three \{B-\( \beta \)-SiW₈O₃₁\} fragments. Later, our group isolated another cobalt-substituted tungstosilicate \[(\text{Co}_5(\text{B-\( \beta \)-SiW₈O₃₃(OH)})_(\text{B-\( \beta \)-SiW₈O₂₀(OH)_₂})_2)_1^5 \] containing the similar fragment.\[131\] However, there, the fragment contains two \( \mu_2 \)-hydroxo (W–O–W) bridges in the \{Si₈W₈\} unit. Moreover, the \[B-\( \beta \)-GeW₈O₃₁]⁰\-fragment was first presented in \[\text{Cu}_3(2,2′-\text{bpy})_6(\text{H}_2\text{O})][\text{GeW₈O₃₁}] \] under hydrothermal reaction,\[132\] as well as the \[\beta\)-PW₈O₃₁]⁰\- was first exhibited in \[\{\text{Cu}_8(2,2′-\text{bpy})_8\}(\text{PW₈O₃₁})_2 \]^².\[133\] Up to now, the tetravacant Keggin species are
rarely documented. We would also like to mention that this moiety was synthesized mostly starting from $[\gamma\text{-SiW}_{10}\text{O}_{36}]^8_-$, which undergoes structural transformation in aqueous media. Table 3.7 gives the examples of reported compounds containing $\{\text{XW}_8\}$ fragments. The sandwich-type POMs composed of lacunary POMs and metal ions are important sub-family with brilliant prospects. Various POM nuclearities and topologies of encapsulated metal ions ranging from mononuclear to heptanuclear between the sandwich POMs have been recorded by Kortz, Yamase, Wang et al.[37, 134-142] However, no sandwich-type structure constructed by the unusual octatungstate unit $\{\text{XW}_8\}$ has been reported so far.

Table 3.7 Survey of polyoxotungstate based on tetralacunary building blocks.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicotungstate ${\text{SiW}_8}$</td>
<td></td>
</tr>
<tr>
<td>$[\text{Co}_6(\text{H}_2\text{O})_5{\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_6(\beta\text{-SiW}<em>8\text{O}</em>{31})}]^{3+}$</td>
<td>[130]</td>
</tr>
<tr>
<td>$[{\text{Co}_3(\beta\text{-SiW}<em>9\text{O}</em>{33}(\text{OH}))(\beta\text{-SiW}<em>8\text{O}</em>{29}(\text{OH}_2)}_2]^{2+}$</td>
<td>[131]</td>
</tr>
<tr>
<td>$[{\text{Cu}_3(\text{SiW}<em>8\text{O}</em>{31})(\text{OH})(\text{H}_2\text{O})_2(N_3)}_3(N_3)]^{19+}$</td>
<td>[143]</td>
</tr>
<tr>
<td>$[\text{Co}(\text{H}_2\text{O})_2{\text{Co}_3(\text{H}_2\text{O})(\beta\text{-SiW}<em>9\text{O}</em>{33}(\text{OH}))(\beta\text{-SiW}<em>8\text{O}</em>{29}(\text{OH}_2)}_2]^{20-}$</td>
<td>[144]</td>
</tr>
<tr>
<td>$[\text{Co}_1.5(\text{H}_2\text{O})_7][\text{Co}_4(\text{OH})(\text{H}<em>2\text{O})<em>7(\gamma\text{-SiW}</em>{10}\text{O}</em>{36})(\beta\text{-SiW}<em>8\text{O}</em>{30}(\text{OH}))]^{1+}$</td>
<td>[144]</td>
</tr>
<tr>
<td>$[\text{Cu}_{14}(\text{OH})_4(\text{H}<em>2\text{O})</em>{16}(% \text{SiW}<em>8\text{O}</em>{31})_4]^{16-}$</td>
<td>[145]</td>
</tr>
<tr>
<td>$[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\beta\text{-SiW}<em>9\text{O}</em>{34})(\text{B}-\beta\text{-SiW}<em>8\text{O}</em>{29}(\text{OH}_2))]^{12-}$</td>
<td>[146]</td>
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<tr>
<td>$[\text{Co}_3(\text{H}_2\text{O})(\text{B}-\beta\text{-SiW}<em>9\text{O}</em>{34})(\text{B}-\beta\text{-SiW}<em>8\text{O}</em>{31})]]^{14-}$</td>
<td>[146]</td>
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<tr>
<td>$[\text{Co}_9\text{Cl}_2(\text{OH})_3(\text{H}_2\text{O})_6(\beta\text{-SiW}<em>8\text{O}</em>{31})_3]^{17-}$</td>
<td>[146]</td>
</tr>
<tr>
<td>$[\gamma\text{-Cu}_2(\text{H}_2\text{O})\text{SiW}<em>8\text{O}</em>{31}]^{12-}$</td>
<td>[147]</td>
</tr>
<tr>
<td>${\text{Cu}(\text{Cu}_{7.5}(\text{SiW}<em>8\text{O}</em>{30}(\text{OH}_2))_2(\text{H}_2\text{O})_4}_2]^{7-}$</td>
<td>[148]</td>
</tr>
<tr>
<td>$[\text{Mn}^\text{III}_2\text{Mn}^\text{II}_4(\text{H}<em>2\text{O})<em>4(\beta\text{-SiW}<em>9\text{O}</em>{31})(\beta\text{-SiW}<em>8\text{O}</em>{34})(\gamma\text{-SiW}</em>{10}\text{O}</em>{36})]^{18-}$</td>
<td>[149]</td>
</tr>
<tr>
<td>$[[\text{Mn}(\text{H}_2\text{O})_3]_2[\text{Mn}(\text{H}_2\text{O})_2][(\text{B}-\beta\text{-SiW}<em>9\text{O}</em>{33}(\text{OH}))\text{Mn}_3(\text{H}_2\text{O})(\text{B}-\beta-\text{SiW}<em>8\text{O}</em>{31})_2]]^{150}$</td>
<td></td>
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</tbody>
</table>
The two structurally equivalent Cr$^{III}$ cation in 4 presents an almost ideal octahedral environment comprising four corner sharing $\mu_2$-O atoms from the tungsten-oxo framework with Cr–O distances of 1.954(7)–1.968(6) Å and two $\mu_3$-O (GeCrCr') bridging atoms with Cr–O distances of 1.990(6) and 1.996(6) Å. Additionally, two $\mu_3$-O atoms bridge the two central transition metal ions. The [B-β-SiW$_{8}$O$_{31}$]$^{10-}$ unit is derived from saturated β-Keggin [SiW$_{12}$O$_{40}$]$^{3-}$ isomer by removing one {W$_3$O$_{13}$} triad and one neighboring WO$_6$ of the rotated triad. The four kinds of W–O bond lengths fall within the anticipated ranges for the different types of oxo ligands with an increasing trend: terminal (1.726(2)–1.756(5) Å), $\mu_2$-bridging bonding (1.817(8)–2.102(8) Å), $\mu_3$-bridging bonding (2.212(7)–2.235(7) Å) and central $\mu_4$-bridging (2.279(7)–2.301(7) Å).

The Ge center, in the distorted tetrahedron GeO$_4$, is connected to two $\mu_4$-O atoms from two triads, a $\mu_3$-O atom from the two edge-shared WO$_6$ octahedra, and a $\mu_3$-O atom from two chromium centers. The Ge–O bond lengths are in the range of 1.730(7)–1.759(7) Å. In the case of [SiW$_8$O$_{31}$]$^{10-}$, the Si–O bond lengths are in the range of 1.627(10)–1.651(10) Å. Bond valence sum (BVS) calculations for 4 suggest that there
are no well-defined protonation sites. The same observation is true for 3.

Polyanions 3a and 4a have two key features that make them unique. Firstly, these two compounds represent the first sandwich-type POM constructed by the unusual octatungstate \([\text{XW}_8\text{O}_{31}]^{10-}\) (X = Si, Ge) units. We believe that the other transition metal analogues of this kind of sandwich-type structure could also be obtained and thus further investigation is needed. Secondly, the dimeric polyanion 4a is the first reported Cr\(^{III}\)-containing germanotungstate known to data.

Fig.3.20 View of polyanion 3a, Na\(^+\)···OH\(_2\) interactions and hydrogen bonds are drawn as thin dashed lines.

As known, the magnetic properties are usually influenced by the magnetic interactions between metal atoms as well as the M1–O–M2 angle. Interestingly, the distance between the two transition metals is 2.97 Å, which is shorter than that in \([\text{A-}\alpha-\cdots \text{B}]\).
SiW₉O₃₄Cr₃(OH)₆(1) with 3.61–3.62 Å,[71] as well as that in Cr(III) acetate fragment of [γ-SiW₁₀O₃₆Cr₂(OH)(OOCCH₃)₂(H₂O)₂]⁵⁻ with 3.05–3.07 Å,[73] and also shorter than the 5 Å of the discrete oxalate-bridged dinuclear (Cr(III)–M(II) (M = Cu, Ni, Co, Fe, Mn) complexes, which are also studied in magnetochemistry.[152, 153] The antiferromagnetic interactions in 4 were weaker than those in 4. This fact is in agreement with the fact that Cr–O–Cr bridging angles in 4 (99.757(5) are larger than those in 3 (96.338(18)).

Fig.3.21 View of polyanion 4a, Na⁺···OH₂ interactions and hydrogen bonds are drawn as thin dashed lines.
3.4.2.2 Electrochemistry

(The electrochemistry was performed by our collaborators Prof. Dr. Pedro de Oliveira, Université Paris-Sud, France)

The electrochemical characterisation of compounds 3 and 4 was carried out in 0.5 M Li$_2$SO$_4$ + H$_2$SO$_4$ media at pH 1, 2 and 3 and in 1.0 M LiCH$_3$COO + CH$_3$COOH media at pH 4, 5 and 6. The CVs obtained in these different media exhibit the same overall features for the two compounds, namely a single reversible redox wave assigned to the reduction of W$^{VI}$ centres present in these species. Beyond this single redox process the solvent limit is reached, which corresponds to the electro-catalytic reduction of protons by a reduced form of the POMs. This reduction of the POMs is irreversible and encompasses the modification of the electrode surface, rendering it particularly active towards the hydrogen evolution reaction (HER). As expected, the midpoint redox potential values, $E^0' = (E_{pa} + E_{pc})/2$, ($E_{pa}$, and $E_{pc}$, being the anodic and the cathodic peak potentials, respectively) decrease as the electrolyte pH increases.[154] Fig.3.22 shows the CVs of compound 4 obtained at the six pH values selected for the present study (see Fig.3.23 for compound 3). The redox waves shift towards the negative potentials as the pH rises from 1 up to 7. This behaviour indicates that the reduction of the two compounds encompasses proton uptake, as is the case for the majority of POMs in aqueous solution. The reduction is facilitated (less negative $E^0'$ values) when the proton concentration is higher (smaller pH values) and gets more and more difficult as protons in the medium become scarce (higher pH values). The existence of a mechanism composed of an electrochemical step, $E$ (electron transfer), coupled to a chemical reaction, $C$ (proton exchange), is further confirmed by the relative reduction peak current intensities at the different pH values. In fact, the peak currents should be
very close, if not similar, irrespective of the pH, since the POM concentration is the same for all the experiments. However, when the cathodic peak current intensities, $I_{pc}$, obtained at the selected pH values are compared, an obvious trend is observed: the absolute value of $I_{pc}$ increases when the electrolyte pH decreases (i.e. when the proton concentration increases) going from $I_{pc} = -3.4 \ \mu A$ at pH 6 to $I_{pc} = -4.4 \ \mu A$ at pH 1, proving that protons are implicated in the process. This constitutes another evidence of the fact that POM reduction follows an $EC$ mechanism, i.e. an electrochemical reaction is coupled to a chemical reaction. Nevertheless, we would expect the shape of the redox waves on the CVs to change as they keep shifting towards the negative potentials upon increasing the pH, which is not really the case.

We know that for $EC$ processes for which protonation is the coupled chemical reaction, a drastic fall of the proton concentration or the eventual absence of protons in the medium renders the electron transfer energetically more demanding (higher energy input required, therefore the reduction occurs at more negative potentials) and also kinetically slower (less reversible). Hence, for high pH values, the redox waves are supposed to lose some of their reversibility (slower electron transfer kinetics). Also, for multi-electron waves, as is the case for the present compounds, a progressive splitting of the main peak into several peaks, possibly via intermediate steps exhibiting shoulders, was the expected behaviour. Reversible, single peak redox waves at low pH values would evolve into less reversible, composite waves and finally into an ensemble of several waves more or less separated from each other. In the present case, it is surprising that in such a large pH range (1 to 7), the sole multi-electron wave observed does not undergo any pronounced evolution in its shape which might be attributed to the slowdown of the electron transfer, nor there is any hint of a peak splitting phenomenon,
even at a small scan rate (2 mV s\(^{-1}\)). For small pH values, especially at pH 1, the CVs of
the two compounds show a slight shoulder after the reduction peak which is possibly
due to the partial decay of the two species in this medium. This shoulder progressively
disappears upon increasing the pH, and beyond pH 3 (Fig.3.23b) there is a perfectly
defined reversible redox wave, exhibiting a single reduction peak during the forward
scan and a single oxidation peak during the reverse scan.

Controlled potential coulometry did not allow to determine the total number of
exchanged electrons during the redox process. In fact, even at pH 6, a medium where
protons are relatively scarce, the electrolysis carried out at a potential of -0.94 V vs.
SCE (i.e. before the cathodic peak), the beginning of the reduction process encompasses
also the HER. Under these conditions, the total charge that crosses the circuit is 10-fold
the charge recovered upon re-oxidising at a potential of 0.0 V vs. SCE. A similar
behaviour was observed in a previous study concerning a Ni\(^{2+}\) centre-containing
tungstic POM.[155]

Fig.3.22 CVs of 4 (a) in different 0.5 M Li\(_2\)SO\(_4\) + H\(_2\)SO\(_4\) media: pH 1 (black); pH 2
(red) and pH 3 (blue) and (b) in different 1.0 M LiCH\(_3\)COO + CH\(_3\)COOH media: pH 4
(black) ; pH 5 (red) and pH 6 (blue). Each scan is started in the sense of the negative
potentials and the waves are associated to the redox response of the W\(^{VI}\) centres. Scan
rate: 10 mV s\(^{-1}\). Working electrode: EPG; counter electrode: Pt; reference electrode: SCE.

Fig.3.23 CVs of 3 (a) in different 0.5 M \(\text{Li}_2\text{SO}_4 + \text{H}_2\text{SO}_4\) media: pH 1 (black); pH 2 (red) and pH 3 (blue) and (b) in different 1.0 M \(\text{LiCH}_3\text{COO} + \text{CH}_3\text{COOH}\) media: pH 4 (black); pH 5 (red) and pH 6 (blue). Each scan is started in the sense of the negative potentials and the waves are associated to the redox response of the \(\text{W}^{VI}\) centres. Scan rate: 10 mV s\(^{-1}\). Working electrode: EPG; counter electrode: Pt; reference electrode: SCE.

Table 3.8 Cathodic peak potentials, \(E_{pc}\), anodic peak potentials, \(E_{pa}\), and midpoint redox potentials, \(E_{0^\circ} = (E_{pa} + E_{pc})/2\), for the W centre reduction steps of 3 and 4 in 0.5 M \(\text{Li}_2\text{SO}_4 + \text{H}_2\text{SO}_4\), from pH 1 to 3, and in 1.0 M \(\text{LiCH}_3\text{COO} + \text{CH}_3\text{COOH}\), from pH 4 to pH 6. The CVs were recorded at a scan rate of 10 mV s\(^{-1}\). Working electrode: EPG.

Potentials are quoted against the SCE reference electrode.

<table>
<thead>
<tr>
<th>(V vs. SCE)</th>
<th>(3)</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.0</td>
</tr>
<tr>
<td>(E_{pc})</td>
<td>-0.480</td>
</tr>
<tr>
<td>(E_{pa})</td>
<td>-0.440</td>
</tr>
<tr>
<td>(E_{0^\circ})</td>
<td>-0.460</td>
</tr>
<tr>
<td>(V vs. SCE)</td>
<td>(4)</td>
</tr>
</tbody>
</table>
The comparison of the CVs of compounds 3 and 4 recorded in the same experimental conditions reveals that for pH values below 3 (Fig.3.24a), the reduction of the tungstic centres of 4 happens before that of 3, as expected.[156] Indeed, recent works have shown that there is a general trend for a series of POMs having the same structure and charge and differing just in the nature of the central hetero-element (e.g. Si or Ge; P or As; etc.): the species that is reduced first is the one containing the hetero-element having the largest atomic radius (Si: \( r \approx 110 \text{ pm} \) and Ge: \( r \approx 125 \text{ pm} \)).[157, 158] These observations have been confirmed and rationalised by DFT calculations. However, in the present case and for pH value higher than 3, there is an inversion of the expected trend, compound 3 being reduced before compound 4 (Fig.3.24b). This phenomenon may be explained by the pK\(_a\) values for the two compounds, which must fall around 4, matching the redox potential inversion when this pH reached.
Fig. 3.24 CVs of 3 (blue) and of 4 (red) in (a) 0.5 M Li$_2$SO$_4$ + H$_2$SO$_4$ / pH 2.0 and in (b) 1.0 M LiCH$_3$COO + CH$_3$COOH / pH 5.0. Each scan is started in the sense of the negative potentials and the waves are associated to the redox response of the W$^\text{VI}$ centres. Scan rate: 10 mV s$^{-1}$. Working electrode: EPG; counter electrode: Pt; reference electrode: SCE. (c) Dependency of the midpoint potential, E$^{0'}$, on the electrolyte pH (from pH 1.0 to pH 6.0) for compound 3 (blue squares) and for compound 4 (red squares). The values were obtained from the CVs recorded with an EPG working electrode at a scan rate of 10 mV s$^{-1}$.

In both compounds 3 and 4, the Cr centres are at the +III oxidation state. It is possible, then, to observe their conversion to higher oxidation states, such as Cr$^{V}$, by cyclic voltammetry, and make use of them in order to carry out electro-catalytic...
oxidation processes. In the case of the mono-substituted derivatives $\alpha_2$-[P$_2$W$_{17}$O$_{61}$Cr$^{\text{III}}$(OH$_2$)]$^{7-}$ and [PW$_{11}$O$_{39}$Cr$^{\text{III}}$(OH$_2$)]$^{4+}$, Anson et al. described an irreversible oxidation wave attributable to the Cr$^V$/Cr$^{\text{III}}$ couple.[159] However, in other cases, namely in sandwich-type molecules possessing several Cr centres,[73] it is hard to make out clearly this oxidation wave of Cr$^{\text{III}}$, because it takes place at rather positive potentials and may be concealed by the solvent limit, i.e. the electro-catalytic oxidation of water. In order to avoid this interference, we have worked at pH 6, at which the Cr$^{\text{III}}$ oxidation occurs at potentials values not so positive. In fact, in the CV of compound 3 obtained at pH 6, there is a hump around +0.870 V vs. SCE assigned to the oxidation of Cr$^{\text{III}}$, followed by the electro-catalytic oxidation of water which takes place around +1.100 V vs. SCE (Fig.3.25). The oxidation process of Cr$^{\text{III}}$ is totally irreversible, with its corresponding reduction wave appearing at -0.480 V vs. SCE. The electrode surface is modified upon the oxidation of the Cr$^{\text{III}}$ centres, which renders it less reactive. Indeed, when two consecutive cycles are recorded, the reduction of the W$^{\text{VI}}$ centres upon the second cycle is shifted by 70 mV towards the negative potentials. Similar results are observed with the CVs for compound 4 recorded in the same conditions (Fig.3.26). The working electrode fouling related to the oxidation of the Cr$^{\text{III}}$ centres happens in the six media used in the present study. It may be rationalised by the formation of a film of insoluble oxides that covers the electrode surface and is not totally removed upon the reduction scan.
Fig. 3.25 CVs of 3 in 1.0 M 1.0 M LiCH₃COO + CH₃COOH / pH 6. The scan (2 cycles) is started in the sense of the negative potentials, followed by the sense of the positive potentials, in order to assess the redox behaviour of the waves attributed to the Cr^{III} centres. Working electrode: EPG; counter electrode: Pt; reference electrode: SCE.

Fig. 3.26 CVs of 4 in 1.0 M 1.0 M LiCH₃COO + CH₃COOH / pH 6. The scan (2 cycles) is started in the sense of the negative potentials, followed by the sense of the positive potentials, in order to assess the redox behaviour of the waves attributed to the Cr^{III} centres. Working electrode: EPG; counter electrode: Pt; reference electrode: SCE.
3.4.2.3 Biological Studies

(The biological studies were performed by our collaborator Prof. Dr. Jamshed Iqbal.)

**Enzymatic assays**

POMs have shown remarkable significance against chronic metabolic diseases especially diabetes and its complications.[121] Two novel compounds 3 and 4 were tested against Glucosidases (α- β) to evaluate their antidiabetic potential. The compound 4 showed a good inhibition potential against both enzymes with IC$_{50}$ 3.58 ± 0.672 µM (α-Glucosidases) and 5.87 ± 0.124 µM (β-Glucosidases). Compound 3 showed comparatively less inhibition for Glucosidases with IC$_{50}$ 12.13 ± 2.26 µM (α-Glucosidases) and 17.42 ± 6.45 µM (β-Glucosidases) [see Table 3.9].

Alkaline phosphatase enzymes can cause impaired mineralization especially in old age chronic diseases including osteoporosis, osteoarthritis, cardiovascular tissue calcification and bone metastasis.[160-162] Compounds 3 and 4 were also evaluated for alkaline phosphatases (TNAP and CIAP). The compound 4 was very active against alkaline phosphatases with Ki values 1.09 ± 0.152 µM (TNAP) and 1.54 ± 0.025 µM (CIAP). 3 showed similar inhibition for TNAP (Ki = 1.96 ± 0.526 µM) and less inhibition for CIAP 8.06 ± 1.52 µM [see Table 3.9].

**Anticancer studies**

The compounds 3 and 4 were also tested for anticancer activity on different cell lines (BHK-21 and H157) and comparison was made with standard drug Vincristine. The compound was also tested on vero cells to evaluate its safety for noncancerous cells. The cytotoxicity results of 4 were reported with IC$_{50}$ 2.07 ± 0.381 µM (BHK-21) and 1.01 ± 0.084 µM (H157). The results were comparable with standard drug Vincristine which showed inhibition on both cell lines with IC$_{50}$ 1.08 ± 0.09 µM. The
compound has showed minimum inhibition on vero cells 18 ± 2 (%) which demonstrates its safety. The compound Na$_{14}$[Cr$_{12}$\(\beta\)-\(\beta\)-Si$^{IV}$W$_8$O$_{31}$]$\cdot$45H$_2$O showed slightly different cytotoxicity behavior with IC$_{50}$ 7.37 ± 1.04 µM (BHK-21) and 5.16 ± 2.87 µM (H157) [see Table 3.9].

To the best of our knowledge POMs have never been reported to have antiparasitic activity. The novel compounds 3 and 4 were tested against Leishmania and showed an excellent inhibition with IC$_{50}$ 0.32 ± 0.08 µM and 1.34 ± 0.42 µM respectively that is quite similar when compared with standard Amphotericin B (IC$_{50}$ 0.29 ± 0.05 µM) used as standard drug [see Table 3.9].

Table 3.9 Biological activities of Cr$^{III}$-substituted polyoxotungstates

<table>
<thead>
<tr>
<th>Activities</th>
<th>Compound</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Glucosidase IC$_{50}$ (µM)</td>
<td>12.13 ± 2.26</td>
<td>3.58 ± 0.672</td>
<td></td>
</tr>
<tr>
<td>β-Glucosidase IC$_{50}$ (µM)</td>
<td>17.42 ± 6.45</td>
<td>5.87 ± 0.124</td>
<td></td>
</tr>
<tr>
<td>TNAP K$_i$ (µM)</td>
<td>1.96 ± 0.526</td>
<td>1.09 ± 0.152</td>
<td></td>
</tr>
<tr>
<td>CIAP K$_i$ (µM)</td>
<td>8.06 ± 1.52</td>
<td>1.54 ± 0.025</td>
<td></td>
</tr>
<tr>
<td>BHK-21 IC$_{50}$ (µM)</td>
<td>7.37 ± 1.04</td>
<td>2.07 ± 0.381</td>
<td></td>
</tr>
<tr>
<td>H157 IC$_{50}$ (µM)</td>
<td>5.16 ± 2.87</td>
<td>1.01 ± 0.084</td>
<td></td>
</tr>
<tr>
<td>Anti- Leishmania IC$_{50}$ (µM)</td>
<td>1.34 ± 0.42</td>
<td>0.32 ± 0.08</td>
<td></td>
</tr>
</tbody>
</table>

3.4.2.4 Magnetic Studies

The magnetic data were corrected for the sample holder and diamagnetism using Pascal constants.[163] The temperature dependence of the effective magnetic moment ($\mu_{\text{eff}}$) per Cr$_2$ unit for the complexes is shown in Fig.3.27. The $\mu_{\text{eff}}$ values at room temperature are 5.71 and 5.67 for 3 and 4 respectively. Below 50 K the values decrease
sharply, presumably because of antiferromagnetic interaction between the Cr$^{\text{III}}$ centers. The data were evaluated using the Hamiltonian of an interacting spin system:

$$\mathcal{H} = \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \beta \mathbf{H} \cdot g \cdot \sum_i \mathbf{S}_i$$

Where the first sum $\langle i,j \rangle$ is restricted to nearest neighbor (nm), $J < 0$ indicates antiferromagnetic interactions, and the Zeeman (second) term includes the Bohr magneton ($\beta$), and the presence of an externally applied magnetic field ($\mathbf{H}$) and the Lande $g$ factor.

The magnetic susceptibility data for both compounds were adequately described using essentially the same parameters of $S_{1,2} = 1.5$, $J = -3.3 \text{ cm}^{-1}$, and $g_{1,2} = 2.10$ for 3 and $S_{1,2} = 1.5$, $J = -4.1 \text{ cm}^{-1}$, and $g_{1,2} = 2.08$ for 4 as indicated by the acceptable fit of the solid line in Fig.3.27 to the experimental data (circles). The small negative $J$ value indicates the presence of a weak antiferromagnetic spin-exchange interaction between Cr$^{\text{III}}$ centers. The $J$ values of 3 and 4 are comparable with those determined for several other Cr$^{\text{III}}$ dimers.[164-166] Much more work about electron paramagnetic resonance is still needed to understand these spectra and is planned for the future.

---

**Fig.3.27** Temperature dependence of $\mu_{\text{eff}}$ for (a) 3 and (b) 4. The solid line is the best fit with the parameters listed in the text.
3.4.2.5 Thermogravimetric Analysis

The thermal analysis of 3 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 200 °C and involving loss of 45 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 15.5 (13.5)]. A weight loss for 4 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 50 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 16.6 (15.5)].

Fig.3.28 Thermogram for 3 from room temperature to 800 °C.
Fig. 3.29 Thermogram for 4 from room temperature to 800 °C.

3.4.3 Conclusions

We report the synthesis and structure of two dinuclear Cr$^{III}$ complexes, $\text{Na}_{14}[\text{Cr}^{III}_2(\text{B}-\beta-\text{Si}^{IV} \text{W}_8\text{O}_{31})_2]\cdot 45\text{H}_2\text{O}$ (3) and $\text{Na}_{14}[\text{Cr}^{III}_2(\text{B}-\beta-\text{Ge}^{IV} \text{W}_8\text{O}_{31})_2]\cdot 50\text{H}_2\text{O}$ (4) which represent the first chromium-containing sandwich-type polyanion structure constructed by the unusual octatungstate unit $[\text{XW}_8\text{O}_{31}]^{10-}$ ($\text{X} = \text{Si, Ge}$). Remarkably, this assembly of architectural versatility in POMs can be tuned by changing the heteroatom template from phosphorous and arsenic to silicon and germanium. Susceptibility measurements of the title compounds were performed, making it possible to determine the exchange coupling constants. The solution stability has been examined by UV-Vis spectroscopy. The stability of both compounds in water and in media having pH values ranging from 1 to 7 at least, allowed us to extend the compounds into
solution study. The present study also reported on the first signs of antiparasitic activity in POM chemistry.

3.5 Synthesis and Structure of Dichromium-Containing 12-tungstoarsenate, \([H_3Cr_2(As^{III}W_6O_{23})_2(As^{III}O_3)_2]^{11+}\) (5a)

\[
2Cr^{3+} + 4As^{III}O_4^{3-} + 12WO_4^{2-} + 19H^+ \xrightarrow{H_2O} [H_3Cr^{III}_2(As^{III}W_6O_{23})_2(As^{III}O_3)_4]^{11+} + 8H_2O \quad (5a)
\]

3.5.1 Synthesis of \(Na_{11}[H_3Cr_2(As^{III}W_6O_{23})_2(As^{III}O_3)_2]\cdot45H_2O\) (5)

A sample of \(Cr(NO_3)_3\cdot9H_2O\) (0.1 g, 0.25 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of \(As_2O_3\) (0.07 g, 0.34 mmol) and \(Na_2WO_4\cdot2H_2O\) (1.32 g, 4 mmol). The mixture was later stirred for 1 h at 80°C, then after cooling to room temperature and filtration the obtained pH was 8. 5 were obtained as a pure crystalline phase after evaporation of the solution at room temperature within 2 days (yield 0.5 g, 44% based on Cr). The crude powder was dissolved in minimal amount of sodium acetate buffer (1M, pH 6) at 50°C. The resulting solution was cooled down to room temperature and then kept in a closed vial, green block crystals of 5 suitable for X-ray diffraction were collected the next day. IR (cm\(^{-1}\)): 932 (m), 851 (s), 723 (s), 618 (s), 504 (w), 451 (m). Elemental analysis % calc. (Found): Na 5.61 (5.6), As 6.65 (6.9), W 48.93 (48.32), Cr 2.31 (2.41). Mw = 4508.33 g/mol.
3.5.2 Results and discussion

3.5.2.1 Synthesis and Structure

Crystallographic structural analysis revealed that 5 crystallizes in the triclinic space group $P\bar{1}$ (see Table 3.10). The polyanionic entity $[H_3Cr_2As_2W_{12}O_{52}]^{11-}$ consists of two equivalent hexatungstate moieties $\{(AsW_6O_{21})(AsO_3)\}$, which then sandwich two Cr$^{III}$ centers bridged by four “planar” Cr–O–W and two ‘axial’ Cr–O–X bridges. Each moiety consists of two $\{W_3O_{13}\}$ triads fused together through corner-sharing and the uppermost $\{AsO_3\}$ group, with both units stabilized by the central triangular pyramid $\{AsO_3\}$ group, which is previously unreported building block. Therefore this structure results in a $C_{2h}$ point-group symmetry with a $C_2$ axis passing through the two Cr$^{III}$ centers. (Fig.3.31).
Table 3.10 Crystal data for Na$_{11}$[H$_3$Cr$_2$(AsW$_6$O$_{23}$)$_2$(AsO$_3$)$_2$]·45H$_2$O (5).

<table>
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<th>Compound</th>
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<tbody>
<tr>
<td>Formula</td>
<td>Na$_{11}$[H$_3$Cr$_2$(AsW$<em>6$O$</em>{23}$)$_2$(AsO$_3$)$_2$]·45H$_2$O</td>
</tr>
<tr>
<td>Formula weight, g/mol</td>
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</tr>
<tr>
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<tr>
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<td>I &gt; 2\sigma(I)</td>
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<tr>
<td>wR$_2$(all data)$^{[b]}$</td>
<td>0.1107</td>
</tr>
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</table>

[a] $R = \sum|F_0| - |F_c|/\sum|F_0|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

The central Cr$^{III}$ ion adopts a distorted octahedral geometry with three different types of $\mu$-oxo bridges: two from four {WO$_6$} octahedra of the {W$_3$O$_{13}$} triads (Cr–O, 1.961(5)–1.987(5) Å) and one from the hetero group AsO$_3$ (Cr–O, 2.008(8) Å). Throughout the structure of 5a, three kinds of W–O bond lengths fall within the
anticipated ranges for the different types of oxo ligands with an increasing trend: terminal (1.725(2)–1.799(5) Å), $\mu_2$-bridging (1.883(5)–2.030(9) Å), and $\mu_4$-bridging (2.323(4)–2.353(4) Å). The As$^{III}$–O bond lengths of 1.766(9)–1.799(5) Å in the central group and 1.755(7)–1.780(5) Å in the terminal group are as anticipated. In the solid state, the polyanions are surrounded by sodium countercations, which in turn coordinate to crystal water molecules. (Fig.3.32).

Fig.3.31 Combined polyhedral and ball-and stick representation of polyanions 5a. Color code: As (pink), Cr (green), O (red), {WO$_6$} blue octahedra.
3.5.2.2 Thermogravimetric Analysis

The thermal analysis of the sodium-salt 5 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 200 °C and involving loss of 45 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 17.97 (18.0)]. The second weight loss occurs between 200 and 500 °C, corresponding to the further loss of two arsenic groups {AsO$_3$} per formula unit [% calc. (found): 5.45 (5.5)].
Fig. 3.33 Thermogram curve for 5 from room temperature to 1000 °C.

3.5.3 Conclusions

We have prepared the first examples of di-Cr\textsuperscript{III}-containing tungstoarsenate(III), [H\textsubscript{3}Cr\textsubscript{2}As\textsubscript{4}W\textsubscript{12}O\textsubscript{52}]\textsuperscript{11-} (5a), by reaction of the composing elements in sodium acetate medium. The compound 5 was fully characterized by IR spectroscopy, single-crystal XRD, elemental and thermal analysis. The SQUID measurement is underway. Polyanion 5a comprises two octahedrally coordinated Cr\textsuperscript{III} ions, sandwiched by two \{As\textsubscript{2}W\textsubscript{6}\} units, which adds a novel type of sandwich-type POM. This once again demonstrate that the remarkable effect of hetero templates in the isolation of new POMs archetypes. More importantly, the synthetic procedure which we discovered here allow us to expand this story. Possibly, the \{As\textsubscript{2}W\textsubscript{6}\} units present in 5a could be used as building blocks for other POMs. The embedded Cr\textsuperscript{III} ions could be substituted by other transition metal ions, which have great potential to explore the magnetic properties of such type structure.
3.6 Synthesis and Structure of Anderson-Evans Hexatungstochromate(III), \([\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]^{6-}\) (6a)

\[\text{Cr}^{3+} + 6\text{WO}_4^{2-} + 3\text{H}^+ \xrightarrow{\text{H}_2\text{O}} [\text{H}_3\text{Cr}^{\text{III}}\text{O}_6\text{W}_6\text{O}_{18}]^{6-}\] (6a)

3.6.1 Synthesis of \(\text{Na}_6[\text{H}_3\text{Cr}^{\text{III}}\text{W}_6\text{O}_{24}]\cdot22\text{H}_2\text{O}\) (6)

*Method 1*: A sample of \(\text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O}\) (0.20 g, 0.50 mmol) was dissolved in 20 mL of 1 M sodium acetate solution at pH 6.9, followed by addition of \(\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O}\) (0.99 g, 3 mmol). The mixture was stirred for 1 h at 80°C, allowed to cool to room temperature, and then filtered (final pH 8). Slow evaporation at room temperature led to the formation of green crystals of 6 within three days (yield 0.15 g, 14% based on Cr). IR (cm\(^{-1}\)): 947 (m), 880 (s), 656 (s), 559 (w), 511 (m), 440 (m). Anal. Calcd (Found): Na 6.71 (7.15), W 53.65 (53.76), Cr 2.53 (2.69). Mw = 2076.4 g/mol.

*Method 2*: A sample of \(\text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O}\) (0.40 g, 1 mmol) was dissolved in 20 mL of 0.5 M sodium acetate solution at pH 6, followed by addition of \(\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O}\) (2.64 g, 8 mmol). The mixture was stirred for 1 h at 80°C, allowed to cool to room temperature, and then filtered (final pH 8). Slow evaporation at room temperature led to the formation of green crystals of 6 within two days (yield 0.4 g, 19% based on Cr). The identity of 6a was established by XRD and IR.
3.6.2 Results and Discussion

3.6.2.1 Synthesis and Structure

The novel polyanion \([\text{H}_3\text{Cr}^{III}\text{W}_6\text{O}_{24}]^{6-}\) (6a) was synthesized in a one-pot procedure under conventional “open beaker” conditions, by reaction of Cr(NO\(_3\))\(_3\)·9H\(_2\)O with Na\(_2\)WO\(_4\)·2H\(_2\)O in aqueous NaOAc solution at 80 °C. The results show that the optimal ratio of Cr\(^{3+}\)/WO\(_4\)^{2-} is 1:6 for method 1 and 1:8 for method 2. Apparently, the ratio of Cr\(^{3+}\)/WO\(_4\)^{2-} is equivalent to its stoichiometric ratio in method 1, not for the case of 2. The reason for that is the final pH is crucial for the successful isolation of 6, which should be carefully adjusted to 7.5–8.5. The starting pH in method 1 is 6.9, whereas 6 in method 2, therefore, the excess of Na\(_2\)WO\(_4\)·2H\(_2\)O in method 2 is needed to keep the final pH as in the range of 7.5–8.5.

Single crystal X-ray analysis revealed that \([\text{H}_3\text{Cr}^{III}\text{W}_6\text{O}_{24}]^{6-}\) has the so-called
Anderson-Evans structure, consisting of a ring of six edge-shared WO$_6$ octahedra surrounding the central CrO$_6$ unit (Fig.3.35). Polyanion 6a represents the first Anderson-Evans type heteropolytungstate with a trivalent hetero element. Also, 6a is isostructural with the molybdenum derivative [Cr(OH)$_6$Mo$_6$O$_{18}$]$^{3-}$, first reported in 1970.[74] The central Cr$^{III}$ ion has an almost ideal octahedral coordination environment with the Cr–O distances being in the range of 1.962(5)–2.006(5) Å. These distances are very similar to the ones observed in the molybdenum derivative (Cr–O: 1.968(3)–1.986(3) Å). The W–O distances in 6a can be grouped in three sets, terminal (W=O, 1.722(6)–1.763(6) Å), doubly-bridging (W–O$_b$, 1.916(6)–1.965(5) Å), and triply-bridging (W–O$_c$: 2.094(5)–2.413(5) Å). The same trend has been found in the Anderson-Evans polyanion of [Cr(OH)$_6$Mo$_6$O$_{18}$]$^{3-}$ (see table 3.12). Bond valence sum (BVS) calculations for 6a suggest that the triply bridging $\mu_3$-oxo groups O1CR, O3CR and O5CR are monoprotonated (1.09, 1.18, and 1.22 respectively). Polyanion 6a is tri-protonated, whereas Perloff’s [Cr(OH)$_6$Mo$_6$O$_{18}$]$^{3-}$ is hexa-protonated, which is probably due to the pH differences during synthesis (pH 8 versus 4.5).

Fig.3.35 Polyhedral (left) and ball-and-stick (right) representation of polyanion 6a. The positions of the three oxygens carrying non-disordered protons are indicated. Color code:
W atoms and WO$_6$ octahedra (blue), Cr atom and CrO$_6$ octahedron (green), O atoms (red).

Table 3.11 Crystal data for Na$_6$[H$_3$Cr$^{III}$W$_6$O$_{24}$]·22H$_2$O (6).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Na$_6$[H$_3$Cr$^{III}$W$<em>6$O$</em>{24}$]·22H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight, g/mol</td>
<td>2076.4</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>11.6313(10)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>12.3305(11)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>16.5066(13)</td>
</tr>
<tr>
<td>$\alpha$, °</td>
<td>68.336(2)</td>
</tr>
<tr>
<td>$\beta$, °</td>
<td>85.209(2)</td>
</tr>
<tr>
<td>$\gamma$, °</td>
<td>71.109(3)</td>
</tr>
<tr>
<td>Volume, Å$^3$</td>
<td>2079.9(3)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$D_{\text{calc}}$, g/cm$^3$</td>
<td>3.316</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>16.962</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>1898</td>
</tr>
<tr>
<td>Crystal size, mm</td>
<td>0.24 x 0.19 x 0.18</td>
</tr>
<tr>
<td>Theta range for data collection, °</td>
<td>3.491 – 27.877</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>64511</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9767</td>
</tr>
<tr>
<td>R(int)</td>
<td>0.0435</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.064</td>
</tr>
<tr>
<td>$R$,</td>
<td>[I &gt; 2$\sigma$(I)]$^{[a]}$</td>
</tr>
<tr>
<td>wR$_2$ (all data)$^{[b]}$</td>
<td>0.1041</td>
</tr>
</tbody>
</table>

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

In 1948, Evans[167] reported the first example by determining the structure of
[TeMo₆O₂₄]⁶⁻, which had originally been proposed by Anderson in 1937.[1] To date, a large number of Anderson-Evans type polyanion derivatives [HₓXM₆O₂₄]ᵐ⁺ (M = W, Mo) is known, with many different p- and d- block elements acting as octahedrally coordinated hetero groups XO₆, with the oxidation states for X ranging from +2 to +6. The structural characterized tungsten-based derivatives [HₙX₉W₆O₂₄]ᵐ⁻ include the following hetero elements: Te⁶⁺,[22] Sb⁵⁺,[21, 168] V⁵⁺[169], Pt⁴⁺,[170-172] Mn⁴⁺,[23] Ni⁴⁺,[173] Ni²⁺,[174, 175] and Mn²⁺.[168] On the other hand, the molybdate family [HₙXMo₆O₂₄]ᵐ⁻ is known for the following hetero elements: I⁷⁺,[176-178] Te⁶⁺,[1, 167] Sb⁵⁺,[179] V⁵⁺,[180] Pt⁴⁺,[181-186] Pd⁴⁺[187] Al³⁺,[188-191] Cr³⁺,[74, 75, 192-194] Fe³⁺,[189] Co³⁺,[189, 195] Ga³⁺,[196] Rh³⁺,[197] Mn²⁺,[189] Co²⁺,[188, 198-200] Ni²⁺,[189, 201] Cu²⁺,[202] Zn²⁺.[189, 203] There are some reports on mixed addenda Anderson-Evans ions, such as [Ni²⁺(OH)ₓMo₆₋ₓW₆ₓO₁₈]⁴⁺,[204] which was reinvestigated by Miwa’s group.[189]

It has been demonstrated that organic functionalities can be attached to one or both sides of the Anderson-Evans framework, in particular by the groups of Hasenknopf,[205-208] Cronin,[209, 210] Wang,[211, 212] Wei,[213, 214] Wu,[215, 216] and Song,[217, 218].

Table 3.12 Comparison of bond lengths between [H₃Cr³⁺W₆O₂₄]⁶⁻ and [Cr(OH)ₓMo₆O₁₈]³⁺.

<table>
<thead>
<tr>
<th></th>
<th>[H₃Cr³⁺W₆O₂₄]⁶⁻</th>
<th>[Cr(OH)ₓMo₆O₁₈]³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths /Å</td>
<td>Average bond</td>
<td>Bond lengths /Å</td>
</tr>
<tr>
<td></td>
<td>length /Å</td>
<td></td>
</tr>
<tr>
<td>Cr–O</td>
<td>1.962(5) – 2.006(5)</td>
<td>1.982</td>
</tr>
</tbody>
</table>

93
In the solid state lattice of 6, individual polyanions are surrounded by five Na\(^+\) ions through six terminal O atoms. Two nearest neighboring polyanions are linked by two Na(1) ions, and the distance between the two central Cr atoms of the neighboring polyanions is about 6.771(4) Å. Moreover, the two neighboring \([\text{H}_3\text{Cr}^{III}\text{W}_6\text{O}_{24}]^{6-}\) polyanions further link with other Na\(^+\) ions to can extend to a 3D structure.

Fig. 3.36 Solid state lattice of 6 showing the polyanions being surrounded by Na\(^+\) counter cations (large pink balls). Water molecules are shown as small red balls, and the Na\(^+\)···OH\(_2\) interactions as dashed lines. Notice that not all Na\(^+\) ions could be found by single crystal XRD (see text for details).

### 3.6.2.2 Fourier-transform infrared spectrum (FTIR)

The Fourier transform infrared (FTIR) spectrum of 1a shows a fingerprint region characteristic for the tungsten-oxo framework. The bands at about 947 cm\(^{-1}\) and 880 cm\(^{-1}\)
arise from the antisymmetric stretching vibrations of the terminal W=O bonds and Cr–O–W bridges, respectively. The strong band at approximately 656 cm⁻¹ is associated with the antisymmetric stretching of the W–O–W bridges, whereas medium peak at 511 cm⁻¹ and a weak peak at 559 cm⁻¹ correspond to bending vibrations of W–O–W bridges. Medium to strong band at around 440 cm⁻¹ originate from the bending vibrations of the Cr–O–W bridges.

3.6.2.3 Thermogravimetric Analysis

The thermal analysis of the sodium-salt 6 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 240 °C and involving loss of 22 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 17.2 (17.2)].

Fig. 3.37 Thermogram for 6 from room temperature to 800 °C.
3.6.3 Conclusions

The Cr$^{III}$-containing hexatungstate $[\text{H}_3\text{Cr}^{III}\text{W}_6\text{O}_{24}]^{6-}$ (6a) has been prepared by simple, one pot reaction of $\text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O}$ in sodium acetate medium. Polyanion 6a represents the first chromium-derivative of the Anderson-Evans-type heteropolytungstate family. The title compound was characterized in the solid state by IR spectroscopy, single-crystal XRD, elemental and thermal analyses. As we know, Anderson-Evans-type structures could be used as building block to attach additional metal-oxo units onto these basic sites. What the project, in the long run, is profound.
4. Results: Synthesis and Structure of Hexa, Hepta, Octa-
heteropolytungstates

The terminal and bridging oxygen of saturated POMs are very difficult to be activated. Therefore, one class of lacunary POMs with polydentate oxygen donor accommodating metal ions has opened up a new path for POMs functionalization. Of the potential lacunary POMs, monovant \( \{XW_{11}\} \) and \( \{X_2W_{17}\} \), divacant \( \{XW_{10}\} \), trivacant \( \{XW_9\} \) and \( \{X_3W_{15}\} \), and multivacant derivatives \( \{X_2W_{12}\} \) and \( \{X_8W_{48}\} \) (\( X = P, \ As, \ Si, \ Ge, \) etc.), are comprehensively studied due to the fact that these building blocks can be linked to form various POMs structures. However, priori design and discovery of new types of low nuclearity POM clusters that fall outside these precursors remain a great challenge. The highly vacant hexa, hepta, octametalate subunits are very few in POM literature. Moreover, the sandwich-type POMs composed of lacunary POMs and metal ions form an important sub-family with brilliant prospects. Various nuclearities and topologies of encapsulated metal ions ranging from mononuclear to heptanuclear between the sandwich POMs have been recorded by Kortz, Yamase, Wang et al.[37, 134-142] However, no sandwich-type structure constructed by the unusual hexatungstate \( \{AsW_6\} \) or octatungstate unit \( \{XW_8\} \) (\( X = Si, \ Ge \)) has been reported so far.

To understand structure-activity relationship of POMs is still a challenge because the self-assembly processes of a certain structure are affected and controlled by many complex parameters, such as synthesis strategies, reaction conditions, and
crystallization methods.[219, 220] In the last two decades, many novel POMs were prepared by different synthesis methods like the conventional synthesis, hydrothermal synthesis, ionic liquid method, solid state reaction route, liquid phase contact reaction, microwave, photochemical, and electrochemical method,[58, 221-223] which could be summarized as two architectural principles and strategy, the conventional bottom-up, one pot solution synthesis and the building block self-assembly synthesis. In recent years, many interesting novel POMs were prepared by building block method that involves preformed lacunar keggin as secondary building units and incorporated transition metal ions. In comparison, much less new POMs were prepared by conventional bottom-up one pot reaction in self-assembly of simple oxoanions, the necessary heteroatom and metal ions. The advantage is that they have more chances to obtain novel structures and they are relatively easy to operate.

Following the newly developed synthetic strategy that we discovered here, it is possible to isolate some other novel polyanions comprising hexa-, hepta-, and octaheteropolytungstates by substituting Cr ions to other s, p, d-block metal ions. According to the structural type described in Chapter 3, compounds 1 - 5 can be abbreviated as three breeds: Type A \{MXW_7\} (X = P^V, As^V); Type B \{M_2(XW_8)_2\} (X = Si^{IV}, Ge^{IV}); Type C \{M_2(As^{III}W_6)_2\}.

The ability to study other transition metals, such as Fe^{III}, Mn^{II}, Mn^{III}, Co^{II}, Ni^{II}, Cu^{II} ions in such well-defined and magnetically isolated environments, combined with the recent discovery of the fact that Cr^{III} ions coordinated by similar polyoxotungstate ligands are characterized by unusually large magnetic anisotropy, provided the impetus for synthesizing magnetic POMs analogue of type A \{MXW_7\}. Magnetic studies of type A are of fundamental theoretical importance since the paramagnetic ions sit in a
well-defined oxo-ligand environment, which is sterically protected and magnetically isolated by the large lacunary polyoxotungstate ligands. In essence, these compounds provide a platform for studying the magnetism of A type structure at the single ion level. Such compounds are particularly suitable for EPR spectroscopic studies since the lack of magnetic interactions leads to narrow spectral line widths. The interest of studying type B \( \{M_2(XW_8)_2\} \) (\( X = \text{Si}^{IV}, \text{Ge}^{IV} \)) is due to its high stability, which has exhibited interesting antidiabetic and anticancer activities in compounds 3 and 4. Substantially, type B compounds not only provide a platform for their biological study, but also show interesting magnetic properties. The value of studying type C \( \{M_2(\text{As}^{III}W_6)\} \) could also extend into the magnetic field because two or more paramagnetic ions incorporated in a POM could be regarded as exchange-coupled centers.

4.1 General Methods and Materials

All chemicals were commercially purchased and used in this study without further purification. Infrared spectra were recorded on a Nicolet Avatar 370 FT-IR spectrophotometer using KBr pellets. The following abbreviations were used to assign the peak intensities: \( w = \) weak; \( m = \) medium; \( s = \) strong; \( br = \) broad. Thermogravimetric analyses were carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL/min flow of nitrogen; the temperature was ramped from 20 to 800 °C/1000 °C at a rate of 5 °C/min. Elemental analyses were performed by CNRS, Service Central d’Analyse, Solaize, France. Temperature-dependent magnetic susceptibility measurements were made using a Quantum Design MPMS-XL SQUID magnetometer (see Chapter 3.1) over a temperature range of 300 K to 1.8 K at a measuring field of 0.01 T. The powdered samples were contained in a gel capsule and fixed in a non-
magnetic sample holder. The data were corrected for the diamagnetic contribution of the sample holder and the gel capsule. The molar susceptibility data were corrected for the diamagnetic contribution using Pascal’s constants.[102, 163] Magnetization measurements at variable temperature and variable field (VTVH) were performed at 1, 2, 3, 4, and 5 T over the temperature range of 300 K to 1.8 K. Variable-temperature Electron paramagnetic resonance (EPR) spectra between 290 K and 140 K were recorded on a Bruker E500 spectrometer (see Chapter 3.1). Low-temperature (4-295 K) high-frequency EPR measurements (240 GHz) were conducted at the Florida State University National High Magnetic Field Laboratory (FSU-NHMFL) in Tallahassee, FL. In all measurements the magnetic field was calibrated using a DPPH standard (g = 2.0036), as discussed in chapter 3.1.

4.2 X-ray Crystallography

Single crystals were mounted on a Hampton cryoloop in light oil for data collection at 100 K. Indexing and data collection were measured on a Bruker D8 SMART APEX II CCD diffractometer with kappa geometry [graphite monochromator, \( \lambda(\text{Mo }K\alpha) = 0.71073 \) Å. Data integration was performed using SAINT.[90] Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using SADABS.[91] Direct methods (SHELXS) successfully located the tungsten atoms, and successive Fourier syntheses (SHELXL) revealed the remaining atoms.[91] Refinements were full- matrix least-squares against \(|F|^2\) using all data. In the final refinement, the Fe, Ni, Mn, Ga, In, W, P, As, and Na atoms were refined anisotropically, whereas the O atoms were refined isotropically.
4.3 Mononuclear Containing Polytungstophosphate Family based on \{XW_7\} Building Blocks, \([M(HP^VW_7O_{28})_2]^{n-}\) (M = Fe (7a), Mn (8a), Ga (9a), In(10a), Mg (11a))

\[
\begin{align*}
\text{Fe}^{3+} + 2\text{PO}_4^{3-} + 14\text{WO}_4^{2-} + 18\text{H}^+ &\quad \xrightarrow{\text{H}_2\text{O}} \quad [\text{Fe}^{\text{III}}\text{O}_4\text{H}_2(\text{PO}_4)_2(\text{W}_7\text{O}_{21})_2]^{13-} + 8\text{H}_2\text{O} (7a) \\
\text{Mn}^{3+} + 2\text{PO}_4^{3-} + 14\text{WO}_4^{2-} + 18\text{H}^+ &\quad \xrightarrow{\text{H}_2\text{O}} \quad [\text{Mn}^{\text{III}}\text{O}_6\text{H}_2(\text{PO}_4)_2(\text{W}_7\text{O}_{21})_2]^{13-} + 8\text{H}_2\text{O} (8a) \\
\text{Ga}^{3+} + 2\text{PO}_4^{3-} + 14\text{WO}_4^{2-} + 18\text{H}^+ &\quad \xrightarrow{\text{H}_2\text{O}} \quad [\text{Ga}^{\text{III}}\text{O}_6\text{H}_2(\text{PO}_4)_2(\text{W}_7\text{O}_{21})_2]^{13-} + 8\text{H}_2\text{O} (9a) \\
\text{In}^{3+} + 2\text{PO}_4^{3-} + 14\text{WO}_4^{2-} + 18\text{H}^+ &\quad \xrightarrow{\text{H}_2\text{O}} \quad [\text{In}^{\text{III}}\text{O}_6\text{H}_2(\text{PO}_4)_2(\text{W}_7\text{O}_{21})_2]^{13-} + 8\text{H}_2\text{O} (10a) \\
\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 14\text{WO}_4^{2-} + 18\text{H}^+ &\quad \xrightarrow{\text{H}_2\text{O}} \quad [\text{Mg}^{\text{II}}\text{O}_6\text{H}_2(\text{PO}_4)_2(\text{W}_7\text{O}_{21})_2]^{14-} + 8\text{H}_2\text{O} (11a)
\end{align*}
\]

4.3.1 Synthetic Procedures

4.3.1.1 Synthesis of \(\text{Na}_{13}\)[Fe^{III}(HP^VW_7O_{28})_2] \cdot 42\text{H}_2\text{O} (7)

A sample of Fe(NO\text{3})_3 \cdot 9\text{H}_2\text{O} (0.1 g, 0.25 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of 85\% \text{H}_3\text{PO}_4 (70 \mu\text{L}, 1.0 mmol) and \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} (1.65 g, 5 mmol). The mixture was later stirred for 1 h at 80°C. Then after cooling to room temperature and filtration the obtained pH was 8. Slow evaporation of the solution at room temperature led to the formation of yellow crystals of 7 within one week. (yield 0.5 g, 43% based on Fe). IR (cm\(^{-1}\)): 1071 (s), 1010 (m), 942 (s), 914 (w), 682 (s,br) 523 (m), 439 (w). Elemental analysis \% calc. (found): Na 6.43 (6.47), Fe 1.20 (1.17), P 1.33 (1.32), W 55.40 (55.39). Mw = 4645.04 g/mol.
4.3.1.2 Synthesis of Na$_{13}$[Mn$_{13}$ (HP$^\text{V}$W$_{28}$O$_{88}$)$_2$]·43H$_2$O (8)

A sample of Mn$_{13}$ (CH$_3$COO)$_3$·2H$_2$O (0.13 g, 0.5 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of 85% H$_3$PO$_4$ (85 µL, 1.2 mmol) and Na$_2$WO$_4$·2H$_2$O (1.65 g, 5 mmol). The mixture was later stirred for 1 h at 80°C. Then after cooling to room temperature and filtration the obtained pH was 8. Slow evaporation of the solution at room temperature led to the formation of green crystals of 8 within three days. (yield 0.34 g, 15% based on Cr). IR (cm$^{-1}$): 1103 (m), 1070 (m), 1009 (w), 942 (s), 904 (s), 670 (s,br), 517 (s). Elemental analysis % calc. (found): Na 6.41 (6.57), Mn 1.18 (1.23), P 1.33 (1.34), W 55.20 (54.91). Mw = 4662.15 g/mol.
4.3.1.3 Synthesis of Na$_{13}$[Ga$^{III}$](HP$^V$W$_7$O$_{28}$)$_2$·48H$_2$O (9)

A sample of Ga(NO$_3$)$_3$ (0.13 g, 0.5 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of 85% H$_3$PO$_4$ (85 µL, 1.2 mmol) and Na$_2$WO$_4$·2H$_2$O (1.65 g, 5 mmol). The mixture was later stirred for 1 h at 80°C. Then after cooling to room temperature and filtration the obtained pH was 8. Slow evaporation of the solution at room temperature led to the formation of colorless block crystals of 9 within three days. (yield 0.46 g, 19% based on Ga). IR (cm$^{-1}$): 1079 (s), 1014 (m), 942 (s), 920 (m), 895 (w), 853 (w), 787 (w), 691 (s,br) 525 (s). Elemental analysis % calc. (found): Na 6.25 (6.56), Ga 1.46 (1.46), P 1.29 (1.32), W 53.78 (53.4). Mw = 4767.01 g/mol.

4.3.1.4 Synthesis of Na$_{13}$[In$^{III}$](HP$^V$W$_7$O$_{28}$)$_2$·44H$_2$O (10)

A sample of InCl$_3$ (0.11 g, 0.5 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of 85% H$_3$PO$_4$ (85 µL, 1.2 mmol) and Na$_2$WO$_4$·2H$_2$O (1.65 g, 5 mmol). The mixture was later stirred for 1 h at 80°C. Then after cooling to room temperature and filtration the obtained pH was 8. Slow evaporation of the solution at room temperature led to the formation of colorless block crystals of 10 within one week. (yield 0.12 g, 5% based on In). IR (cm$^{-1}$): 1081 (s), 1014 (m), 942 (s), 911 (w), 892 (w), 688 (s,br) 519 (m), 439 (w). Elemental analysis % calc. (found): Na 6.31 (6.72), In 2.42 (2.55), P 1.30 (1.27), W 54.29 (54.29). Mw = 4740.05 g/mol.
4.3.1.5 Synthesis of Na$_{14}$[Mg$^{II}$$(HP^{V}W_{28}O_{7})_2$]·44H$_2$O (11)

A sample of MgCl$_2$·6H$_2$O (0.1 g, 0.5 mmol) was first dissolved in 20 mL of sodium acetate buffer (0.5 M, pH 4.8) followed by the addition of Na$_3$PO$_4$ (0.5 g, 3 mmol) and Na$_2$WO$_4$·2H$_2$O (1.32 g, 4 mmol). The mixture was later stirred for 1 h at 80°C. Then after cooling to room temperature and filtration the obtained pH was 8. Slow evaporation of the solution at room temperature led to the formation of green crystals of 11 within three days. (yield 0.5 g, 19% based on W). IR (cm$^{-1}$): 1107 (s), 1076 (w), 1009 (w), 931 (s), 898 (m), 869 (w), 802 (w), 695 (s,br), 524 (m). Elemental analysis % calc. (found): Na 6.89 (7.00), Mg 0.52 (0.52), P 1.33 (1.37), W 55.08 (54.71). Mw = 4672.52 g/mol.

Fig.4.2 Polyhedral (a) and ball-and-stick (b) representation of polyanions 8a. Color code: P (yellow), W (blue), Mn (dark brown), O (red).
4.3.2 Results and discussion

4.3.2.1 Synthesis and Structure

As mentioned in Chapter 3.1, the discovery of two mononuclear chromium$^{III}$-containing heteropolytungstates that exhibit unusually large magnetic anisotropy provided the impetus for synthesizing the similar polyoxotungstate compounds by changing the central atom to study their properties. We present here five s, p, d-block metal substituted heptatungstophosphates, $\text{Na}_{13}[\text{Fe}^{III}(\text{HP}^{V}\text{W}_{7}\text{O}_{28})_{2}]\cdot42\text{H}_{2}\text{O}$ (7), $\text{Na}_{13}[\text{Mn}^{III}(\text{HP}^{V}\text{W}_{7}\text{O}_{28})_{2}]\cdot43\text{H}_{2}\text{O}$ (8), $\text{Na}_{13}[\text{Ga}^{III}(\text{HP}^{V}\text{W}_{7}\text{O}_{28})_{2}]\cdot48\text{H}_{2}\text{O}$ (9), $\text{Na}_{13}[\text{In}^{III}(\text{HP}^{V}\text{W}_{7}\text{O}_{28})_{2}]\cdot44\text{H}_{2}\text{O}$ (10), $\text{Na}_{14}[\text{Mg}^{III}(\text{HP}^{V}\text{W}_{7}\text{O}_{28})_{2}]\cdot44\text{H}_{2}\text{O}$ (11) by interaction of the respective hetero group ($\text{H}_{3}\text{PO}_{4}/\text{Na}_{3}\text{PO}_{4}$) with respective $\text{Fe}^{III}(\text{NO}_{3})_{3}\cdot9\text{H}_{2}\text{O}$, $\text{Mn}^{III}(\text{CH}_{3}\text{COO})_{3}\cdot2\text{H}_{2}\text{O}$, $\text{Ga}^{III}(\text{NO}_{3})_{3}$, $\text{In}^{III}\text{Cl}_{3}$, $\text{Mg}^{II}\text{Cl}_{2}\cdot6\text{H}_{2}\text{O}$ and $\text{Na}_{2}\text{WO}_{4}\cdot2\text{H}_{2}\text{O}$ in aqueous NaOAc solution at 80 °C. Polyanions 7a - 11a comprise an octahedrally coordinated single metal ion, sandwiched by two $\{\text{PW}_{7}\}$ units. The successful synthesis of 7a - 11a requires careful control of the final pH, temperature and choice of solvent, the same as 1a and 2a described in Chapter 3.1. Surprising, the synthetic procedure we discovered here could be used for almost the whole elements in periodic table. Such work is underway.
### Table 4.1 Crystal data for 7 - 11.

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<thead>
<tr>
<th></th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
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<td><strong>Empirical formula</strong></td>
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<td>Na$<em>{13}$MnP$<em>2$W$</em>{14}$O$</em>{98}$H$_8$</td>
<td>Na$<em>{13}$GaP$<em>2$W$</em>{14}$O$</em>{98}$H$_8$</td>
<td>Na$<em>{13}$InP$<em>2$W$</em>{14}$O$</em>{98}$H$_8$</td>
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<td>2032</td>
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<td>9592</td>
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<tr>
<td><strong>R1[I &gt; 2σ(I)][a]</strong></td>
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[a] $R = \Sigma |F_o| - |F_c|/\Sigma |F_o|$. [b] $R_w = \left[ \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2 \right]^{1/2}$.

Crystallographic structural analysis revealed that 7a - 11a are isomorphous, both crystallizing in the triclinic space group Pǐ (see Table 4.1). Therefore, only the polyanion 8a is discussed here. The polyanionic entities [Mn$^{III}$(HP$^V$W$_7$O$_{28}$)$_2$]$^{13-}$ consist of two equivalent heptatungstophosphate moieties [HPW$_7$O$_{28}$]$^{8-}$, which are arranged almost orthogonally to each other and linked via a single Mn$^{III}$ ion through four ‘planar’ Cr–O–W and two ‘axial’ Cr–O–X bridges. Each moiety consists of a {W$_3$O$_{13}$} triad.
linked to an edge-shared half-ring \{W_4O_{10}\} via corner-sharing, with both units stabilized by the central \{PO_4\} group. In the \{W_3O_{13}\} triad, three edge-shared WO_6 octahedra are aggregated together by sharing one central O atom, leaving one terminal O atom at each WO_6 octahedron. In the \{W_4O_{19}\} unit, four edge-shared WO_6 octahedra are assembled together without sharing a common O atom, leaving two cis-related terminal O atoms at each WO_6 octahedron. Therefore, these newly obtained polyanions comply with the Lipscomb principle,[17] which states that no MO_6 octahedra in a POM have more than two unshared oxygens. This structure results therefore in a C_{2h} point-group symmetry, with the C_2 axis passing through the Mn^{III} center (Fig.4.2).

![Fig.4.3 Representation of polyanion 8a and its surrounding Na^+ counter cations (large rose balls). Water molecules are shown as small red balls, and the Na^+···OH_2 interactions as dashed lines.](image)

Structural analysis and bond valence sum (BVS) calculations for 8 suggest that the
double-bridging $\mu_2$-oxo group at O34A is monoprotonated with W–O bond length of 2.182(2) and 2.168(8) Å and a BVS of 0.9960, which is the value expected for a hydroxo group. This gives a total charge of $-13$ for 7a - 10a, and $-14$ for 11a, which is stabilized in the solid state by sodium countercations (Fig.4.3).

**4.3.2.2 Magnetic Studies**

(The magnetic studies were performed by our collaborators Prof. Dr. Naresh S. Dalal, Florida State University, USA.)

The magnetic susceptibility of powder samples of both compounds was measured over the temperature range of 1.8 K to 300 K. The effective magnetic moment of 7 (Fig. 4.4a) was 6.38 $\mu_B$ over most of the measured temperature range, which is somewhat higher than the spin only magnetic moment of an $S=5/2$ system, i.e. Fe$^{III}$ with $g = 2$ (5.92 $\mu_B$). The effective magnetic moment of 8 (Fig.4.4b) was 5.25 $\mu_B$ over most of the measured temperature range, which is slightly higher than the spin only magnetic moment of an $S=2$ system i.e. Mn$^{III}$ with $g = 2$ (4.89 $\mu_B$). In both cases we attribute the slightly elevated $\mu_{\text{eff}}$ values to orbital contributions to the magnetic moment. The observation that the magnetic center of both compounds is in the $+3$ oxidation state is consistent with bond-valence sum calculations, and with previous studies of similar Cr$^{III}$ compounds (vide supra).[129] In both 7 and 8 the magnetic moment decreases sharply below 20 K, indicating there are interactions within the each compound, namely spin-spin and spin-orbit coupling, since the intermolecular M–M distance in both compounds is substantial ($\approx 10$ Å) and thus likely rules out the possibility of intermolecular magnetic exchange. Thus, the magnetic properties of both compounds were evaluated using the standard spin Hamiltonian with axial zero-field splitting: $\mathcal{H} = \beta \mathcal{H} \cdot g \cdot S +$
The experimental data were well simulated using the magnetic parameters: $S = \frac{5}{2}$ $g_{\text{average}} = 2.17$, and $|D| = 3.6 \text{ cm}^{-1}$ for 7 and, $S = 2$ $g_{\text{average}} = 2.08$ and $|D| = 6.0 \text{ cm}^{-1}$ for 8. The hyperfine (hf) term was neglected because no hf splitting was discernible in the EPR spectra of Fe$^{\text{III}}$ and the simulation was not sensitive to the small hyperfine energy observed in the EPR of Mn$^{\text{III}}$ (vide infra).

Fig.4.4 The effective magnet moment of 7 and 8 are shown as a function of temperature (black circles). (a) $\mu_{\text{eff}}$ remains constant around 6.38 $\mu_B$ above 20 K for 7 (b) $\mu_{\text{eff}}$ remains constant around 5.08 $\mu_B$ above 20 K for 8. The data of 7 is fit using the parameters $S = \frac{5}{2}$ $g_{\text{average}} = 2.17$, and $|D| = 3.6 \text{ cm}^{-1}$. For 8 the data is fit using, $S = 2$ $g_{\text{average}} = 2.08$ and $|D| = 6.0 \text{ cm}^{-1}$.

Since the accuracy of $D$ values obtained from such powder measurements is not guaranteed, magnetization measurements at variable temperature and variable field (VTVH) were performed. VTVH magnetization at 1, 2, 3, 4 and 5 T between 1.8 and 300 K was measured for 7 and 8 and the data were simulated using the same parameters as listed above for the $\mu_{\text{eff}}$ plots. The data of both compounds fit quiet well to their respective magnetic parameters, as shown in Fig.4.5.
Fig. 4.5 Variable-temperature-variable field magnetization measurements of 7 and 8 at 1, 2, 3, 4 and 5 T. The solid lines represent the best fit simulations to the experimental data.

The sign of $D$ is not reliably obtained from such measurements. On the other hand, the data strongly suggest that the magnitude of $D$ in these compounds is uncommonly large for both Mn$^{III}$ [224, 225] and Fe$^{III}$ [225, 226] in an $O_6$ coordination sphere. Typical absolute $D$ values for Fe$^{III}$ octahedral complexes in an $O_6$ coordination sphere range from 0.1683 cm$^{-1}$ to 1.176 cm$^{-1}$ [225, 227, 228]. For Mn$^{III}O_6$ complexes they range from 3.35 cm$^{-1}$ to 4.524 cm$^{-1}$ [224, 225]. To investigate the magnetic parameters of these compounds further, a detailed EPR study was undertaken.

### 4.3.2.3 EPR Measurements

(The EPR measurements were performed by our collaborators Prof. Dr. Naresh S. Dalal, Florida State University, USA.)

The room temperature, X-band (9.4 GHz) powder EPR spectrum of 7 is shown in Fig. 4.6. The spectrum of 7 shows an intense peak around 0.16 T, which corresponds to a $g$ value of 4.27. Additionally there is a small feature at slightly lower fields and a low intensity broad peak at high field around 0.5 T. A DPPH standard (2,2-diphenyl-1-
picrylhydrazyl) was used to calibrate the field and is shown with the spectrum of 7 to demonstrate the significant deviation of the peaks from 7 with $g = 2.0036$. Such a large deviation from $g \sim 2$ suggests that the molecule has significant ZFS, an observation which is consistent with magnetic susceptibility and magnetization analysis (vide supra).

To further investigate the role of $D$ in 7, variable-temperature Q-band (34.5 GHz) EPR was measured between 290 and 140 K (Fig.4.7). At Q-band frequency, three intense peaks are observed between 0.5 T and 0.7 T. Additionally, at $T < 180$ K a small peak begins to appear below 0.2 T. Once again, the observed peaks of 7 appear at a much lower $g$ values than the signal from the DPPH standard. For an $S = 5/2$ system with ZFS, many EPR transitions should become evident if $D < h\nu$, which is clearly not the case here. This suggests that $D$ in these compounds is at least greater than 34 GHz.

Fig.4.6 Room temperature X-band (9.4 GHz) EPR spectrum of 7 (black) and DPPH (red). The significant deviation of the most intense peak in 7 from the DPPH ($g = 2.0036$) signal, suggests the ZFS in this molecule is large.
Repeated efforts to accurately simulate the X and Q-band spectra of 7 were unsuccessful, although the best fit simulations are shown in Fig.4.8. The simulation parameters used were: \( S = \frac{5}{2}, g_x = 1.73, g_y = 1.32, g_z = 3.95, D = 3.6 \text{ cm}^{-1}, \) and \( E/D = 0.046. \) Although the simulations are not a perfect fit to the experimental data, it is clear from the combined results of magnetic susceptibility and EPR that the magnitude of \( D \) appears is \( \approx 3.6 \text{ cm}^{-1}. \)

In systems with more than 3 unpaired electrons, dipole interactions become increasingly more complex, thus the Hamiltonian describing such a system becomes:

\[
\hat{H} = \beta \vec{H} \cdot \vec{g} \cdot \vec{S} + D \left( \vec{S}_z^2 - \frac{\vec{S}^2}{3} \right) + E \left( \vec{S}_x^2 - \vec{S}_y^2 \right) + B_4^0 \vec{O}_4^0 + B_4^2 \vec{O}_4^2 + B_4^4
\]

(4.1)

Where \( B_4^0, B_4^2, B_4^4 \) are higher-order ZFS terms and the \( O_4^m \) terms are operators. In a highly anisotropic \( S = 5/2 \) system like 7, the EPR simulation parameters become \( g_x, g_y, g_z, D, E, B_4^0, B_4^2, \) and \( B_4^4. \) Due to the large number of magnetic parameters, accurate EPR simulations are exceedingly difficult and there is a strong risk of over-parameterization. Thus, we were unable to obtain good fit simulations for 7.
Variable-temperature Q-band (34 GHz) EPR spectrum of 7 and DPPH. The peaks show increased intensity upon cooling, but the relative intensity between peaks remains constant; therefore, it is not possible within the measured temperature range to determine which are ground or excited state transitions. The Q-band spectra show more peaks than X-band, but the absence of a large number of peaks and the significant deviation of the peaks from $g = 2$, implies the zero-field splitting is at least larger than $h\nu$.

Fig. 4.8 (a) Room temperature X-band (9.4 GHz) EPR spectrum of 7 (black) and the best fit simulation (red) using the parameters $S = \frac{5}{2}$, $g_x = 1.73$, $g_y = 1.32$, $g_z = 3.95$, $D = 3.6$ cm$^{-1}$, and $E/D = 0.046$. (b) 140 K Q-band (34 GHz) spectrum of 7 and the best fit simulation using the same parameters as (a).

Variable-temperature high-frequency EPR (240 GHz) was measured between 290 and 5 K in an effort to gain further insight into the magnetic properties of 7. The 10 K and 5 K HF-EPR spectra are shown in Fig. 4.9. The appearance of many EPR peaks at 240 GHz clearly indicates that $D$ is less than the microwave frequency; however, as mentioned above, the complexity of such spectra and the large amount of magnetic parameters, make simulating the spectra very difficult. Nonetheless, these EPR results provide unambiguous proof that $D$ is greater than 34 GHz but less than 240 GHz, a
result consistent with magnetic susceptibility. Furthermore, these results indicate the $D$ in these compounds is larger than any observed for an octahedral Fe$^{III}$ complex with a O$_6$ coordination sphere.[225, 226]

Fig.4.9 EPR spectra of 7 at 5 K and 10 K at 240 GHz. Although the spectra are exceedingly difficult to simulate due to the large number of magnetic parameters, it is evident that the zero-field splitting is less than 240 GHz (8 cm$^{-1}$).

The room temperature X-band (9.4 GHz) powder EPR spectrum of 8 and a DPPH standard is shown in Fig.4.10. As was the case with 7, the EPR peaks are significantly deviated from $g = 2.0036$. The spectrum of 8 also shows 13 peaks due to the $^{55}$Mn hyperfine ($I = 5/2$, $\mu/\mu_N = 3.45$). There appear to be two different sextets of peaks as shown in Fig.4.11a. The first sextet has a hyperfine value, $A_1 = 4.349$ mT ($40.65 \times 10^{-4}$ cm$^{-1}$) and the second sextet has $A_2 = 4.651$ mT ($43.47 \times 10^{-4}$ cm$^{-1}$). The additional feature in the spectrum is likely due to a third unresolved hyperfine sextet, thus suggesting the existence of rhombic symmetry in this molecule. At Q-band (Fig.4.11b) the hyperfine structure of $^{55}$Mn is still evident although the peaks become broader,
presumably due to D-strain and possibly A-strain, from various conformational distributions, which lead to insuperable spectral line broadening. Thus, it becomes difficult to accurately calculate the hyperfine constants at Q-band.

Interestingly, although many EPR studies have been performed on Mn$^{III}$,[224-226] very few examples exist where the hyperfine structure is well resolved. This is unfortunate since many SMMs are comprised of Mn$^{III}$ clusters [229, 230], and the hyperfine interaction is a critical component in quantum tunnelling of magnetization. Thus, the observation and accurate measurement of the hyperfine structure of Mn$^{III}$ is of high importance.

Fig. 4.10 Room temperature X-band (9.4 GHz) spectrum of 8 (black) and DPPH (red). The significant deviation of the peak positions in 8 from $g \sim 2$ suggests the ZFS in this molecule is large.
Fig.4.11 (a) Room temperature X-band (9.4 GHz) spectrum of 8 with the hyperfine structure labeled (red). (b) Room-temperature Q-band (34 GHz) spectrum of 8. The spectrum is noticeably broader at high frequency presumably due to $D$-strain broadening.

Fig.4.12 The room temperature Q-band (34 GHz) spectrum of 8 is shown with the best fit simulation.

To further investigate the role of $D$ in 8 and the broadening of the hyperfine structure at high microwave frequency, HF-EPR was measured at 240 GHz. The spectra at 100 K and 20 K spectra are shown in Fig.4.12. The hyperfine structure is completely
absent at such high frequency; however, it is clear from the presence of 6 peaks that $D$ is less than 240 GHz in this case. Accurate EPR simulations were not obtained due to the large amount of magnetic parameters in this system (vide supra); however, these EPR results provide unambiguous proof that the $D$ in 8 is greater than 34 GHz but less than 240 GHz, a result consistent with magnetic susceptibility. Furthermore, these results seem to indicate the $D$ is larger than any previously reported value for Mn$^{III}$O$_6$ compounds, where the literature values range from 3.35 cm$^{-1}$ to 4.524 cm$^{-1}$.[224, 225] Additionally, to the best of our knowledge, a $|D|$ value of 6.0 cm$^{-1}$ seems to be the highest yet reported for any Mn$^{III}$ single-ion compound [224-226], with the most comparable compound being [Mn$^{III}$(taa)] (taa = tris(1-(2-azolyl)-2-azabuten-4-yl)amine)$^{34}$ where $|D|$ is reported as 5.90 cm$^{-1}$.

![Fig.4.13 HF EPR (240 GHz) spectra at 20 K and 100 K of 8. Accurate simulations could not be obtained due to the large amount of magnetic parameters.](image)
4.3.2.4 Thermogravimetric Analysis

The thermal analysis of the sodium-salt 7 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 200 °C and involving loss of 43 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 16.3 (16.3)].

Fig.4.14 Thermogram for 7 from room temperature to 800 °C.

A weight loss for 8 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 43 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 16.6 (16.7)].
Fig. 4.15 Thermogram for 8 from room temperature to 800 °C.

A weight loss for 9 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 48 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 18.1 (15.2)].

Fig. 4.16 Thermogram for 9 from room temperature to 800 °C.
A weight loss for 10 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 44 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 16.7 (14.5)].

Fig. 4.17 Thermogram for 10 from room temperature to 1000 °C.

A weight loss for 11 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 44 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 16.9 (16.02)].
4.3.3 Conclusions

We have prepared five mononuclear containing polytungstophosphate based on \{PW\_7\} building blocks, \([\text{M(HP}^{V}\text{W}_7\text{O}_{28})_2]^{n-}\) (\(n = 13\), M = Fe (\(7a\)), Mn (\(8a\)), Ga (\(9a\)), In(\(10a\)); \(n = 14\), Mg (\(11a\))), by reaction of the composing elements in sodium acetate medium. All of the compounds were fully characterized in the solid state by IR spectroscopy, single-crystal XRD, elemental and thermal analyses. \(7\) and \(8\) were fully characterized by SQUID and EPR measurements. Attempted to study the NMR spectra, electrochemistry, and biological properties of diamagnetic containing POMs \(9\) – \(11\) were failed due to the low stability in solution. Detailed SQUID and EPR spectroscopic measurements on the hydrated sodium salts showed that the axial zero-field splitting parameter \((D)\) is unexpectedly large at \(\approx 3.6\ \text{cm}^{-1}\) for \(7\) and \(\approx 6.0\ \text{cm}^{-1}\) for \(8\). Although accurate simulation of the EPR spectra was unsuccessful due to the complex nature of these systems, (i.e. highly distorted with S > 3/2) the significant deviation of the main
EPR peaks from $g = 2.0036$, are a clear indicator that $D$ in these compounds is large. The unusually large values of $D$ in 7 and 8 is believed to exist because the M–O bonding in these compounds is strongly modified by the polarizing, highly charged W$^{IV}$ and P$^{V}$ ions. These ions can cause misaligned lone pairs and charge density deviating from the X-ray geometry of the CrO$_6$ core, similar to the results observed in isostructural Cr$^{III}$ compounds (vide supra). The large distortion in the axial direction as well as in the equatorial plane of the MO$_6$ octahedron reduces the gap between the d orbitals and imposes a large trigonal splitting of the metal-centered multiples. This distortion splits the excited state and the splitting reacts back through the spin-orbit coupling to remove the degeneracy of the ground spin states. Future quantum calculations are still needed to support this suggestion.

4.4 Dinuclear Ga$^{III}$ and In$^{III}$ Containing Tungstogermanate Complexes based on \{XW$_8$\} Building Blocks, [M$^{III}_2$(B-$\beta$-Ge$^{IV}$W$_8$O$_{31}$)$_2$]$^{14-}$ (M=Ga (12a), In (13a))

4.4.1 Synthetic Procedures

$$2\text{Ga}^{3+} + 2\text{GeO}_4^{3-} + 16\text{WO}_4^{2-} + 20\text{H}^+ \xrightarrow{\text{H}_2\text{O}} [\text{Ga}^{\text{III}}_2\text{(GeO}_4)\text{W}_{16}\text{O}_{62}]^{14-} + 10\text{H}_2\text{O} \quad (12a)$$

$$2\text{In}^{3+} + 2\text{GeO}_4^{3-} + 16\text{WO}_4^{2-} + 20\text{H}^+ \xrightarrow{\text{H}_2\text{O}} [\text{In}^{\text{III}}_2\text{(GeO}_4)\text{W}_{16}\text{O}_{62}]^{14-} + 10\text{H}_2\text{O} \quad (13a)$$

4.4.1.1 Synthesis of Na$_{14}[\text{Ga}^{\text{III}}_2(\text{B}-\beta\text{-Ge}^{\text{IV}}\text{W}_8\text{O}_{31})_2]\cdot46\text{H}_2\text{O} \quad (12)$

A sample of Ga(NO$_3$)$_3$ (0.13 g, 0.5 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of GeO$_2$ (0.05 g, 0.50 mmol) and Na$_2$WO$_4$·2H$_2$O (1.32 g, 4 mmol). The mixture was later stirred for 1 h at 60°C, then
after cooling to room temperature and filtration the obtained pH was 8.7. Slow evaporation of the solution at room temperature led to the formation of colorless crystals of 12 within one week (yield 0.2 g, 14% based on Ge). IR (cm⁻¹): 936 (s), 809 (w), 775 (s), 721 (s), 636 (w), 464 (m), 428 (w). Elemental analysis % calc. (found): Na 5.8 (5.97), Ga 2.51 (2.65), Ge 2.62 (3.05), W 53.01 (52.72). Mw = 5548.84 g/mol.

4.4.1.2 Synthesis of Na₁₄[In³⁺₂(B-β-Ge⁴⁺W₈O₃₁)₂]·46H₂O (13)

A sample of InCl₃ (0.11 g, 0.5 mmol) was first dissolved in 20 mL of sodium acetate buffer (1M, pH 6) followed by the addition of GeO₂ (0.05 g, 0.50 mmol) and Na₂WO₄·2H₂O (1.32 g, 4 mmol). The mixture was later stirred for 1 h at 60°C, then after cooling to room temperature and filtration the obtained pH was 8.7. Slow evaporation of the solution at room temperature led to the formation of colorless crystals of 13 within two days (yield 0.33 g, 23% based on Ge). IR (cm⁻¹): 936 (s), 823 (m), 767(s), 718 (m), 518 (w), 457 (w). Elemental analysis % calc. (found): Na 5.71 (6.24), In 4.07 (4.19), Ge 2.58 (2.69), W 52.16 (51.42). Mw = 5639.03 g/mol.
4.4.2 Results and discussion

4.4.2.1 Synthesis and Structure

As expected, the polyanions \([\text{Ga}^{III}_2(\text{B-β-Si}^{IV} \text{W}_8\text{O}_{31})_2]^{14+} \) (12a) and \([\text{In}^{III}_2(\text{B-β-Ge}^{IV} \text{W}_8\text{O}_{31})_2]^{14+} \) (13a) self-assembles in the reaction of Ga\(^{III}\) nitrate for 12 or In\(^{III}\) chloride for 13, sodium tungstate, and germanium dioxide at stoichiometric ratio in a sodium acetate buffer (pH 6.0) at 60°C. Variation of the \(\text{M}^{III} : \text{GeO}_2 : \text{Na}_2\text{WO}_4 \) ratios does of influence the composition of the final product. Also the pH is not crucial for the successful synthesis of type B \(\{\text{M}_2(\text{XW}_8)\}_2\) (\(\text{X} = \text{Si}^{IV}, \text{Ge}^{IV}\)). Once again we found that the heteroatom templates are the most distinguishing mark of the isolation of new POMs archetypes.
Crystallographic structural analysis revealed that 12a and 13a are isomorphous, both crystallizing in the triclinic \( P\bar{1} \) space group (see Table 4.2). Therefore, only the structure 13a is discussed here. The polyanionic entities \([\text{In}^{III}_2(B-\beta-\text{Ge}^{IV}\text{W}_8\text{O}_{31})_2]^{14-}\) consist of two equivalent octatungstogermanate moieties \([\text{GeW}_8\text{O}_{31}]^{10+}\), which are sandwiched between two \( \text{In}^{III} \) ion through four ‘planar’ \( \text{In}--\text{O}--\text{W} \) and two ‘axial’ \( \text{In}--\text{O}--\text{Ge} \) bridges. Each moiety consists of two \{W\(_3\)O\(_{13}\)\} triads (see Fig.4.20, W5, W6, W8 as a triad, W1, W2, W7 as a triad) linked to two edge-shared WO\(_6\) octahedra (see Fig.4.20, W3 and W4), with both units are stabilized by the central GeO\(_4\) hetero group. Both molecules possess \( C_{2h} \) point-group symmetry, with the \( C_2 \) axis passing through the metal center, which is positioned between two distorted octahedral \( \text{In}^{III} \) centers. The polyanions are surrounded by sodium countercations, which in turn result into a 3D framework by Na···OH\(_2\) interactions, as shown in Fig.4.21.

![Fig.4.20 Polyhedral (left) and ball-and-stick (right) representation of polyanion 13a. Color code: W atoms and WO\(_6\) octahedra (blue), In atoms (gold), O atoms (red).](image-url)
Table 4.2 Crystal data for 12 and 13.

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[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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Fig. 4.21 Connection of $[\text{In}_2(\text{GeW}_{8}\text{O}_{31})_2]^{14+}$ polyanions into a 3D framework by Na···OH$_2$ interactions.

4.4.2.2 Thermogravimetric Analysis

The thermal analysis of the sodium-salt 12 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 200 °C and involving loss of 46 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 14.9 (15.0)].
A weight loss for 13 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 46 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 14.68 (13.62)].
4.4.3 Conclusions

We have prepared the first examples of dinuclear Ga$^{III}$ and In$^{III}$-containing POMs, [Ga$_2$(GeW$_8$O$_{31}$)$_2$]$^{14-}$ (12a) and [In$_2$(GeW$_8$O$_{31}$)$_2$]$^{14-}$ (13a), by reaction of the composing elements in sodium acetate medium. Both compounds were fully characterized in the solid state by IR spectroscopy, single-crystal XRD, elemental and thermal analysis. Polyanions 12a and 13a consist of two octahedrally coordinated metal centers, sandwiched by two {GeW$_8$} units. In addition to these two new compounds, the Si derivatives could also be obtained, and such work is underway. They are also found to be stable in solution in a wide range of pH 1 – 7. Their biological studies are underway.

4.5 Dinuclear Mn$^{II}$, Fe$^{III}$, Sc$^{III}$, In$^{III}$, and Ti$^{IV}$ Containing Tungstoarsenate(III) Complexes,

\[ [H_3Mn^{II}_2(As^{III}W_6O_{21})_2(As^{III}O_3)_4Na_2(H_2O)_6]^{11-} \] (14a) and

\[ [M_2(As^{III}W_6O_{23})_2(As^{III}O_3)_2]^{n-} (n = 14, M = Fe (15a), Sc (16a), In (17a); n = 14, M = Ti (18a)) \]

4.5.1 Synthetic Procedures

\[ 2Mn^{III} + 6AsO_3^{3-} + 12WO_4^{2-} + 27H^+ \xrightarrow{H_2O} [H_3Mn^{III}_2(AsW_6O_{21})_2(AsO_3)_4]^{11-} + 12H_2O \] (14a)

\[ 2Fe^{III} + 4AsO_3^{3-} + 12WO_4^{2-} + 18H^+ \xrightarrow{H_2O} [H_2Fe^{III}_2(AsW_6O_{21})_2(AsO_3)_4]^{12-} + 8H_2O \] (15a)

\[ 2Sc^{III} + 4AsO_3^{3-} + 12WO_4^{2-} + 18H^+ \xrightarrow{H_2O} [H_3Sc^{III}_2(AsW_6O_{21})_2(AsO_3)_4]^{12-} + 8H_2O \] (16a)

\[ 2In^{III} + 4AsO_3^{3-} + 12WO_4^{2-} + 18H^+ \xrightarrow{H_2O} [H_3In^{III}_2(AsW_6O_{21})_2(AsO_3)_4]^{12-} + 8H_2O \] (17a)

\[ 2Ti^{IV} + 4AsO_3^{3-} + 12WO_4^{2-} + 17H^+ \xrightarrow{H_2O} [H_3Ti^{IV}_2(AsW_6O_{21})_2(AsO_3)_4]^{11-} + 8H_2O \] (18a)
4.5.1.1 Synthesis of Na$_{11}$[H$_3$Mn$^{II}_2$(As$^{III}$W$_6$O$_{21}$)$_2$(AsO$_3$)$_4$]·44H$_2$O (14)

A sample of Mn(CH$_3$COO)$_2$·4H$_2$O (0.061 g, 0.25 mmol) was dissolved in 20 ml NaOAc buffer (1 M, pH 6). Next, As$_2$O$_3$ (0.1 g, 0.5 mmol) and Na$_2$WO$_4$·2H$_2$O (1.32 g, 4 mmol) were added to the solution under constant stirring. The solution was heated for 1 hour at 80°C, resulting in a clear yellowish orange solution. Then, the solution was filtered into a glass vial, and left to crystallize for about a day. The resulting crystals were yellowish orange. (Yield: 0.09 g, 15% based on Mn). IR (cm$^{-1}$): 936 (m), 873 (s), 789 (w), 735 (s), 635 (w), 456 (m), 419 (w). Elemental analysis % calc. (found): Na 5.4 (5.36), As 10.12 (9.61), Mn 2.35 (2.51), W 47.15 (46.43). Mw = 4678.04 g/mol.

4.5.1.2 Synthesis of Na$_{12}$[H$_2$Fe$^{III}_2$(As$^{III}$W$_6$O$_{23}$)$_2$(AsO$_3$)$_2$]·48H$_2$O (15)

A sample of Fe(NO$_3$)$_3$·9H$_2$O (0.05 g, 0.125 mmol) was dissolved in 20 ml NaOAc buffer (0.5 M, pH 6). Next, As$_2$O$_3$ (0.1 g, 0.5 mmol) and Na$_2$WO$_4$·2H$_2$O (1.65 g, 5 mmol) were added to the solution under constant stirring. The solution was heated for 1 hour at 80°C, resulting in a clear reddish orange solution. Then, the solution was filtered into a glass vial, and left to crystallize for about a day. The resulting crystals were reddish orange. (Yield: 0.15 g, 42% based on Fe). IR (cm$^{-1}$): 929 (m), 850 (s), 719 (s), 503 (w), 460 (w). Elemental analysis % calc. (found): Na 6.12 (6.01), W 47.69 (48.06). Mw = 4592.05 g/mol.

4.5.1.3 Synthesis of Na$_{12}$[H$_2$Sc$^{III}_2$(As$^{III}$W$_6$O$_{23}$)$_2$(As$^{III}$O$_3$)$_2$]·39H$_2$O (16)

A sample of Sc(NO$_3$)$_3$·6H$_2$O (0.09 g, 0.3 mmol) was dissolved in 20 ml NaOAc buffer (0.5 M, pH 6). Next, As$_2$O$_3$ (0.1 g, 0.5 mmol) and Na$_2$WO$_4$·2H$_2$O (1.65 g, 5 mmol) were added to the solution under constant stirring. The solution was heated for
30 minutes at 80°C. After the mixture was cooled to room temperature and filtered, the obtained pH was 8. Slow evaporation of the colorless solution at room temperature led to the formation of block crystals of 16 within one day (Yield: 0.36 g, 54% based on Fe). IR (cm⁻¹): 929 (m), 845 (s), 721 (s), 608 (m), 504 (w), 461 (w). Elemental analysis % calc. (found): Na 6.46 (6.26), As 6.89 (6.8), Sc 2.04 (2.08), W 50.04 (49.87). Mw = 4408.14 g/mol.

4.5.1.4 Synthesis of Na₁₂[H₂In⁴⁺(As⁵⁺W₆O₂₃)₂(As⁵⁺O₃)₂]·49H₂O (17)

A sample of InCl₃ (0.055 g, 0.25 mmol) was dissolved in 20 ml NaOAc buffer (1 M, pH 6). Next, As₂O₃ (0.1 g, 0.5 mmol) and Na₂WO₄·2H₂O (1.65 g, 5 mmol) were added to the solution under constant stirring. The solution was heated for 30 minutes at 80°C. After the mixture was cooled to room temperature and filtered, the obtained pH was 8. Slow evaporation of the colorless solution at room temperature led to the formation of block crystals of 16 within one day (Yield: 0.28 g, 47% based on In). IR (cm⁻¹): 930 (m), 854 (s), 725 (s), 621 (w), 501 (m). Mw = 4483.96 g/mol. Elemental analysis % calc. (found): Na 5.97 (5.84), As 6.34 (6.4), In 4.87 (4.86), W 46.65 (46.34). Mw = 4728.01 g/mol.

4.5.1.5 Synthesis of Na₁₁[HTi⁴⁺₂(As⁵⁺W₆O₂₃)₂(As⁵⁺O₃)₂]·41H₂O (18)

A sample of TiOSO₄ (0.05 g, 0.3 mmol) was dissolved in 20 ml NaOAc buffer (1 M, pH 6). Next, As₂O₃ (0.1 g, 0.5 mmol) and Na₂WO₄·2H₂O (1.65 g, 5 mmol) were added to the solution under constant stirring. The solution was heated for 1 hour at 80°C, resulting in a clear reddish orange solution. Then, the solution was filtered into a glass vial, and left to crystallize for about a day. The resulting crystals were reddish orange. (Yield: 0.34 g, 51% based on Ti). IR (cm⁻¹): 940 (m), 877 (m), 827 (w), 707 (s),
618 (m), 502 (w), 444 (m). Elemental analysis % calc. (found): Na 5.73 (5.71), As 7.32 (6.77), Ti 2.42 (2.16), W 49.72 (49.84). Mw = 4425.99 g/mol.

Fig.4.24 IR spectra of compounds 14-18.
Table 4.3 Crystal data for 14 - 18.

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<td>0.0663</td>
<td>0.0380</td>
<td>0.0384</td>
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<td>Goodness-of-fit on F$^2$</td>
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<td>1.075</td>
<td>1.017</td>
<td>1.042</td>
<td>1.007</td>
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<tr>
<td>R1[I &gt; 2σ(I)][a]</td>
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<td>0.0473</td>
<td>0.0418</td>
<td>0.0463</td>
<td>0.0532</td>
</tr>
<tr>
<td>wR2 (all data)[b]</td>
<td>0.0807</td>
<td>0.1908</td>
<td>0.1038</td>
<td>0.1103</td>
<td>0.1304</td>
</tr>
</tbody>
</table>

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

4.5.2 Results and discussion

4.5.2.1 Synthesis and Structure

Compound Na$_{11}$[H$_3$Mn$_2$(As$_6$O$_{21}$)$_2$(As$_3$O$_9$)$_3$]·44H$_2$O (14) crystallizes in the monoclinic symmetry in the space group C2/c. As seen in Fig.4.25, the polyanion 14a...
exhibits a dimeric structure, being built up of two equivalent \{\text{AsW}_6\text{O}_{21}\}(\text{AsO}_3)_2\} units linked by two Mn$^{\text{II}}$ centers, leading to a sandwich-like structure with $C_{2h}$ point-group symmetry with a $C_2$ axis along the two Mn$^{\text{II}}$ centers and a perpendicular $\sigma_h$ mirror plane. The tungstoarsenate fragment is composed of two corner sharing \{W_3\text{O}_{13}\} triads which is stabilized by a central AsO$_3$ triangular pyramid, which can be formulates as \{AsW$_6$O$_{21}$\}. Two terminal arsenate groups then decorate each of these \{W$_3$O$_{13}$\} triad through a single $\mu_2$-bridging oxo to each tungsten metal centre with six As-O bonds in the range 1.780(6)-1.797(6). The \{AsW$_6$O$_{21}$\}(AsO$_3$)$_2$\} unit is structurally realated to the tetralacunary \{B-$\beta$-SiW$_8$O$_{31}$\} fragment by swapping two WO$_6$ octahedra to two arsenate groups. The As center, in the distorted triangular pyramid AsO$_3$, is connected to two $\mu_4$-O atoms from two \{W$_3$O$_{13}$\} triads and a $\mu_3$-O atom from two manganese centers, with three As-O bonds falling in the range of 1.732(5)-1.829(5). The terminal arsenate group then coordinate to additional sodium cations resulting into 1D chain, as shown in Fig.4.26.
Fig. 4.25 Polyhedral (left) and ball-and-stick (right) representation of polyanions 14a. Color Code: W atoms and WO$_6$ octahedra (blue), As atoms (pink), Mn atoms (gold), O atoms (red).

Fig. 4.26 Connection of polyanion 14a into 1D Chain by Na···OH$_2$ interactions.

Crystallographic structural analysis revealed that 14 – 18 are isomorphous, both crystallizing in the triclinic space group $P\bar{1}$ (see Table 4.3). Therefore, only the
structure of 15 is discussed here. The polyanionic entity \([\text{H}_2\text{Fe}_2\text{As}_2\text{W}_{12}\text{O}_{52}]^{11-}\) (15a) consists of two equivalent hexatungstate moieties \(\{(\text{AsW}_6\text{O}_{21})(\text{AsO}_3)_2\}\), which then sandwich two \(\text{Fe}^{III}\) centers bridged by four “planar” \(\text{Fe}–\text{O}–\text{W}\) and two ‘axial’ \(\text{Fe}–\text{O}–\text{As}\) bridges. Each moiety consists of two \(\{\text{W}_3\text{O}_{13}\}\) triads fused together through corner-sharing and the uppermost \(\{\text{AsO}_3\}\) group, with both units stabilized by the central triangular pyramid \(\{\text{AsO}_3\}\) group, which is previously unreported building block. However, the compounds differ in the amount of \(\{\text{AsO}_3\}\) groups present, as 13 contains six arsenic groups, while 14 – 18 only contains four. This lower amount of arsenic groups being present in the iron compound versus the manganese compound can be attributed to the oxidation state of central metals, where iron is +3, while manganese is +2. The polyanion molecules of 15a are surrounded by sodium countercations, forming a three-dimension framework, as shown in Fig.4.28.
Fig. 4.27 Polyhedral (left) and ball-and-stick (right) representation of polyanions 15a. Color Code: W atoms and WO$_6$ octahedra (blue), As atoms (pink), Fe atoms (orange), O atoms (red).

Fig. 4.28 Connection of [H$_2$Fe$_2$(AsW$_6$O$_{23}$)$_2$(AsO$_3$)$_2$]$^{12-}$ polyanions into a 3D framework by Na···OH$_2$ interactions.
4.5.2.2 Thermogravimetric Analysis

The thermal analysis of the sodium-salt 14 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 200 °C and involving loss of 44 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 16.93 (16.0)]. The second weight loss occurs between 200 and 430 °C, corresponding to the further loss of four arsenic group \{AsO_3\} per formula unit [% calc. (found): 10.47 (9.2)]. A weight loss for 15 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 48 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 18.81 (16.21)]. The second weight loss occurs between 200 and 500 °C, corresponding to the further loss of two arsenic group \{AsO_3\} per formula unit [% calc. (found): 5.35 (3.20)]. A weight loss for 16 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 48 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 15.9 (16.2)]. The second weight loss occurs between 200 and 450 °C, corresponding to the further loss of one arsenic group \{AsO_3\} per formula unit [% calc. (found): 2.74 (2.90)]. Above 450 °C, the framework is collapsed. A weight loss for 17 begins at room temperature and is complete at ca. 400 °C, which corresponds to the loss of 49 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 18.6 (18.4)]. The second weight loss occurs between 400 and 600 °C, corresponding to the further loss of four arsenic group \{AsO_3\} per formula unit [% calc. (found): 5.2 (5.6)]. A weight loss for 18 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 41 water molecules per formula unit based
on TGA combined with the elemental analysis results [% calc. (found): 16.67 (16.8)].

The second weight loss occurs between 200 and 450 °C, corresponding to the further loss of two arsenic groups \{AsO_3\} per formula unit [% calc. (found): 5.56 (6.1)]. Above 450 °C, the framework is collapsed.

Fig.4.29 Thermogram for 14 from room temperature to 1000 °C.

Fig.4.30 Thermogram for 15 from room temperature to 1000 °C.
Fig. 4.31 Thermogram for 16 from room temperature to 1000 °C.

Fig. 4.32 Thermogram for 17 from room temperature to 800 °C.
In summary, two novel types of hexa-heteropolytungstates \([\text{H}_3\text{Mn}_2(\text{AsW}_6\text{O}_{21})_2(\text{AsO}_3)_4]^{11-}\) (14a) and \([\text{H}_2\text{X}_2(\text{AsW}_6\text{O}_{23})_2(\text{AsO}_3)_2]^{12-}\) (\(X = \text{Fe, 15a}; \text{Sc, 16a}; \text{In, 17a}; \text{Ti, 18a}\)) have been isolated successfully and structurally characterized. Polyanion 14a is composed of two equivalent \(\{(\text{AsW}_6\text{O}_{21})(\text{AsO}_3)_2\}\) units with four terminal arsenate groups. In comparison, polyanion 15a - 18a comprise two equivalent \(\{(\text{AsW}_6\text{O}_{23})(\text{AsO}_3)\}\) units with two terminal arsenate groups. The reason for the different number of \{AsO\_3\} antenna groups is probably the oxidation state of Fe\(^{III}\) versus Mn\(^{II}\). As a result, all polyanions should have the total compensative charge, independent of protonation, forming the most stable archetype structure. More importantly, 14a - 18a could be used as promising reaction precursors in the isolation of POM-based materials. Moreover, their magnetic and EPR studies are in progress.
4.6 Sandwich-Type Dimeric, Dinuclear Containing Tungstophosphate Complexes, \([\{\text{Na(H}_2\text{O)}\text{M(P}_4\text{W}_6\text{O}_{34})\}\text{]}_2^{18-}\) (M=Ni (19a), Mn (20a))

4.6.1 Synthetic Procedures

4.6.1.1 Synthesis of Na$_{14}$H$_4$\([\{\text{Na(H}_2\text{O)}\text{Ni(P}_4\text{W}_6\text{O}_{34})\}\text{]}_2\cdot30\text{H}_2\text{O}$ (19)

A sample of NiCl$_2$·6H$_2$O (0.1165 g, 0.49 mmol) was first dissolved in 20 mL of sodium acetate buffer (0.5 M, pH 4.8) followed by the addition of 85% H$_3$PO$_4$ (106 µL, 1.6 mmol) and Na$_2$WO$_4$·2H$_2$O (1 g, 3 mmol). The mixture was later stirred for 1 h at room temperature. Then after filtering any solid off, 1M KCl (0.5 mL) was added to the resulting orange solution. Slow evaporation of the solution at room temperature led to the formation of orange crystals of 19 after three weeks (Yield: 0.5 g, 44% based on Ni). IR (cm$^{-1}$): 1137 (m), 1054 (m), 1027 (w), 936 (s), 896 (m), 845 (s), 708 (s,br), 575 (w), 526 (m), 459 (w). Elemental analysis % calc. (found): Na 5.6 (5.61), P 6.9 (6.65), Ni 2.41 (2.31), W 48.93 (48.32). Mw = 4607.51 g/mol.

![Fig.4.34 IR spectra of 19 and 20.](image-url)
4.6.1.2 Synthesis of Na_{14}\{H_4\{Na(H_2O)Mn(P_4W_6O_{34})}\}_2\cdot30H_2O (20)

A sample of MnCl_2\cdot6H_2O (0.1146 g, 0.49 mmol) was first dissolved in 20 mL of sodium acetate buffer (0.5 M, pH 4.8) followed by the addition of 85% H_3PO_4 (106 \mu L, 1.6 mmol) and Na_2WO_4\cdot2H_2O (1 g, 3 mmol). The mixture was later stirred for 1 h at room temperature. Then after filtering any solid off, 1M KCl (0.5 mL) was added to the resulting orange solution. Slow evaporation of the solution at room temperature led to the formation of orange crystals of 20 after three weeks (Yield: 0.5 g, 44% based on Mn). IR (cm\(^{-1}\)): 1137 (m), 1045 (s), 934 (s), 892 (m), 839 (m), 708 (s, br), 573 (w), 521 (m), 450 (w). Mw = 4590.48 g/mol.

4.6.2 Results and Discussion

4.6.2.1 Synthesis and Structure

Crystallographic structural analysis revealed that [H_4\{Na(H_2O)Ni(P_4W_6O_{34})\}_2\]^{14-} (19a) and [H_4\{Na(H_2O)Ni(P_4W_6O_{34})\}_2\]^{14-} (20a) are isomorphous, both crystallizing in the triclinic \(P\bar{1}\) space group. Therefore, only the polyanion 19a is discussed here. This polyanion is assembled by fusion of two unprecedented hexalacunary “Keggin” [PW_6O_{28}]^{15-} via two divalent nickel and two monovalent sodium centers, resulting in a sandwich-like structure capped with three \{PO_4\} groups at its opposing ends (Fig.4.35). To the best of our knowledge, this bridging cluster [PW_6O_{28}]^{15-}, which can be considered as a dicapped hexavacant B-Keggin subunit with a central PO_4 group, has not been observed independently. The [PW_6O_{28}]^{15-} fragment can be generated by elimination of an edge-shared triad from the top and a corner-shared triad from the bottom, forming a belt-shape bridging ligand. On the basis of structural arguments we
believe that six “outer” \{PO$_4$\} groups connected to the bridging cluster [PW$_6$O$_{28}$]$^{15-}$ play an important role by reducing the charge of this compound from –24 to –18, independent of protonation. Bond valence sum (BVS) calculations for 19a suggest that the terminal ligand at each Na(I) center are water molecules.

Fig.4.35 Combined polyhedral and ball-and-stick representation of 19a. Color code: PO$_4$ tetrahedron (yellow), WO$_6$ octahedra (blue), Ni (bright green), Na (sky blue), O (red).

**4.6.2.2 Thermogravimetric Analysis**

The thermal analysis of the sodium-salt 19 shows a weight loss which starts at room temperature with a dehydration step ending at ca. 200 °C and involving loss of 30
water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 11.72 (12.20)]. A weight loss for 20 begins at room temperature and is complete at ca. 200 °C, which corresponds to the loss of 30 water molecules per formula unit based on TGA combined with the elemental analysis results [% calc. (found): 11.76 (12.0)].

Fig.4.36 Thermogram for 19 from room temperature to 800 °C.
4.6.3 Conclusions

In summary, we have synthesized the novel nickel (II)- and manganese (II)-containing polyanions [{Na(H$_2$O)M$^{II}$P$_4$W$_6$O$_{34}$})$_2$$]^{18-}$ (M = Ni$^{II}$ (19a), Mn$^{II}$ (20a)) by one pot reaction. Interestingly, both polyanions comprise two unprecedented hexalacunary “Keggin” [PW$_6$O$_{28}$]$^{15-}$ via two divalent nickel and two monovalent sodium centers, resulting in a sandwich-like structure capped by three phosphate groups on either side. Further work will be concentrated on its detailed magnetic studies. Moreover, the existing of polydentate O donor in 19a and 20a allows us to isolate POM-based materials by utilizing such compounds as reaction precursors.
5 Summary and Outlook

In the course of this thesis a novel synthetic strategy has been developed which has led to the discovery of six novel Cr$^{III}$-containing POMs 1a – 6a. The two polyanions [Cr$^{III}$(HX$^\mathrm{V}$W$_7$O$_{28}$)$_2$]$^{13-}$ (X = P (1a), As (2a)) are the first examples of mononuclear Cr-containing POMs, being composed of the unusual heptatungstate \{PW$_7$\} or \{AsW$_7$\} units sandwiched between a single Cr$^{III}$ ion. Detailed SQUID and EPR spectroscopic measurements on the hydrated sodium salts of 1a and 2a showed that the axial zero-field splitting parameter (D) is unexpectedly large (2.4 cm$^{-1}$) for a Cr$^{III}$ ion in an octahedral oxo-coordination. The unusually large value of D has been rationalized using \textit{ab-initio} calculations and subsequent ligand field analysis. Systematic evolution of this structural family by heteroatom substitution has resulted in the two di-Cr$^{III}$-containing heteropolytungstates, [Cr$^{III}$_2(B-$\beta$-SiW$_8$O$_{31}$)$_2$]$^{14+}$ (3a) and [Cr$^{III}$_2(B-$\beta$-GeW$_8$O$_{31}$)$_2$]$^{14+}$ (4a). Polyanions 3a and 4a represent the first examples of sandwich-type POMs comprising two \{XW$_8$O$_{31}$\} (X = Si, Ge) units, and they are stable in solution from pH 1 – 7. Biological studies on 3a and 4a demonstrated interesting antidiabetic and anticancer activity. This is the first report of antiparasitic activity of POMs. The polyanion [Cr$^{III}$_2(As$^{III}$W$_6$O$_{23}$)(As$^{III}$O$_5$)$_2$]$^{14+}$ (5a) exhibits the first example of a di-Cr$^{III}$-containing tungstoarsenate(III) and comprises two \{(AsW$_6$O$_{21}$)(AsO$_3$)\} units linked by two Cr$^{III}$ centers. The preparation of 1a - 5a demonstrates a remarkable heteroatom template effect in the formation of new POM archetypes. The Cr$^{III}$-containing hexatungstate
Following the newly developed synthetic strategy we discovered here, it was possible to isolate some other novel polyanions comprising hexa-, hepta-, and octaheteropolytungstates by substituting Cr ions to other s, p, d-block metal ions, which are described in Chapter 4. Five mononuclear containing polytungstophosphate based on \(\{\text{PW}_7\}\) building blocks, \([\text{M}(\text{HP}^\text{V}\text{W}_{28})_2]^{n-}\) \((n = 13, \text{M} = \text{Fe} (7a), \text{Mn} (8a), \text{Ga} (9a), \text{In}(10a); n = 14, \text{Mg} (11a))\) has been synthesized and structurally characterized. Detailed SQUID and EPR spectroscopic measurements on the hydrated sodium salts of \(7a\) and \(8a\) showed that the axial zero-field splitting parameter \((D)\) is unexpectedly large at \(\approx 3.6\) cm\(^{-1}\) for \(7\) and \(\approx 6.0\) cm\(^{-1}\) for \(8\). The compounds were found to possess, to our knowledge, the largest zero-field splitting parameter of any previously reported \(\text{Fe}^{\text{III}}\text{O}_6\) compound and \(\text{Mn}^{\text{III}}\text{O}_6\) containing moiety. Attempted study the NMR spectra and electrochemistry of the diamagnetic containing POMs \(9 - 11\) were failed due to the low stability in solution. We have also prepared the first examples of dinuclear \(\text{Ga}^{\text{III}}\) and \(\text{In}^{\text{III}}\)-containing POMs, \([\text{Ga}_2(\text{GeW}_8\text{O}_{31})_2]^{14-}\) (12a) and \([\text{In}_2(\text{GeW}_8\text{O}_{31})_2]^{14+}\) (13a). They consist of two octahedrally coordinated metal centers, sandwiched by two \(\{\text{GeW}_8\}\) units. In addition to these two new compounds, the Si derivatives would also be obtained, and such work is underway. They are also found to be stable in solution in a wide range of pH 1 – 7, and their biological studies are in progress. The two novel types of hexa-heteropolytungstates \([\text{H}_3\text{Mn}_2(\text{AsW}_6\text{O}_{21})_2(\text{AsO}_3)_3]^{11-}\) (14a) and \([\text{H}_2\text{X}_2(\text{AsW}_6\text{O}_{23})_2(\text{AsO}_3)_2]^{12-}\) \((X = \text{Fe}, 15a; \text{Sc}, 16a; \text{In}, 17a; \text{Ti}, 18a)\) have been isolated successfully and structurally characterized. Polyanion 14a is composed of two equivalent \(\{(\text{AsW}_6\text{O}_{21})(\text{AsO}_3)_2\}\) units with four terminal arsenate groups. In
comparison, polyanion 15a - 18a comprise two equivalent \{(AsW_{6}O_{21})(AsO_{3})_{2}\} units with two terminal arsenate groups. The reason for the different number of \{AsO_{3}\} antenna groups is probably the different oxidation states of Fe^{III} versus Mn^{II}. By a slightly modified synthetic procedure the nickel (II)- and manganese (II)-containing polyanions \{\{Na(H_{2}O)M^{II}(P_{4}W_{6}O_{34})\}_{2}\}^{18-} (M = Ni^{II} (19a), Mn^{II} (20a)) could be prepared, which have a sandwich-type structure capped by three phosphate groups on either side.

According to the structural types described in this work, compounds 1 - 20 can be abbreviated as three breeds: Type A \{MXW_{7}\} (X = P^{V}, As^{V}); Type B \{M_{2}(XW_{8})_{2}\} (X = Si^{IV}, Ge^{IV}); Type C \{M_{2}(As^{III}W_{6})_{2}\}, Tpye D \{M_{2}(As^{III}W_{6})_{4}\}, Tpye E \{M_{2}(P_{4}^{V}W_{6})_{2}\}. The ability to study other transition metals, such as Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} ions in such well-defined and magnetically isolated environments, combined with our discovery of the fact that Cr^{III}, Fe^{III}, Mn^{III} ions coordinated by similar polyoxotungstate ligands are characterized by unusually large magnetic anisotropy, provided the impetus for synthesizing magnetic POMs analogue of type A \{MXW_{7}\}. In essence, this archetype of compounds provides a platform for studying the magnetism at the single ion level. The interest of studying type B \{M_{2}(XW_{8})_{2}\} (X = Si^{IV}, Ge^{IV}) is due to its high stability which has exhibited interesting antidiabetic and anticancer activities in compounds 3 and 4. The value of studying type C \{M_{2}(As^{III}W_{6})_{2}\}, Tpye D \{M_{2}(As^{III}W_{6})_{4}\} and Tpye E \{M_{2}(P_{4}^{V}W_{6})_{2}\} may extend into the magnetic field because two or more paramagnetic ions incorporated in a POM could be regarded as exchange-coupled centers.

We are now working on the manuscript. At the same time, magnetic and EPR studies on the hydrated sodium salts of 5a, 14a, 15a, 19a, and 20a are in progress, biological studies on the hydrated sodium salts of 12a and 13a and theoretical studies of
7a and 8a are underway. The synthetic strategy we discussed in the thesis has opened a new door for investigating the derivatives of those five type structures and even synthesizing numerous novel structures. For future studies, we propose the utilization of the isomers dichlorotetraaquachromium(III) chloride dehydrate [CrCl$_2$(OH)$_2$]Cl·2H$_2$O and chloropentaaquachromium(III) chloride hydrate [CrCl(OH)$_2$]Cl$_2$·H$_2$O instead of hexaaquachromium(III) nitrate [Cr(OH)$_2$]$_6$(NO$_3$)$_3$·3H$_2$O as starting compounds. Possibly, the \{XW$_6$\}, \{XW$_7$\}, \{XW$_8$\} fragments present in these structures can be used as building blocks for other POM structures, and such work is currently underway. We also propose to synthesize derivatives of the dinuclear octatungstate where one or two Cr$^{III}$ centers are replaced by Fe$^{III}$ or Mn$^{III}$ salts, to obtain homometallic or heterometallic sandwich-type POMs, both of which have very interesting magnetic properties. We could also extend the synthetic strategy by utilizing organo cations to manipulate the assembly of POM structures and to trap a diverse range of compounds prior to their reorganization into more stable structures.
~ CHAPTER ~

6. References


90. SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.


102. Simulation of the experimental magnetic data was performed with the julX program: Bill E.j.M.-P.I.f.C.E.C.M.l.a.d.R., Germany.


115. Simulation of the experimental magnetic data was performed with the julX program (E. Bill: Max-Planck Institute for Chemical Energy Conversion M.R., Germany).


