Titanium(IV)- and Lanthanide(III)-Containing Heteropolytungstates

by

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a Thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

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Acknowledgements

Composing the acknowledgements is the hardest for me because no amount of words will suffice to thank all the people who have influenced me and be part of my life during the past four years.

The mentorship of my advisor, Prof. Ulrich Kortz, made this whole journey possible and enjoyable. I express my sincere gratitude to Prof. Ulrich Kortz for his inspiring motivation, valuable suggestions, and constant encouragement throughout my graduate studies. He set such a great example for me through his hard work and concentration on the task at hand.

I would also like to thank Prof. Tatjana N. Parac-Vogt, Prof. Cristian Silvestru, Prof. Hans Joachim Breunig, and Prof. Bassem S. Bassil and Prof. Gerd-Volker Röschenthaler for being on my committee.

I deeply appreciate Prof. Dr. Bassem S. Bassil for giving me great, instructive help in many ways during my doctoral study. Thanks to Dr. Zhengguo Lin for XRD support; Dr. Ali Haider for his instructions on NMR measurements; Xiaolin Xing for the electrochemical characterization. My laboratoray was my second home and I am pretty thankful to the entire lab fellows for giving conform, support and joy during the time of my research. In addition, I want to thank Anastasia Resetnic, Tim Sudmeier, and Obida Bawadkji for being part of my research project as undergraduate students.

Many thanks to my collaborators: (i) Dr. Bineta Keita for electrochemical analysis (retired from Université Paris-Sud, France); (ii) Prof. Tatjana N. Parac-Vogt and Dr. Stef Vanhaeckt for photoluminescence analysis (KU Leuven, Belgium); (iii) Prof. Cristian Silvestru for supplying the organoantimony complex (Babes-Bolyai University, Romania); (iv) Dr. Cristina Sáenz de Pipaón and Prof. José Ramón Galán-Mascarós for magnetic property analysis; (v) Dr. Jasleen Kaur Bindra, Kariem Diefenbach and Prof. Naresh S. Dalal for magnetic property analysis and EPR test (Florida State University, United States); (vi) Prof. Jie Cao and Dr. Linyuan Fan for ESI-MS analysis (Beijing Institute of Technology, P.R. China).

I gratefully acknowledge China Scholarship Council (CSC) for a doctoral fellowship and ECOST program for funding my short-term scientific mission (STSM). I specially want to thank Prof. Xiao-Ying Huang (Fujian institute of research on the structure of matter, Chinese academy of sciences, P. R. China) for his support all the time.
I definitely need to mention my gratitude and love to my parents for their strongest support and my wife Lin Cheng for her encouragement overseas over the whole time of my PhD study. They stand by my side at this important moment of my life.
Abstract

Extensive studies on polyoxometalates (POMs), from synthesis to structural examination, have revealed a versatile structural evolution and its relevance to technological applications of these materials in green catalysis, medicine, magnetism, materials science, and molecular recognition, and so on. Lacunary (vacant) POMs can incorporate additional electrophiles from the $p$-, $d$-, and $f$-blocks by virtue of their exposed, reactive oxo ligands, resulting in products with enhanced structural and compositional diversity.

Titanium(IV)-containing heteropolytungstates are highly interesting for their diverse structural chemistry as well as their catalytic properties. The Ti$^{4+}$ ion fits well into the vacant addenda sites of various types of Keggin or Wells-Dawson heteropolytungstate precursors. The first part of this thesis is dedicated to the reaction of the $[\text{TiO}]^{2+}$ cation and lone-pair containing, lacunary POM precursors of the type $[\alpha\text{-XIII}W_9O_{33}]^{9-}$ (X = As, Sb). This work has resulted in seven novel Ti$^{IV}$-containing heteropolytungstates.

Lanthanide-containing heteropolyanions are of interest due to their highly diverse structural and chemical nature. Due to the large size of the lanthanide (Ln) ions they cannot be fully incorporated into lacunary heteropolyanions, and hence coordinate to several terminal water ligands, resulting in large coordination numbers and compounds with Lewis acidic properties. In the second part of this thesis the reactivity of lanthanide ions with trilacunary Keggin-type polyanions such as $[\alpha\text{-X}W_9O_{34}]^{10-}$ (X = Si, Ge) has been investigated. This work has resulted in three novel Ln$^{III}$-containing heteropolytungstates.

This dissertation comprises five chapters.

Chapter 1 contains a general introduction of the historical background, classification, and structural description of POMs, and a comprehensive state of the art overview of Ti$^{IV}$- and Ln$^{III}$-containing polyoxotungstates.

Chapter 2 comprises a description of the analytical techniques used for the characterization of the obtained products, as well as the synthetic procedures of the lacunary POM precursors used in this work.

In Chapter 3 the synthesis of two novel Ti$^{IV}$-containing tungstoarsenates(III), $[\text{Ti}_{6}(\text{Ti}^{}\text{IV}O_6)(\text{As}^{III}W_9O_{33})_4]^{20-}$ (Thr) and $[\text{Ti}^{IV}O_2(\alpha\text{-As}^{III}W_9O_{33})_2]^{14+}$ (Ti2), by reaction of $[\text{TiO}]^{2+}$ and the $[\alpha\text{-As}^{III}W_9O_{33}]^{9-}$ POM precursor was discussed. The tetrameric
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polyanion Ti7 features a compact structure with an unprecedented Ti7-core, comprising a central TiO6 octahedron surrounded by six TiO5 square-pyramids, which is capped by four {AsIIIW9} fragments. The sandwich-type polyanion Ti2 comprises two {TiO} groups capped by two {AsIIIW9} fragments, leaving a vacant site in the central belt position.

In Chapter 4 the reactivity of Ti2 with the {C6H5SbIII}2+ electrophile or 3d metal ions such as Co2+, Ni2+, Cu2+, and Zn2+ was investigated, resulting in a series of mono-substituted Ti2 derivatives, namely, [C6H5SbIII(TiIVO)2(α-AsIIIWO33)]12- (SbTi2) and [M(H2O)(TiIVO)2(α-AsIIIWO33)]12- (M = Co (CoTi2), Ni (NiTi2), Cu (CuTi2), and Zn (ZnTi2)). Besides, the electrochemical and magnetic properties of all new compounds were also studied. It was demonstrated that Ti2 represents a heterometallic, monolacunary POM host platform for selective incorporation of various main-group and d-block metal-ion guests, allowing for flexible tuning of the physicochemical properties.

In Chapter 5 a new class of hexameric Ln12-containing 60-tungstogermanates is introduced, [Na(H2O)6⊂Eu12(OH)12(H2O)18Ge2(GeW10O38)6]39- (Eu12), [Na(H2O)6⊂Gd12(OH)6(H2O)24Ge(GeW10O38)6]37- (Gd12), and [(H2O)6⊂Dy12(H2O)24(GeW10O38)6]36- (Dy12), all comprising six di-Ln-embedded {β(4,11)-GeW10} subunits. Depending on the size of the LnIII ion, the POM assemblies feature selective capture of two (for Eu12), one (for Gd12) or zero (for Dy12) extra GeIV guest ions. Selective incorporation of a cationic [Na(H2O)6]3+ complex was observed for Eu12 and Gd12, whereas Dy12 incorporates a neutral, distorted-octahedral (H2O)6 cluster.
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<td>(\text{Na}_{20}[\text{Ti}^{IV}_6(\text{Ti}^{IV}_6\text{O}_6)(\alpha-\text{As}^{III}\text{W}<em>9\text{O}</em>{33})_4]\cdot63\text{H}_2\text{O})</td>
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<td>(\text{Na}<em>{17.5}\text{Cs}</em>{2.5}[\text{Ti}^{IV}_6(\text{Ti}^{IV}_6\text{O}_6)(\alpha-\text{As}^{III}\text{W}<em>9\text{O}</em>{33})_4]\cdot72\text{H}_2\text{O}\cdot2\text{CH}_3\text{COONa})</td>
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<td>(\text{Na}_{14}[(\text{Ti}^{IV}_4\text{O})_2(\alpha-\text{As}^{III}\text{W}<em>9\text{O}</em>{33})_2]\cdot50\text{H}_2\text{O}\cdot\text{CH}_3\text{COONa})</td>
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</tr>
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<td>(\text{Cs}<em>{2.5}\text{Na}</em>{9.5}[\text{Cs}_6\text{H}_5\text{Sb}^{III}(\text{Ti}^{IV}_4\text{O})_2(\alpha-\text{As}^{III}\text{W}<em>9\text{O}</em>{33})_2]\cdot40\text{H}_2\text{O})</td>
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<td>(\text{Cs}<em>{0.5}\text{Na}</em>{11.5}[\text{Co}(\text{H}_2\text{O})(\text{Ti}^{IV}_4\text{O})_2(\alpha-\text{As}^{III}\text{W}<em>9\text{O}</em>{33})_2]\cdot32\text{H}_2\text{O}\cdot0.5\text{CH}_3\text{COONa})</td>
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<td>(\text{Cs}<em>{0.5}\text{Na}</em>{11.5}[\text{Cu}(\text{H}_2\text{O})(\text{Ti}^{IV}_4\text{O})_2(\alpha-\text{As}^{III}\text{W}<em>9\text{O}</em>{33})_2]\cdot40\text{H}_2\text{O}\cdot0.5\text{CH}_3\text{COONa})</td>
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<td>(\text{Cs}<em>{0.5}\text{Na}</em>{11.5}[\text{Zn}(\text{H}_2\text{O})(\text{Ti}^{IV}_4\text{O})_2(\alpha-\text{As}^{III}\text{W}<em>9\text{O}</em>{33})_2]\cdot47\text{H}_2\text{O}\cdot0.5\text{CH}_3\text{COONa})</td>
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<td>(\text{Na}<em>{39}[\text{Na}(\text{H}<em>2\text{O})<em>6\subset\text{Eu}</em>{12}(\text{OH})</em>{12}(\text{H}<em>2\text{O})</em>{18}\text{Ge}<em>2(\text{GeW}</em>{10}\text{O}</em>{38})_6]\cdot159\text{H}_2\text{O})</td>
<td>Na-Eu12</td>
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<tr>
<td>(\text{Na}<em>{37}[\text{Na}(\text{H}<em>2\text{O})<em>6\subset\text{Gd}</em>{12}(\text{OH})</em>{6}(\text{H}<em>2\text{O})</em>{24}\text{Ge}(\text{GeW}</em>{10}\text{O}_{38})_6]\cdot129\text{H}_2\text{O})</td>
<td>Na-Gd12</td>
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<tr>
<td>(\text{Na}<em>{36}[(\text{H}<em>2\text{O})<em>6\subset\text{Dy}</em>{12}(\text{H}<em>2\text{O})</em>{24}(\text{GeW}</em>{10}\text{O}</em>{38})_6]\cdot122\text{H}_2\text{O})</td>
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Chapter 1 Introduction

Polyoxometalates (POMs) represent a class of anionic metal-oxygen clusters built up by Group VB or VIB metal ions in their highest oxidation states (i.e. V(V), Nb(V), Ta(V), Mo(VI), W(VI)). The study on POMs have developed fast during the last 200 years, and these materials are remarkable due to their oxygen-rich surfaces and a controllable size, composition, charge density, redox potential, and acid strength, which give rise to their wide applications in analytical and clinical chemistry, catalysis, biochemistry, medicine, and solid-state devices.\[1\] According to the different chemical compositions, the POMs can be mainly classified in two groups: the isopolyanions (IPAs, \([M_nO_{y-n}]^n\)−) and heteropolyanions (HPAs, \([X_mM_6O_{y-n}]^{m+n}\)). Apart from the addenda M atom, the X atom is the heteroatom which is usually located in the center of the polyanion, covering more than 60 elements across the periodic table. This thesis will focus on the heteropolyanion units.

1.1 Historical perspective

In 1826, Berzelius observed a yellow precipitate after mixing ammonium molybdate with phosphoric acid, which was originally formulated as 3(NH\(_4\))\(_2\)O-P\(_2\)O\(_5\)-24MoO\(_3\)-aq, and nowadays are well-known 12-molybdophosphate (NH\(_4\))\(_3\)[PMo\(_{12}\)O\(_{40}\)]\(_{\cdot}\)nH\(_2\)O.\[2\] This is the first synthesis of the heteropolyanion. In 1862, Marignac prepared and precisely analyzed the two isomers of silicotungstate (α- and β-[SiW\(_{12}\)O\(_{40}\)]\(4^+\)) by adopting analytical techniques, accelerating the study of POM chemistry.\[3\] After that, this research field developed rapidly so that more than 700 heteropolyanions were reported and analyzed by several scientists in the following 50 years, especially Scheibler, Gibbs, Sprenger, Klein, Mauro, Copaux, and Miolati. In 1929, Pauling made a breakthrough in the structural chemistry of the POMs.\[4\] He proposed a structure of heteropolyanion with M:X=12:1 model, where the central tetrahedral hetero group XO\(_4\) (X= Si, P) was surrounded by twelve corner-shared addenda MO\(_6\) octahedra. The cage-like W\(_{12}\)O\(_{18}\)(OH)\(_{36}\) expected to be electrical neutrality. It was in 1933 that Keggin performed powder X-ray diffraction on the free acid H\(_3\)PW\(_{12}\)O\(_{40}\) and solved its structure as H\(_3\)[PW\(_{12}\)O\(_{40}\)]\(_{\cdot}\)5H\(_2\)O, proposing the Keggin-type structure (Figure 1-1a).\[5\] This structure contains four 3-fold W\(_3\)O\(_{13}\) triads, where each pair of neighboring WO\(_6\) octahedra are edge-shared. Four W\(_3\)O\(_{13}\) triads interlink with each other by corner-sharing and surround one center XO\(_4\)
tetrahedron, where each O atom around the hetero X atom act as a $\mu_4$ atom, connecting one X atom and three M atoms in one triad. In 1937, Anderson speculated the 6:1 type of polyanion to adopt a planar configuration, where six MO$_6$ octahedra attach one another to form a circle, while the center is occupied by a hexa-coordinate X atom.$^6$ In 1948, Evans determined this type of structure by using single-crystal X-ray analysis on the salt of [TeMo$_6$O$_{24}$]$^{6-}$ polyanion.$^7$ So this type of polyanion was later referred to Anderson-Evans structure (Figure 1-1b). In 1953, B. Dawson used the single-crystal X-ray analysis to determine the structure of the K$_6$[P$_2$W$_{18}$O$_{62}$]-14H$_2$O (referred to the Wells-Dawson structure), confirming the structural model speculated by A. F. Wells in 1945 (Figure 1-1c).$^8$

![Figure 1-1. Structures of (a) Keggin, (b) Anderson-Evans and (c) Wells-Dawson types of heteropolyoxotungstates.]

### 1.2 Keggin-type polyanions

The Keggin structure and its derivatives are most widely studied. As for the composition, the Keggin polyanion is a combination of twelve addenda octahedral MO$_6$ groups and one hetero tetrahedral XO$_4$ group. The typical addenda metal atoms are molybdenum (Mo) and tungsten (W). In contrast, the heteroatom in the center of the Keggin ion can be any of a wide range of elements (i.e. B, Al, Ga, Si, Ge, Sn, P, As, Sb, Bi, Se, Te, I), among which the P$^V$, As$^V$, Si$^{IV}$, Ge$^{IV}$ are most commonly investigated. For example, the synthesis of the Keggin-type polyanion [PW$_{12}$O$_{40}$]$^{3-}$ can be represented by the following equation 1-1:

$$12\text{WO}_4^{2-} + \text{PO}_4^{3-} + 24\text{H}^+ \rightleftharpoons [\text{PW}_{12}\text{O}_{40}]^{3-} + 12\text{H}_2\text{O} \quad (1-1)$$

From the viewpoint of structure, the Keggin structure is based on one central XO$_4$ tetrahedron surrounded by four M$_3$O$_{13}$ triads of three edge-shared MO$_6$ octahedra, resulting in a $T_d$ symmetry. One triad interlinks with the neighboring ones by corner-sharing two $\mu_2$-O atoms, simultaneously connects with the central heteroatom by sharing one $\mu_4$-O atom. Each addenda M atom has a $\pi$-bonded terminal O atom.
This double bond results in a short terminal M=O (O₁) bond length and a relative longer M–O (μ₄-O) bond length on the trans position, leading to the polarization as well as the distortion of the MO₆ octahedron.

1.2.1 Baker-Figgis isomers

Keggin-type polyanion have five different geometrical isomers, known as Baker-Figgis isomers. The structure shown in the center of Figure 1-2 is referred to the α-Keggin, which consists of four equivalent triads. And the four isomers of the α-Keggin structure are formed by rotating one (β-isomer), two (γ-isomer), three (δ-isomer), and four (ε-isomer) triads by 60° around the related μ₄-O–X axes. The α-, β-, γ-, δ- and ε-Keggin isomers of Keggin polyanion possess Tₐ, C₃ᵥ, C₂ᵥ, C₃ᵥ and Tₐ symmetries, respectively.

Figure 1-2. The formation of the different geometrical isomers of the Keggin ion starting from the parent α-Keggin structure.

A review of theoretical studies on POMs written by Bo and Poblet indicates the sequence of the stabilities of the five isomers should be as follows: α > β > γ > δ >
C. \[10\] Obviously, when two neighboring triads in the $[\alpha\text{-X}M_{12}\text{O}_{40}]^{n-}$ are rotated by 60°, the linkage mode between them will transform from corner-sharing to edge-sharing, resulting in a much closer M···M distance and more acute W–O–W angles than the \(\alpha\)-Keggin isomer. Thus, the \(\alpha\)- and \(\beta\)-Keggin isomers with 0 and 1 rotated triads are the most stable forms because they do not have the close M···M contacts. However, for the \(\gamma\)-, \(\delta\)-, to the \(\varepsilon\)-Keggin isomers, their respective 2, 3, and 4 rotated triads give rise to an increasing number of M···M contacts from 1, 3 to 6.

1.2.2 Lacunary derivatives of Keggin-type polyanions

Lacunary (or vacant) derivatives from the Keggin structures can be obtained from the removal of variable number of M addenda atoms from the plenary Keggin structure upon basification.\[1\] Due to the scarce examples of the lacunary \(\delta\)- and \(\varepsilon\)-Keggin polyanions, herein, we will discuss in more detail the mono-, di-, tri-lacunary species of the \(\alpha\)-, \(\beta\)-, and \(\gamma\)-Keggin polyanions. These lacunary polyanions can act as multi-dentate oxo ligands to coordinate to the main-group elements, transition metal, and Lanthanide atoms, which bind to the vacant sites of the POMs.

![Diagram](image_url)

Figure 1-3. Structures of the mono-lacunary polyanions derived from the \(\alpha\)- and \(\beta\)-Keggin structures.
1.2.2.1 Mono-lacunary Keggin ions

The elimination of one M atom from the plenary Keggin polyanion give rise to the mono-lacunary derivatives, as shown in Figure 1-3. For the \([\alpha\text{-}\text{XM}_{12}\text{O}_{40}]^-\), the removal of the M will result in only one type of mono-lacunary polyanion, \([\alpha\text{-}\text{XM}_{11}\text{O}_{39}]^-\). This is due to equivalent positions of the twelve M atoms in such a high symmetry (\(T_d\)) of the \([\alpha\text{-}\text{XM}_{12}\text{O}_{40}]^-\). In contrast, the non-equivalent addenda M atoms due to the lower symmetry (\(C_{3v}\)) of the \([\beta\text{-}\text{XM}_{12}\text{O}_{40}]^-\) implies three different types of mono-lacunary \([\beta\text{-}\text{XM}_{11}\text{O}_{39}]^-\) depending on the position of the M atom removed. (a) \([\beta_1\text{-}\text{XM}_{11}\text{O}_{39}]^-\): the M atom is removed from the “base” position (three octahedra unconnected with the rotated triad); (b) \([\beta_2\text{-}\text{XM}_{11}\text{O}_{39}]^-\): the M atom is removed from the “belt” position (six octahedra connected with the rotated triad); (c) \([\beta_3\text{-}\text{XM}_{11}\text{O}_{39}]^-\): the M atom removed belongs to the rotated triad.

1.2.2.2 Di-lacunary Keggin polyanions

The di-lacunary \(\alpha\)-Keggin polyanion can be viewed as the derivative of the \([\alpha\text{-}\text{XM}_{12}\text{O}_{40}]^-\) by removing two addenda M atoms. However, such polyanions are not stable in solution, so they are usually in-situ formed during the reaction, evidenced by the \{\(\alpha(1,2)\text{-}\text{XW}_{10}\text{O}_{37}\)\}, \{\(\alpha(1,5)\text{-}\text{XW}_{10}\text{O}_{38}\)\}, and \{\(\alpha(1,8)\text{-}\text{XW}_{10}\text{O}_{38}\)\}. Here, the notification “(x, y)” refers to the numberial positions of M atoms in the structure according to the IUPAC rules.\(^{[14]}\)

The di-lacunary \(\beta\)-Keggin polyanion have ten types of configurations due to the lower symmetry than \(\alpha\)-Keggin structure, including \{\(\beta(1,5)\text{-}\text{XW}_{10}\text{O}_{38}\)\}, \{\(\beta(1,8)\text{-}\text{XW}_{10}\text{O}_{38}\)\}, \{\(\beta(4,11)\text{-}\text{XW}_{10}\text{O}_{38}\)\}, \{\(\beta(5,10)\text{-}\text{XW}_{10}\text{O}_{38}\)\}, \{\(\beta(4,5)\text{-}\text{XW}_{10}\text{O}_{37}\)\}, \{\(\beta(4,10)\text{-}\text{XW}_{10}\text{O}_{37}\)\}, \{\(\beta(1,10)\text{-}\text{XW}_{10}\text{O}_{38}\)\}, \{\(\beta(5,6)\text{-}\text{XW}_{10}\text{O}_{37}\)\}, \{\(\beta(1,9)\text{-}\text{XW}_{10}\text{O}_{37}\)\}, and \{\(\beta(5,11)\text{-}\text{XW}_{10}\text{O}_{37}\)\}.

\[ \begin{align*}
&\text{\([\gamma\text{-}\text{XM}_{12}\text{O}_{40}]^-\)} \quad \text{\([\gamma\text{-}\text{XM}_{10}\text{O}_{36}]^-\)} \quad \text{\([\gamma\text{-}\text{XM}_{12}\text{O}_{40}]^-\)} \\
\end{align*} \]

**Figure 1-4.** Structures of di-lacunary polyanions derived from the \(\gamma\)-Keggin structure.
Typically, there is only one lacunary specie observed from the $\gamma$-Keggin polyanion, i.e. the dilacunary $[\gamma\text{-}XM_{10}\text{O}_{36}]^{z-}$, which can be obtained by removing two adjacent M atoms from two rotated triads (Figure 1-4).  

1.2.2.3 Tri-lacunary Keggin polyanions

The tri-lacunary Keggin polyanion forms upon the removal of three addenda M atoms from the plenary Keggin structure. Here, we will discuss the structural features of the tri-lacunary spcies derived from the $\alpha$- and $\beta$-Keggin polyanions (Figure 1-5). For the $\alpha$-isomer, the tri-lacunary spcies can be either “$A$-$\alpha$-” type, where the three M atoms removed are corner-shared by O bridges, or “$B$-$\alpha$-” type, where three M atoms in one triad are lost. It is noteworthy that one terminal O atom of the XO$_4$ group in the $[B$-$\alpha$-$XM_9O_{34}]^{q}$ points outwards, not bonding to other metal atoms. Such a configurational feature allows the formation of the lone pair-containing analogs $[B$-$\alpha$-$XM_9O_{33}]^{q}$, where the X atoms (e.g. As$^{III}$, Sb$^{III}$, Bi$^{III}$, Se$^{IV}$, and Te$^{IV}$) contains a lone pair of electrons. The case for the $\beta$-isomer is similar. The removal of three corner-shared M atoms from different non-rotated triads give rise to the $[A$-$\beta$-$XM_9O_{34}]^{p}$, while the elimination of one non-rotated triad results in the formation of $[B$-$\beta$-$XM_9O_{34}]^{p}$.

![Figure 1-5. Structures of tri-lacunary polyanions derived from the $\alpha$- and $\beta$-Keggin structures.](image-url)
1.3 Ti$^{IV}$-substituted heteropolytungstates

1.3.1 Ti$^{IV}$-substituted Keggin heteropolytungstates with tetrahedral XO$_4$ (X = Si$^{IV}$, Ge$^{IV}$, P$^{IV}$, As$^{V}$) or lone electron pair-containing XO$_3$ (X = As$^{III}$, Sb$^{III}$) hetero groups

1.3.1.1 Ti$^{IV}$-substituted Keggin POM monomers

In 1968, Tourné pioneered the research territory of Ti$^{IV}$-substituted heteropolytungstates by reporting on reactions of several mono-lacunary Keggin-type POM precursors [$XW_{11}O_{39}$]$^{(p+4)-}$ (X = B, Si, Ge, P, As, Zn, H$_2$; p is the negative charge of the parent [$XW_{11}O_{39}$]$^p$ polymerion) and Ti$^{4+}$ ions, and isolated corresponding mono-Ti$^{IV}$-substituted [XTi$W_{11}O_{40}$]$^{(p+2)-}$ (X = P (1a), B (1b), Si (1c), Ge (1d), As (1e), Zn (1f), H$_2$ (1g)) polyanions.$^{[21]}$ Later on, Knöth et al. prepared the tetra-$n$-butyl ammonium (TBA) salt of the [PTi$W_{11}O_{40}$]$^5^-$ (1a) (Figure 1-6a) through two different ways: (1) the hydrolytic conversion from [CITi$PW_{11}O_{39}$]$^{4^+}$ (2), (2) the direct reaction of TiCl$_4$ and [PW$_{11}O_{39}$]$^{7^-}$.\(^{[22]}\) The $^{183}$W NMR spectrum of polyanion 1a in CH$_3$CN/CD$_3$CN gives six peaks with intensity ratio of 2:2:1:2:2:2, supporting for the expected C$_5$ point group symmetry. Due to the well resolution of the spectrum, a detailed assignment of the peaks to the magnetically inequivalent W atoms of this polyanion was made on the basis of the spin-spin couplings.$^{[22]}$ Subsequently, a third method by reacting the (Bu$_4$N)$_3$H$_3$PW$_{11}O_{39}$ with Ti(NEt)$_2$$_4$ was proven by Keana et al. to be effective to prepare polyanion [PTi$W_{11}O_{40}$]$^5^-$ (1a).\(^{[23]}\) Notably, the structural determination work through X-ray crystallography by Yamase et al.$^{[24]}$ and Nomiya et al.$^{[25]}$ revealed that the polyanion 1a possesses the same structure as the plenary Keggin POM, nevertheless it was not possible to determine the Ti$^{IV}$ sites from the statistically disordered W and Ti atoms, as is expected due to the high symmetry of the Keggin POM. In addition, Knöth et al. initially synthesized the methoxo derivative of polyanion 1a, [PTi(OCH$_3$)$_3$W$_{11}$O$_{39}$]$^{4+}$ (3) by the substitution reaction between the [CITi$PW_{11}O_{39}$]$^{4^+}$ (2) and sodium methoxide.$^{[22]}$ Later on, Kholdeeva et al. reported another effective synthetic procedure for this polyanion 3 through the fragmentation of μ-hydroxo dimeric species, which were also extended to other substituting ligands (L = OH, OAr (ArOH = 2,3,6-trimethylphenol)), resulting in the corresponding monomeric [PTi(L)$_2$W$_{11}$O$_{39}$]$^{p^+}$ (L = OH (H1a), OAr (ArOH = 2,3,6-trimethylphenol) (4)) derivatives.$^{[26]}$ Notably, as the negative charge of the
Keggin polyanion increased upon the successive substitution of W\textsuperscript{VI} group by Ti\textsuperscript{IV}, the basicity should undoubtedly increase, which has been indicated by the reversible protonation of the mono-Ti\textsuperscript{IV}-substituted [ClTiPW\textsubscript{11}O\textsubscript{39}]\textsuperscript{4-} (2) under conditions where [PW\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-} does not protonate.\textsuperscript{[22]}

Replacement of two W atoms of the Keggin [PW\textsubscript{12}O\textsubscript{40}]\textsuperscript{3-} polyanion results in the di-Ti\textsuperscript{IV}-substituted polyanion [PTi\textsubscript{2}W\textsubscript{10}O\textsubscript{40}]\textsuperscript{7-} (5) (Figure 1-6b). In 1983, Knoth et al. reported the synthesis of this polyanion from the direct reaction of TiCl\textsubscript{4}, NaWO\textsubscript{4} and NaH\textsubscript{2}PO\textsubscript{4} in aqueous solution at pH 8-8.6.\textsuperscript{[27]} \textsuperscript{31}P NMR spectrum revealed that one isomer (δ = -11.43 ppm) predominates in the isolated product, together with small amounts of other isomers according to the presence of several other weak resonances. The high-resolution \textsuperscript{183}W NMR spectrum on \textsuperscript{5} gives five peaks with equal intensity, which must be ascribed to the C\textsubscript{2} isomer generated by the 1,5-substitution (according to the IUPAC rules).\textsuperscript{[14]} The spin-spin couplings observed in the \textsuperscript{183}W NMR spectrum was successfully used to assign the chemical shifts of each W site in [PTi\textsubscript{2}W\textsubscript{10}O\textsubscript{40}]\textsuperscript{7-} (5) \textsuperscript{[27]} in a manner similar to that reported earlier for [PTiW\textsubscript{11}O\textsubscript{40}]\textsuperscript{5-} (1a).\textsuperscript{[22]} As would be expected, the increase in basicity of the [PTi\textsubscript{2}W\textsubscript{10}O\textsubscript{40}]\textsuperscript{7-} (5) is more strikingly in comparison with the mono-Ti\textsuperscript{IV}-substituted Keggin polyanion. It can not only protonate reversibly to form [H\textsubscript{2}PTi\textsubscript{2}W\textsubscript{10}O\textsubscript{40}]\textsuperscript{5-} (H\textsubscript{2}5), but also form 1:1 complexes with series of M\textsuperscript{2+} ions (M = Mn, Fe, Co, Ni, Zn).\textsuperscript{[27]} In 1991, Yamase et al. carried out the X-ray crystal structure analysis on the mixed diethylammonium sodium salt of the polyanion [H\textsubscript{2}PTi\textsubscript{2}W\textsubscript{10}O\textsubscript{40}]\textsuperscript{5-} (H\textsubscript{2}5), whose substituted sites were distinguishable due to the preservation of the preferred orientation.\textsuperscript{[28]} The predominant configuration has a C\textsubscript{2} symmetry, which confirms the results of earlier \textsuperscript{183}W NMR work.\textsuperscript{[27]} Moreover, the terminal Ti–O distances are determined as 1.77 and 1.75 Å, whose bond valence summary are 1.13 and 1.19, respectively, indicating they are protonated.

![Figure 1-6. Proposed structures of (a) [PTiW\textsubscript{11}O\textsubscript{40}]\textsuperscript{5-} (1a) and (b) [PTi\textsubscript{2}W\textsubscript{10}O\textsubscript{40}]\textsuperscript{7-} (5).](image-url)
to form the OH groups. This is in good agreement with the hypothesis proposed by Ho [29] and Knoth [27], that is, the terminal oxygen on titanium is the most likely protonation site.

Infrared spectra (IR) of the mono- or di-Ti$^{IV}$ substituted polyanions described above all are closely related to the spectrum of [PW$_{12}$O$_{40}$]$^{3-}$ in the 700-1000 cm$^{-1}$ range, except for slight changes of the band positions.[22] However, it should be noted that the triply degenerate phosphate stretch (~1080 cm$^{-1}$) in the spectrum of [PW$_{12}$O$_{40}$]$^{3-}$ split into two bands for [PTiW$_{11}$O$_{40}$]$^{5-}$ (1a) [22] and three bands for [PTi$_2$W$_{10}$O$_{40}$]$^{7-}$ (5)[27], respectively, because of loss of tetrahedral symmetry when one or two WO$_4^{4+}$ group is replaced by the TiO$_2^{2+}$ group. This phenomenon was also observed on other heterometal-substituted {PW$_{12}$} species, and the degree of splitting varies with the nature of the hetero group and the strength of the bond between it and its associated phosphate oxygen.[22,30,31,32,33,34] Interestingly, the infrared spectra of [Ti(OH)$_2$]PO$_3$ [29] and [H$_2$Ti$_2$W$_{10}$PO$_{40}$]$^{5-}$ (H$_2$5) [27] display a triply degenerate asymmetric phosphate stretch at 1060 cm$^{-1}$, in contrast to the nondegenerate absorption described above for the unprotonated species [PTiW$_{11}$O$_{40}$]$^{5-}$ (1a) and [PTi$_2$W$_{10}$O$_{40}$]$^{7-}$ (5). This has been ascribed to the significant restoration of the tetrahedral symmetry about the phosphorus upon protonation of the anion, which is in consist with the fact that the terminal oxygen on titanium is the most likely protonation site.[29]

Further reactions of [PTiW$_{11}$O$_{40}$]$^{5-}$ (1a) and [PTi$_2$W$_{10}$O$_{40}$]$^{7-}$ (5) with hydrogen peroxide result in their corresponding peroxo derivatives [PTiW$_{11}$O$_{39}$(O$_2$)$_2$]$^{5-}$ (6)[24,34] and [PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$]$^{7-}$ (7).[24] respectively. Crystalline salt of both polyanions are statistically disordered according to the X-ray crystal structure examination. Therefore, the locations of Ti atoms and peroxo ligands in the polyanions were not determined. However, it is clearly shown that the α-Keggin configuration was retained in both peroxo polyanions, and the final difference Fourier map indicated the existence of the side-on O$_2$ groups attached to some of the metal atoms. $^{183}$W NMR spectrum of [PTiW$_{11}$O$_{39}$(O$_2$)$_2$]$^{5-}$ (6) gives six lines in the intensity order of 2:2:1:2:2:2, indicating the retention of the C$_5$ symmetry from its parent polyanion [PTiW$_{11}$O$_{40}$]$^{5-}$ (1a). The small change in the chemical shift for the W atom on the mirror plane strongly suggests the bonding of the O$_2$ group to the Ti atom. By analogy, [PTi$_2$W$_{10}$O$_{38}$(O$_2$)$_2$]$^{7-}$ (7) also maintain the C$_2$ symmetry as that in [PTi$_2$W$_{10}$O$_{40}$]$^{7-}$ (5). In addition, the
appearance of the new absorption band at 390 nm in the electronic spectra of these polyanions also support the peroxidation at the Ti sites. The protonated derivative of the \([\text{PTiW}_{11}\text{O}_{39}(\text{O}_2)]^{5+}\) (6) can be obtained in situ by adding 1 equiv of \(\text{H}^+\), but decompose during the precipitation according to the work by Kholdeeva et al.\[34,35\] Subsequently, they optimized the synthesis procedure via interaction of the \(\mu\)-oxo dimeric heteropolytungstate \(\{\text{PTiW}_{11}\text{O}_{39}\text{O}_2\}\)^8\- (10) with an excess of 30% aqueous \(\text{H}_2\text{O}_2\) in MeCN.\[36\] The electronic and vibrational spectra of 10 are very similar to those of the unprotonated polyanion \([\text{PTiW}_{11}\text{O}_{39}(\text{O}_2)]^{5-}\) (6), while \(^{31}\text{P}\) and \(^{183}\text{W}\) NMR spectra differ significantly. The resonance Raman (RR) deuterium labeling experiments, in consistent with the DFT calculation results, shows that the extra proton is most likely localized at a Ti–O–W bridging oxygen rather than at the peroxo group. Moreover, protonation of the titanium peroxo complex results in an increase of the redox potential of the peroxo group, as well as the activation of this complex toward the oxidation of organic substrates under both stoichiometric and turnover conditions.\[34,35,37\]

![Figure 1-7. Proposed structures of (a) \([\alpha\text{-CpTiPW}_{11}\text{O}_{39}]^{2+}\) (8a) and (b) \([\beta\text{-CpSiW}_{9}\text{V}_{3}\text{O}_{40}]^{2+}\) (9).](image)

During the past few decades, organometallic POM derivatives have stemmed not only for their large structural variety, but also for the new and/or enhanced properties due to the synergistic association between the organic and inorganic components.\[38,39,40\] In the field of catalysis, the isolation of this type of compounds can provide more mechanistic insights into the obscure interactions between organic molecules and the surface of oxides, leading to novel efficient recyclable multifunctional catalysts. For the Ti\(^{IV}\)-substituted POM, such organometallic derivatives can be classified into two subclasses according their different binding
modes between the organometallic species and POM block: (1) organometallics-incorporated POMs that features direct incorporation of organometallics into the vacant site of the polyoxoanion lattice; (2) POM-supported organometallics where the organometallic group(s) is/are covalently attached to a polyoxoanion surface.

Subclass (1). In 1978, Klemperer et al. reported the synthesis of the first organotitanium-incorporated POM, the \( [\alpha\text{-CpTiPW}_{11}\text{O}_{39}]^{4-} \) (8a), by reaction of \( \text{CpTiCl}_3 \) and \((n\text{-Bu}_4\text{N})_4\text{H}_3\text{PW}_{11}\text{O}_{39}\) in the organic solvent \( 1,2\text{-C}_2\text{H}_4\text{Cl}_2 \).\(^{[30]}\) Subsequently, this polyanion and its polytungstosilicate analog, \( [\alpha\text{-CpTiSiW}_{10}\text{O}_{39}]^{5-} \) (8b), were synthesized by Knoth in the aqueous solution.\(^{[31]}\) The appearance of two peaks at 575 and 558 ppm in the \( ^{17}\text{O} \) NMR can be assigned to two types of W–O–Ti bridging oxygens, indicating a structure with an overall \( C_3 \) point group symmetry (Figure 1-7a).\(^{[30]}\) This was later on confirmed by the \( ^{183}\text{W} \) NMR spectrum, which showed six doublets of intensity ratios 2:1:2:2:2:2.\(^{[41]}\) FTIR spectrum on the potassium salt of 8a displays a single, sharp absorption at 1445 cm\(^{-1}\) in the 1300 - 1500 cm\(^{-1}\) region, which is the characteristic C–C stretch for a \( \eta^5\text{-C}_5\text{H}_5 \) ligand bonded to Ti\(^{IV} \) center.\(^{[30]}\) Therefore, the Ti\(^{IV} \) atom in polyanion 8a adopts a formal octahedral coordination geometry, where three coordination sites are occupied by the \( \pi \)-bonded cyclopentadienyl ring while the remaining five coordination sites are bonded to the \{PW\(_{11}\)\} Keggin fragment. Notably, the polyanion 8a differs markedly from other mononuclear oxygen-bonded complexes of the CpTi\(^{3+} \) with regard to its hydrolytic stability. Such an unprecedented stability toward hydrolysis is undoubted due in part to steric factors, but also related the function of the “charge sink”-like POM ligand in delocalizing the additional negative charge, cause by the substitution of \{W=O\}\(^{4+} \) by CpTi\(^{3+} \), over the surface of the entire polyanion. For the latter, a \( \text{trans} \) bond alternation mechanism was proposed, which provided a self-consistent interpretation of \( ^{183}\text{W} \) NMR chemical shifts observed for the polyanion 8a.\(^{[41]}\) This improved hydrolytic stability (up to pH 6) suggested Keana et al. a new approach to prepare small, highly electron dense labels for electron microscopy (EM), namely, the attachment of reactive organic functional groups to the cyclopentadienyl ring. In 1986, they reported a series of cyclopentadienyltitanium-substituted Keggin- and Dawson-type heteropolytungstates that bear reactive organic groups suitable for chemoselective covalent bonding to macromolecular sites.\(^{[23,42]}\)
Subclass (2). In 1986, Finke et al. reported the reaction of the trivanadium-substituted polyoxometalate \( [\text{SiW}_9\text{V}_3\text{O}_{40}]^{7-} \) and an equimolar amount of \( \text{CpTi}^{3+} \) in the \( \text{CH}_3\text{CN} \) medium, resulting in the polyoxometalate-supported organometallic complex \( [\beta\text{-CpTiSiW}_9\text{V}_3\text{O}_{40}]^{4-} \) (9). And a full report of characterization of this polyanion was documented according to their later work.\(^{[44]}\) In the FTIR spectrum of polyanion 9, a strong perturbation of the ca. 800 cm\(^{-1}\) band (M–O–M edge shared octahedra) was observed compared to that of the parent \( [\text{SiW}_9\text{V}_3\text{O}_{40}]^{7-} \), suggesting the tight attachment of \( \text{CpTi}^{3+} \) group onto these edge shared bridging oxygens. The \( ^{51}\text{V} \) NMR spectrum for 9 shows two resonances of 1:2 intensity at -561 and -604 ppm and thus reveals that the symmetry of the complex is \( C_s \), a change from the \( C_{3v} \) symmetry for the starting \( [\text{SiW}_9\text{V}_3\text{O}_{40}]^{7-} \) (one peak at \( \delta = -531 \) ppm). This was confirmed by the five-peak \( ^{183}\text{W} \) NMR spectrum with relative intensities of 2:2:1:2:2. Due to the failure to obtain suitable crystals for X-ray structural analysis, two plausible \( C_s \) symmetry structures for 9 was proposed at that time: (A) the \( \text{CpTi}^{3+} \) group is attached to two bridging W–O–V oxygens plus one terminal V=O oxygen; (B) the \( \text{CpTi}^{3+} \) group is attached to two bridging W–O–V oxygens plus one bridging W–O–W oxygen.\(^{[44]}\) Recently, the electronic structures of 9 investigated by Density Functional Theory (DFT) methods indicates that the former structure (type A; Figure 1-7b) is more stable than the latter one (type B).\(^{[45]}\) Such type of inner-sphere Ti\(^{IV}\)-to-Polyoxoanion binding, i.e. the rest of titanium’s coordination sphere in \( \text{CpTi}^{3+} \) are fully and irreversibly occupied by three polyoxoanion surface oxygens, leads to an enhanced stability of 9 toward moist air, which is further confirmed by the nonexchangeability of the polyoxoanion surface attached \( \text{CpTi}^{3+} \) from the experiments performed employing ion-exchange resins.\(^{[44]}\)

### 1.3.1.2 Ti\(^{IV}\)-substituted Keggin POM dimers

In 2000, Kholdeeva et al. reported the dimerization of the \( [\text{PTiW}_{11}\text{O}_{40}]^{5-} \) (1a) via acidification treatment, resulting in the \( \mu\)-hydroxo dimer of the mono-Ti-substituted Keggin polyanion, namely \( [(\alpha\text{-PTiW}_{11}\text{O}_{39})_{2}\text{OH}]^{7-} \) (H10), where the two \( [\text{PTiW}_{11}\text{O}_{39}]^{3-} \) subunits are interlinked by forming a Ti–OH–Ti bridge.\(^{[34]}\) The \( \text{pH} \) varied \( ^{31}\text{P} \) NMR spectroscopic measurements facilitated the direct observation of \( \mu\)-hydroxo dimer formation, and suggested a plausible mechanism for the formation of H10 upon acidification of 1a, which can be represented by equations 1-2 to 1-4:
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\[ [\text{PTiW}_{11}\text{O}_{40}]^{5-} (1\text{a}) + \text{H}^+ \rightleftharpoons [\text{PTi(OH)}\text{W}_{11}\text{O}_{39}]^{4+} (\text{H1a}) \]  \hspace{1cm} (1-2)

\[ [\text{PTi(OH)}\text{W}_{11}\text{O}_{39}]^{4+} (\text{H1a}) + [\text{PTi(OH)}\text{W}_{11}\text{O}_{39}]^{4+} (\text{H1a}) \rightleftharpoons \]  \hspace{1cm} (1-3)

\[ [(\alpha\text{-PTiW}_{11}\text{O}_{39})_2\text{O}]^{8-} (10) + \text{H}_2\text{O} \]  \hspace{1cm} (1-4)

This mechanism is consistent with those proposed for the dimerization process in Lindqvist and Keggin POMs by using DFT methods.\[^[46]\] Subsequently, the same group presented their further progress on the synthesis of the unprotonated \(\mu\)-oxo dimeric intermediate \([(\alpha\text{-PTiW}_{11}\text{O}_{39})_2\text{O}]^{8-} (10)\) by the basification of \([(\alpha\text{-PTiW}_{11}\text{O}_{39})_2\text{OH}]^{7-} (\text{H10})\) or \(\text{H}_3\text{PW}_{11}\text{TiO}_{40}\).\[^[26]\] The FTIR spectra of 10 and H10 are similar and shows a pronounced band at 640-655 cm\(^{-1}\), which is characteristic of a Ti–O–Ti (or Ti–OH–Ti) vibration.\[^[26,34]\] X-ray crystal structure of polyanion 10 (Figure 1-8) was determined by Nomiya and coworkers for the first time in 2013.\[^[25]\] The two Keggin units in this polyanion are crystallographically independent due to the slight twist between them, thus resulting in the overall \(C_1\) symmetry of the polyoxoanion molecule in the solid state. However, in solution, the twist was averaged and thus resulted in an overall \(C_{2v}\) symmetry of 10, which was confirmed by the six-peak \(^{183}\text{W}\) NMR spectrum in \(\text{D}_2\text{O}/\text{CD}_3\text{CN} (1:3 \text{ v/v})\) with a relative intensity ratio of 2:2:1:2:2:2. Bond valence sum (BVS) calculations based on the solid structure strongly suggested that the bridging oxygen atom was not protonated.

**Figure 1-8.** Structure of \([(\alpha\text{-PTiW}_{11}\text{O}_{39})_2\text{O}]^{8-} (10)\).

For the di-Ti\(^{IV}\)-substituted Keggin polyoxotungstates, there are two types of structures:

\[ [(\alpha-1,2-\text{PTi}_2\text{W}_{10}\text{O}_{38})_2(\mu\text{-O})_2]^{10-} (11),[^{[47]}] \hspace{1cm} (1) \]

\[ [(\gamma\text{-XTi}_2\text{W}_{10}\text{O}_{36}(\text{OH})_2)_2(\mu\text{-O})_2]^{8-} (\text{X = Si (12a), Ge (12b)}) \]  \hspace{1cm} (2)

\[ [(\gamma\text{-SiTi}_2\text{W}_{10}\text{O}_{36}(\text{OH})(\text{OMe}))_2(\mu\text{-O})_2]^{8-} (13),[^{[48,49]}] \]

The type (1) polyanion 11 was initially found by Nomiya et al. as a minor product in the preparation of the dimeric, tri-Ti\(^{IV}\)-1,2,3-substituted species, \([(\alpha\text{-PTi}_3\text{W}_9\text{O}_{37})(\mu\text{-O})_3]^{12-} (14c)\) (see below for detailed discussion),\[^[50]\] and was
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Optimized as a main product in their later work and structurally characterized by X-ray diffraction technique (Figure 1-9a).[47] The molecular structure of 11 consists of a dimeric anhydride formed by two Ti–O–Ti bonds linking two [(α-1,2-PW_{10}Ti_{2}O_{40})]^{7-} Keggin units, exhibiting an overall C_{2v} symmetry, which is consistent with a 2:2:2:1:1 ^{183}W NMR spectrum. Furthermore, ultracentrifugation molecular weight (MW) measurements of polyanion 11 in aqueous solution showed the pH-dependent interconversion between the dimeric [(α-1,2-PTi_{2}W_{10}O_{38})(μ-O)]^{10-} (11) and monomeric [(α-1,2-PW_{10}Ti_{2}O_{40})]^{7-}, where the dimer predominates under more acidic conditions (pH 1.0-2.2), while the monomer presents as the main species under less acidic conditions (pH 7.8).[47] The pH-dependent interconversion can be shown as the following equation 1-5:

\[
[(α-1,2-PTi_{2}W_{10}O_{38})(μ-O)]^{10-} (11) + 4OH^- \rightleftharpoons 2[α-1,2-PW_{10}Ti_{2}O_{40}]^{7-} + 2H_2O \quad (1-5)
\]

Nevertheless, the attempt to isolate analytically pure solid of the monomeric [(α-1,2-PW_{10}Ti_{2}O_{40})]^{7-} was unsuccessful, because the polyanion readily reverted to the dimer in solution.

![Figure 1-9. Structures of (a) [(α-1,2-PTi_{2}W_{10}O_{38})(μ-O)]^{10-} (11) and (b) [γ-XTi_{2}W_{10}O_{46}(OH)_{2}](μ-O)]^{9+} (X = Si (12a), Ge (12b)].](image)

Polyanions 12a and 12b in type (2), on the other hand, were synthesized by reaction of titanium(IV) sources and the divacant lacunary γ-Keggin-type
silicotungstate of $[\gamma$-X$W_{10}O_{36}]^{8-}$ (X = Si (12a), Ge (12b)). Both of them feature isomorphic dimeric structures, where each half $\gamma$-Keggin fragment contains a dinuclear titanium center bridged by two hydroxo groups, and the resulting Ti$_2$(\(\mu\)-OH)$_2$ core connects to the other Ti$_2$(\(\mu\)-OH)$_2$ core of the paired $\gamma$-Keggin subunit through Ti–O–Ti linkages (Figure 1-9b). The X-ray analysis revealed the overall $C_{2h}$ molecular symmetry of these two polyanions, which were confirmed by their $^{183}$W NMR spectra exhibiting three peaks with intensity ratio of 1:2:2. Further reaction of the polyanion 12a and excess amount of MeOH resulted in the formation of the methoxo derivative, namely, $[\{\gamma$-SiTi$_2W_{10}O_{36}(OH)(OMe)\}_2(\mu-O)\}_2]^{8-}$ (13).$^{[48]}$ $^{183}$W NMR spectrum of this polyanion showed six peaks with intensities of 1:2:2:2:1:2, which suggested the transfer of the original $D_{2h}$ symmetry to a lower $C_2$ one. The X-ray analysis indicated that the overall structure of 13 is similar to that of 12a, except for the replacement of one OH bridge in the Ti$_2$(\(\mu\)-OH)$_2$ core with one OMe group, therefore giving rise to novel Ti$_2$(\(\mu\)-OH)(\(\mu\)-OMe) core in each $\gamma$-Keggin fragment.

Figure 1-10. Structures of (a) [(\(\alpha\)-XTi$_3W_9O_{37})(\mu-O)\}_3]^{14-}$ (X = Ge (14a), Si (14b), n = 14; X = P (14c), n = 12) and (b) [(\(\beta\)-XTi$_3W_9O_{37})(\mu-O)\}_3]^{14+}$ (X = Si (15a), Ge (15b)).

In 1993, Yamase et al. reported the first tri-Ti$^{IV}$-substituted polyoxotungstate, the dimeric [(\(\alpha\)-GeTi$_3W_9O_{37})(\mu-O)\}_3]^{14-}$ (14a), which was synthesized by reaction of Na$_{10}$[(\(\alpha\)-GeW$_9$O$_{34}$)-18H$_2$O and TiCl$_4$ under acidic condition (pH < 1.0).$^{[51]}$ This polyanion consists of two $C_{3v}$ [(\(\alpha\)-GeTi$_3W_9O_{40})]^{10-}$ fragments fused together at the terminal O atoms of the six Ti$^{IV}$ atoms (Figure 1-10a). The $^{183}$W NMR spectrum...
showed 2 peaks with intensity ratio of 1.94:1, in consistent with the two types of W atoms revealed by X-ray crystal structural analysis. Later on, Nomiya et al. reported the silicate- and phosphate-analogs of the polyanion 14a, namely, [(α-SiTi₃W₉O₃7)(μ-O)₃]^{14-} (14b) and [(α-PTi₃W₉O₃7)(μ-O)₃]^{12-} (14c). In 1993, Finke et al. reported the synthesis of [(β-SiTi₃W₉O₃7)(μ-O)₃]^{14-} (15a) (Figure 1-10b) polyanion by reaction of TiOSO₄ and A-β-Na₉HSiW₉O₃₄ under acidic (pH 1.0) condition. Both two [SiW₉Ti₃O₄₀]^{10-} units in this structure have the “β-” configuration, different from the aforementioned [α-GeTi₃W₉O₄₀]^{10-}. In 2007, Yamase et al. reported the germanate-analog [(β-GeTi₃W₉O₃₇)(μ-O)₃]^{14-} (15b).

In 2007, Kortz et al. reported the synthesis of a dititanium-containing 19-tungstodiarsenate(III) [Ti₂(OH)₂As₂W₁₉O₆₇(H₂O)]^{8-} (16) (Figure 1-11) by reaction of TiOSO₄ and K₁₄[As₂W₁₉O₆₇(H₂O)] in aqueous, acidic medium (pH 2). This polyanion comprises two [B-α-AsW₉O₃₃]^{9-} linked by one {WO(OH)} and two {Ti(OH)} groups, resulting in a sandwich-like structure with C₂ symmetry. Each Ti⁴⁺ ion adopts an unprecedented square-pyramidal coordination geometry, with the apical –OH ligand pointing outwards. This polyanion can be isolated as TBA salt, which shows high catalytic activity (TOF = 11.3 h⁻¹) in H₂O₂-based cyclohexene oxidation reactions.

1.3.1.3 Ti⁴⁺-substituted Keggin POM trimers

In 2008, U. Kortz et al. reported the cyclic Ti₉ Keggin trimmers
Chapter 1 Introduction

\[ [(\alpha{-}\text{Ti}_3\text{PW}_{9}\text{O}_{38})(\text{PO}_4)]^{18-} \] (17) (Figure 1-12a) and
\[ [(\alpha{-}\text{Ti}_3\text{SiW}_{9}\text{O}_{37}\text{OH})_3(\text{TiO}_3(\text{OH}_2)_3)]^{17-} \] (18a) (Figure 1-12b), both of which consist of three \{Ti_3XW_{9}O_{37}\} subunits (X= P or Si) linked via three Ti–O–Ti bridges and one capping group, either one tetrahedral \{PO_4\} or one octahedral \{TiO_6\}.\[56\] $^{31}$P NMR and $^{183}$W NMR spectroscopical analysis indicated the $C_{3v}$ symmetry of both two polyanions. In the same year, Liu et al. reported two similar tungstogermanate derivatives of the trimeric, Ti$_9$-containing POMs, namely the \{[K∩(Ge(OH)O$_3$)(GeW$_9$Ti$_3$O$_{38}$H$_2$)$_3$)]$^{14-}$ (19) and \{[K∩[(SO$_4$)(GeW$_9$Ti$_3$O$_{38}$H$_3$)$_3$)]$^{10-}$ (20), the cavities of which are occupies by K$^+$ ions.\[57\] Recently, the tungstogermanate derivative \{[(\alpha{-}\text{Ti}_3\text{GeW}_9\text{O}_{37}\text{OH})_3(\text{TiO}_3(\text{OH}_2)_3)]^{17-} \} (18b) (Figure 1-12b) was also isolated by U. Kortz and coworkers.\[58\]

![Figure 1-12. Structures of (a) \{[(\alpha{-}\text{Ti}_3\text{PW}_{9}\text{O}_{38})(\text{PO}_4)]^{18-} \} (17) and (b) \{[(\alpha{-}\text{Ti}_3\text{XW}_{9}\text{O}_{37}\text{OH})_3(\text{TiO}_3(\text{OH}_2)_3)]^{17-} \} (X = \text{Si (18a), Ge (18b))}.](image)

![Figure 1-13. Structure of \{[(\text{Ti}_2(\beta{-}\text{SiW}_{10}\text{O}_{39}))_4]^{24-} \} (21).](image)
1.3.1.4 TiIV-substituted Keggin POM tetramers

In 2004, Kortz et al. reported a unique tetrameric and cyclic polytungstosilicate, the $\{[\text{Ti}_2(\beta\text{-}\text{SiW}_{10}\text{O}_{39})]\}_4^{24+}$ (21) (Figure 1-13).[18] This polyanion was synthesized by reaction of TiOSO$_4$ and $[\gamma\text{-}\text{SiW}_{10}\text{O}_{36}]^{8-}$ in aqueous acidic medium (pH 2), during which the $\gamma$-Keggin unit underwent a transformation to the $\beta$-Keggin structure. The polyanion is composed of four $\{\text{Ti}_2(\beta(1,10)-\text{SiW}_{10})\}$ fragments, which are linked via Ti–O–Ti bridges. The two Ti atoms of each fragment are located in the 1 and 10 positions (according to the IUPAC rules), not allowing the formation of a dimeric product. Due to the $C_2$ symmetry of the polyanion, 10 expected peaks of equal intensities were identified in the $^{183}\text{W}$ NMR spectrum recorded in solution. Significantly, the isolation of this polyanion indicated that very large TiIV-substituted Keggin polyanions can be formed.

1.3.1.5 Other TiIV-substituted Keggin heteropolyoxotungstates

In 2005, Nomiya et al. reported a mono-lacunary Keggin POM connected with a Ti–O–Ti bonding complex, namely $[[\text{Ti(OH)}(\text{ox})]_2(\mu-O)][(\alpha-\text{PW}_{11}\text{O}_{39})]^{7-}$ (22) (Figure 1-14a). This polyanion was synthesized by reaction of tri-lacunary Na$_9[A-\text{PW}_{9}\text{O}_{34}]-19\text{H}_2\text{O}$ (or mono-lacunary K$_7[\text{PW}_{11}\text{O}_{39}]-10\text{H}_2\text{O}$) and K$_2\text{TiO(ox)}_2\cdot2\text{H}_2\text{O}$ in a HCl-acidic solution (pH 0.08).[59] The polyanion features the composition of one host (mono-lacunary unit) and two guests (two octahedral Ti groups), in contrast to most Ti-substituted POMs comprising one host and one guest. $^{31}\text{P}$ NMR spectroscopical analysis revealed there is a dissociation equilibrium of the POM in aqueous solution which depends on the temperature and pH. In 2006, the same group reported the preparation and structural characterization of a Ti–O–Ti bonding complex constructed in a dilacunary $\alpha$-Keggin POM, namely the $[[[\text{Ti(ox)}(\text{H}_2\text{O})]_4(\mu-O)]_3[(\alpha-\text{PW}_{10}\text{O}_{37})]^{7-}$ (H$_2$ox = oxalic acid) (23) (Figure 1-14b).[60] It is prepared by reaction of K$_{10}[(\alpha-1,2-\text{PW}_{10}\text{Ti}_2\text{O}_{39})_2]-18\text{H}_2\text{O}$ and K$_2[\text{TiO(ox)}_2]\cdot2\text{H}_2\text{O}$ in acidic solution (pH 0.08). The structure of the polyanion is composed of four octahedral TiIV-O groups (guests) incorporated to the two adjacent vacant sites (hosts) of the $\alpha$-Keggin unit, giving rise to a “two hosts-four guests” POM.

In 2010, Nomiya et al. reported the synthesis of two new TiIV-substituted POMs, $[[\text{Ti}_4(\mu-O)_3(\text{SO}_4)_2(\text{H}_2\text{O})_8][(\alpha-\text{PW}_{9}\text{O}_{34})]^{3-}$ (24) (Figure 1-15a) and $[[[\text{Ti(H}_2\text{O})_3]_2(\mu-O)][(\alpha-\text{PW}_9\text{Ti}_2\text{O}_{38})]^{26-}$ (25) (Figure 1-15b), by using the preformed $[(\alpha-1,2,3-\text{PW}_9\text{Ti}_3\text{O}_{17})_2\text{O}_3]^{12-}$ as precursor.[61] The former polyanion features a
monomeric $\alpha$-Keggin species containing four octahedral $\text{Ti}^{\text{IV}}$-O groups and two $\text{SO}_4^{2-}$ ligands, whereas the second polyanion is a dimer of tetra-$\text{Ti}^{\text{IV}}$-embeded tri-lacunary $\alpha$-Keggin units linked by two $\text{Ti}--\text{O}--\text{Ti}$ bridges. From the viewpoint of the host-guest chemistry, these two products exhibit the “three hosts-four guests” and a combination of “one host-one guest” and “one host-two guests” relations, respectively. In 2010, Nomiya et al. published a review to summary the Group IV Metal Ion ($\text{Ti}^{\text{IV}}$, $\text{Zr}^{\text{IV}}$ and $\text{Hf}^{\text{IV}}$)-Containing POMs.$^[62]$
1.3.2 Ti$^{IV}$-substituted Wells-Dawson heteropolyoxotungstates with tetrahedral PO$_4$ hetero groups

1.3.2.1 Ti$^{IV}$-substituted Wells-Dawson POM monomers

Compared to the Keggin Ti-POMs, the Wells-Dawson Ti-POMs were less extensively studied. In 1968, Tourné reported the reaction of [X$'$$_2$W$_{17}$O$_{61}$]$^{q+4}$- (X$'$ = P, As; $q$ is the negative charge of the parent [X$'$$_2$W$_{18}$O$_{62}$]$^{q-}$ polyanion) and the Ti$^{4+}$ ions, which resulted in the monomeric [X$'$$_2$TiW$_{17}$O$_{62}$]$^{(q+2)-}$ (X$'$ = P (26a), As (26b)) polyanions.$^{[21]}$ Later on, Keana, Finke and their coworkers carried out systematically synthetic and structural studies on a series of organometallic derivatives of the monolacunary [P$_2$W$_{17}$O$_{61}$]$^{10-}$ polyanions.$^{[23,44]}$ The coordination environment of the Ti$^{IV}$ center and the linkage between the organotitanium(IV) group and the POM fragment are similar to that observed in the aforementioned Keggin systems, which will not be discussed in detail here.

1.3.2.2 Ti$^{IV}$-substituted Wells-Dawson POM dimers

In 2008, the synthesis of the dimer of mono-Ti$^{IV}$-substituted species based on the Wells-Dawson $\alpha_2$-{P$_2$W$_{17}$O$_{62}$} was reported by Nomiya et al.$^{[63]}$ The anionic part features a 2:2 dimer [($\alpha_2$-P$_2$W$_{17}$TiO$_{61}$)$_2$(µ-O)]$^{14+}$ (27), in which two equivalent $\alpha_2$-mono-Ti$^{IV}$-substituted Wells-Dawson POM subunits are connected through one Ti–O–Ti bond (Figure 1-16). They also obtained the free-acid form of the POM, while BVS (bond valence sum) calculation showed that one O atom in one of the two Wells-Dawson subunits is protonated, therefore two subunits are unequivalent. The pH-varied $^{31}$P NMR spectra of both compounds showed the monomer, the dimer, the mono-protonated species of the dimer are the predominant species in the solutions, at pH 7.0, pH 1.0-3.0 and pH 0.5, respectively.

![Figure 1-16. Structure of [($\alpha_2$-P$_2$W$_{17}$TiO$_{61}$)$_2$(µ-O)]$^{14+}$ (27).](image-url)
Kortz and coworkers have been interested in the interaction of Ti$^{IV}$ with lacunary Wells-Dawson POMs for a long time. In 2003, they firstly use the XRD analysis to characterize another 2:2 dimeric polytungstophosphate, namely $[\text{TiP}_2\text{W}_{15}\text{O}_{55}\text{OH}]^{14-}$ (28), which consists of two $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ linked by two Ti$^{IV}$ atoms in a sandwich fashion (Figure 1-17). BVS calculation indicated that one O atom attached to one of the two Ti$^{IV}$ atoms is protonated, resulting in the chiral distortion within each $\{\text{P}_2\text{W}_{15}\text{Ti}\}$ fragment in the polyanion $[\text{TiP}_2\text{W}_{15}\text{O}_{55}\text{OH}]^{14-}$ (28).

Figure 1-17. Structure of $[\text{TiP}_2\text{W}_{15}\text{O}_{55}\text{OH}]^{14-}$ (28).

1.3.2.3 Ti$^{IV}$-substituted Wells-Dawson POM tetramers

As for the Ti$^{IV}$-substituted Wells-Dawson POM tetramers, some successful work by Kortz and Nomiya will be discussed. In 2003, Kortz et al. firstly reported the a tetrameric giant polyanion $\{[\text{Ti}_3\text{P}_2\text{W}_{15}\text{O}_{57.5}(\text{OH})_3]_4\}^{24+}$ (29) (Figure 1-18a). This polyanion is composed of four identical $\{\text{P}_2\text{W}_{15}\text{Ti}_3\}$ fragments, resulting to an overall $T_d$ point group symmetry. Notably, from crystallographical analysis results, the authors believe that the counter cations (especially the NH$_4^+$) play a crucial templating role in the self-assembly process and the crystallization, evidenced by the fact that an ammonium ion is located in the middle of the central cavity of the molecule, surrounded by twelve protonated O atoms of the Ti-O fragments. Later on, Nomiya et al. reported an isostructural non-protonated polyanion, where the central cavity is occupied by a Cl$^-$ ion, rather than NH$_4^+$. Hitherto, the POM with the largest number
of TiIV centers is the $\left[(\alpha-1,2,3-P_2W_{15}Ti_3O_{62})_4\{\mu_3-Ti(OH)_3\}_4Cl\right]^{45-}$ (30), reported by Nomiya and coworkers in 2003. This polyanion was prepared by reaction of $\{P_2W_{15}O_{56}\}^{12-}$ and excess of TiCl4 in aqueous solution. The polyanion unit was revealed to be a giant, inorganic molecule, which is composed of four tri-TiIV-substituted $\alpha$-Dawson substructures linked by four $\{Ti(OH)_3\}$ bridging groups and one encapsulated Cl\(^-\) ion located in the central cavity (Figure 1-18b). Thus, it can be viewed as a derivative from the tetrameric $\{Ti_3P_2W_{15}\}_4$ by adding four extra $\{TiO_3(OH)_3\}$ octahedra.

The reaction of the $\left[(\alpha-1,2,3-P_2W_{15}Ti_3O_{62})_4\{\mu_3-Ti(OH)_3\}_4Cl\right]^{45-}$ (30) and excess of 30% aqueous hydrogen peroxide gave rise to a water-soluble monomeric peroxoderivative, $\left[\alpha-1,2,3-P_2W_{15}(TiO_2)_3O_{56}(OH)_3\right]^9-$ (31), which contains three peroxy groups with side-on coordination to the three Ti atoms.

1.4 Multinuclear lanthanide(III)-containing heteropolytungstates

The synthesis of lanthanide(III)-containing polyoxotungstates are attracting increasing interest due to the structural variety and some chemical and physical properties, such as photoluminescence, Lewis acid catalysis and magnetism. Due to the larger ion radius than that of transition metal ions, the lanthanide(III) ion can not completely incorporate into vacant sites of the precursor. Therefore, additional sites are available for further derivatization, which leads to the formation of large polyanions. This feature has been successfully used by several research groups to
synthesize giant, discrete molecular POM materials. In 2010, a research report by Kortz et al. gave the recent advances in the lanthanide-containing POMs.\[^{68}\] Hence, the following introduction will only focus on the supramolecular chemistry based on the large 4f ions-containing assemblies with more than four polyanion building blocks.

### 1.4.1 Tetrameric Ln\textsuperscript{III}-containing polyoxotungstates

In 2001, Francesconi reported the octa-Ln\textsuperscript{III}-containing polyanions, [(PM\textsubscript{2}W\textsubscript{10}O\textsubscript{38})\textsubscript{4}(W\textsubscript{3}O\textsubscript{14})]\textsuperscript{30-} (M= Eu (32a), Y(32b)) (Figure 1-19a), \[^{11}\] They were synthesized by reaction of Eu\textsuperscript{3+} (or Y\textsuperscript{3+}) and the tri-lacunary precursor [PW\textsubscript{9}O\textsubscript{34}]\textsuperscript{9-} in a 2:1 molar ratio and were isolated as K salts. Their structures can be viewed as an assembly of four di-Ln\textsuperscript{III}-substituted \{α-XW\textsubscript{10}O\textsubscript{37}\} blocks, which are linked via a \{W\textsubscript{3}O\textsubscript{14}\} group.

In 2003, Pope et al. reported the synthesis of a U\textsuperscript{IV}\textsubscript{12} containing tetrameric polyanion of [(UO\textsubscript{2})\textsubscript{12}(μ\textsubscript{3}-O)(μ\textsubscript{2}-H\textsubscript{2}O)\textsubscript{12}(P\textsubscript{2}W\textsubscript{15}O\textsubscript{56})\textsubscript{4}]\textsuperscript{32-} (33) (Figure 1-19b) by reaction of Na\textsubscript{12}[P\textsubscript{2}W\textsubscript{15}O\textsubscript{56}] and of UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}.\[^{69}\]

In 2003, Yamase et al. reported a α-AsW\textsubscript{9}O\textsubscript{33}-based unique crown-shaped ring architecture containing Eu\textsuperscript{3+} ions, namely the [Cs{Eu(H\textsubscript{2}O)\textsubscript{2}(α-AsW\textsubscript{9}O\textsubscript{33})}\textsubscript{4}]\textsuperscript{23-} (34) (Figure 1-20).\[^{70}\] It was isolated as a mixed Cs\textsuperscript{+}/Na\textsuperscript{+} salt. The structure of this polyanion is a Cs\textsuperscript{+}-ion encapsulated tetramer of [Eu(H\textsubscript{2}O)\textsubscript{2}(α-AsW\textsubscript{9}O\textsubscript{33})]\textsuperscript{6-} with a C\textsubscript{4h} symmetry.
Kortz and coworkers did some interesting work in the Wells-Dawson based Ln$^{III}$-containing polyoxotungstates. In 2007, they reported the reaction of K$_{28}$Li$_5$H$_7$[P$_8$W$_{48}$O$_{184}$]·92H$_2$O and early lanthanide ions under hydrothermal and conventional conditions, which resulted in novel structures of the molecular formula Ln$_4$(H$_2$O)$_{28}$K$_6$Li$_7$[KP$_8$W$_{48}$O$_{184}$][H$_4$W$_4$O$_{12}$]$_2$Ln$_2$(H$_2$O)$_{10}$·57H$_2$O (Ln = La (35a), Ce (35b), Pr (35c) and Nd (35d)) (Figure 1-21a). And in 2008, they successively reported a U-shaped trimeric polyanion [Li(H$_2$O)K$_4$(H$_2$O)$_3${((UO$_2$)$_4$(O$_2$)$_4$(H$_2$O)$_2$)$_2$(PO$_3$OH)$_2$P$_6$W$_{36}$O$_{136}$]$_{25}$ (36), encapsulating a cubic {U$_8$} cluster (Figure 1-21b).
In 2007, Wang et al. reported two \{As\_2W\_19\} -based Ln\textsuperscript{III} containing polyanions, namely the \([\text{[Ce}_2\text{O}_2\text{(H}_2\text{O})_3\text{(As}_2\text{W}\_19\text{O}_{68})]_2]^{16-}\) (37) (Figure 1-22) and \([\text{[Ce}_4\text{As}_4\text{W}_{44}\text{O}_{151}\text{(ala)}_4\text{(OH)}_2\text{(H}_2\text{O})_{10}]]^{12-}\) (ala = \(\alpha\)-alanine) (38) (Figure 1-23a). The former is composed of two di-Ce\textsuperscript{IV} -substituted \{As\_2W\_19\} groups, which are dimerized through two Ce–O–W bridges. The reaction of the former compound and the \(\alpha\)-alanine at pH = 2 gave rise to the later alanine-decorated cryptand compound. It can be viewed as a dimer of two \{As\_2W\_19\} linked via a \{W\_6\} groups, in which there are four cavities occupied by four Ce\textsuperscript{IV} ions. Furthermore, the reaction of \([\text{[Ce}_2\text{O}_2\text{(H}_2\text{O})_3\text{(As}_2\text{W}\_19\text{O}_{68})]_2]^{16-}\) (37) and MnCl\_2 at pH = 5 resulted in a third \{AsW\_9\} -based polyanion, \([\text{[Ce}_4\text{As}_4\text{W}_{41}\text{O}_{149}]]^{24+}\) (39) (Figure 1-23b). Electrochemical analyses of the compounds suggested that tetravalent cerium ion can be stabilized by the polyanions with high negative charges.\textsuperscript{[73]}

Figure 1-22. Structures of \([\text{[Ce}_2\text{O}_2\text{(H}_2\text{O})_3\text{(As}_2\text{W}\_19\text{O}_{68})]_2]^{16-}\) (37).

Figure 1-23. Structures of (a) \([\text{[Ce}_4\text{As}_4\text{W}_{44}\text{O}_{151}\text{(ala)}_4\text{(OH)}_2\text{(H}_2\text{O})_{10}]]^{12-}\) (38) and (b) \([\text{[Ce}_4\text{As}_4\text{W}_{41}\text{O}_{149}]]^{24+}\) (39).
1.4.2 Hexa- and octameric Ln<sup>III</sup>-containing polyoxotungstates

For the aforementioned \([\text{Cs}\{\text{Eu}(\text{H}_2\text{O})_2(\alpha-\text{AsW}_9\text{O}_{33})\}_4]^{23-}\) (34), if change the central Cs<sup>+</sup> ion as K<sup>+</sup> ion, a different crown-shaped hexamer of \([\text{Eu}(\text{H}_2\text{O})_2(\alpha-\text{AsW}_9\text{O}_{33})]^{6-}\) with an overall \(S_6\) symmetry can be formed, namely the \([\text{K}\{\text{Eu}(\text{H}_2\text{O})_2(\alpha-\text{AsW}_9\text{O}_{33})\}_6]^{35-}\) (40) (Figure 1-24a).<sup>170</sup> Both the tetramer 34 and hexamer 40 were obtained by reaction of \([\alpha-\text{AsW}_9\text{O}_{33}]^{9-}\) and Eu<sup>3+</sup> ions in a 1:1 ratio in an aqueous solution containing alkali-metal cations and characterized by FTIR, single crystal X-ray diffraction, elemental analysis in solid state, as well as \(^{31}\text{P}\) NMR and electrochemistry studies in solution.

![Figure 1-24. Structures of (a) \([\text{K}\{\text{Eu}(\text{H}_2\text{O})_2(\alpha-\text{AsW}_9\text{O}_{33})\}_6]^{35-}\) (40) and (b) \([\text{CsLn}_6\text{As}_6\text{W}_{65}\text{O}_{218}(\text{OH})_4(\text{H}_2\text{O})_{12}(\text{OAc})_2]^{38-}\) (Ln = Eu (41a), Gd (41b), Tb (41c), Dy (41d), Ho (41e), and Er (41f)).](image1)

![Figure 1-25. Structures of (a) \([\text{Gd}_{10}\text{As}_{10}\text{W}_{88}\text{O}_{308}(\text{OH})_{16}(\text{H}_2\text{O})_{28}(\text{OAc})_4]^{38-}\) (42) and (b) \([\text{Yb}_{10}\text{As}_{10}\text{W}_{88}\text{O}_{308}(\text{OH})_{16}(\text{H}_2\text{O})_{28}(\text{OAc})_4]^{38-}\) (43).](image2)
In 2003, Patzke et al. reported the synthesis and characterization of a family of novel $\text{Ln}^{III}$-containing polytungstoarsenate(III) polyanions, $[\text{CsLn}_6\text{As}_6\text{W}_{63}\text{O}_{218}(\text{H}_2\text{O})_{14}((\text{OH})_4)]^{25-}$ (Ln = Eu (41a), Gd (41b), Tb (41c), Dy (41d), Ho (41e), and Er (41f)) (Figure 1-24b). These polyanions were synthesized by reaction of $[\alpha-\text{AsW}_9\text{O}_{33}]^9-$ and $\text{Ln}^{3+}$ in a 1 : 3 molar ratio in 1 M NaOAc/HOAc buffer at pH 4.7. The structure of this type of polyanion is composed of six $\{\alpha-\text{AsW}_9\}$, two $\{\text{W}_2\text{O}_{10}\}$, three $\{\text{WO}_6\}$, two $\{\text{WO}_5\}$ groups and six $\text{Ln}^{3+}$ ions, which get together under the templating role of the Cs$^+$ ions.

In 2009, Boskovic et al. reported two $\{\text{AsW}_9\}$-based hexameric and octameric POM, $[\text{Gd}_6\text{As}_6\text{W}_{65}\text{O}_{229}(\text{OH})_4(\text{H}_2\text{O})_{12}((\text{OAc})_2)]^{38-}$ (42) (Figure 1-25a) and $[\text{Yb}_{10}\text{As}_{10}\text{W}_{88}\text{O}_{308}(\text{OH})_8(\text{H}_2\text{O})_{28}((\text{OAc})_4)]^{10-}$ (43) (Figure 1-25b). Both polyanions were obtained by reaction of $[\alpha-\text{AsW}_9\text{O}_{33}]^9-$ and $\text{Gd}^{3+}/\text{Yb}^{3+}$ in a 1 : 3 molar ratio in the NaOAc/HOAc buffer at pH 4.7. From a viewpoint of structure, both two polyanions are composed $\{\text{B-}\alpha-\text{AsW}_9\}$ or $\{\text{B-}\beta-\text{AsW}_9\}$ groups linked by $\text{Ln}^{3+}$ ions and W-O fragments.

1.4.3 Large $\text{Ln}^{III}$-containing polyoxotungstates with more than ten building blocks

In 1997, Pope et al. reported the synthesis of a giant Ce$_{16}$-containing polytungstoarsenate(III), $[\text{As}_{12}\text{Ce}_{16}(\text{H}_2\text{O})_{38}\text{W}_{148}\text{O}_{524}]^{76-}$ (44) (Figure 1-26a), by reaction of Na$_2$WO$_4$-2H$_2$O, As$_2$O$_3$ and Ce(NO$_3$)$_6$-6H$_2$O in aqueous solution. This polyanion represented the largest discrete-molecular polyoxotungstinate known at that time. X-ray diffraction revealed that the structure of this polyanion contains twelve $[\text{B-}\alpha-\text{AsW}_9\text{O}_{33}]^9-$ and four $[\text{W}_5\text{O}_{13}]^{10-}$ connected by 16 Ce$^{3+}$ ions via Ce–O–W bridges, giving rise to the final folded wheel with a $D_{2d}$ symmetry. The well-resolved $^{183}$W NMR spectrum of this polyanion indicated its solution stability.

In 2007, Kortz et al. reported a Ce$_{20}$-containing tungstogermanate, $[\text{Ce}_{20}\text{Ge}_{10}\text{W}_{100}\text{O}_{376}(\text{OH})_4(\text{H}_2\text{O})_{30}]^{56-}$ (45) (Figure 1-26b). This polyanion was synthesized by reaction of the Ce$^{3+}$ and trilacunary POM precursor $[\alpha-\text{GeW}_9\text{O}_{34}]^{10-}$ in a 1:1 molar ratio in the solution at pH 5.0 and was isolated as a mixed cesium-sodium salt. The structure of the polyanion 45 can be described as a dimeric entity composed of two half units of $[\text{Ce}_{10}\text{Ge}_3\text{W}_{50}\text{O}_{188}(\text{OH})_2(\text{H}_2\text{O})_{15}]^{28-}$ related by an inversion center ($C_i$ symmetry). Every half unit comprises five $\{\beta(4,11)-\text{GeW}_{10}\text{O}_{38}\}$ units linked by
ten Ce$^{3+}$ ions to give an asymmetric configuration. Notably, the $\beta(4,11)$-GeW$_{10}$O$_{38}$ units transformed from the $\alpha$-GeW$_9$O$_{34}$ block was unprecedented before this work.

In 2009, Patzke et al. reported a Gadolinium-Bridged Polytungstoarsenate, [Gd$_8$As$_{12}$W$_{124}$O$_{432}$(H$_2$O)$_{122}$]$^{60-}$ (46) (Figure 1-27a).\textsuperscript{[77]} It was synthesized by reaction of [As$_2$W$_{19}$O$_{67}$(H$_2$O)]$^{14+}$ and Gd$^{3+}$ in a 1:2 ratio in the NaOAc/HOAc buffer at pH 4.7. This polyanion can be viewed as a dimer of two subunits of {Gd$_4$As$_6$W$_{62}$O$_{216}$(H$_2$O)$_{11}$}$^{30-}$, which are related by an inversion center. Such an arrangement renders the polyanion an overall dimension of about 4.8 nm. Later, in 2011, the same group reported the isolation of another series of giant [Ln$_{16}$As$_{16}$W$_{164}$O$_{576}$(OH)$_{8}$(H$_2$O)$_{42}$]$^{80-}$ (Ln = Eu$^{3+}$ (47a), Gd$^{3+}$ (47b), Tb$^{3+}$ (47c), Dy$^{3+}$ (47d), and Ho$^{3+}$ (47e)) POMs, whose structures are composed of [As$_2$W$_{19}$O$_{67}$(H$_2$O)]$^{14-}$ (Figure 1-27b).\textsuperscript{[78]}

![Figure 1-26. Structures of (a) [As$_{12}$Ce$_{16}$(H$_2$O)$_{36}$W$_{148}$O$_{524}$]$^{76-}$ (44) and (b) [Ce$_{20}$Ge$_{10}$W$_{106}$O$_{576}$(OH)$_{4}$(H$_2$O)$_{30}$]$^{56-}$ (45).](image1)

![Figure 1-27. Structures of (a) [Gd$_8$As$_{12}$W$_{124}$O$_{432}$(H$_2$O)$_{122}$]$^{60-}$ (46) and (b) [Ln$_{16}$As$_{16}$W$_{164}$O$_{576}$(OH)$_{8}$(H$_2$O)$_{42}$]$^{80-}$ (Ln = Eu$^{3+}$ (47a), Gd$^{3+}$ (47b), Tb$^{3+}$ (47c), Dy$^{3+}$ (47d), and Ho$^{3+}$ (47e)).](image2)
Figure 1-28. Structure of \([\text{KK}_7\text{Ce}_{24}\text{Ge}_{12}\text{W}_{120}\text{O}_{456}(\text{OH})_{12}(\text{H}_2\text{O})_{64}]^{52-}\) (48).

In 2010, Reinoso et al. reported the synthesis of a giant crown-shaped polyoxotungstate containing 24 $\text{Ce}^{3+}$ ions, \([\text{KK}_7\text{Ce}_{24}\text{Ge}_{12}\text{W}_{120}\text{O}_{456}(\text{OH})_{12}(\text{H}_2\text{O})_{64}]^{52-}\) (Figure 1-28). This polyanion can be viewed as a product of the $\text{K}^+$-directed self-assembly of twelve \([\text{Ce}_2\text{GeW}_{10}\text{O}_{38}]^{6-}\) subunits formed in situ, where as many as three distinct types of \{\text{GeW}_{10}\} skeletons are observed, namely the $\beta(1,8)$-, $\beta(1,5)$- and the $\gamma(3,4)$-Keggin species.

1.5 References


Chapter 1 Introduction


Chapter 1 Introduction


Chapter 2 Experimental details

2.1 Instrumentation

2.1.1 Crystallography

Single crystals of the compounds were mounted on a Hampton cryo-loop for indexing and intensity data collection at 100 K on a Bruker D8 APEX II CCD using Mo-Kα radiation ($\lambda = 0.71073$ Å). Data integration was performed using SAINT.\[^{[1]}\] Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.\[^{[2]}\] Direct methods (SHELXS) successfully located the tungsten and lanthanide atoms, and successive Fourier syntheses (SHELXL) revealed the remaining atoms.\[^{[3]}\] Refinements were full matrix least-squares against $|F|^2$ using all data. Due to the high number of parameters, only heavy atoms (W, Ln, As, Sb, Ti, Co, Ni, Cu, Zn, and non-disordered counter cations) were refined anisotropically, whereas the lighter O and C atoms, as well as disordered counter cations were refined isotropically. Anisotropic refinement of the oxygen atoms within the POM lead to a large increase in the number of parameters, rendering the refinement unstable, without significant reduction in the residual factor values. The relevant crystallographic data and structure refinement details of the compounds can be found in the corresponding chapters.

2.1.2 Nuclear magnetic resonance spectroscopy

The NMR spectra of all the compounds dissolved in D$_2$O/H$_2$O or D$_2$O/buffer solutions were recorded on a JEOL ECX 400 instrument at room temperature, using 5 mm tubes for $^1$H and $^{13}$C NMR and 10 mm tubes for $^{183}$W NMR. The respective resonance frequencies were 400.53 MHz ($^1$H), 100.71 MHz ($^{13}$C) and 16.69 MHz ($^{183}$W). The chemical shifts are reported with respect to the references Si(CH$_3$)$_4$ ($^1$H and $^{13}$C), and 1 M Na$_2$WO$_4$(aq) ($^{183}$W).

2.1.3 Electrochemistry

All reagents and chemicals were of high-purity grade and were used as purchased without further purification. The solutions were thoroughly deoxygenated for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The working electrode was well cleaned ITO glass or glassy carbon. The electrochemical set-up was a CHI workstation using a PC with the CHI660 software.
Potentials are quoted against a saturated calomel electrode (SCE), in a compartment separated from the test solution by a fine porosity glass frit. The counter electrode was a platinum plate with large surface area in a compartment separated from the test solution by a medium porosity glass frit. All experiments were performed at room temperature.

2.1.4 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra (KBr pellets) of all the compounds were recorded on a Nicolet-Avatar 370 spectrometer.

2.1.5 UV-vis absorption spectroscopy

The UV-vis absorption spectra were recorded on a Varian Cary 100 Bio UV-vis spectrophotometer.

2.1.6 Thermogravimetry

Thermogravimetric analyses of all the compounds were carried out on a TA Instruments Q 600 device at a heating rate of 5 °C/min under a nitrogen atmosphere.

2.1.7 Elemental analysis

Elemental analyses were performed at CNRS, Service Central d’Analyze, Solaize, France; or at Zentralabteilung für Chemische Analysen (ZCH), Forschungszentrum Jülich, 52425 Jülich.

2.2 Synthesis of lacunary precursors

2.2.1 Na₉[α-As⁺³WO₃₃]·27H₂O

The title compound was prepared according to the literature. As₂O₃ (11 g, 0.056 mol) was added to a hot solution of Na₂WO₄·2H₂O (330 g, 1.0 mol) in 350 ml water. After the addition of 83 ml 11M HCl with vigorous stirring over 2 min, the solution was heated at 95°C for 10 min and then transferred to a teflon beaker. The product crystallized overnight. Yield: 280 g (90%). Purity of this material was verified by FTIR spectroscopy. FTIR (KBr disk): 933, 897, 781, 724, 511, 469, 440, 411 cm⁻¹.

2.2.2 Na₉[α-Sb⁺³WO₃₃]·19.5H₂O

The title compound was prepared according to the literature. Sb₂O₃ (1.96 g, 6.72 mmol) dissolved in concentrated HCl (10 mL) was added dropwise to a boiling solution of Na₂WO₄·2H₂O (40 g, 121 inmmol) in 80 mL water. The mixture was
refluxed for 1 h and allowed to cool slowly. Colourless crystals were formed after evaporation of one-third of the solution volume. Yield: 28.0 g (72%). Purity of this material was verified by FTIR spectroscopy. FTIR (KBr disk): 920, 890, 767, 715 cm\(^{-1}\).

2.2.3 \( \text{Na}_{10}[\alpha-\text{SiW}_{9}\text{O}_{34}]-18\text{H}_{2}\text{O} \)

The preparation of the title compound is according to the literature.\textsuperscript{[6]} \( \text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O} \) (182 g, 551.8 mmol) and \( \text{NaSiO}_3 \) (11g, 72.0 mmol) were dissolved in 200 mL of water. Hydrochloric acid (6 M, 130 mL) was added with stirring. The solution was then boiled for 1 h and concentrated to 300 mL. Eventually, insoluble stuff was filtered off. A solution of 50 g of \( \text{Na}_2\text{CO}_3 \) in 50 mL of water was added. Then, the lukewarm solution was gently stirred and the title product precipitated.

2.2.4 \( \text{Na}_{10}[\alpha-\text{GeW}_{9}\text{O}_{34}]-18\text{H}_{2}\text{O} \)

The preparation of the title compound is according to the literature.\textsuperscript{[6]} \( \text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O} \) (182 g, 551.8 mmol) and \( \text{GeO}_2 \) (7.53g, 72.0 mmol) were dissolved in 200 mL of water. Hydrochloric acid (6 M, 130 mL) was added with stirring. The solution was then boiled for 1 h and concentrated to 300 mL. Eventually, insoluble stuff was filtered off. A solution of 50 g of \( \text{Na}_2\text{CO}_3 \) in 50 mL of water was added. Then, the lukewarm solution was gently stirred and the title product precipitated.

2.3 References

Chapter 3 Plenary and lacunary Ti\textsuperscript{IV}-containing heteropolytungstates prepared by reaction of [TiO]\textsuperscript{2+} and [\(\alpha\)-AsW\textsubscript{9}O\textsubscript{33}]\textsuperscript{9-}

This chapter is based on two published articles (Communication):

“Ti\textsuperscript{-}containing, tetrahedral 36-tungsto-4-arsenate(III) [Ti\textsubscript{6}(TiO\textsubscript{6})(AsW\textsubscript{9}O\textsubscript{33})\textsubscript{4}]\textsuperscript{20-}”,

and

“Ti\textsubscript{2}-Containing 18-Tungsto-2-Arsenate(III) Monolacunary Host and the Incorporation of a Phenylantimony(III) Guest”,

All experiments regarding the preparation, crystallization, X-ray diffraction and other characterizations of all the polyanions were performed by Kai-Yao Wang. The structural refinement was executed by Prof. Bassem. S. Bassil and Dr. Zhengguo Lin. The electrochemical property tests were performed by Xiaolin Xing and Dr. Bineta Keita. The ESI-mass spectroscopic measurement and analysis were supplied by Dr. Zheng-Guo Lin and Prof. Jie Cao. The text was written by Kai-Yao Wang, with valuable contribution and corrections by Prof. Ulrich Kortz.
3.1 Abstract

The plenary Ti$_7$-containing, tetrahedral 36-tungsto-4-arsenate(III) \([\text{Ti}^\text{IV}_6(\text{Ti}^\text{IV}O_6)(\text{As}^\text{III}W_9O_{33})_4]^{20^-}\) (Ti$_7$) and monolacunary Ti$_2$-containing, 18-tungsto-2-arsenate(III) \([(\text{Ti}^\text{IV}O)_2(\text{As}^\text{III}W_9O_{33})_2]^{14^-}\) (Ti$_2$) were successfully synthesized by reaction of [TiO]$^{2+}$ species with \( [\text{As}^\text{III}W_9O_{33}]^9^- \) \( ([\text{As}^\text{III}W_9]) \) by a simple, one pot procedure at different pH 4.6 and 6.0, respectively. The polyanion Ti$_7$ contains a novel Ti$_7$-core, comprising a central TiO$_6$ octahedron surrounded by six TiO$_5$ square-pyramids, and capped by four \( \{\text{As}^\text{III}W_9\} \) trilacunary fragments. The polyanion Ti$_2$ features a sandwich-type structure composed of two \( \{\text{As}^\text{III}W_9\} \) units interlinked by two \{TiO\} groups, leaving a vacant site in the central belt position. Both polyanions were characterized by single-crystal X-ray diffraction, elemental analysis, Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) in the solid-state and by UV-vis, and multinuclear NMR in solution. Electrospray-ionization mass spectrometry (ESI-MS) was also performed on polyanion Ti$_7$. Electrochemical study was performed on polyanion Ti$_2$.

3.2 Introduction

Polyoxometalates (POMs) are a well-known class of discrete, molecular metal oxides comprising early transition metal ions in high oxidation states. POMs are of fundamental importance and technological relevance.\[1\] Lacunary heteropolytungstates can act as inorganic ligands, allowing for incorporation of \( p-, d-, \) and \( f\)-block metal ions, resulting in products with large structural and compositional versatility and a manifold of properties applicable to catalysis, magnetism, medicine, and materials science.\[2\]

The area of Ti$^\text{IV}$-containing POMs is well-established nowadays, and many compounds have been isolated. The ionic radius of Ti$^{4+}$ (0.75 Å) is very similar to that of W$^{6+}$ (0.74 Å), and hence Ti$^{4+}$ fits well into the lacunary site of Keggin or Wells-Dawson type POMs, usually adopting octahedral coordination geometry. In terms of Keggin-derivatives, much progress has been made for mono-, di- and tri-Ti$^{4+}$-substituted species,\[3\] ranging from monomers to oligomers, comprising Ti–O–Ti’ bonds between neighbouring Keggin units, such as dimers, trimers, as well as tetraters. Besides, some work has also been carried out on the Ti$^\text{IV}$-containing Keggin-type heteropolytungstates with diverse host/guest features.\[4\]

A milestone in recent years was the discovery of the di-Ti$^\text{IV}$-containing
Na₉Na₂Cs[6]h case 14 in a 52% yield. The synthesis of sodium acetate solution at pH 6 resulted in the Ti₄⁺ ions.[5] The two square-pyramidal TiO₄(OH) groups are apparently vital for the unique catalytic properties of this polyanion.[6] Now we decided to investigate the reaction of [TiO]²⁺ and the lone-pair containing POM precursors [α-XIII₃W₉O₃₃]⁰ (X = As, Sb) ([XIII₃W₉]) in aqueous solution further.

3.3 Results and discussion

3.3.1 Synthesis

Reaction of TiOSO₄ and Na₀[α-AsIII₃W₉O₃₃]-27H₂O[7a] in 1 M NaOAc buffer solution at pH 4.6 resulted in the Ti₇-containing, tetrahedral 36-tungsto-4-arsenate(III) [TiIV₆(TiIVO₆)(AsIII₃W₉O₃₃)₄]²⁻ (Ti₇), which was isolated as the hydrated sodium salt Na₂₀[TiIV₆(TiIVO₆)(α-AsIII₃W₉O₃₃)₄]·63H₂O (Na-Ti₇, yield 10%). The synthesis of polyanion Ti₇ can be represented as equation 3-1:

\[
4[α-AsIII₃W₉O₃₃]⁰ + 7TiOSO₄ + 2H⁺ ⇌ [TiIV₆(TiIVO₆)(AsIII₃W₉O₃₃)₄]²⁻ (Ti₇) + 7SO₄²⁻ + H₂O \tag{3-1}
\]

Because the crystals of Na-Ti₇ were not suitable for single crystal X-ray analysis, we also isolated the hydrated, mixed sodium–cesium salt Na₁₇.₅Cs₂.₅[TiIV₆(TiIVO₆)(AsIII₃W₉O₃₃)₄]·72H₂O·2CH₃COONa (NaCs-Ti₇, yield 3%), which was suitable for X-ray analysis. As expected, the FTIR spectra of Na-Ti₇ and NaCs-Ti₇ (Figure 3-1) are virtually identical in the POM fingerprint region 400-1000 cm⁻¹, indicating the presence of the same polyanion in both cases. Elemental analysis on NaCs-Ti₇ indicates the presence of cocrystallized sodium acetate, which is supported by FTIR (extra peaks at 1559 and 1411 cm⁻¹) (Figure 3-1) and ¹³C NMR (two peaks at 181.5 and 23.3 ppm, respectively) (Figure 3-2a). In the present work, all bulk studies were performed on Na-Ti₇, due to the higher yield as compared to NaCs-Ti₇.

The similar reaction of TiOSO₄ and the Na₀[α-AsIII₃W₉O₃₃]-27H₂O[7a] in 2 M sodium acetate solution at pH 6 resulted in the Ti₁₂-containing, 18-tungsto-2-arsenate(III) [(TiIVO₂)(α-AsIII₃W₉O₃₃)₂]¹⁺ (Ti₁₂), which was also isolated as a hydrated sodium salt Na₄₁[(TiIVO₂)(α-AsIII₃W₉O₃₃)₂]·50H₂O·CH₃COONa (Na-Ti₁₂) in a 52% yield. The synthesis of polyanion Ti₁₂ can be represented as equation 3-2:

\[
2[α-AsIII₃W₉O₃₃]⁰ + 2TiOSO₄ ⇌ [(TiIVO₂)(α-AsIII₃W₉O₃₃)₂]¹⁺ (Ti₁₂) + 2SO₄²⁻ \tag{3-2}
\]
Chapter 3 Plenary and lacunary Ti\textsuperscript{IV}-containing heteropolytunstates

Figure 3-1. FTIR spectra of Na\textsubscript{9}[$\alpha$-AsW\textsubscript{9}O\textsubscript{33}]·27H\textsubscript{2}O (black), Na-Ti\textsubscript{7} (blue), and NaCs-Ti\textsubscript{7} (red) and Na-Ti\textsubscript{2}.

Figure 3-2. $^{13}$C NMR spectra of (a) CsNa-Ti\textsubscript{7}, Na-Ti\textsubscript{7} and (b) Na-Ti\textsubscript{2} dissolved in D\textsubscript{2}O/H\textsubscript{2}O recorded at room temperature.
By analogy, the elemental analysis, FTIR spectrum (Figure 3-1) and $^{13}$C NMR spectrum (Figure 3-2b) of this compound indicate the presence of cocrystallized sodium acetate.

Polyanions Ti$_7$ and Ti$_2$ are related to our previously reported [Ti$_{IV}$$_2$(OH)$_2$As$_{III}$W$_9$O$_{67}$(H$_2$O)]$_8^-$ (\{(Ti$_2$As$_2$W$_19$)\}).\cite{5} All three polyanions Ti$_7$, Ti$_2$, \{Ti$_2$As$_2$W$_19$\} can be prepared by reaction of TiOSO$_4$ with $[$α-As$_{III}$W$_9$O$_{33}$]$^9$, but at different reagent ratios (2.2:1 vs 1.25:1 vs 4:1), pH (4.6 vs 6.0 vs 4.0), and solvent (1M CH$_3$COONa/CH$_3$COOH vs 2M CH$_3$COONa/CH$_3$COOH vs H$_2$O).

Unfortunately, the attempt to obtain the polytungstoantimonate(III) analogues of Ti$_7$ and Ti$_2$ by reaction of TiOSO$_4$ and Na$_5$[α-Sb$_{III}$W$_9$O$_{33}$]·19.5H$_2$O\cite{7b} was unsuccessful, which could probably caused by the conformational transform of the POM precursor during the reaction.

### 3.3.2 Structure description

[\{Ti$_{IV}$$_6$(Ti$_{IV}$O$_6$)(As$_{III}$W$_9$O$_{33}$)$_4$\}]$_{20b}^{-}$ (Ti$_7$)

Single crystal X-ray analysis revealed that the polyanion Ti$_7$ contains a novel Ti$_7$-core, comprising a central TiO$_6$ octahedron surrounded by six TiO$_5$ square-pyramids, capped by four \{As$_{III}$W$_9$\} fragments, leading to an assembly with $T_d$ point group symmetry (Figures 3-3a,b). The plenary structure of Ti$_7$ somewhat resembles the tetra-Keggin polyanion [Nb$_4$O$_6$(Nb$_7$SiW$_{40}$O$_{140}$)$_4$]$^{20-}$\cite{8} as well as the Wells-Dawson based tetramer \{(Ti$_3$P$_2$W$_{15}$)$_4$\}$_{9}^{-}$\cite{9} which also have an overall tetrahedral shape. However, in Ti$_7$ the lone pair of electrons on the As$_{III}$ heteroatom in \{As$_{III}$W$_9$\} does not allow the formation of a tri-Ti$_{IV}$-substituted Keggin unit. As a result, the four \{As$_{III}$W$_9$\} units in Ti$_7$ are linked via six square-pyramidal Ti$_{IV}$O$_5$ groups, with the apical oxo ligand O12T ($d_{Ti2-O12T}$ = 1.75(2) Å) pointing to the centre of the polyanion, and bridging to the central, unique Ti$_{IV}$ ion, which is hence octahedrally coordinated. As a result, Ti$_7$ contains Ti$_{IV}$ ions in two different coordination geometries, square-pyramidal and octahedral. In the other known polyanions containing square-pyramidal TiO$_5$ groups the apical oxygen is terminal.\cite{5,10} The central Ti$_7$ core in Ti$_7$ has an octahedral shape, with ideal bond angles of 90° and 180°, respectively, around the central Ti1 (Figure 3-3c). BVS values for selected atoms in NaCs-Ti$_7$ are shown in Table 3-2.\cite{11} The BVS calculations for oxygen atoms confirmed that the polyanion Ti$_7$ is not protonated. For structural clarity, we can simplify the four \{As$_{III}$W$_9$\} groups in Ti$_7$ as the four vertices of a regular tetrahedron, with the six
penta-coordinate Ti$^{4+}$ ions being located at the edge centers, thus forming an ideal octahedron, surrounding the central, unique Ti$^{4+}$ ion (Figure 3-3d).

Figure 3-3. (a) and (b) Combined polyhedral/ball-and-stick representations of polyanion Ti$_{17}$. (c) Ball-and-stick representation of the Ti$_{17}$ core in Ti$_{17}$. (d) Topological skeleton representation of Ti$_{17}$, reflecting the high symmetry as shown by a Ti$_6$ octahedron and an As$_4$ tetrahedron. Colour code: WO$_6$ octahedra (red), TiO$_5$ square-pyramids and TiO$_6$ octahedron (light blue), W (black), Ti (light blue), As (yellow), O (red).

Figure 3-4. $^{183}$W NMR spectrum of Na-Ti$_{17}$ dissolved in D$_2$O/H$_2$O recorded at room temperature. The signal at -129.3 ppm originates from the 12 capping tungstens (green WO$_6$ octahedra), whereas the signal at -138.1 ppm corresponds to the 24 equatorial tungstens (blue WO$_6$ octahedra).
As Na-Ti\textsubscript{7} is well-soluble in water, we also performed \textsuperscript{183}W NMR in D\textsubscript{2}O/H\textsubscript{2}O. The resulting spectrum (Figure 3-4) consists of two singlets at -129.3 and -138.1 ppm, respectively, with relative intensities of 1:2, in complete agreement with the solid state structure of Ti\textsubscript{7}, indicating that the tetrahedral assembly is maintained in solution.

\[
[\text{Ti}^{IV}\text{O})_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2]^{14-} \text{(Ti}_2\text{)}
\]

Single-crystal XRD indicated that Na-Ti\textsubscript{2} crystallizes in the triclinic space group \textit{P}-1. The novel Ti\textsubscript{2} has a sandwich-type structure, with two [TiO\textsuperscript{2+}]\textsubscript{2} groups encapsulated by two \{As\textsuperscript{III}W\textsubscript{9}\} moieties (Figure 3-5a). Both Ti\textsuperscript{4+} ions are penta-coordinate in a square-pyramidal fashion, being bound to two pairs of corner shared WO\textsubscript{6} octahedra via oxo bridges, and a terminal oxo-ligand pointing outwards, resulting in an overall assembly with idealized \textit{C}\textsubscript{2v} symmetry. The Ti–O bond lengths in the square plane of Ti\textsubscript{2} range from 1.957(10) to 1.992(10) Å, and the average terminal Ti=O bond length is 1.665(12) Å. The O–Ti–O angles range from 85.7(4) to 88.2(4) °. The third addenda site in the central belt is occupied by a hexa-coordinate sodium ion (Na1) in the solid state (Figure 3-5a,b). The interstices in the belt are filled by additional three sodium ions (Na2, Na3, Na4), in complete analogy to earlier polyanions with the \{M\textsubscript{2}As\textsuperscript{III}W\textsubscript{19}\}, \{M\textsubscript{3}(As\textsuperscript{III}W\textsubscript{9})\textsubscript{2}\}, and \{M\textsubscript{4}(As\textsuperscript{III}W\textsubscript{9})\textsubscript{2}\} structural types.\textsuperscript{[12]} Due to the absence of the third addenda atom in the central belt, the polyanion Ti\textsubscript{2} might be considered as an monolacunary Hervé-type dimeric POMs.

\[\text{Figure 3-5.} \text{(a) Structure of polyanion Ti}_2 \text{ with incorporated, weakly bound Na}^+ \text{ ions. (b) The central belt of Ti}_2 \text{ with the unique Na1 occupying an addenda site, whereas Na2, Na3, and Na4 occupy the interstitial sites between Ti1, Ti2 and Na1. Colour code: WO}_6 \text{ octahedra (red), balls: Ti (turquoise), Sb (pink), As (yellow), O (red), Na1 (light blue), Na2, Na3, and Na4 (dark blue). H atoms are omitted for clarity.}\]
BVS values for selected atoms in Na-Ti$_2$ are shown in Table 3-2. The BVS calculations for oxygen atoms confirmed that the polyanion Ti$_2$ is not protonated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaCs-Ti$_7$</th>
<th>Na-Ti$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{44}$H$</em>{150}$As$<em>4$Cs$</em>{2.5}$Na$<em>{19.5}$O$</em>{214}$Ti$<em>7$W$</em>{36}$</td>
<td>C$<em>{2}$H$</em>{103}$As$<em>2$Na$</em>{15}$O$_{120}$Ti$<em>2$W$</em>{18}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>11657.39</td>
<td>5947.63</td>
</tr>
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<td>Crystal system</td>
<td>Cubic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
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<tr>
<td>$b/\AA$</td>
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<td>17.1828(6)</td>
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<tr>
<td>$c/\AA$</td>
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<tr>
<td>$\gamma^\circ$</td>
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<td>Measured refls.</td>
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<td>147097</td>
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<td>0.0511</td>
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<td>711</td>
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<tr>
<td>$GOF$</td>
<td>1.013</td>
<td>1.004</td>
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<tr>
<td>$R_1, wR_2$ [I &gt; 2$\sigma$(I)]</td>
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<td>0.0504, 0.1199</td>
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<tr>
<td>$R_1$, wR$_2$ (all data)</td>
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<td>0.0573, 0.1234</td>
</tr>
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</table>

$[a] R_1 = \sum ||F_o|-|F_c||/\sum |F_o|, \ R_2 = \sqrt{\sum w[(F_o)^2-(F_c)^2]}/\sum w[(F_o)^2]^{1/2}$
Table 3-2. Bond valence sum values for selected atoms in \( \text{NaCs-Ti}_7 \) and \( \text{Na-Ti}_2 \).

<table>
<thead>
<tr>
<th>Atom</th>
<th>BVS value</th>
<th>Atom</th>
<th>BVS value</th>
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</thead>
<tbody>
<tr>
<td>( \text{NaCs-Ti}_7 )</td>
<td>( \text{NaCs-Ti}_7 )</td>
<td>( \text{Na-Ti}_2 )</td>
<td></td>
</tr>
<tr>
<td>W1</td>
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<td>As</td>
<td>3.14</td>
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<td>As2</td>
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</tr>
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<td>4.11</td>
<td>W7</td>
<td>6.08</td>
</tr>
<tr>
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<td>W4</td>
<td>6.14</td>
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<td>6.07</td>
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Figure 3-6. \(^{183}\text{W}\) NMR spectrum of \( \text{Na-Ti}_2 \) dissolved in \( \text{H}_2\text{O/}D_2\text{O} \) recorded at room temperature. Inset: Representation of five different types of magnetically inequivalent W centers (different colors) in polyanion \( \text{Ti}_2 \), in accordance with its \( C_2 \) point group symmetry.
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We also performed \textsuperscript{183}W NMR on Na-Ti\textsubscript{2} dissolved in D\textsubscript{2}O/H\textsubscript{2}O (pH 7.5). The resulting spectrum (Figure 3-6) consists of five peaks at -104.1, -105.6, -109.6, -110.1, and -153.5 ppm, respectively, with the expected relative intensities of 2:2:2:2:1, which is fully consistent with the C\textsubscript{2v} point group symmetry of polyanion Ti\textsubscript{2} in the solid-state. The \textsuperscript{183}W NMR spectrum of Ti\textsubscript{2} remained unchanged for two weeks, indicating that this polyanion is solution-stable.

3.3.3 Thermogravimetric analysis

![Figure 3-7. Thermogram of Na-Ti\textsubscript{2} from room temperature to 800 °C under N\textsubscript{2} atmosphere.](image)

![Figure 3-8. Thermogram of Na-Ti\textsubscript{2} from room temperature to 800 °C under N\textsubscript{2} atmosphere.](image)
Chapter 3 Plenary and lacunary Ti\textsuperscript{IV}-containing heteropolytunstates

The thermogram of Na-Ti\textsubscript{7} and Na-Ti\textsubscript{2} are shown in Figures 3-7 and 3-8, respectively, both of which feature the two-step weigh loss. The first weight loss step (9.5\% for Na-Ti\textsubscript{7} in 20 - 400 °C; 12.5\% for Na-Ti\textsubscript{2} in 20 - 325 °C) can be attributed to the removal of crystal waters, and the following weight loss step up to 650 °C (3.3\% for Na-Ti\textsubscript{7}; 3.6\% for Na-Ti\textsubscript{2}) can be assigned to the decomposition of the organic species and structural transformation/decomposition of the polyanions.

3.3.4 UV-vis spectroscopy

![UV-vis spectra of Na-Ti\textsubscript{7} in different solutions.](image)

Figure 3.9. UV-vis spectra of Na-Ti\textsubscript{7} in (a) H\textsubscript{2}O, (b) LiCH\textsubscript{3}COO/CH\textsubscript{3}COOH (1M, pH = 4), (c) LiCH\textsubscript{3}COO/CH\textsubscript{3}COOH (1M, pH = 5), (d) LiCH\textsubscript{3}COO/CH\textsubscript{3}COOH (1M, pH = 6) and (e) LiCH\textsubscript{3}COO/CH\textsubscript{3}COOH (1M, pH = 7). The POM concentration is 0.0025 mM.
The UV-vis spectra of Na-Ti$_7$ dissolved in water and 1 M CH$_3$COOLi/CH$_3$COOH solutions at different pH values (4 to 7) displays an absorption maximum at 256 nm in the UV range, which can be attributed to the O → W charge transfer transition (Figure 3-9). In addition, time-dependent UV-vis spectra (0 h, 0.5 h, 1 h, 2 h, 4 h and 24 h) recorded in each solvent showed identically overlap, suggesting the stability of Ti$_7$ in the above-mentioned solvents. By analogy, the polyanion Ti$_2$ also exhibits a characteristic absorption of the O → W charge transfer transition at around 250 nm (Figure 3-10). And it shows a stability in the 1 M CH$_3$COOLi/CH$_3$COOH solution at pH 6 for at least four hours.

### 3.3.5 Electrospray-ionization mass spectrometry (ESI-MS)

Electrospray-ionization mass spectrometry (ESI-MS) has proven to be a valuable analytical technique.$^{[13]}$ Due to the stability of the polyanion Ti$_7$ in water, we carried out the ESI-MS measurement to extract structural information of the POM in the gas phase. The major peaks observed in the mass spectrum of Na-Ti$_7$ dissolved in water showed an ensemble of adducts derived from [Na$_x$H$_y$Ti$_7$As$_4$W$_{36}$O$_{138}$(H$_2$O)$_z$]$^{(20-x-y)}$ with different numbers of sodium ions, protons and water molecules associated with
Figure 3-11. Negative ion mass spectrum of Na-Ti dissolved in water.

polyanion Ti\textsuperscript{7} (Figure 3-11). For instance, the most intense peaks centred at \(m/z\) 1375.17 and 1608.02, respectively, can be assigned to the 7- charged \([\text{Na}_2\text{H}_1\text{Ti}_7\text{As}_4\text{W}_{36}\text{O}_{136}(\text{H}_2\text{O})_6]^{-}\) and the 6- charged \([\text{Na}_3\text{H}_1\text{Ti}_7\text{As}_4\text{W}_{36}\text{O}_{136}(\text{H}_2\text{O})_6]^{6-}\) adducts. These results indicate that Ti\textsuperscript{7} is also stable in the gas phase, as expected based on our solution \textsuperscript{183}W NMR and UV-vis studies.

### 3.3.6 Electrochemistry

The electrochemistry properties of Ti\textsubscript{2} was studied in 1 M lithium acetate solution at pH 6, where the polyanion is stable as confirmed by UV-vis spectroscopy (Figure 3-10d). Figure 3-12a shows the cyclic voltammogram (CV) of Ti\textsubscript{2} obtained at 100 mV s\textsuperscript{-1} and restricted to the chemically reversible wave. Whatever the scan rate from 100 mV s\textsuperscript{-1} down to 5 mV s\textsuperscript{-1}, no splitting of the single reduction wave of Ti\textsubscript{2} was observed, but at a scan rate as small as 2 mV s\textsuperscript{-1} the reduction peak (-0.972 V versus SCE) presents a small pre-wave at ca. -0.850 V versus SCE (Figure 3-12b). Upon potential reversal, the re-oxidation CV pattern features two waves located at -0.867 V and -0.809 V versus SCE, respectively, which confirms the composite nature of the reduction wave. Two closely spaced reduction waves were also reported for Kortz’s polyanion \([\text{Ti}_2(\text{OH})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})_2]^{8-}\) and attributed to the reduction of the Ti and W centers, respectively.\textsuperscript{[5]} Figure 3-13 shows the CV of the redox processes of Ti\textsubscript{2} as a function of the potential scan rate. The variation of the reduction peak current as a function of the square root of the potential scan rate shows a good linearity (inset of Figure 3-13), indicating a diffusion-controlled reduction process. We also performed preliminary qualitative tests of Ti\textsubscript{2} on the electrocatalytic activity towards nitrate.
Figure 3-12. Cyclic voltammograms of 0.086 mM Ti₂ in 1 M aqueous CH₃COOLi/CH₃COOH (pH 6) medium, at a scan rate of 100 mV s⁻¹ (a) and 2 mV s⁻¹ (b), respectively.

Figure 3-13. Cyclic voltammograms as a function of the scan rate for 0.086 mM Ti₂ in 1 M LiCH₃COO/CH₃COOH at pH 6. Inset: variation of the cathodic peak current intensity of the main reduction peak as a function of the square root of the scan rate.
Figure 3-14. (a) Cyclic voltammograms of 0.086 mM Ti\textsubscript{2} in 1 M aqueous CH\textsubscript{3}COOLi/CH\textsubscript{3}COOH at pH 6 medium at 2 mV s\textsuperscript{-1} and in the presence of increasing amounts of nitrate with the excess parameter $\gamma = C_{\text{nitrate}}/C_{\text{POM}}$ (C = concentration). (b) Variation of the catalytic efficiency $\text{CAT}$ (at -1.0 V versus SCE) as a function of $\gamma$. $\text{CAT} = 100 \times [I_{\text{POM+nitrate}}] - I_{\text{POM}}]/I_{\text{POM}}$, where $I_{\text{POM}}$ and $I_{\text{POM+nitrate}}$ represent the measured reduction current of the POM alone and in the presence of nitrate, respectively.

reduction. Several examples of POM-based nitrate reduction electrocatalysts have been reported, but the challenge remains to develop efficient POM electrocatalysts in media at pH $> 4$.\textsuperscript{[14]} Figure 3-14a shows that Ti\textsubscript{2} is an efficient nitrate reduction electrocatalyst in the pH 6 acetate medium. Moreover, a linear correlation is found between nitrate concentration and current (Figure 3-14b), in the range from 4.3 to 94.6 mM. Therefore, Ti\textsubscript{2} is a promising candidate for nitrate detection, quantification and transformation.

3.4 Conclusion

In summary, we have prepared the plenary Ti\textsubscript{7}-containing, tetrahedral 36-tungsto-4-arsenate(III) [Ti\textsuperscript{IV}\textsubscript{6}(Ti\textsuperscript{IV}O\textsubscript{6})(As\textsuperscript{III}W\textsubscript{9}O\textsubscript{33})\textsubscript{4}]\textsuperscript{20-} (Ti\textsubscript{F}) and monolacunary
Chapter 3 Plenary and lacunary Ti\textsuperscript{IV}-containing heteropolytungstates

Ti\textsubscript{2}-containing, 18-tungsto-2-arsenate(III) \([(\text{Ti}^{\text{IV}}\text{O})_{2}(\alpha-\text{As}^{\text{III}}\text{W}_{9}\text{O}_{33})_{2}]^{14-}\) (T\text{I}_{2}) by reaction of [TiO]\textsuperscript{2+} species and [\(\alpha-\text{As}^{\text{III}}\text{W}_{9}\text{O}_{33}\)]\textsuperscript{9-} (\(\{\alpha-\text{As}^{\text{III}}\text{W}_{9}\}\)) at different pH 4.6 and 6.0, respectively. The polyanion Ti\textsubscript{7} comprises a Ti\textsubscript{7} core comprising penta- and hexa-coordinate Ti\textsuperscript{4+} ions, surrounded by four \(\{\alpha-\text{As}^{\text{III}}\text{W}_{9}\}\) capping units, resulting in a tetrahedral assembly. The polyanion Ti\textsubscript{2} features a sandwich-type structure composed of two \{As\textsuperscript{III}W\textsubscript{9}\} units interlinked by two (TiO) groups, leaving a vacant site in the central belt position. Both polyanions were characterized in the solid state by single-crystal XRD, Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), and elemental analysis and in solution by UV–vis and NMR spectroscopy. Electrospray-ionization mass spectrometry (ESI-MS) was performed on polyanion Ti\textsubscript{7}. Electrochemical study was performed on polyanion Ti\textsubscript{2}.

3.5 Experimental section

3.5.1 General methods and reagents

The reagents were used as purchased without further purification. The Na\textsubscript{20}[\(\alpha-\text{As}\text{W}_{9}\text{O}_{33}\)]\cdot27\text{H}_{2}\text{O}\textsuperscript{[7a]} and Na\textsubscript{8}[\(\alpha-\text{Sb}^{\text{III}}\text{W}_{9}\text{O}_{33}\)]\cdot19.5\text{H}_{2}\text{O}\textsuperscript{[7b]} were synthesized according to the published procedures and characterized by FTIR spectroscopy. Na FTIR spectra (KBr pellets) were recorded on a Nicolet-Avatar 370 spectrometer. Thermogravimetric analyses were carried out with a TA Instruments Q 600 device at a heating rate of 5 °C/min under a nitrogen atmosphere. The UV-vis absorption spectra were recorded on a Varian Cary 100 Bio UV-vis spectrophotometer. Mass spectra were obtained in the negative ion mode by direct injection using an Agilent 6520 Q-TOF LC/MS mass spectrometer. The general strategy includes assignment of the polyanion species and determination of the clusters stability in aqueous solution. The NMR spectra of the compounds dissolved in D\textsubscript{2}O/H\textsubscript{2}O were recorded on a JEOL ECX 400 instrument at room temperature, using 5 mm tubes for \(\text{^{13}C}\) NMR and 10 mm tubes for \(\text{^{183}W}\) NMR. The respective resonance frequencies were 100.71 MHz (\(\text{^{13}C}\)) and 16.69 MHz (\(\text{^{183}W}\)). The chemical shifts are reported with respect to the references Si(CH\textsubscript{3})\textsubscript{4} (\(\text{^{13}C}\)), and 1 M Na\textsubscript{2}WO\textsubscript{4}(aq) (\(\text{^{183}W}\)). Elemental analyses for Na, Cs, Ti, As, W and C were performed at CNRS, Service Central d’Analyse, Solaize, France.

3.5.2 Synthesis

Na\textsubscript{20}[\(\text{Ti}^{\text{IV}}\text{O}_{6}(\text{Ti}^{\text{IV}}\text{O})_{2}(\alpha-\text{As}^{\text{III}}\text{W}_{9}\text{O}_{33})_{4}\)]\cdot63\text{H}_{2}\text{O} (Na-T\text{I}_{7}):

TiOSO\textsubscript{4} (0.128 g, 0.80 mmol) was dissolved in 20 mL of sodium acetate buffer (1 M, pH 4.6) followed by addition of Na\textsubscript{8}[\(\alpha-\text{As}\text{W}_{9}\text{O}_{33}\)]\cdot27\text{H}_{2}\text{O}\textsuperscript{[7a]} (1.10 g, 0.37 mmol). The
solution was kept at room temperature for 1 h with constant stirring. Then the solution was filtered and allowed to evaporate in an open beaker. Colourless crystals of Na-Ti7 started to appear after one day and were collected after ten days (yield: 0.105 g, 10%, based on Na9[α-AsW9O33]-27H2O). The Na-Ti7 can be prepared in sodium acetate buffer (1M) with variable pH range from 4.2 to 5. As an optimum condition, the procedure at pH 4.6 is described in detail. IR of Na-Ti7: 1619(m), 966 (m), 898 (m), 823 (s), 763 (s), 729 (m), 662 (m), 475 (w), 453 (m) cm\(^{-1}\). Anal. Calcd (Found) for Na-Ti7: Na 4.16 (4.02), W 59.86 (59.90), As 2.71 (2.68), Ti 3.03 (2.99).

Na14_{7.5}Cs_{2.5}[Ti^{IV}_6(Ti^{IV}_O6)(As^{III}W9O33)_4]\cdot72H2O\cdot2CH3COONa (NaCs-Ti7)

The procedure was analogous to that of Na-Ti7, but the pH of the 1M sodium acetate buffer used was 5.0 instead of 4.6, and 40 μL of 1 M CsCl was added to the reaction solution after stirring. Colourless crystals of NaCs-Ti7 started to form after one day and were collected after ten days. (yield: 0.030 g, 3%, based on Na9[α-AsW9O33]-27H2O). FTIR of NaCs-Ti7: 1623(m), 1559(w), 1411(w), 958 (m), 890 (m), 820 (s), 764 (s), 728 (m), 667 (m), 474 (w), 452 (m) cm\(^{-1}\). Anal. Calcd (Found) for NaCs-Ti7: Na 3.85 (4.29), Cs 2.85 (2.91), W 56.8 (56.7), As 2.57 (2.68), Ti 2.87 (2.53), C 0.41 (0.24).

Na14[Ti^{IV}_O2(α-As^{III}W9O33)]\cdot50H2O-CH3COONa (Na-Ti2)

TiOSO4 (1.60 g, 10.00 mmol) and Na9[B-α-As^{III}W9O33]-27H2O\[^{7a}\] (23.60 g, 8.00 mmol) were added in 400 mL of 2 M aqueous sodium acetate medium at pH 6 solution with constant stirring. Upon heating at 80 °C for 1 h the solution became almost completely transparent. After cooling down to room temperature, the solution was filtered in order to remove a small amount of white precipitate, and then allowed to evaporate in an open beaker. Colorless crystals of Na-Ti2 started to appear after one week and were collected after 15 days when the volume of the solution had decreased to about 250 ml (yield 12.4 g, 52% based on Na9[α-AsW9O33]-27H2O). FTIR of Na-Ti2: 1636 (m), 1415 (w), 1384 (w), 945 (m), 897 (m), 748 (s), 673 (m), 495 (w), 473 (w), 453(w) cm\(^{-1}\). Anal. Calcd (Found) for Na-Ti2: Na 5.80 (5.95), Ti 1.61 (1.64), As 2.52 (2.60), W 55.64 (55.23), C 0.40 (0.33).

3.5.3 Crystallography

Colorless single crystals of NaCs-Ti7 and Na-Ti2 were mounted on a Hampton cryo-loop for indexing and intensity data collection at 100 K on a Bruker D8 APEX II CCD using Mo-Kα radiation (λ = 0.71073 Å). Data integration was performed using
Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program. Direct methods (SHELXS) successfully located the tungsten and lanthanide atoms, and successive Fourier syntheses (SHELXL) revealed the remaining atoms. Refinements were full matrix least-squares against $|F|^2$ using all data. The heavy atoms and non-disordered Na$^+$ ions were refined anisotropically, whereas all other atoms were refined isotropically. For NaCs-Ti$_7$, the refinement suggests an occupancy of 0.16667 on Cs atom at special position, resulting in 4 Cs atoms in the formula, whereas the elemental analysis shows that the bulk material contains only 2.5 Cs in the formula. Herein, the latter formula is shown throughout the paper due to the bulk material was used for all further characterizations. The relevant crystallographic data and structure refinement details NaCs-Ti$_7$ and Na-Ti$_2$ can be found in Table 3-1.

3.6 References


Chapter 3 Plenary and lacunary Ti$^{IV}$-containing heteropolytungstates


Chapter 3 Plenary and lacunary Ti$^{IV}$-containing heteropolytunstates


Chapter 4 Incorporation of electrophilic guests into the Ti$_2$-containing 18-tungsto-2-arsenate(III) monolacunary host

This chapter is based on

“Ti$_2$-Containing 18-Tungsto-2-Arsenate(III) Monolacunary Host and the Incorporation of a Phenylantimony(III) Guest”


and

“Rational incorporation of Transition Metal (Co, Ni, Cu, Zn) Guests into the Ti$_2$-containing 18-Tungsto-2-Arsenate(III) Monolacunary Host”


All experiments regarding the preparation, crystallization, X-ray diffraction and other characterizations of all the polyanions were performed by Kai-Yao Wang. The structural refinement was executed by Prof. Bassem. S. Bassil. The electrochemistry section was executed by Xiaolin Xing and Dr. Bineta Keita. The magnetic properties of the polyanions were measured by Jasleen Kaur Bindra, Dr. Kariem Diefenbach and Prof. Naresh S. Dalal. The organo-Sb precursor was supplied by Prof. Dr. Cristian Silvestru. The text was written by Kai-Yao Wang, with valuable contribution and corrections by Prof. Dr. Ulrich Kortz.
4.1 Abstract

The novel Ti\textsubscript{2}-containing, sandwich-type 18-tungsto-2-arsenate(III) [(Ti\textsuperscript{IV}O)\textsubscript{2}(α-As\textsuperscript{III}W\textsubscript{9}O\textsubscript{33})\textsubscript{2}]\textsuperscript{14-} (Ti\textsubscript{2}) was successfully used as monolacunary host to react with main group or 3d transition metal electrophiles, resulting in a series of mono-substituted derivatives, namely, the [C\textsubscript{6}H\textsubscript{5}Sb\textsuperscript{III}(Ti\textsuperscript{IV}O)\textsubscript{2}(α-As\textsuperscript{III}W\textsubscript{9}O\textsubscript{33})\textsubscript{2}]\textsuperscript{12-} (SbTi\textsubscript{2}) and [M(H\textsubscript{2}O)(Ti\textsuperscript{IV}O)\textsubscript{2}(α-As\textsuperscript{III}W\textsubscript{9}O\textsubscript{33})\textsubscript{2}]\textsuperscript{12-} (M = Co (CoTi\textsubscript{2}), Ni (NiTi\textsubscript{2}), Cu (CuTi\textsubscript{2}), Zn (ZnTi\textsubscript{2})) polyanions. All the polyanions were characterized by single-crystal X-ray diffraction, elemental analysis, Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) in the solid-state and by UV-vis, and multinuclear NMR and electrochemistry in solution. Variable temperature magnetic susceptibility and variable field magnetization characterization indicate their antiferromagnetic interactions with the nearest neighbours for the paramagnetic NaCs-CoTi\textsubscript{2}, NaCs-NiTi\textsubscript{2}, NaCs-CuTi\textsubscript{2} samples. The resolved hyperfine structure of the NaCs-CuTi\textsubscript{2} obtained from the multifrequency EPR measurements assists us to assign the ground state to mainly the Cu d\textsubscript{x2-y2} orbital.

4.2 Introduction

Polyoxometalates (POMs) are a large class of molecular metal-oxygen anions with a remarkable structural variety and manifold properties,\cite{1} which can be applied in areas such as catalysis,\cite{2} magnetism,\cite{3} photochemistry,\cite{4} materials science,\cite{5} medicine and biology.\cite{6} The development of rational synthetic pathways for the formation of novel, functionalized POMs has always been a challenging task. In most cases, the formation mechanism of POMs is not fully understood and is usually described as “self-assembly”. Subsequently, even some very large and complex POM structures were synthesized in one-step procedures by the simple reaction of water-soluble sources of composing elements.\cite{7} Such a process could lead to unpredictable structural types, sometimes restricted to relatively low yields, which is not beneficial for the transfer towards industrial applications. Therefore, it is highly desirable to develop controllable synthesis and/or derivatization of POMs, similar to that of organic chemistry.

Within the rich POM family, lacunary tungstoarsenates(III) represent a unique subclass, where the lone pair of electrons on the As\textsuperscript{III} heteroatom doesn’t allow the formation of plenary Keggin ions, largely enriching the structural variety of this
Early reports on the synthetic procedure and structural characterization for some members in this subclass are known, including the monomeric, trilacunary $[{\alpha-As^{III}W_{9}O_{33}}]$ and the dimeric, dilacunary $[{As^{III}_{2}W_{19}O_{67}(H_{2}O)}]$ monolacunary host subclass. Their solution stability is pH dependant, with more acidic conditions needed as the W:As ratio increases. Reactions of the preformed lacunary $[{\alpha-As^{III}W_{9}O_{33}}]$, $[{As^{III}_{2}W_{19}O_{68}(H_{2}O)}]$ and plenary $[{As_{2}W_{21}O_{69}(H_{2}O)}]^{9-}$ $({As_{2}W_{21}})$, $[{Ti_{2}As_{2}W_{19}}]$ and plenary $[{Ti_{2}As_{2}W_{19}}]$ $({Ti_{2}As_{2}W_{19}})$, $[{Ti_{2}As_{2}W_{19}}]$ precursors with $p$-, $d$-, and $f$-block metal ions have lead to various substituted products. However, their structures display a great variety in geometry and aggregation modes, due to the precursor’s chemical transformation and conformational isomerization during the reaction. Such synthetic routes can hence seldom contribute to a rational synthetic pathway for the formation of predictable target compounds. The design and synthesis of solution-stable POM precursors with fixed lacunary site/sites will undoubtedly improve this situation.

One significant progress is our recent discovery of the Ti$_2$-containing 18-tungsto-2-arsenate(III) $[{(Ti^{IV}O)_{2}(\alpha-As^{III}W_{9}O_{33})_{2}}]$ (Ti$_2$) (see Chapter 3), which features a sandwich-type structure, with two [TiO]$^{2+}$ groups encapsulated by two $[{\alpha-As^{III}W_{9}O_{33}}]$ moieties. This polyanion is strucutrally related to the previously reported, catalytically active $[{Ti_{2}(OH)_{2}As_{2}W_{19}O_{67}(H_{2}O)}]$ $({Ti_{2}As_{2}W_{19}})$, but replace the extra WO(H$_2$O) group in the belt position by a vacant site. Such a structural feature suggests the promising utilization of Ti$_2$ as a monolacunary POM host platform for further encapsulation of metal-ion guests, realizing the required post functionalization.

Incorporation of main group and transition metal electrophiles into lacunary POM precursors represents an extensively investigated subject for the generation of novel POMs with a great strucutral variety as well as interesting properties. We thus decided to investigate the reactivity of the monolacunary Ti$_2$ precursor with some selected main group (e.g. C$_6$H$_5$Sb$^{III}$, C$_6$H$_5$Sn$^{IV}$) and 3d metal (Mn$^{2+}$, Mn$^{3+}$, Fe$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Zn$^{2+}$) electrophilic guest.

### 4.3 Results and Discussion

#### 4.3.1 Incorporation of main group electrophiles

The subclass of polyoxoanions modified by organotin(IV) and organoantimony(III) groups has drawn extensive attention during the past years.
because of the good fitness of SnIV and SbIII into the addenda sites of Keggin- and Wells-Dawson types of POM skeletons as well as the potential applications of these resultant POMs in medicinal or biological chemistry.\cite{15,16} Here, we choose the phenyltin(IV) and phenylantimony(III) as the candidates to react with the Ti2 monolacunary precursor. As a result, we isolated the phenylantimony(III) embedded derivative of Ti2, namely, the [C6H5SbIII(TiIVO)2(α-AsIIIW9O33)2]12- (SbTi2). On the contrary, unfortunately, the reaction of Ti2 and phenyltin(IV) group didn’t give the isolatable products. This may be caused by the higher oxidation state of tin(IV) compared to that of antimony(III), the former of which, coupled with two TiIV centers, could lead to a thermodynamically-unfavorable central belt in the polyanion.

### 4.3.1.1 Synthesis

The polyanion [C6H5SbIII(TiIVO)2(α-AsIIIW9O33)2]12- (SbTi2) was prepared by reaction of Ti2 and C6H5SbCl2 in a nearly stoichiometric ratio in a 1 M sodium acetate solution at pH 6, and was isolated as a mixed Na/Cs salt Cs2.5Na9.5[C6H5SbIII(TiIVO)2(α-AsIIIW9O33)2]·40H2O (NaCs-SbTi2) in 62% yield. The synthesis of polyanion SbTi2 can be represented as the following equation 4-1:

\[
[(TiIVO)2(α-AsIIIW9O33)2]^{14+} + C6H5SbCl2 \rightleftharpoons [C6H5SbIII(TiIVO)2(α-AsIIIW9O33)2]^{12-} (SbTi2) + 2Cl^- \quad (4-1)
\]

![Figure 4-1. FTIR spectra of Na-Ti2 (black) and NaCs-SbTi2 (red) measured at room temperature (KBr pellets).](image-url)
In the FTIR spectrum of NaCs-SbTi$_2$ (Figure 4-1), two weak peaks at 1475 and 1423 cm$^{-1}$, respectively, are assigned to the C=C stretching vibrations of the phenyl ring, and a third peak at 1064 cm$^{-1}$ represents the $q$ vibration mode of the (C$_6$H$_5$)Sb$^{2+}$ groups.$^{[17]}$ Two points should be noted about the synthesis of SbTi$_2$: (1) C$_6$H$_5$SbCl$_2$ can hardly dissolve in aqueous solution, thus this chemical need to be dissolved in a minimum amount of ethanol before to achieve a fast, complete reaction with Ti$_2$; (2) A recrystallization process is necessary for obtaining single crystals with good quality for XRD diffraction measurement.

4.3.1.2 Structure description

NaCs-SbTi$_2$ crystallizes in the monoclinic space group $P2_1/n$ (Table 4-1). The polyanion SbTi$_2$ is the expected phenylantimony(III)-embedded derivative of Ti$_2$, with the Sb$^{III}$ ion occupying the vacant site and the phenyl group pointing outwards (Figure 4-2), resulting in a structure with idealized point group $C_{2v}$ symmetry. The Sb$^{III}$ ion is penta-coordinate and exhibits a square-pyramidal coordination geometry, with basal Sb–O bonds ranging from 2.179(8) to 2.234(8) Å, and O–Sb–O angles from 84.8(3) to 94.3(3) °. The Sb–C bond length is 2.185(12) Å. BVS values for selected atoms in NaCs-SbTi$_2$ are shown in Table 4-2.$^{[18]}$ In addition, the BVS values for oxygen atoms confirmed that the polyanion SbTi$_2$ is not protonated.

Replacement of the unique, labile sodium ion in the addenda site of Ti$_2$ by the phenylantimony(III) electrophile results in an increased distance between the opposite

![Figure 4-2](image_url)
pairs of tungsten oxygens at the Na/Sb binding site from around 2.99 Å to 3.20 Å. This is also reflected by an increase in the dihedral angle between the two planes passing through the six ‘belt’ W atoms of each \{As^{III}W_9\} unit in Ti_2 and SbTi_2 from about 3.1 ° to 6.3 °. In addition, a slight distortion at the TiO_5 units is observed, where for example the O–Ti1–O bond angle facing the vacant site increases from 88.2° to 92.8° when comparing Ti_2 and SbTi_2. We believe that this structural flexibility at the

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<tr>
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</tbody>
</table>

[^a] R_1 = \sum||F_o||-|F_c||/\sum|F_o|, wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}
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Table 4-2. Bond valence sum values for selected atoms in NaCs-SbTi$_2$. The BVS calculations were performed on the KDist software (Version 3.75) distributed by K. Knížek.

<table>
<thead>
<tr>
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<th>Atom</th>
<th>BVS value</th>
<th>Atom</th>
<th>BVS value</th>
</tr>
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<td>6.13</td>
<td>W17</td>
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<td>W11</td>
<td>6.18</td>
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</tr>
</tbody>
</table>

Figure 4-3. $^{183}$W NMR spectrum of NaCs-SbTi$_2$ dissolved in H$_2$O/D$_2$O recorded at room temperature. Inset: Representation of five different types of magnetically inequivalent W centers (different colors) in polyanion SbTi$_2$, in accordance with its C$_2$v point group symmetry.

Vacant site of Ti$_2$ is key for the smooth substitution of Na1 by the phenylantimony(III) electrophile, rendering Ti$_2$ a highly interesting monolacunary POM precursor.

We carried out $^{183}$W NMR studies on NaCs-SbTi$_2$ dissolved in D$_2$O/H$_2$O (pH 6.6) and observed the expected spectrum with peaks at -99.5, -108.7, -120.8, -122.6, and -159.3 ppm and relative intensities of 2:2:2:2:1 (Figure 4-3). The $^{13}$C NMR spectrum of SbTi$_2$ shows four peaks at 170.1, 134.1, 128.3, and 127.8 ppm, as expected for the phenyl group on Sb$^{III}$ (Figure 4-4a). This observation is further supported by the
Figure 4-4. (a) $^{13}$C NMR and (b) $^1$H NMR spectra of NaCs-SbTi$_2$ dissolved in D$_2$O/H$_2$O recorded at room temperature.

Figure 4-5. Thermogram of NaCs-SbTi$_2$ from room temperature to 800 °C under N$_2$ atmosphere.
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$^1$H NMR spectrum (Figure 4-4b). The NMR spectra of SbTi$_2$ remained unchanged after two weeks, indicating that this polyanion is solution-stable.

4.3.1.3 Thermogravimetric analysis

The thermogram of NaCs-SbTi$_2$ is shown in Figure 4-5, which features a two-step weigh loss. The first weight loss step (6.2%) in 20 - 325 °C can be attributed to the removal of crystal waters, and the following weight loss step (5.3%) up to 675 °C can be assigned to the decomposition of the organic species and structural transformation/decomposition of the polyanion.

4.3.1.4 UV-vis spectroscopy

The UV-vis spectra of NaCs-SbTi$_2$ dissolved in water and 1 M CH$_3$COOLi/CH$_3$COOH solutions at different pH values (4 to 6) displays an absorption maximum at around 250 nm in the UV range, which can be attributed to the O → W charge transfer transition (Figure 4-6). In addition, time-dependent UV-vis spectra (0 h, 1 h, 2 h and 4 h) suggested the stability of SbTi$_2$ in the 1 M CH$_3$COOLi/CH$_3$COOH solution at pH 4.

Figure 4-6. UV-vis spectra of NaCs-SbTi$_2$ in (a) H$_2$O, (b) LiCH$_3$COO/CH$_3$COOH (1M, pH = 4), (c) LiCH$_3$COO/CH$_3$COOH (1M, pH = 4.8) and (d) LiCH$_3$COO/CH$_3$COOH (1M, pH = 6). The POM concentration is 0.01 mM.
4.3.1.5 Electrochemistry

The electrochemistry of SbTi$_2$ was studied in 1 M LiCH$_3$COO/CH$_3$COOH solution at pH 4, where the polyanion is stable, as confirmed by UV-vis spectroscopy (Figure 4-6b). The CV pattern of SbTi$_2$ also shows a well-defined quasi-reversible and composite reduction wave followed by a wave close to the solvent limit peaking respectively at -0.760 V and ca. -0.920 V versus SCE (Figure 4-7). Figure 4-8 exhibits the CV of the first redox processes of SbTi$_2$ as a function of the potential scan rate. The peak current varies linearly with the square root of the scan rate as expected for diffusion controlled processes (inset of Figure 4-8).

![Figure 4-7](image_url)

**Figure 4-7.** Cyclic voltammograms obtained at different reverse potentials with 0.086 mM SbTi$_2$ in 1 M LiCH$_3$COO/CH$_3$COOH at pH 4, at a scan rate of 100 mV s$^{-1}$.

![Figure 4-8](image_url)

**Figure 4-8.** Cyclic voltammograms as a function of the scan rate for 0.086 mM SbTi$_2$ in 1 M LiCH$_3$COO/CH$_3$COOH at pH 4. Inset: variation of the cathodic peak current intensity of the main reduction peak as a function of the square root of the scan rate.
4.3.2 Incorporation of d-block electrophiles

Incorporation of 3d transition metal ions into POMs represents one extensively investigated subject, and their interesting magnetic, and electrochemical properties have raised wide interest.\cite{13,19} We thus decided to investigate the reactivity the POM precursor $\text{Ti}_2$ and 3d transition metal ion guests $\text{Mn}^{2+}$, $\text{Mn}^{3+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$ as well as the functionalization of the resultant products. As a result, we isolated a series of mono-embeded derivatives of $\text{Ti}_2$, namely, the $[\text{M(H}_2\text{O})(\text{Ti}^{IV}\text{O})_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2]^{12-}$ ($\text{M} = \text{Co}^{2+} (\text{CoTi}_2)$, $\text{Ni}^{2+} (\text{NiTi}_2)$, $\text{Cu}^{2+} (\text{CuTi}_2)$, $\text{Zn}^{2+} (\text{ZnTi}_2)$) polyanions. Unfortunately, the attempt to isolate $\text{Mn}^{2+}$, $\text{Mn}^{3+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$ metal ions-embeded derivatives were not successful. The reason for this is still unclear, but it should be related to the chemical nature (e.g. oxidation state, ionic radius, polarizability) of the metal ions.

4.3.2.1 Synthesis

The four polyanions $\text{MTi}_2$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) were prepared by reactions of the $\text{M(OAc)}_2\cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu} \text{and } \text{Zn}; n = 1, 2 \text{ and } 4$) and precursor $\text{Ti}_2$ in a 1 M sodium acetate solution at pH 6 (for details, see Experimental Section). All four polyanions were isolated as hydrated, mixed sodium/cesium salts, $\text{Cs}_{0.5}\text{Na}_{11.5}[\text{M(H}_2\text{O})(\text{Ti}^{IV}\text{O})_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2]\cdot n\text{H}_2\text{O}\cdot 0.5\text{CH}_3\text{COONa}$ ($\text{NaCs-MTi}_2$). The synthesis of polyanions $\text{MTi}_2$ can be represented as the following equation 4-2:

$$[\text{Ti}^{IV}\text{O})_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2]^{14+} + \text{M}^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{M(H}_2\text{O})(\text{Ti}^{IV}\text{O})_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2]^{12-} (\text{MTi}_2) \quad (4-2)$$

The FTIR spectra of the four salts are virtually identical and reflect their isostructural relation (Figure 4-9). Elemental analysis, FTIR spectra (two peaks at 1560 and 1415 cm$^{-1}$) of the $\text{NaCs-MTi}_2$ compounds indicate the presence of cocrystallized sodium acetate, which is confirmed by the appearance of two peaks at 181.5 and 23.3 ppm in the $^{13}$C NMR spectrum of $\text{NaCs-ZnTi}_2$ dissolved in H$_2$O/D$_2$O (Figure 4-10).

The molar ratio of reactants ($\text{M}^{2+}:\text{Ti}_2$) was optimized as 1.2:1, close to the stoichiometric ratio, but reflecting the need of a small excess of metal salts, alongside moderate heating, for optimized yield. A weakly acidic medium (pH 6) was required for successful synthesis of the TM-incorporated derivatives of $\text{Ti}_2$. This pH was also needed for our reported $\text{SbTi}_2$, and seems to be required to stabilize $\text{Ti}_2$ in solution prior to incorporation of the electrophile, evidenced by the previous UV-vis test result.
(see Section 3.3.4).\textsuperscript{13} Furthermore, a minimal amount of Cs\textsuperscript{+} ions was needed for the successful crystallization of the resulting product polyanions in single-crystals suitable for the X-ray analysis. The absence of Cs\textsuperscript{+} leads to a slow crystallization process, whereas a large amount caused the formation of a polycrystalline precipitate with low solubility in aqueous solution.

**Figure 4-9.** FTIR spectra of Na-Ti\textsubscript{2} and NaCs-MTi\textsubscript{2} (M = Co, Ni, Cu, Zn) measured at room temperature (KBr pellets).
4.3.2.2 Structure description

Single-crystal X-ray diffraction (XRD) indicated that all four NaCs-MTi₂ compounds crystallize in the same triclinic space group P\textoverline{1}, and are hence isomorphous (Table 4-3). The main POM entity features a typical Hervé-type dimeric assembly, with the belt filled by two titanium(IV) and one TM(II) cations, with three weakly coordinating sodium counter ions filling the interstitial sites (Figure 4-11). Both Ti\textsuperscript{IV} ions are penta-coordinate in a square-pyramidal fashion, with a terminal oxo ligand (as checked by Bond Valence Sum (BVS) calculations; see Table 4-5).\[^{[18]}\] As is listed in Table 4-4, the average equatorial Ti–O\textsubscript{l} bond lengths vary from 1.958(15) to 1.971(11) Å, slightly shorter than that in the Ti\textsubscript{2} precursor (1.973(10) Å).\[^{[13]}\] Consequently, MTi\textsubscript{2} features longer average terminal Ti=O\textsubscript{t} bond lengths (1.714(11) Å for CoTi\textsubscript{2}; 1.701(16) Å for NiTi\textsubscript{2}; 1.729(17) Å for CuTi\textsubscript{2}; 1.690(12) Å for ZnTi\textsubscript{2}) compared to Ti\textsubscript{2} (1.665(12) Å). The reason probably lies in the substitution of the sodium counter cation by the M\textsuperscript{2+} ions in the vacant site, resulting in shorter Ti–O\textsubscript{l} bonds and hence a decreased distance between the two \{AsW\textsubscript{9}\} units, see Figure 4-12, Tables 4-4 and 4-6. The third addenda site in the central belt is occupied by a M\textsuperscript{2+} ion, which adopts a square-pyramidal coordination geometry as Ti\textsuperscript{4+}, but with a terminal aqua ligand pointing outwards, in agreement with BVS calculations.\[^{[18]}\] The terminal Cu–O\textsubscript{w} bond (2.160(30) Å) in CuTi\textsubscript{2} is longer than the corresponding ones in the other MTi\textsubscript{2} (M = Co, Ni, Zn) (2.003(15) Å for CoTi\textsubscript{2}; 2.000(20) Å for NiTi\textsubscript{2};

Figure 4-10. $^{13}$C NMR spectrum of NaCs-ZnTi\textsubscript{2} dissolved in D\textsubscript{2}O/H\textsubscript{2}O recorded at room temperature.
Table 4-3. Crystal data for NaCs-MTi$_2$ (M = Co, Ni, Cu, Zn).

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<td>Measured refls.</td>
<td>215919</td>
<td>192255</td>
<td>93594</td>
<td>188910</td>
</tr>
<tr>
<td>Independent refls.</td>
<td>23051</td>
<td>20559</td>
<td>20478</td>
<td>22342</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.0690</td>
<td>0.0767</td>
<td>0.0854</td>
<td>0.0794</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>700</td>
<td>700</td>
<td>708</td>
<td>732</td>
</tr>
<tr>
<td>GOF</td>
<td>1.003</td>
<td>1.002</td>
<td>1.003</td>
<td>1.004</td>
</tr>
<tr>
<td>$R_1$, w$R_2$, [I &gt; 2$\sigma$(I)]</td>
<td>0.0472, 0.1262</td>
<td>0.0685, 0.1709</td>
<td>0.0616, 0.1478</td>
<td>0.0528, 0.1248</td>
</tr>
<tr>
<td>$R_1$, w$R_2$, (all data)</td>
<td>0.0682, 0.1393</td>
<td>0.0866, 0.1818</td>
<td>0.1030, 0.1680</td>
<td>0.0750, 0.1359</td>
</tr>
</tbody>
</table>

$[a]$ $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]\}^{1/2}/\sum w[(F_o)^2]^{1/2}$
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2.035(13) Å for ZnTi$_2$ derivatives due to the Jahn-Teller effect, which also results in shorter average equatorial M–O$_1$ bond lengths for CuTi$_2$ (1.925(14) Å vs 1.973(15)-2.001(10) Å).

The replacement of the sodium ion in Ti$_2$ by M$^{2+}$ leads to subtle, but measureable geometric changes in the ‘belt’ of the Hervé structure (Figure 4-12 and Table 4-6). As mentioned above, the mean interatomic distance between the opposite pairs of oxygens bound to at the Na/M binding sites ($l_1$) decreases significantly from ~3.01 to ~2.75 Å, reaching a similar range of distances at the Ti sites ($l_2$ and $l_3$). As a result, two {As$^{III}$W$_9$} units in MTi$_2$ are almost parallel to each other, where the dihedral angle ($\theta_1$) between the two planes passing through the six “belt” W atoms of each {As$^{III}$W$_9$} unit is very close to 0°. This renders the average O–Ti–O bond angles at the belt, mainly $\theta_2$ (86.4 - 88.4°) and $\theta_3$ (87.4 - 88.0°), almost equal compared to those in Ti$_2$ ($\theta_2 = 88.7°$, $\theta_3 = 85.0°$). This renders the average O–Ti–O bond angles at the belt, mainly $\theta_2$ (86.4 - 88.4°) and $\theta_3$ (87.4 - 88.0°), almost equal compared to those in Ti$_2$ ($\theta_2 = 88.7°$, $\theta_3 = 85.0°$). This conformational flexibility within the Ti$_2$ skeleton supports our previous hypothesis of the precursor’s efficiency of encapsulating a multitude of electrophilic, cationic centers within its vacant site.[13] We plan to continue further the study of this characteristic.

Figure 4-11. (a) Representation of polyanion MTi$_2$ with incorporated, weakly bound Na$^+$ ions. (b) Central belt of MTi$_2$, with the Na1, Na2, and Na3 occupying the interstitial sites between Ti1, Ti2, and M1. Color code: WO$_6$ octahedra (red); Ti (turquoise); M (green); As (yellow); O (red); Na1, Na2, and Na3 (dark blue). H atoms are omitted for clarity.
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Table 4-4. Average Ti−O/Ti=O and M−O bond lengths in the NaCs-MTi$_2$ (M = Co, Ni, Cu, Zn).

<table>
<thead>
<tr>
<th>bond lengths$^a$</th>
<th>CoTi$_2$</th>
<th>NiTi$_2$</th>
<th>CuTi$_2$</th>
<th>ZnTi$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti−O$_l$</td>
<td>1.969(10)</td>
<td>1.970(15)</td>
<td>1.958(15)</td>
<td>1.971(11)</td>
</tr>
<tr>
<td>Ti=O$_t$</td>
<td>1.714(11)</td>
<td>1.701(16)</td>
<td>1.729(17)</td>
<td>1.690(12)</td>
</tr>
<tr>
<td>M−O$_l$</td>
<td>1.984(10)</td>
<td>1.973(15)</td>
<td>1.925(14)</td>
<td>2.001(10)</td>
</tr>
<tr>
<td>M−O$_w$</td>
<td>2.003(15)</td>
<td>2.000(20)</td>
<td>2.160(30)</td>
<td>2.035(13)</td>
</tr>
</tbody>
</table>


Table 4-5. Bond valence sum (BVS) values for the selected atoms in compounds NaCs-MTi$_2$ (M = Co, Ni, Cu, Zn). The BVS calculations were performed on the KDist software (Version 3.75) distributed by K. Knížek.

<table>
<thead>
<tr>
<th>Atom</th>
<th>BVS value</th>
<th>Atom</th>
<th>BVS value</th>
<th>Atom</th>
<th>BVS value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCs-CoTi$_2$</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>W1</td>
<td>6.13</td>
<td>W9</td>
<td>6.11</td>
<td>W17</td>
<td>6.11</td>
</tr>
<tr>
<td>W2</td>
<td>6.07</td>
<td>W10</td>
<td>6.10</td>
<td>W18</td>
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<tr>
<td>W3</td>
<td>6.08</td>
<td>W11</td>
<td>6.12</td>
<td>As1</td>
<td>3.09</td>
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<tr>
<td>W4</td>
<td>6.21</td>
<td>W12</td>
<td>6.10</td>
<td>As2</td>
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<tr>
<td>W5</td>
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<td>W13</td>
<td>6.20</td>
<td>Ti1</td>
<td>3.89</td>
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<tr>
<td>W6</td>
<td>6.07</td>
<td>W14</td>
<td>6.17</td>
<td>Ti2</td>
<td>4.05</td>
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<tr>
<td>W7</td>
<td>6.25</td>
<td>W15</td>
<td>6.16</td>
<td>Co1</td>
<td>2.21</td>
</tr>
<tr>
<td>W8</td>
<td>6.14</td>
<td>W16</td>
<td>6.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| NaCs-NiTi$_2$ | | | | | |
| W1   | 6.27      | W9   | 6.07      | W17  | 6.00      |
| W2   | 6.07      | W10  | 6.25      | W18  | 6.30      |
| W3   | 6.13      | W11  | 6.13      | As1  | 3.04      |
| W4   | 6.39      | W12  | 6.12      | As2  | 3.20      |
| W5   | 6.02      | W13  | 6.14      | Ti1  | 4.00      |
| W6   | 6.22      | W14  | 6.15      | Ti2  | 4.02      |
| W7   | 6.34      | W15  | 6.26      | Ni1  | 2.18      |
| W8   | 5.98      | W16  | 6.38      |      |           |

| NaCs-CuTi$_2$ | | | | | |
| W1   | 6.18      | W9   | 5.98      | W17  | 6.12      |
Chapter 4 Guest incorporation into Ti$_2$-containing monolacunary host

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<td>W2</td>
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<td>W10</td>
<td>6.28</td>
<td>W18</td>
<td>6.07</td>
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<td>W3</td>
<td>6.08</td>
<td>W11</td>
<td>6.14</td>
<td>As1</td>
<td>3.21</td>
</tr>
<tr>
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<td>6.24</td>
<td>W12</td>
<td>6.12</td>
<td>As2</td>
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</tr>
<tr>
<td>W5</td>
<td>6.08</td>
<td>W13</td>
<td>6.28</td>
<td>Ti1</td>
<td>4.00</td>
</tr>
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<td>6.05</td>
<td>Ti2</td>
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<td>W16</td>
<td>6.36</td>
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**NaCs-ZnTi$_2$**

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<td>W9</td>
<td>6.17</td>
<td>W17</td>
<td>6.10</td>
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<tr>
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<td>6.08</td>
<td>W11</td>
<td>6.21</td>
<td>As1</td>
<td>3.17</td>
</tr>
<tr>
<td>W4</td>
<td>6.17</td>
<td>W12</td>
<td>6.15</td>
<td>As2</td>
<td>3.04</td>
</tr>
<tr>
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<td>6.19</td>
<td>W13</td>
<td>6.33</td>
<td>Ti1</td>
<td>4.03</td>
</tr>
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<td>6.17</td>
<td>W14</td>
<td>6.12</td>
<td>Ti2</td>
<td>4.05</td>
</tr>
<tr>
<td>W7</td>
<td>6.21</td>
<td>W15</td>
<td>6.06</td>
<td>Zn1</td>
<td>2.21</td>
</tr>
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<td>6.18</td>
<td>W16</td>
<td>6.19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Figure 4-12.* Representations of the parameters $l_1$, $l_2$, $l_3$, $\theta_1$, $\theta_2$, and $\theta_3$ the MTi$_2$ (M = Co, Ni, Cu, Zn) polyanions from a side view. The representation of $l_4$ is omitted for clarity. All the measurements and calculations are performed by the Diamond, version 3.2k (copyright Crystal Impact GbR).

*Table 4-6.* Average interatomic distances and angles in the Ti$_2$, SbTi$_2$ and MTi$_2$ (M = Co, Ni, Cu, Zn) polyanions shown in Figure 4-12.

<table>
<thead>
<tr>
<th>parameters$^{[a]}$</th>
<th>Ti$_2$</th>
<th>CoTi$_2$</th>
<th>NiTi$_2$</th>
<th>CuTi$_2$</th>
<th>ZnTi$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_1$</td>
<td>3.01</td>
<td>2.77</td>
<td>2.71</td>
<td>2.70</td>
<td>2.77</td>
</tr>
<tr>
<td>$l_2$</td>
<td>2.77</td>
<td>2.72</td>
<td>2.75</td>
<td>2.70</td>
<td>2.72</td>
</tr>
</tbody>
</table>

73
To study the solution behavior of the diamagnetic ZnTi₂, we performed $^{183}$W NMR spectroscopy on NaCs-ZnTi₂ dissolved in 1M LiOAc, H₂O/D₂O solution adjusted to the synthesis pH 6.0. In the same medium, the $^{183}$W NMR spectrum of Ti₂ (Figure 4-13a) gives five peaks at -106.4, -107.7, -109.7, -115.8, and -148.9 ppm in a respective 2:2:2:2:1 intensity ratio, resulting from $C_{2v}$ symmetry. The derivative ZnTi₂ has the same symmetry as the parent Ti₂ and is expected to give five peaks as well, which are observed in its spectrum (Figure 4-13b) at -107.6, -112.7, -112.9,
-137.3, and -165.8 ppm, with respective 2:2:2:1:2 intensities.

The $^{183}$W spectrum of Ti$_2$ undergoes significant changes after incorporation of zinc(II) to give ZnTi$_2$. For example, the resonance of intensity 1 (-148.9 ppm) in the spectrum of Ti$_2$ (Figure 4-13a), which can be assigned easily to the unique “cap” W atom (shown in green in Figure 4-13) in the edge-shared W$_3$O$_{13}$ that connect with two [TiO]$^{2+}$ groups, is shifted up-field to -137.3 ppm (Figure 4-13b). Moreover, the only resonance without obvious large couplings (~20 ± 4 Hz; corner-sharing mode between WO$_6$ octahedra) is the one at -115.8 ppm (Figure 4-13a), because two small couplings (~9 ± 2 Hz; edge-sharing mode between WO$_6$ octahedra) produce spectral overlap. Therefore, it is reasonable to correlate this resonance to the four magnetically equivalent W atoms that close to the third addenda site occupied by Na$^+$/Zn$^{2+}$ groups (shown in lavenda in Figure 4-13). This resonance move substantially to a high-field position at -165.8 ppm (Figure 4-13b) upon the substitution, which is consistent with the changes of the magnetic environment of the W centers due to the formation of Zn–O dative covalent bond.

4.3.2.3 Thermogravimetric analysis

![Figure 4-14. Thermogram of NaCs-CoTi$_2$ from room temperature to 800 °C under N$_2$ atmosphere.](image)
Figure 4-15. Thermogram of NaCs-NiTi$_2$ from room temperature to 800 °C under N$_2$ atmosphere.

Figure 4-16. Thermogram of NaCs-CuTi$_2$ from room temperature to 800 °C under N$_2$ atmosphere.
Figure 4-17. Thermogram of NaCs-ZnTi$_2$ from room temperature to 800 °C under N$_2$ atmosphere.

The thermograms of NaCs-CoTi$_2$, NaCs-NiTi$_2$, NaCs-ZnTi$_2$ (Figures 4-14, 4-15 and 4-17) feature two-step weight loss. The first step (8.6% for NaCs-CoTi$_2$, 10.2% for NaCs-NiTi$_2$, 8.9% for NaCs-ZnTi$_2$ in 20 - 300 °C) can be attributed to the removal of crystal waters, and the following weight loss step (2.7% for NaCs-CoTi$_2$, 2.6% for NaCs-NiTi$_2$ up to 650 °C; 2.5% for NaCs-ZnTi$_2$ up to 600 °C) can be assigned to the decomposition of the organic species and structural transformation/decomposition of the polyanions. In comparison, the removal of crystal waters of NaCs-CuTi$_2$ (Figure 4-16) results in a weight loss of 8.0% in 20-150 °C. More interestingly, there is a rebounding increase of the weight after 450 °C, which may be caused by the reaction of the residue and N$_2$ during the structural transformation/decomposition of the polyanion.
4.3.2.4 UV-vis spectroscopy

![Absorption spectra of the polyanions MTi$_2$ (M = Co, Ni, Cu and Zn) recorded in 1 M LiCH$_3$COO/CH$_3$COOH solution at pH 6 with a 1 cm optical path quartz cuvette. (a) Spectra recorded in the UV range; the POM concentration was 0.03 mM. (b) Spectra recorded in the visible region; the POM concentration was 0.5 mM.](image)

The absorption spectra of polyanions MTi$_2$ (M = Co, Ni, Cu and Zn) were recorded in the 1M LiCH$_3$COO/CH$_3$COOH solution at pH 6. In the UV region, all four MTi$_2$ polyanions exhibit intense absorption bands (at around 250 nm) attributed to O → W charge transfer transition (Figure 4-18a). As expected, the absorption bands due to the Co, Cu and Ni centers are observed at higher wavelengths (Figure 4-18b). The spectrum of NiTi$_2$ presents a well-defined bands located at 450 nm followed by a O → W charge transfer transition (Figure 4-18a). As expected, the absorption bands
due to the Co, Cu and Ni centers are observed at higher wavelengths (Figure 4-18b). The spectrum of NiTi$_2$ presents a well-defined bands located at 450 nm followed by a slight shoulder at around 520 nm while that of CoTi$_2$ is characterized by two bands at 540 and 640 nm. The spectra of all MTi$_2$ polyanions were reproducible with respect to absorptions and wavelengths for at least the period of time matching the duration of an electrochemical experiment (which may last up to several hours). The stability tests of CoTi$_2$ assessed in 0.4 M NaH$_2$PO$_4$/NaOH (pH 6 or 7) also show that it is sufficiently stable in these media to afford electrochemical characterization.

4.3.2.5 Electrochemistry

The redox properties of MTi$_2$ (M = Co, Ni, Cu and Zn) polyanions were studied in a pH 6 acetate medium by cyclic voltammetry (CV). In the previous chapter, we have described the electrochemistry of the precursor Ti$_2$ (see Section 3.3.6). The UV-visible stability carried out in this medium revealed that all these polyanions are sufficiently stable to stand electrochemical characterization (see Section 4.3.2.4). For clarity, the redox processes observed in the negative and positive potential domains (versus SCE) are described separately. In our experimental conditions, the MTi$_2$ polyanions have only one potentially electro-oxidizable metal cation (Co$^{II}$). Figure 4-19 exhibits the CVs of CoTi$_2$, NiTi$_2$ and ZnTi$_2$ in the negative potential domain. These CVs patterns are characterised by two more or less closely spaced and chemically reversible reduction waves. In line with the previous observations for Ti$_2$,[13] these composite waves are assigned to the reduction of the Ti$^{IV}$ and W$^{VI}$ centers respectively. The CVs patterns display features allowing for a facile distinction of the MTi$_2$ polyanions, despite the fact that they are isostructural and have the same overall negative charge and non-electro reducible substituent metal cations (Co$^{II}$, Ni$^{II}$ and Zn$^{II}$) in our experimental conditions. Such observation is most likely related to the interplay of other parameters such as the substituent metal ion properties and its influence on the basicity of reduced or oxidised forms of the POM.[20] This influence is reflected both in the potential locations and separations of the redox waves.[20] As main differences, the number of reduction waves and their cathodic peak potential separations ($\Delta E_{pc}$) depend on the nature of the metal ion substituent. Thus the CV of CoTi$_2$ exhibits one well-defined reduction wave (at -0.968 V versus SCE) preceded by a very low intensity wave (at ca. -0.875 V versus SCE). On the reverse scan, two reoxidation waves are observed at -0.900 V and
-0.810 V versus SCE, which confirms the composite nature of the reduction wave. In contrast, two reduction waves are observed at -0.890 V and -0.950 V versus SCE for ZnTi2 and -0.867 V and -0.960 V versus SCE for NiTi2. However, the ΔEpc values are ca. 0.060 V and 0.093 V for ZnTi2 and NiTi2 respectively, which means that the electrochemical-chemical-electrochemical (ECE) or EEC process is favored in the case of ZnTi2. Therefore, the basicity of the reduced forms of the POMs decreases as follows CoTi2 > ZnTi2 > NiTi2. The CV run for Ti2, under the same conditions, shows the same general shape as that of CoTi2 characterized by one chemically reversible reduction wave at -0.972 V versus SCE preceded by a low intensity wave at ca. -0.850 V versus SCE.[13] However, the influence of the CoII center is revealed by the fact that the overall electron transfer process associated with the redox couples, evaluated from the anodic-to-cathodic peak potentials difference (ΔEp), is faster for CoTi2 (ΔEp =

![Figure 4.19. Cyclic voltammograms of the quasi-reversible WVI-waves of CoTi2, NiTi2 and ZnTi2, respectively, run in a 1 M CH3COOLi/CH3COOH medium a pH 6. The scan rate was 2 mV s\(^{-1}\), and the reference electrode was a saturated calomel electrode (SCE). The POM concentration of was 0.1 mM.](image)

0.068 V) than for Ti2 (ΔEp = 0.105 V).[13] Moreover, despite the difference in the overall negative charges of CoTi2 and Ti2, their reduction peak potentials are similar.

This observation might, at least partly, be due to the differences in the acid-base properties of their reduced forms. For all three polyanions, the peaks currents remain proportional to the square root of the scan rate (from 2 to 100 mV/s), indicating that the processes are diffusion-controlled, in agreement with the behavior previously
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reported for Ti$_2$.[13]

As shown in Figure 4-20a, the CV of CuTi$_2$ is composed by the W$^{VI}$ reduction waves preceded by those of Cu$^{II}$ labelled I and II, in line with observations reported for Cu$^{II}$-substituted POMs.[21] The characteristics of the CV pattern of the Cu$^{II}$ center depend strongly on the value of the scan rate. Specifically, the reduction wave II is ill-defined at scan rates higher than 10 mV/s as illustrated by the CV obtained at 100 mV/s and shown in Figure 4-20a. In contrast, well-behaved waves I and II are observed at lower scan rates. In order to better highlight this behaviour, the CV of CuTi$_2$ obtained at a scan rate as slow as 2mV/s and restricted to the Cu$^{II}$ waves is displayed in Figure 4-20b. Indeed, this CV exhibits well-defined reduction waves I and II peaking at -0.259 V and -0.383 V versus SCE respectively. In agreement with previous reports on Cu$^{II}$-substituted POMs, these waves are attributed to the stepwise reduction of Cu$^{II}$ center into Cu$^0$ through Cu$^I$ state.[21] On potential reversal, two reoxidation wave I’ and II’ are observed at -0.0140 V and -0.063 V versus SCE respectively. The latter displays the roughly symmetrical shape of desorptive reoxidation of surface-confined species because it features the oxidation of the deposited Cu$^0$.[21] Figure 4-20c exhibits the CV as a function of the scan rate for CuTi$_2$ restricted to the potential domain of the Cu$^{II}$ to Cu$^I$ process (waves I). This quasi-reversible process is diffusion-controlled as revealed by the linear variation of the reduction peak current as a function of the square-root of the scan rate (inset of Figure 4-20c). The results altogether, underscore the good stabilization of the Cu$^I$ state by the ligand Ti$_2$. Whatever the value of the scan rate (from 100 to 2 mV/s), the Ti$^{IV}$ and W$^{VI}$ centers reduction processes are featured be a composite quasi-reversible reduction wave as shown in Figure 4-20a but the comparison of its characteristics with those of the other MTi$_2$ or Ti$_2$ is not straightforward because the copper deposition comes into play in the potential domain of this wave.
Figure 4-20. (a) Cyclic voltammograms of a 0.1 mM solution of CuTi$_2$, in a 1 M CH$_3$COOLi/CH$_3$COOH medium at pH 6; the scan rate was 100 mV s$^{-1}$. The reference electrode was a saturated calomel electrode (SCE). (b) Cyclic voltammograms of CuTi$_2$ restricted to the Cu$^{II}$ to Cu$^{0}$ redox process; the scan rate was 2 mV s$^{-1}$. (c) Cyclic voltammograms of CuTi$_2$ restricted to the Cu$^{II}$ to Cu$^{I}$ redox process; the scan rate (from inner to outer curve) was 2, 10, 20, 40, 60, 80, and 100 mV s$^{-1}$. Inset: variation of cathodic peak current intensities as a function of the square root of the scan rate.
Figure 4-21. Redox activity of the Co$^{II}$ center of 0.1 mM CoTi$_2$ in 0.4 M NaH$_2$PO$_4$/NaOH medium at pH 7 or pH 6. The cyclic voltammogram of the electrolyte alone is superimposed for comparison. The scan rate was 100 mV s$^{-1}$, and the reference electrode was a saturated calomel electrode (SCE). (a) Cyclic voltammogram observed at pH 7 with a glassy carbon (GC) working electrode. (b) Cyclic voltammogram observed at pH 7 with an ITO working electrode. (c) Comparison of the cyclic voltammograms obtained with GC at pH 6 and 7 respectively.
As expected based on earlier works,[22] the oxidation processes associated with the CoII center in CoTi2 are complex. In particular, they are accompanied by film deposition and the characteristics of the CV depend on the working electrode material and the supporting electrolyte composition. For example, Figure 4-21a shows that the CV of CoTi2 obtained with glassy carbon (GC) electrode in pH 7 phosphate medium features a well-defined quasi-reversible CoII oxidation wave peaking at +1.100 V versus SCE and followed by a large irreversible wave, whereas for ITO, these two waves are completely merged (Figure 4-21b). However, for both electrodes, the large wave, which is not observed in the absence of CoTi2, is attributed to the oxygen evolution reaction (OER). As shown in Figure 4-21c, a less-defined CoII oxidation wave is observed in pH 6 medium. Moreover, the pH 6 medium (acetate or phosphate) is more favorable for the working electrode modification by concomitant partial film deposition during the successive scans (not shown). Such a phenomenon was attributed to at least partial transformation of the POM during the oxidation processes.[22]

4.3.2.6 Preliminary evaluation towards nitrate reduction electrocatalysis

We also performed preliminary study of the influence of the nature of the metal ion guests (CoII, NiII, CuII, and ZnII) within MTi2 on the electrocatalytic activity of the precursor Ti2 towards nitrate reduction that we have reported recently.[13] Analogous studies were described for a large series of Dawson-type metal-ion-substituted (VIV, MnII, FeIII, CoII, NiII, CuII and ZnII) POMs in the pioneering work on the electrocatalytic reduction of nitrate by reduced POMs.[23] Since then, the multi-copper substituted POMs were demonstrated to show the highest electrocatalytic activity towards this reaction.[19] However, a high-performance nitrate reduction electrocatalyst was recently obtained with Mialane’s heptanuclear POM based on NiII centers, bisphosphonates and polyoxotungstates.[24] The tests carried out for 0.1 mM solutions of the MTi2 and Ti2 in a pH 6 acetate medium revealed that the presence of the ZnII or CoII center does not induce significant improvement of the efficiency of Ti2 as electrocatalyst for nitrate reduction. By contrast, NiTi2 and CuTi2 present significantly higher electrocatalytic activities towards this reaction compared to Ti2. Similarly, it was shown for the above mentioned Dawson-type POMs that only those substituted with NiII and CuII are effective for this reaction.[23] Figures 4-22a,b feature the CVs as a function of the excess parameter \( \gamma = C_{\text{nitrate}}/C_{\text{POM}} \) for NiTi2 and
CuTi$_2$, respectively. For clarity, the backward scans recorded in the presence of nitrate are omitted. Representative CVs featuring the backward scans are shown in Figures 4-23a,b for NiTi$_2$ and CuTi$_2$, respectively. In accordance with previous observations,$^{[21,23,24]}$ the addition of nitrate induced a current increase, and concomitantly the reversibility of the W$^{VI}$ centers waves was suppressed (Figures 4-23a,b). Moreover, the catalytic current rises upon increasing the nitrate concentration (Figures 4-22a,b). Figure 4-23a, shows that no appreciable nitrate reduction occurs in the absence of POM. Altogether, these observations indicate an efficient reduction of nitrate by the reduced POMs. The current increase observed in the presence of nitrate can be expressed more quantitatively, as usual, through the catalytic efficiency CAT defined as

$$\text{CAT} = 100 \times \frac{I_{\text{POM + nitrate}} - I_{\text{POM}}}{I_{\text{POM}}}$$

where the $I_{\text{POM}}$ and $I_{\text{POM + nitrate}}$ represent the reduction currents observed for the POM alone and in the presence of nitrate, respectively. The CAT values measured at -1.020 V versus SCE for NiTi$_2$ vary from ca. 99% to 833% when $\gamma$ increases from 50 to 300. The CAT values of NiTi$_2$ are 4.2 to 5.6 times higher than those of Ti$_2$ obtained under the same conditions, which confirms the expected beneficial effect of the Ni$^{II}$ center on the nitrate reduction electrocatalysis.$^{[23]}$ To our knowledge, NiTi$_2$ represents the first example of a very efficient Ni$^{II}$-monosubstituted POM electrocatalyst for nitrate reduction. Importantly, these CAT values are obtained with relatively low $\gamma$ values at a remarkably favorable potential and in a pH 6 medium for a Cu$^{II}$-free POM electrocatalyst. In line with previous reports,$^{[22]}$ the catalytic efficiency of CuTi$_2$ is significantly higher that of the NiTi$_2$. Indeed, the CAT values obtained with CuTi$_2$ at -1.00 V versus SCE, vary from 1286% to 3903% for $\gamma =$50 and 300 respectively. It is worth noting that relatively high CAT values were also obtained for much smaller $\gamma$ values. For example, CAT value varies from 180% to 403% when $\gamma$ increases from 5 to 10. To our knowledge, CuTi$_2$ constitutes the first example of Cu$^{II}$-containing POM electrocatalyst for nitrate reduction in a medium at pH 6. It is well-known that the activity of POMs towards this reaction decreases sharply with increasing the pH of the supporting electrolyte. The CAT values of CuTi$_2$ compare favorably with those obtained with various Cu$^{II}$-substituted POMs in a medium at pH 5.$^{[19a]}$ The electrocatalytic process is mainly triggered by the electrodeposited copper, however, it was shown for a series of Cu$^{II}$-containing Dawson-type POMs that the nature of the POM ligand influences the electrocatalysis intensity.$^{[25]}$ The authors resorted to CV coupled with electrochemical quartz microbalance (EQCM) and atomic force
microscopy (AFM) to demonstrate that the morphology and size of the deposited copper particles depend strongly on POM structure and composition, thus explaining the differences between observed electrocatalytic activities. As expected, the smaller particles were the most efficient. Moreover, whatever the POM, the size of the deposited particles was greatly smaller than that obtained with CuSO$_4$\textsuperscript{2-}\textsuperscript{25} which underscores the beneficial effect of the POM ligand on the electrocatalytic process. Although, we did not perform EQCM and AFM characterizations for the films obtained with CuTi$_2$, we tentatively attribute its high performance to at least partly

**Figure 4-22.** Cyclic voltammograms of (a) NiTi$_2$ and (b) CuTi$_2$, respectively, run in a 1 M CH$_3$COOLi/CH$_3$COOH medium at pH 6 and in the presence of increasing amounts of nitrate with the excess parameter $\gamma = C_{\text{nitrate}}/C_{\text{POM}}$ (C = concentration); the scan rate was 2 mV s$^{-1}$, and the reference electrode was a saturated calomel electrode (SCE). The concentration of the POMs was 0.1 mM.
such beneficial effect. We have also performed complementary electrocatalytic tests with nitrite because it is likely an intermediate or final product in the reduction of nitrate. Interestingly, the results show that nitrite is reduced at more positive potential than nitrate. For example, the CAT value of CuTi$_2$ for nitrite reduction obtained at -0.320 V versus SCE with $\gamma = 300$ is about 6.2 higher than for nitrate under the same conditions. Therefore, it is likely that nitrate is reduced beyond the state of nitrite. This observation is in line with previous reports which demonstrated that even purely tungstic POMs are effective for the electrocatalysis of nitrite reduction.$^{[2a]}$
4.3.2.7 Magnetic susceptibility and magnetization studies

In order to support the bonding information from the X-ray structural data, and to elucidate the magnetic properties of the newly synthesized compounds, we carried out temperature-dependent magnetic susceptibility, \( \chi \), measurements. Figure 4-24 presents the measured \( \chi \) and their inverses for NaCs-CoTi\(_2\), NaCs-NiTi\(_2\) and NaCs-CuTi\(_2\), respectively. The measurements were performed under an applied field of 0.01 T and diamagnetic corrections to the measured susceptibility were subtracted.\(^{[26]}\) The magnetic susceptibility was fit to the Curie-Weiss law using eqn (4-3) and eqn (4-4) for all three samples and compared to theoretical values.\(^{[27]}\)

\[
\frac{1}{\chi} = 1/T - \theta + C = N \mu_{\text{eff}}^2 \mu_B^2 / 3k_B
\]  
(4-3), where

\[
\mu_{\text{eff}}^2 = \frac{3k_B C}{N \mu_B^2} = g^2 (S(S + 1))
\]  
(4-4)

In eqn (4-3) and (4-4), \( C \) and \( \theta \) represent the Curie constant and the Weiss temperature, respectively. \( N, \mu_B, \) and \( k_B \) are Avogadro’s number, Bohr magneton, and the Boltzmann constant. The electron Zeeman factor, \( g \), coupled with the total spin, \( S \), yields the theoretical effective magnetic moment, \( \mu_{\text{eff}} \). The effective magnetic moments for NaCs-CoTi\(_2\), NaCs-NiTi\(_2\) and NaCs-CuTi\(_2\) were calculated to be 5.45.

Figure 4-24. Temperature dependence of DC magnetic susceptibility of (a) NaCs-CoTi\(_2\), (b) NaCs-NiTi\(_2\) and (c) NaCs-CuTi\(_2\) (Inset: Curie-Weiss fit (solid black line) to temperature dependent inverse susceptibility), and field-dependent magnetization of (d) NaCs-CoTi\(_2\), (e) NaCs-NiTi\(_2\) and (f) NaCs-CuTi\(_2\) measured at 1.8K.
3.11, and 2.12 Bohr magnetons (B.M.) per molecule, respectively. Theoretical values taken from literature\cite{28} are presented in Table 4-7 with the calculated magnetic moments. The negative Weiss constants indicate antiferromagnetic interactions with the nearest neighbours for these paramagnetic samples.\cite{29}

The magnetic moments for NaCs-CoTi₂, NaCs-NiTi₂ and NaCs-CuTi₂ were measured by varying the field from 0 T to 7 T at a temperature of 1.8 K as shown in Figures 4-24d,e.f. The NaCs-NiTi₂ plot does not saturate up to our highest available magnetic field of 7 T, while the other two samples saturate, near to the values expected.

4.3.2.8 Electron paramagnetic resonance (EPR) studies

EPR is an ideal technique to directly probe unpaired electrons and determine the electronic structure of materials. In particular by identifying the $g$-values and hyperfine splittings the nature of the bonds, oxidation states, and several other electromagnetic properties may be assessed in a paramagnetic species.\cite{3b} Therefore, EPR measurements were conducted on all three compounds, NaCs-CoTi₂, NaCs-NiTi₂ and NaCs-CuTi₂, to further confirm the oxidation states and site symmetry of the metal ions. Initial measurements were made at X-band (9.8 GHz). Unfortunately, NaCs-NiTi₂ and NaCs-CoTi₂ yielded no detectable EPR response, most likely due to their fast spin-lattice relaxation that broadens the EPR peaks beyond detection. But the SQUID data on these compounds were deemed to be sufficient for assigning their oxidation state since the geometry and bonding was well established via X-ray structure and NMR measurements. On the other hand, NaCs-CuTi₂ yielded a sharp spectrum, with well resolved hyperfine structure in the

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental moment $\mu_{\text{eff}}$/molecule</th>
<th>Theoretical moment $\mu_{\text{eff}}$/molecule (spin only)</th>
<th>Theoretical moment $\mu_{\text{eff}}$/molecule (L + S)</th>
<th>Weiss constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCs-CoTi₂</td>
<td>5.45</td>
<td>3.87</td>
<td>5.21</td>
<td>-41</td>
</tr>
<tr>
<td>NaCs-NiTi₂</td>
<td>3.11</td>
<td>2.83</td>
<td>4.49</td>
<td>-4</td>
</tr>
<tr>
<td>NaCs-CuTi₂</td>
<td>2.12</td>
<td>1.73</td>
<td>3.01</td>
<td>-17</td>
</tr>
</tbody>
</table>

Table 4-7. Experimental and theoretical magnetic moments and Weiss constants for NaCs-CoTi₂, NaCs-NiTi₂ and NaCs-CuTi₂.
low field \((g_z)\) part of the spectrum, as shown in Figure 4-25a. After multiple simulations, it was noted that the hyperfine structure exhibits contributions from both \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\) isotopes, their peaks overlap because they have same nuclear spin, \(I = 3/2\), and nearly the same magnetic moments. By using two hyperfine constants, with the ratio of their isotopic abundance, 69:31, and respective magnetic moments, a reasonably well simulated spectrum was obtained, as can be seen in Figure 4-25b. Since the hyperfine splitting was not resolved on the perpendicular \((g_x\) or \(g_y\)) components, the \(A_\perp\) value was assumed to be much smaller than the linewidth, essentially zero.\(^{29-30}\)

To interpret the EPR spectrum, we noted that the spectrum in Figure 4-25 had three \(g\)-tensor components\((g_x \neq g_y \neq g_z)\), revealing that the \(\text{Cu}^{2+}\) ion has a rhombic symmetry, but close to a square-planar geometry, since the peaks representing \(g_x\) and \(g_y\) are nearly overlapping. The spectrum was simulated using the computer program “Easy Spin”.\(^{31}\) As can be noted from Figure 4-25, the agreement between the simulated and experimental spectra is satisfactory. The obtained parameters are: \(g_x = 2.0448\), \(g_y = 2.0932\), and \(g_z = 2.410\), but \(A_x \sim A_y = 0\) G, and \(A_z = 90 \pm 3\) G (average of \(A_z\) values of the two main Cu isotopes, \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\)). As discussed earlier,\(^{29}\) these

![Figure 4-25. X-band (9.8 GHz) EPR spectra for both (a) experimental (black) and (b) simulated (red) spectra of NaCs-CuTi2 at 298 K.](image)
parameters enable us to assign the unpaired electron to the copper atom’s orbital. Since \( g_{\parallel} > g_{\perp} \) and \( A_{\perp} \ll A_{\parallel} \), the ground state primarily involves the \( d_{x^2-y^2} \) orbitals of \( \text{Cu}^{2+} \) ions with ligand orbitals in an essentially square planar geometry, in agreement with the X-ray structure as discussed above. No forbidden transition at \( \Delta m_s = \pm 2 \) was observed at half field (~1,700 G). This implies the absence of any strong magnetic exchange or magnetically coupled dimeric species,\(^{32}\) in strong support of the magnetic susceptibility and magnetization results.

### 4.4 Conclusion

We present here the reaction of the novel \( \text{Ti}_2 \)-containing, sandwich-type 18-tungsto-2-arsenate(III) \(((\text{Ti}^{IV}O)_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2)^{14-} \) (\( \text{Ti}_2 \)) and a series of main group or 3d transition metal electrophiles, which resulted in five mono-nuclear-embedded derivatives, namely, the \([\text{C}_6\text{H}_5\text{Sb}^{III}(\text{Ti}^{IV}O)_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2]^{12-} \) (\( \text{SbTi}_2 \)) and \([\text{M(H}_2\text{O})(\text{Ti}^{IV}O)_2(\alpha-\text{As}^{III}\text{W}_9\text{O}_{33})_2]^{12-} \) (\( \text{M} = \text{Co (CoTi}_2), \text{Ni (NiTi}_2), \text{Cu (CuTi}_2), \text{Zn (ZnTi}_2) \)). Both single-crystal XRD and \(^{183}\text{W NMR spectroscopy reveal their isostructural Hervé-type dimers derived from that of } \text{Ti}_2 \text{ precursor, with the replacement of the labile Na}^+ \text{ in the third addenda site of the belt position by the penta-coordinate metal ion guests. The chemically reversible reduction waves of } \text{CoTi}_2, \text{NiTi}_2 \text{ and } \text{ZnTi}_2 \text{ exhibit distinct characteristics allowing for qualitative classification according to the relative basicity of their reduced forms: } \text{CoTi}_2 > \text{ZnTi}_2 > \text{NiTi}_2. \text{ All the POMs are active towards the electrocatalysis of the nitrate reduction, however the catalytic efficiencies (CATs) depend strongly on the nature of the substituent metal ion. In particular, the CAT values of } \text{NiTi}_2 \text{ are up to 5.6 times higher than those of } \text{Ti}_2 \text{ obtained under the same conditions. To our knowledge, } \text{NiTi}_2 \text{ represents the first example of a very efficient Ni}^{II}-\text{monosubstituted POM electrocatalyst for nitrate reduction. The compound } \text{CuTi}_2 \text{ is the most effective for this reaction but as pre-electro catalyst, importantly its CAT values compare favourably with those reported for different Cu}^{II}-\text{substituted POMs. Variable temperature magnetic susceptibility and variable field magnetization characterization on the } \text{NaCs-CoTi}_2, \text{NaCs-NiTi}_2, \text{NaCs-CuTi}_2 \text{ indicate their antiferromagnetic interactions with the nearest neighbours for these paramagnetic samples. The resolved hyperfine structure of the } \text{NaCs-CuTi}_2 \text{ obtained from the multifrequency EPR measurements enabled us to assign the ground state to mainly the Cu } d_{x^2-y^2} \text{ orbital. This work verifies our proposed functionalization of the } \text{Ti}_2 \text{ monolacunary POM host} \)
platform by effective incorporation of various main group and transition metal ion guests, shedding light on greater development of the function-directed, rational POM synthetic chemistry in the future. More exploratory works are currently underway.

4.5 Experimental section

4.5.1 General methods and reagents

The reagents were used as purchased without further purification. The Na$_{14}$[(Ti$^{IV}$O)$_2$(α-As$^{III}$W$_9$O$_{33}$)$_2$]-50H$_2$O·CH$_3$COONa (Na-Ti$_2$) $^{[13]}$ precursor and C$_6$H$_5$SbCl$_2$ $^{[33]}$ were prepared according to the published procedures. FTIR spectra (KBr pellets) were recorded on a Nicolet-Avatar 370 spectrometer. The UV-vis absorption spectra were recorded on a Varian Cary 100 Bio UV-vis spectrophotometer. Thermogravimetric analyses were carried out on a TA Instruments Q 600 device at a heating rate of 5 °C/min under a nitrogen atmosphere. The NMR spectra of the compounds dissolved in D$_2$O/H$_2$O or CH$_3$COOLi/CH$_3$COOH (1 M, pH 6) + D$_2$O were recorded on a JEOL ECX 400 instrument at room temperature, using 5 mm tubes for $^1$H and $^{13}$C NMR and 10 mm tubes for $^{183}$W NMR. The respective resonance frequencies were 400.53 MHz ($^1$H), 100.71 MHz ($^{13}$C) and 16.69 MHz ($^{183}$W). The chemical shifts are reported with respect to the references Si(CH$_3$)$_4$ ($^1$H and $^{13}$C), and 1 M Na$_2$WO$_4$(aq) ($^{183}$W). Elemental analyses were performed at CNRS, Service Central d’Analyze, Solaize, France.

4.5.2 Synthesis

Cs$_{2.5}$Na$_{9.5}$[C$_6$H$_5$Sb$^{III}$](Ti$^{IV}$O)$_2$(α-As$^{III}$W$_9$O$_{33}$)$_2$]-40H$_2$O (NaCs-SbTi$_2$)

Na$_{14}$[(Ti$^{IV}$O)$_2$(α-As$^{III}$W$_9$O$_{33}$)$_2$]-50H$_2$O·CH$_3$COONa (Na-Ti$_2$, 0.500 g, 0.084 mmol) was dissolved in 20 mL of 1 M aqueous sodium acetate medium at pH 6, whereas 0.027 g (0.100 mmol) of C$_6$H$_5$SbCl$_2$ was dissolved in a separate beaker in a minimum amount of ethanol (around 2 mL). The solution of C$_6$H$_5$SbCl$_2$ was added dropwise to the POM precursor solution under vigorous stirring. The resulting solution was stirred for 30 min, and then filtered, followed by addition of around 0.1 mL of 1 M CsCl solution. The final solution was cooled to 4 °C in a fridge. After 2 days an orange crystalline product was collected with a yield of 420 mg. This raw product was recrystallized by dissolution in 10 mL 1 M aqueous sodium acetate medium at pH 6, followed by addition of 0.12 mL of 1 M CsCl solution. The solution was kept in a fridge at 4 °C. Rod-like orange crystals of NaCs-SbTi$_2$ started to appear after several
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hours and were collected after 1 day. Yield: 0.32 g, 62% based on the Na-Ti$_2$
precursor. FTIR of NaCs-SbTi$_2$: 1618 (m), 1475 (w), 1423 (w), 1384 (w), 1064 (w), 945 (m), 871 (m), 756 (s), 726 (s), 507 (sh), 469 (w) 439 (sh) cm$^{-1}$. Anal. Calcd (Found) for NaCs-SbTi$_2$: Cs 5.52 (5.53), Na 3.63 (3.30), Sb 2.02 (1.91), Ti 1.59 (1.60), As 2.49 (2.58), W 54.94 (54.88), C 1.20 (1.05).

Cs$_{0.5}$Na$_{11.5}$[Co(H$_2$O)(Ti$_{IV}$O)$_2$(α-As$_{III}$W$_9$O$_{33}$)$_2$]-32H$_2$O·0.5CH$_3$COONa (NaCs-CoTi$_2$)

Co(CH$_3$COO)$_2$·4H$_2$O (0.049 g, 0.2 mmol) and Na$_{14}$[(Ti$_{IV}$O)$_2$(α-As$_{III}$W$_9$O$_{33}$)$_2$]·50H$_2$O·CH$_3$COONa (Na-Ti$_2$) (1.0 g, 0.17 mmol) were sequentially dissolved in 20 mL of 1 M aqueous sodium acetate medium at pH 6. The solution was kept at 80 °C for 1 h with constant stirring, followed by the addition of 80 μL 1 M CsCl(aq). After cooling down to room temperature, the clear solution was allowed to evaporate in an open beaker for two days (the volume decreased to ~15 mL) and then was cooled to 4 °C in a refrigerator. Dark green plate-like crystals of NaCs-CoTi$_2$ started to form overnight and were collected after two days. Yield: 0.54 g, 56% based on the Na-Ti$_2$ precursor. FTIR of NaCs-CoTi$_2$: 1635 (m), 1619 (m), 1560 (w), 1414 (w), 950 (m), 902 (m), 882 (m), 753 (s), 730 (s), 658 (w), 633 (w), 475 (w), 448 (w) cm$^{-1}$. Anal. Calcd (Found) for NaCs-CoTi$_2$: Cs 1.17 (1.25), Na 4.87 (4.96), Co 1.04 (1.06), Ti 1.69 (1.70), As 2.64 (2.73), W 58.38 (57.74), C 0.21 (0.23).

Cs$_{0.5}$Na$_{11.5}$[Ni(H$_2$O)(Ti$_{IV}$O)$_2$(As$_{III}$W$_9$O$_{33}$)$_2$]-35H$_2$O·0.5CH$_3$COONa (NaCs-NiTi$_2$)

The synthetic procedure for NaCs-NiTi$_2$ is analogues to that for NaCs-CoTi$_2$, but the Ni(CH$_3$COO)$_2$·4H$_2$O (0.05 g, 0.2 mmol) was used as transition metal salt instead of Co(CH$_3$COO)$_2$·4H$_2$O. Golden plate-like crystals of NaCs-NiTi$_2$ were collected. Yield: 0.48 g, 49% based on the Na-Ti$_2$ precursor. FTIR of NaCs-NiTi$_2$: 1636 (m), 1619 (m), 1560 (w), 1416 (w), 950 (m), 907 (m), 882 (m), 753 (s), 732 (s), 658 (w), 637 (w), 477 (w), 448 (w) cm$^{-1}$. Anal. Calcd (Found) for NaCs-NiTi$_2$: Cs 1.16 (1.47), Na 4.82 (4.91), Ni 1.03 (1.03), Ti 1.67 (1.70), As 2.62 (2.69), W 57.83 (57.68), C 0.21 (0.17).

Cs$_{0.5}$Na$_{11.5}$[Cu(H$_2$O)(Ti$_{IV}$O)$_2$(As$_{III}$W$_9$O$_{33}$)$_2$]-40H$_2$O·0.5CH$_3$COONa (NaCs-CuTi$_2$)

The synthetic procedure for NaCs-CuTi$_2$ is analogues to that for NaCs-CoTi$_2$, but the Cu(CH$_3$COO)$_2$·H$_2$O (0.04 g, 0.2 mmol) was used as transition metal salt instead of Co(CH$_3$COO)$_2$·4H$_2$O. Pale green plate-like crystals of NaCs-CuTi$_2$ were collected. Yield: 0.44 g, 44% based on the Na-Ti$_2$ precursor. FTIR of NaCs-CuTi$_2$: 1637 (m), 1619 (m), 1560 (w), 1417 (w), 952 (m), 910 (m), 886 (m), 756 (s), 732 (s), 654 (w), 636 (w), 475 (w), 450 (w) cm$^{-1}$. Anal. Calcd (Found) for NaCs-CuTi$_2$: Cs 1.14 (1.20),
Na 4.74 (4.96), Cu 1.09 (1.10), Ti 1.65 (1.67), As 2.58 (2.66), W 56.89 (56.53), C 0.21 (0.22).

\[ \text{Cs}_0.5\text{Na}_{11.5} [\text{Zn(H}_2\text{O)}(\text{Ti}^{IV}\text{O})_2(\text{As}^{III}\text{W}_9\text{O}_{33})_2] \cdot 47\text{H}_2\text{O} \cdot 0.5\text{CH}_3\text{COONa} \] (NaCs-ZnTi2)

The synthetic procedure for NaCs-ZnTi2 is analogous to that for NaCs-CoTi2, but the Zn(CH3COO)2·2H2O (0.044 g, 0.2 mmol) was used as transition metal salt instead of Co(CH3COO)2·4H2O. Colourless plate-like crystals of NaCs-ZnTi2 were collected. Yield: 0.77 g, 76% based on the Na-Ti2 precursor. FTIR of NaCs-ZnTi2: 1637 (m), 1619 (m), 1560 (w), 1416 (w), 948 (m), 905 (m), 881 (m), 752 (s), 733 (s), 657 (w), 640 (w), 474 (w), 449 (w) cm\(^{-1}\). Anal. Calcd (Found) for NaCs-ZnTi2: Cs 1.12 (0.90), Na 4.64 (5.02), Zn 1.10 (1.18), Ti 1.61 (1.65), As 2.52 (2.61), W 55.67 (55.54), C 0.20 (0.10).

4.5.3 Crystallography

Colorless single crystals of NaCs-SbTi2 and NaCs-MTi2 were mounted on a Hampton cryo-loop for indexing and intensity data collection at 100 K on a Bruker D8 APEX II CCD using Mo-Kα radiation (\(\lambda = 0.71073 \text{ Å}\)). Data integration was performed using SAINT. Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program. Direct methods (SHELXS) successfully located the tungsten atoms, and successive Fourier syntheses (SHELXL) revealed the remaining atoms. Refinements were full matrix least-squares against \(|F|^2\) using all data. The heavy atoms and non-disordered Na\(^+\) ions were refined anisotropically, whereas all other atoms were refined isotropically. The relevant crystallographic data and structure refinement details NaCs-SbTi2 and NaCs-MTi2 can be found in Tables 4-1 and 4-3.

4.5.4 Electrochemistry

All reagents and chemicals were of high-purity grade and were used as purchased without further purification. The solutions were thoroughly deoxygenated for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The working electrode was a polished glassy carbon (0.3 cm\(^2\)) or well cleaned ITO (0.3 cm\(^2\)). The electrochemical set-up was CHI workstation by a PC with the CHI660 software. Potentials are quoted against a saturated calomel electrode (SCE), in a compartment separated from the test solution by a fine porosity glass frit. The counter electrode was a platinum plate with large surface area in a compartment separated from the test solution by a medium porosity glass frit. The composition and
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pH of the supporting electrolytes were 1 M LiCH$_3$COO/CH$_3$COOH solution (pH 6) or 0.4 M NaH$_2$PO$_4$/NaOH (pH 6 and 7). All experiments were performed at room temperature.

4.5.5 Magnetic susceptibility measurements

Magnetization measurements were conducted on polycrystalline CsNa-CoTi$_2$, CsNa-NiTi$_2$, and CsNa-CuTi$_2$ using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Zero field cooled (ZFC) and field cooled (FC) measurements were performed under a constant field of 100 Oe over the temperature range of 1.8-300 K. Isothermal field dependent magnetization measurements were conducted with magnetic field varying between 0 to 7 T at 1.8 K. Sample holders were measured separately under identical conditions, and their magnetic responses were subtracted directly from the raw data. The intrinsic diamagnetic response of the sample was calculated using Pascal’s constants and subtracted from the measured susceptibilities.

4.5.6 EPR measurements

EPR measurements were made at X-band (9.8 GHz), Q-band (35 GHz) using a Bruker Elexsys-500 spectrometer at room temperature. The magnetic field was calibrated using a DPPH standard ($g = 2.0036$), and a digital microwave frequency counter. In all experiments, the modulation amplitudes and microwave power were adjusted for optimal signal intensity and resolution. High frequency (240 GHz) EPR measurements 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.$^{[37]}$

Spectral simulations were performed using the computer program “Easy Spin”.$^{[31]}$

4.6 References

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[34] SAINT, Bruker AXS Inc.: Madison, WI, **2007**.


Chapter 5 Cage-like Ln$_{12}$-Containing 60-Tungstogermanates

This chapter is based on

“Ln$_{12}$-Containing 60-Tungstogermanates: Synthesis, Structure, Luminescence, and Magnetic Studies”


All experiments regarding the preparation, crystallization, X-ray diffraction and other characterizations of all the polyanions were performed by Kai-Yao Wang. The structural refinement was executed by Prof. Dr. Bassem. S. Bassil. The ESI-mass spectroscopic measurement and analysis were supplied by Dr. Zhengguo Lin, Linyuan Fan and Prof. Dr. Jie Cao. The photoluminescence studies were executed by Kai-Yao Wang, Dr. Stef Vanhaecht and Tatjana N. Parac-Vogt. The magnetic properties of the polyanions were measured by Dr. Cristina Sáenz de Pipaón and Prof. Dr. José Ramón Galán-Mascarós. The text was written by Kai-Yao Wang, with valuable contribution and corrections by Prof. Dr. Ulrich Kortz.
5.1 Abstract

A new class of hexameric Ln\(_{12}\)-containing 60-tungstogermanates, 
\[\text{[Na(H}_2\text{O)}_6\subset\text{Eu}_{12}(\text{OH})_{18}\text{Ge}_2(\text{GeW}_{10}\text{O}_{38})_6]}^{39-}\text{ (Eu}_{12}\), 
\[\text{[Na(H}_2\text{O)}_6\subset\text{Gd}_{12}(\text{OH})_{6}\text{Ge}(\text{GeW}_{10}\text{O}_{38})_6]}^{37-}\text{ (Gd}_{12}\), and 
\[\text{[(H}_2\text{O)}_6\subset\text{Dy}_{12}(\text{H}_2\text{O})_{24}(\text{GeW}_{10}\text{O}_{38})_6]}^{36-}\text{ (Dy}_{12}\), comprising six di-Ln-embedded \{\beta(4,11)-\text{GeW}_{10}\} subunits has been prepared by reaction of \([\alpha-\text{GeW}_{9}\text{O}_{34}]^{10-}\) and Ln\(^{III}\) ions in weakly acidic (pH 5) aqueous medium. Depending on the size of the Ln\(^{III}\) ion, the assemblies feature selective capture of two (for \text{Eu}_{12}\), one (for \text{Gd}_{12}\) or zero (for \text{Dy}_{12}\) extra Ge\(^{IV}\) atoms. The selective incorporation of a cationic sodium hexa-aqua complex \([\text{Na(H}_2\text{O)}_6]^+\) was observed for \text{Eu}_{12}\ and \text{Gd}_{12}\, whereas \text{Dy}_{12}\ incorporates a neutral, distorted-octahedral (H\(_2\)O\(_6\)) cluster. The three compounds were characterized by single crystal XRD, ESI-mass spectrometry, photoluminescence, and magnetic studies. \text{Dy}_{12}\ was shown to be a single molecule magnet (SMM).

5.2 Introduction

Polyoxometalates (POMs) are a class of metal-oxygen clusters that comprise early transition metal ions in high oxidation states, and display a wide range of well-defined sizes and shapes.\[^{[1]}\] Lacunary POMs can incorporate additional metallic centers from \(p\)-, \(d\)-, and \(f\)-blocks by virtue of their exposed oxo ligands, resulting in products with large structural and compositional diversity.\[^{[2]}\] Moreover, such incorporation allows POMs to acquire versatile potential applications in fields such as green catalysis, medicine, magnetism, materials science and molecule recognition.\[^{[3]}\]

Lanthanide-containing polyoxotungstates constitute a large POM subclass, owing to their highly diverse structural and chemical nature.\[^{[4]}\] As a result of their higher oxophilicity and coordination number compared to 3d metals, 4f ions display powerful ability to insert into the vacant sites of lacunary POM species as well as linking function, leading to dramatic increases in the number and sizes of resulting products. Since the isolation of the macromolecule \([\text{As}_{12}\text{Ce}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]}^{76-}\,[5]\) the discovery of additional large and lanthanide-based polyoxotungstates allowed for a deeper structural insight into the self-assembly of nanoscale aggregates.\[^{[6]}\] On the other hand, the coordination chemistry of lanthanide(III) ions has consistently been of significant research interest in part because of the large range of coordination numbers and geometries, which mainly arise from the decrease in ionic radius from left to right.
across this period. However, compared to the extended study for lanthanide complexes, research work on ionic size-structure correlation for Ln-POM systems is still in a nascent stage and, ultimately, on a shallow level.

In previous work, we discovered that the reaction of tri-lacunary polyanion \([\alpha-\text{GeW}_9\text{O}_{34}]^{10-}\) and Ce\textsuperscript{III} ions resulted in the very large Ce\textsubscript{20}-containing 100-tungsto-10-germanate \([\text{Ce}_{20}\text{Ge}_{10}\text{W}_{100}\text{O}_{376}\text{(OH)}_4\text{(H}_2\text{O})_{30}]^{56-}\)\textsuperscript{[6a]} This exploration not only reemphasized the feasible synthetic strategy for constructing gigantic assemblies via Ln\textsuperscript{III} linkers, but importantly, opened a door to investigate the essential size-effect of different Ln\textsuperscript{III} ions on this new assembly system. In the work presented here, we explored further the interaction between lanthanide ions such as Eu\textsuperscript{III}, Gd\textsuperscript{III}, Tb\textsuperscript{III}, and Dy\textsuperscript{III} and \([\alpha-\text{XW}_9\text{O}_{34}]^{10-}\) (X = Si, Ge), leading to a novel family of Ln\textsubscript{12}-Containing 60-tungstogermanates with slightly different structural features depending on the size of the incorporated Ln\textsuperscript{III} ion.

5.3 Results and Discussion

5.3.1 Synthesis

Reaction of \([\alpha-\text{GeW}_9\text{O}_{34}]^{10-}\) and Ln\textsuperscript{III} ions in weakly acidic (pH 5) aqueous medium results in three new Ln\textsubscript{12}-containing 60-tungstogermanates,
[Na(H\(_2\)O\(_6\))\(_6\)⊂Eu\(_{12}\)(OH)\(_{12}\)(H\(_2\)O)\(_{18}\)Ge\(_2\)(GeW\(_{10}\)O\(_{38}\))\(_6\)]\(^{39-}\) (\(\text{Eu}_{12}\)),

[Na(H\(_2\)O\(_6\))\(_6\)⊂Gd\(_{12}\)(OH)\(_6\)(H\(_2\)O)\(_{24}\)Ge(GeW\(_{10}\)O\(_{38}\))\(_6\)]\(^{37-}\) (\(\text{Gd}_{12}\)),

and

[(H\(_2\)O)\(_6\)⊂Dy\(_{12}\)(H\(_2\)O)\(_{24}\)Ge(GeW\(_{10}\)O\(_{38}\))\(_6\)]\(^{36-}\) (\(\text{Dy}_{12}\)), which were all isolated as sodium salts, namely,

Na\(_{39}\)[Na(H\(_2\)O\(_6\))\(_6\)⊂Eu\(_{12}\)(OH)\(_{12}\)(H\(_2\)O)\(_{18}\)Ge\(_2\)(GeW\(_{10}\)O\(_{38}\))\(_6\)]·15\(\text{H}_{2}\)O (\(\text{Na-Eu}_{12}\)),

Na\(_{37}\)[Na(H\(_2\)O\(_6\))\(_6\)⊂Gd\(_{12}\)(OH)\(_6\)(H\(_2\)O)\(_{24}\)Ge(GeW\(_{10}\)O\(_{38}\))\(_6\)]·12\(\text{H}_{2}\)O (\(\text{Na-Gd}_{12}\)) and

Na\(_{36}\)[(H\(_2\)O)\(_6\)⊂Dy\(_{12}\)(H\(_2\)O)\(_{24}\)Ge(GeW\(_{10}\)O\(_{38}\))\(_6\)]·12\(\text{H}_{2}\)O (\(\text{Na-Dy}_{12}\)).

**Figure 5-2.** Photos of crystalline products of (a) \(\text{Na-Eu}_{12}\) (\(\text{Na-Gd}_{12}\) is similar), (b) \(\text{Na-Tb}_{12}\), and (c) \(\text{Na-Dy}_{12}\).

Three crucial synthetic parameters needed to be finely tuned for the isolation of pure crystalline products with highest yield for \(\text{Eu}_{12}\), \(\text{Gd}_{12}\) and \(\text{Dy}_{12}\). The reactants ratio was optimal at 1:1(Ln\(^{III}\):[\(\alpha\)-GeW\(_9\)O\(_{34}\)])\(^{10-}\)), different than the suggest 2:1 stoichiometric ratio. This is mostly due to the rearrangement of the \{\(\alpha\)-GeW\(_9\)\} units to \{\(\beta\)-GeW\(_{10}\)\}, thus needing tungsten centers coming from the partial decomposition of other units. Addition of tungstate salts during synthesis did not provide a successful synthesis. This observation underlines the ‘self-assembly’ mechanism most POM species undergo in solution, which was also noticed for [Ce\(_{20}\)Ge\(_{10}\)W\(_{100}\)O\(_{376}\)(OH)\(_4\)(H\(_2\)O)\(_{30}\)]\(^{56-}\).\(^{[6a]}\) A second important parameter is the initial pH, which needed to be adjusted at 5.0. A higher pH led to precipitation and no product, and a lower pH led to the reported [Ln(GeW\(_{11}\)O\(_{39}\))]\(^{13-}\).\(^{[9]}\) Finally, the presence of sodium in solution (by addition of NaCl) was needed, with a moderate ionic strength of 0.25 M. A higher salt concentration led to polycrystalline products, and a lower concentration (or absence) resulted in low or no yield. As such, all polyanions could be isolated as their hydrated sodium \(\text{Na-Eu}_{12}\), \(\text{Na-Gd}_{12}\), and \(\text{Na-Dy}_{12}\). The FTIR spectra of the three salts are virtually identical and reflect their isostructural relation (Figure 5-1). What is notable besides these is a mixture product (abbreviated as \(\text{Na-Tb}_{12}\)) of the reaction by utilizing terbium(III) as Ln source, see the Supporting
Information for detail. Two crystalline phases, isomorphic to Gd₁₂ (minor phase) and Dy₁₂ (major phase), respectively, was observed but extremely difficult to separate (Figure 5-2). Such coexistence is expected owing to the intermediate size of Tb³⁺ that lies between Gd³⁺ and Dy³⁺. Systematic FTIR, XRD, ESI-mass spectroscopy, TGA and elemental analysis were performed on the mixture product.

In addition, we also carried out experimental work on the reactivity of Ln³⁺ ions and the [α-SiW₉O₃₄]₁⁰⁻ precursor under similar conditions in order to obtain the silicon analogues of the Ln₁₂ polyanions. Unfortunately, these attempts were unsuccessful, possibly due to the size difference between Si and Ge in the 4⁺ oxidation state.

5.3.2 Structure description

X-ray diffraction analysis revealed that Eu₁₂ and Gd₁₂ crystallized in the monoclinic space group P2₁/n whereas Dy₁₂ crystallized in the triclinic space group P̅₁ (Tables 5-1). All three polyanions feature cage-like hexameric assemblies.

The polyanion Eu₁₂ consists of six {Eu₂(β(4,11)-GeW₁₀)} subunits, each comprising a dilacunary, β₂⁻³-Keggin fragment with the two Eu³⁺ ions located in the vacant sites in positions 4 and 11 (according to the IUPAC rules), rendering these units chiral (Figure 5-3a). Three such {Eu₂GeW₁₀} units of the same chirality form the cyclic assembly {Ge(Eu₂GeW₁₀)₃} (Eu₆) capped by a distorted-octahedral Ge(OH)₆ unit, and two such trimeric assemblies of opposite chirality are connected to each other in a staggered face-on fashion, leading to a centrosymmetric cage. Interestingly, this cage encapsulates a central cationic [Na(H₂O)₆]⁺ guest complex, resulting in the overall assembly [Na(H₂O)₆⊂Eu₁₂(OH)₁₂(H₂O)₁₈Ge₂(GeW₁₀O₃₈)₆]₃⁹⁻ (Eu₁₂), see Figure 5-3b. The novel polyanion Eu₁₂ has idealized S₆ symmetry, with the S₅ axis passing through the two capping Ge⁴⁺ atoms.

Several examples of polyanions comprising dilacunary β-Keggin units are known.⁶ᵃ,d,g,¹¹ Interestingly, the Ce₂₀-containing 100-tungsto-10-germanate(IV) contains the same dilacunary {β(4,11)-GeW₁₀} Keggin fragments as Eu₁₂.⁶ᵃ Reinoso et al. showed that {GeW₁₀} fragments can also be formed in situ by reaction of Na₂WO₄, GeO₂, and lanthanide sources in acetate buffer.⁶ᵈ,g,¹¹j
Table 5-1. Crystal data for Na-Eu$_{12}$, Na-Gd$_{12}$, and Na-Dy$_{12}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Na-Eu$_{12}$</th>
<th>Na-Gd$_{12}$</th>
<th>Na-Dy$_{12}$</th>
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<tr>
<td>Empirical formula</td>
<td>H$<em>{378}$Eu$</em>{12}$Ge$<em>8$Na$</em>{40}$</td>
<td>H$<em>{324}$Gd$</em>{12}$Ge$<em>7$Na$</em>{38}$</td>
<td>H$<em>{304}$Dy$</em>{12}$Ge$<em>6$Na$</em>{36}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>21503.8</td>
<td>20914.3</td>
<td>20630.6</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/n$</td>
<td>$P2_1/n$</td>
<td>$P\bar{1}$</td>
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<tr>
<td>T/K</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
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<td>$\lambda$ / Å</td>
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<td>0.71073</td>
<td>0.71073</td>
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<td>$a$ / Å</td>
<td>21.163(2)</td>
<td>21.311(3)</td>
<td>21.9637(11)</td>
</tr>
<tr>
<td>$b$ / Å</td>
<td>22.8310(15)</td>
<td>22.778(3)</td>
<td>22.3351(10)</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>38.001(3)</td>
<td>38.014(4)</td>
<td>22.6340(11)</td>
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<td>$\alpha$ /º</td>
<td>90</td>
<td>90</td>
<td>62.131(2)</td>
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<td>$\beta$ /º</td>
<td>94.411(6)</td>
<td>94.584(5)</td>
<td>64.141(3)</td>
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<td>$\gamma$ /º</td>
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<td>90</td>
<td>78.084(2)</td>
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<td>$V$ / Å$^3$</td>
<td>18306(3)</td>
<td>18394(4)</td>
<td>8832.7(8)</td>
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<td>Z</td>
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<td>1</td>
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<td>$D_r$ / Mg·m$^{-3}$</td>
<td>3.901</td>
<td>3.776</td>
<td>3.879</td>
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<td>$\mu$ / mm$^{-1}$</td>
<td>21.615</td>
<td>21.536</td>
<td>22.618</td>
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<td>$F(000)$</td>
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<td>18636</td>
<td>9164</td>
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<td>Measured refls.</td>
<td>441921</td>
<td>524011</td>
<td>203362</td>
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<td>Independent refls.</td>
<td>30068</td>
<td>38788</td>
<td>25090</td>
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<tr>
<td>$R_{int}$</td>
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<td>0.1309</td>
<td>0.1701</td>
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<tr>
<td>No. of parameters</td>
<td>1125</td>
<td>1070</td>
<td>1182</td>
</tr>
<tr>
<td>GOF</td>
<td>1.005</td>
<td>1.003</td>
<td>1.009</td>
</tr>
<tr>
<td>$R_1$, $wR_2$ [I $&gt;$ 2$\sigma$(I)]</td>
<td>0.0619, 0.1465</td>
<td>0.0701, 0.1670</td>
<td>0.0572, 0.1292</td>
</tr>
<tr>
<td>$R_1$, $wR_2$ (all data)</td>
<td>0.1084, 0.1741</td>
<td>0.1050, 0.1931</td>
<td>0.1113, 0.1579</td>
</tr>
</tbody>
</table>

[a] $R_1 = \sum ||F_o|-|F_c||/\sum |F_o|$, $wR_2 = (\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2]^{1/2}$

In Eu$_{12}$, the Eu$^{III}$ ions located in positions 4 (Eu4, belt) and 11 (Eu11, rotated triad) are hepta- and octa-coordinate, respectively. The coordination geometry of the former is capped trigonal-prismatic, and square-antiprismatic for the latter. The coordination sphere of Eu4 comprises four Eu–O–W bridges to the Keggin lacunary site and a Eu–O–W' bridge to another {Eu$_2$(β(4,11)-GeW$_{10}$)} unit of different chirality.
as well as two terminal aqua ligands. On the other hand, Eu11 is coordinated to the lacunary site of the Keggin unit by four Eu–O–W bridges, and linked via one more Eu–O–W’ bridge to another \{\text{Eu}_2(\beta(4,11)-\text{GeW}_{10})\} unit of the same chirality. In addition, each Eu11 carries a terminal aqua ligand, and is bound via two hydroxo-bridges to the capping Ge\text{IV} ion. We presume that the extra Ge\text{IV} originates from the transformation/isomerization of \{\alpha-\text{GeW}_9\} to \{\beta-\text{GeW}_{10}\}. Our attempts to enhance the yield of \textbf{Na-Eu}_{12} by addition of GeO\textsubscript{2} as Ge\text{IV} source during the reaction

**Figure 5.3.** (a) Scheme showing the \{\alpha-\text{GeW}_9\} POM precursor and the two enantiomers of the \{\text{Eu}_2(\beta(4,11)-\text{GeW}_{10})\} subunits. (b) Combined polyhedral/ball-and-stick representations of the trimeric \textbf{Ln}_6 half-units and the hexameric \textbf{Ln}_{12} assemblies (Ln = Eu and Dy). Colour code: WO\textsubscript{6} octahedra (red and rose), GeO\textsubscript{4} tetrahedra (yellow), and for the balls: Eu (turquoise), Dy (pink), O (red). The [Na(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{+} and (H\textsubscript{2}O)\textsubscript{6} guest clusters are not shown for clarity.
were not successful. Protonated oxygens in Eu\(_{12}\) were identified by bond valence sum (BVS) calculations, see Table 5-3.\(^{[12]}\) The presence of 39 sodium counter cations and 159 crystal waters in the solid state was confirmed by elemental and thermogravimetric analysis (TGA), resulting in the overall formula unit Na\(_{39}\)[Na(H\(_2\)O)\(_6\)⊂Eu\(_{12}\)(OH)\(_{12}\)(H\(_2\)O)\(_{18}\)Ge\(_2\)(GeW\(_{10}\)O\(_{38}\))\(_6\)]·159H\(_2\)O (Na-Eu\(_{12}\)), see Experimental Section.

**Figure 5-4.** Representations of the cage-like inner sphere (left), the encapsulated [Na(H\(_2\)O)\(_6\)]\(^+\) complex or (H\(_2\)O)\(_6\) cluster (middle), and the maximum and minimum distances between each pair of centrosymmetrically related Ln4 or Ln11 (right) in the (a) Eu\(_{12}\) and (b) Dy\(_{12}\) polyanions. (c) Representation of the Na\(^+\) encapsulating selectivity coupled with the assembly of Ln\(_{12}\)-containing compounds from Eu to Dy. Colour code: Eu (turquoise), Dy (pink), W (black), Na (blue), O (red).

The [Na(H\(_2\)O)\(_6\)]\(^+\) guest complex encapsulated in the central cavity of the Eu\(_{12}\) host cage exhibits an almost regular octahedral geometry (Figure 5-4a, left and middle). The orientation of [Na(H\(_2\)O)\(_6\)]\(^+\) is enforced by hydrogen bonds between the aqua ligands and oxygens of the host cage (Figure 5-5 and Table 5-4). Such host-guest relationship has been seen in other cage-like POM structures.\(^{[13]}\)

The gadolinium analogue Gd\(_{12}\) is isostructural with Eu\(_{12}\) and comprises the same
Figure 5-5. (a) Front-view (left) and side-view (right) of the ball-and-stick representations of possible hydrogen bonds between the encapsulated [Na(H₂O)₆]⁺ and the Eu₁₂ host cage. (b) Front-view (left) and side-view (right) of the ball-and-stick representations of possible hydrogen bonds between the encapsulated (H₂O)₆ cluster and the Dy₁₂ host cage. The dashed lines represent the O···O interactions by hydrogen bonding between water molecules of the [Na(H₂O)₆]⁺/(H₂O)₆ clusters and bridging O/OH groups (pink dashed lines) or terminal H₂O ligands (green dashed lines).

Figure 5-6. (a) Front view and (b) side view of the combined polyhedral/ball-and-stick representations of Eu₁₂, Gd₁₂, and Dy₁₂. (c) Side view highlighting the extra two, one, and zero Ge⁴⁺ atoms in Eu₁₂, Gd₁₂, and Dy₁₂, respectively.
regular hexameric conformation of its \{Gd_2(\beta(4,11)-GeW_{10})\} building blocks (Figure 5-6). However, only one capping Ge^{IV} atom was found by single crystal XRD, and confirmed in the bulk by elemental analysis (Experimental Section). The opposite site is hence occupied solely by terminal aqua ligands of the respective Gd11 ion (Figure 5-6). This reduces the overall charge of Gd_{12} to 37-, which is balanced in the solid state by 37 sodium ions, resulting in the formula unit Na_{37}[Na(H_2O)_6\subset Gd_{12}(OH)_6(H_2O)_{24}Ge(GeW_{10}O_{38})_6]\cdot129H_2O (Na-Gd_{12}). On the other hand, the cavity in the Gd_{12} host encapsulates the same discrete sodium hexa-aqua complex [Na(H_2O)_6]^+ as seen in Eu_{12}.

![Figure 5-7. Angles between the three Ln11 ions in the \{Ge_2Eu_{12}W_{12}\} inner sphere of Eu_{12} (left), and the \{Dy_{12}W_{12}\} inner sphere of Dy_{12} (right).]

Although the dysprosium analogue Dy_{12} displays the same hexameric topography as Eu_{12} and Gd_{12}, two main structural discrepancies could be observed. First, the Dy^{III} ion at position 11 (Dy11) in the \{Dy_2(\beta(4,11)-GeW_{10})\} building block is hepta-coordinate, in contrast to the octa-coordination for the respective Eu11 and Gd11. This lower coordination resulted in the absence of any extra Ge^{IV} center within the assembly (Figure 5-3b). The empty ‘site’ is therefore occupied by aqua ligands, reducing the overall charge of the polyanion to 36-, which is balanced in the solid state by sodium ions. The overall formula unit is hence Na_{36}[(H_2O)_6\subset Dy_{12}(H_2O)_{24}(GeW_{10}O_{38})_6]\cdot122H_2O (Na-Dy_{12}), as confirmed by TGA (Supporting Information) and elemental analysis (Experimental Section). The second main difference is the absence of the central sodium ion within the cavity of Dy_{12}, and single crystal XRD showed only six water molecules arranged in a distorted octahedral fashion (Figure 5-4b, left and middle). A closer look at the structural shift between Eu_{12} and Dy_{12} revealed a ‘distortion’ of the cavity. The maximum and
minimum distances between each pair of centrosymmetrically related Ln4 and Ln11 was much imbalanced for Dy$_{12}$ (13.0 × 11.2 Å) than for Eu$_{12}$ (12.2 × 11.7Å). In addition, the arrangement of three adjacent Dy11 atoms in Dy$_{12}$ distorts more from a regular triangle than in Eu$_{12}$ (Figure 5-7). This distortion is mirrored by the reduction of unit cell symmetry from monoclinic for Eu$_{12}$ and Gd$_{12}$ to triclinic for Dy$_{12}$. Such structural change is most probably due to the size difference between Eu$^{III}$ and Dy$^{III}$, which affects the coordination number and the overall arrangement of the hexameric assembly (see below).

<table>
<thead>
<tr>
<th>Polyanion</th>
<th>Eu$_{12}$</th>
<th>Gd$_{12}$</th>
<th>Dy$_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination number of Ln4</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Coordination number of Ln11</td>
<td>8</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Total number of the six-coordinated Ge$^{IV}$ in the Ln$_{12}$ polyanion</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Guest encapsulated in the host cage of Ln$_{12}$ polyanion</td>
<td>[Na(H$_2$O)$_6$]$^+$</td>
<td>[Na(H$_2$O)$_6$]$^+$</td>
<td>(H$_2$O)$_6$</td>
</tr>
</tbody>
</table>

**Figure 5-8.** Summary of the characteristic structural discrepancies of the Eu$_{12}$, Gd$_{12}$ and Dy$_{12}$.

**Figure 5-9.** Representation of the “Matryoshka doll” shell structure of the Eu$_{12}$.

Figure 5-8 summarizes the main structural similarities and differences between the three title polyanions, which can be concisely described as follows, (i) for all three polyanions, the Ln$^{III}$ ion at position 4 (Ln4) of the \{Ln$_2$($\beta$(4,11)-GeW$_{10}$)\} subunit is
hepta-coordinate, while the one at position 11 (Ln11) is octa-coordinate for Eu\(_{12}\) and Gd\(_{12}\), and hepta-coordinate for Dy\(_{12}\), (ii) the Eu\(_{12}\), Gd\(_{12}\), and Dy\(_{12}\) encapsulate respectively two, one and zero extra Ge\(^{IV}\) atoms, fully confirmed in the bulk by elemental analysis results, (iii) both Eu\(_{12}\) and Gd\(_{12}\) encapsulate one discrete [Na(H\(_2\)O)\(_6\)]\(^+\) complex, while the Dy\(_{12}\) encloses a (H\(_2\)O)\(_6\) cluster instead, (iv) the POM architecture of Dy\(_{12}\) displays a distortion compared with those of Eu\(_{12}\) and Gd\(_{12}\), which is reflected by the lower symmetry of its unit cell.

As reported for other series of Ln-containing POMs,\(^8\) a correlation between these discrepancies and the decreasing ionic radius can be rationalized. The average Ln-O bonds lengths are displayed in Table 5-5. As clearly shown, a significant reduction in the bond length is observed from Eu\(^{III}\) to Dy\(^{III}\), which has hence resulted in a reduction of the coordination number for Dy11.

It is possible to clarify the complex architecture of the polyanions from a further topological viewpoint involving platonic solids. As an example, Figure 5-9 shows for Eu\(_{12}\) the simplification of the six aqua ligands bonded to the central Na\(^+\) ion, the twelve Eu\(^{III}\) ions and six \{\(\beta(4,11)\)-GeW\(_{10}\)\} subunits as vertexes, respectively giving rise to three platonic solids arranged one inside another. The [Na(H\(_2\)O)\(_6\)]\(^+\) complex, an octahedron, is encircled by an idealized icosahedral arrangement of the twelve Eu\(^{III}\) ions. An additional, external octahedron resulting from the lacunary units engulfs both architectures. Altogether, this topological analysis of three solids inside each other gives Eu\(_{12}\) a Russian “Matryoshka” doll analogy.

**Table 5-2.** Unit cell parameters of the two crystalline phases of Na-Tb\(_{12}\).

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<th>Phase 2</th>
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<td>(\gamma^\circ)</td>
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Table 5.3. Bond valence sum (BVS) values for the metal ions and oxygen atoms bonded to the Ln
ions. The BVS calculations were performed on the KDist software (Version 3.75) distributed by K.

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<th>Atom</th>
<th>BVS value</th>
<th>Atom</th>
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**Na-Gd_{12}**

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<td>O(1D2)</td>
<td>-0.30</td>
<td>O(1D5)</td>
<td>-0.29</td>
<td></td>
</tr>
<tr>
<td>W(22)</td>
<td>6.32</td>
<td>O(24T)</td>
<td>-1.94</td>
<td>O bonded to Dy(6) (position 4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W(23)</td>
<td>6.36</td>
<td>O(2D2)</td>
<td>-0.33</td>
<td>O(16B)</td>
<td>-2.01</td>
<td></td>
</tr>
<tr>
<td>W(24)</td>
<td>6.15</td>
<td>O(5A)</td>
<td>-1.85</td>
<td>O(17A)</td>
<td>-1.79</td>
<td></td>
</tr>
<tr>
<td>W(25)</td>
<td>6.20</td>
<td>O(6B)</td>
<td>-1.86</td>
<td>O(18A)</td>
<td>-1.85</td>
<td></td>
</tr>
<tr>
<td>W(26)</td>
<td>6.25</td>
<td>O(9B)</td>
<td>-1.87</td>
<td>O(3D6)</td>
<td>-2.03</td>
<td></td>
</tr>
<tr>
<td>W(27)</td>
<td>6.17</td>
<td>O bonded to Dy(3) (position 4)</td>
<td>O(2D6)</td>
<td>-0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W(28)</td>
<td>6.41</td>
<td>O(1D3)</td>
<td>-0.22</td>
<td>O(1D6)</td>
<td>-0.25</td>
<td></td>
</tr>
<tr>
<td>W(29)</td>
<td>6.35</td>
<td>O(27T)</td>
<td>-1.96</td>
<td>O(9T)</td>
<td>-1.90</td>
<td></td>
</tr>
</tbody>
</table>
### Table 5-4. Selected hydrogen bond distances for Eu\(_{12}\) and Dy\(_{12}\).

<table>
<thead>
<tr>
<th>D–H⋯A</th>
<th>d(D⋯A)(Å)</th>
<th>D–H⋯A</th>
<th>d(D⋯A)(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(_{12})</td>
<td></td>
<td>Dy(_{12})</td>
<td></td>
</tr>
<tr>
<td>O(2W)–H⋯O(3E3) (b)(^a)</td>
<td>2.73(3)</td>
<td>O(5W)–H⋯O(1E4)#1</td>
<td>2.86(2)</td>
</tr>
<tr>
<td>O(2W)–H⋯O(1E6)#1</td>
<td>2.83(3)</td>
<td>O(25W)–H⋯O(24A) (b)</td>
<td>2.87(5)</td>
</tr>
<tr>
<td>O(2W)–H⋯O(1E4)</td>
<td>2.78(2)</td>
<td>O(25W)–H⋯O(1D1)</td>
<td>2.75(4)</td>
</tr>
<tr>
<td>O(3W)–H⋯O(2E5) (b)</td>
<td>2.77(3)</td>
<td>O(14W)–H⋯O(6B) (b)</td>
<td>2.87(3)</td>
</tr>
<tr>
<td>O(3W)–H⋯O(1E6)</td>
<td>2.75(3)</td>
<td>O(14W)–H⋯O(2D3)</td>
<td>2.73(5)</td>
</tr>
<tr>
<td>O(3W)–H⋯O(2E2)</td>
<td>2.89(3)</td>
<td>O(14W)–H⋯O(2D6)#1</td>
<td>2.86(3)</td>
</tr>
<tr>
<td>O(5W)–H⋯O(3E1) (b)</td>
<td>2.71(3)</td>
<td>O(16W)–H⋯O(2D6)</td>
<td>2.82(3)</td>
</tr>
<tr>
<td>O(5W)–H⋯O(2E2)#1</td>
<td>2.70(3)</td>
<td>O(16W)–H⋯O(1D1)</td>
<td>2.86(5)</td>
</tr>
</tbody>
</table>

\(^a\) “b” represent the acceptor atom is a bridging O atom or OH group, otherwise the O atom belongs to the terminal H\(_2\)O ligands bonded to Ln4. Symmetry transformations used to generate equivalent atoms: for Eu\(_{12}\): #1 -x, 2-y, -z; for Dy\(_{12}\): #1: 1-x, 1-y, -z.

### Table 5-5. Average Ln–O bond length in Eu\(_{12}\), Gd\(_{12}\), and Dy\(_{12}\) polyanions.

<table>
<thead>
<tr>
<th>bond lengths(^a)</th>
<th>Eu(_{12})</th>
<th>Gd(_{12})</th>
<th>Dy(_{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ln4–O(_l) /Å</td>
<td>2.320(18)</td>
<td>2.301(17)</td>
<td>2.275(19)</td>
</tr>
<tr>
<td>Ln4–O(_b) /Å</td>
<td>2.314(18)</td>
<td>2.317(17)</td>
<td>2.287(19)</td>
</tr>
<tr>
<td>Ln4–O(_w) /Å</td>
<td>2.560(18)</td>
<td>2.526(16)</td>
<td>2.505(19)</td>
</tr>
<tr>
<td>Ln11–O(_l) /Å</td>
<td>2.373(18)</td>
<td>2.348(17)</td>
<td>2.292(19)</td>
</tr>
<tr>
<td>Ln11–O(_b) /Å</td>
<td>2.543(19)</td>
<td>2.471(23)</td>
<td>2.343(18)</td>
</tr>
<tr>
<td>Ln11–O(_w) /Å</td>
<td>2.487(23)</td>
<td>2.457(30)</td>
<td>2.462(25)</td>
</tr>
<tr>
<td>Ln11–O(_Ge) /Å</td>
<td>2.491(20)</td>
<td>2.528(28)</td>
<td>\</td>
</tr>
</tbody>
</table>

\(^a\) O\(_l\): O atom that delimit each vacant site. O\(_w\): crystallographically well-defined O atom of the terminal aqua ligand. O\(_b\): bridging O atom from the neighboring subunit. O\(_Ge\): the O atom of the hydroxo bridge between the Ln11 and encapsulated Ge\(^{IV}\) atom.

#### 5.3.3 Thermogravimetric analysis

All the thermograms of Na-Eu\(_{12}\), Na-Gd\(_{12}\), Na-Tb\(_{12}\) and Na-Dy\(_{12}\) (Figures 5-10, 5-11, 5-12, 5-13) feature a one-step weight loss. This weight loss (13.2% for Na-Eu\(_{12}\), 12.3% for Na-Gd\(_{12}\), 11.1% for Na-Tb\(_{12}\) and 15.1% for Na-Dy\(_{12}\)) up to 500 °C can be attributed to the removal of crystal waters, together with some structural transformation/decomposition of the polyanions.
Figure 5-10. Thermogram of Na-Eu\textsubscript{12} from room temperature to 800 °C under N\textsubscript{2} atmosphere.

Figure 5-11. Thermogram of Na-Gd\textsubscript{12} from room temperature to 800 °C under N\textsubscript{2} atmosphere.
5.3.4 ESI mass spectrometry

Structural analysis of the Ln\textsubscript{12} polyanions revealed that only one Ln–O–W bridges connect each pair of adjacent \{Ln\textsubscript{2}GeW\textsubscript{10}\} subunits, which could lead to a plausible fragmentation of the hexameric assemblies upon dissolution. To explore the stability of these polyanions, the negative ion mode mass spectra on the Na-Eu\textsubscript{12}, Na-Gd\textsubscript{12} and Na-Dy\textsubscript{12} dissolved in water have been recorded by ESI-mass spectrometer. In all spectra observed from the freshly prepared solution samples (Figure 5-14), the isotopic pattern inspection together with the m/z spacing indicates a
series of $[\text{Na}_x\text{H}_y\text{LnGeW}_{10}\text{O}_{38}(\text{H}_2\text{O})_z]^{(9-x-y)^-}$ related species containing different numbers of sodium ions, protons and water molecules can be identified as four groups of signals that span from m/z 700 to 1500, see Table 5-6. For example, two most abundant groups of signals centred at m/z 935.98 and 942.97 in the spectrum of Eu$_{12}$ formally corresponds to the $-3$ charged species with the formulas of $[\text{NaH}_5\text{EuGeW}_{10}\text{O}_{38}(\text{H}_2\text{O})_6]^{-3}$ and $[\text{Na}_2\text{H}_4\text{EuGeW}_{10}\text{O}_{38}(\text{H}_2\text{O})_6]^{-3}$, respectively.

**Figure 5-14.** Negative ion ESI-mass spectra of (a) Na-Eu$_{12}$, (b) Na-Gd$_{12}$ and (c) Na-Dy$_{12}$ dissolved in water.

**Figure 5-15.** Negative ion ESI-mass spectrum of Na-Tb$_{12}$ crystals dissolved in water showing a series of $[\text{Na}_x\text{H}_y\text{TbGeW}_{10}\text{O}_{38}(\text{H}_2\text{O})_z]^{(9-x-y)^-}$ related species, resulting from decomposition of the hexameric Tb$_{12}$-containing polyanion.
By analogy, the groups of signals centred at m/z 701.73 and 1434.47 can be readily assigned to the -4 and -2 charged species with the formulas of [NaH₄EuGeW₁₀O₃₈(H₂O)₆]⁴⁻ and [Na₃H₄EuGeW₁₀O₃₈(H₂O)]²⁻. The maximum m/z value accessible with our experimental set-up is 3000. No experimental evidence of the Eu₁₂ related species or those larger than the monomer was obtained. These observation strongly suggests that the intact hexameric Eu₁₂ assembly characterized by XRD is not preserved in solution and completely decomposed into the 1:1 {EuGeW₁₀} monomers upon dissolution. The negative ion ESI-mass spectra for the Gd₁₂, Dy₁₂, and the mixed Tb₁₂ are almost identical with that observed for Eu₁₂ (Figures 5-14, 5-15), except for the slight shifts of the m/z to higher values due to the increasing atomic number from Eu to Dy, indicating the similar decomposition behaviors of them in water. Furthermore, the extension of the time for the dissolution of these compounds did not generate any additional group of signals, suggesting the stability of the monomer species in the solution.

Figure 5-16. Simulated (red) and experimental (black) patterns of the highest peaks observed in the ESI-mass spectra of (a) Na-Eu₁₂, (b) Na-Gd₁₂, (c) Na-Tb₁₂, and (d) Na-Dy₁₂ dissolved in water.
Table 5.6. Assignment of observed peaks in the negative ion mass spectra of Na-Ln\textsubscript{12} compounds dissolved in water.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Species</th>
<th>m/z</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>701.73</td>
<td>[NaH\textsubscript{4}EuGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{4-}</td>
<td>704.23</td>
<td>[Na\textsubscript{2}H\textsubscript{3}GdGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{5}]\textsuperscript{4-}</td>
</tr>
<tr>
<td>935.98</td>
<td>[NaH\textsubscript{5}EuGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{3-}</td>
<td>939.31</td>
<td>[Na\textsubscript{2}H\textsubscript{3}GdGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{5}]\textsuperscript{3-}</td>
</tr>
<tr>
<td>942.97</td>
<td>[Na\textsubscript{2}H\textsubscript{4}EuGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{3-}</td>
<td>946.31</td>
<td>[Na\textsubscript{3}H\textsubscript{3}GdGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{5}]\textsuperscript{3-}</td>
</tr>
<tr>
<td>1135.77</td>
<td>[Na\textsubscript{4}H\textsubscript{5}(EuGeW\textsubscript{10}O\textsubscript{38})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{7}]\textsuperscript{5-}</td>
<td>1139.37</td>
<td>[Na\textsubscript{6}H\textsubscript{7}(GdGeW\textsubscript{10}O\textsubscript{38})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{11}]\textsuperscript{5-}</td>
</tr>
<tr>
<td>1434.47</td>
<td>[Na\textsubscript{4}H\textsubscript{4}EuGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{7}]\textsuperscript{2-}</td>
<td>1440.97</td>
<td>[Na\textsubscript{3}H\textsubscript{2}GdGeW\textsubscript{10}O\textsubscript{38}(H\textsubscript{2}O)\textsubscript{5}]\textsuperscript{2-}</td>
</tr>
</tbody>
</table>

5.3.5 UV-vis spectroscopy

![UV-vis spectra](image)

Figure 5.17. UV-vis spectra of Na-Eu\textsubscript{12}, Na-Gd\textsubscript{12}, Na-Tb\textsubscript{12}, and Na-Dy\textsubscript{12} dissolved in water. Time-dependent UV-vis spectra (5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 4 h, and 24 h) recorded for each solution showed identical spectra, suggesting immediate dissociation of Ln\textsubscript{12} as well as high stability of the resulting monomer \{LnGeW\textsubscript{10}\}.
Chapter 5 Cage-like Ln\textsubscript{12}-Containing 60-Tungstogermanates

The UV-vis spectra of Na-Eu\textsubscript{12}, Na-Gd\textsubscript{12}, Na-Tb\textsubscript{12}, and Na-Dy\textsubscript{12} dissolved in water displays an absorption maximum at around 270 nm in the UV range, which can be attributed to the O → W charge transfer transition (Figure 5-17). The curves remained invariant for at least 24 h. This further confirmed the stability of the monomer \{LnGeW\textsubscript{10}\} species in the solution.

5.3.6 Photoluminescence

Room-temperature photoluminescence experiments were performed on Na-Eu\textsubscript{12} and Na-Dy\textsubscript{12} both in the solid state and in aqueous solution. In the first step, the excitation spectrum of solid Na-Eu\textsubscript{12} was measured monitoring the emission wavelength at 614.7 nm (Figure 5-18a, solid line). The normalized excitation spectrum only displays the characteristic Eu\textsuperscript{III} excitation lines at 362.4 nm (\textsuperscript{5}D\textsubscript{4} ← \textsuperscript{7}F\textsubscript{0}), 376.4, 381.3 and 384.4 nm (combination of \textsuperscript{5}G\textsubscript{2}, \textsuperscript{5}L\textsubscript{7}, \textsuperscript{5}G\textsubscript{3,6} ← \textsuperscript{7}F\textsubscript{0,1}), 394.8 nm (\textsuperscript{5}L\textsubscript{6} ← \textsuperscript{7}F\textsubscript{0}), 415.3 nm (\textsuperscript{5}D\textsubscript{3} ← \textsuperscript{7}F\textsubscript{0,1}), 465.3 nm (\textsuperscript{5}D\textsubscript{2} ← \textsuperscript{7}F\textsubscript{0}) and 473.2 nm (\textsuperscript{5}D\textsubscript{2} ← \textsuperscript{7}F\textsubscript{1}). According to the domination of the \textsuperscript{5}L\textsubscript{6} ← \textsuperscript{7}F\textsubscript{0} transition in this excitation spectrum, the emission spectrum of Na-Eu\textsubscript{12} was measured with the excitation at 394.8 nm (Figure 5-18b). Clearly, two visible peaks at 579.3 and 580.5 nm (\textsuperscript{5}D\textsubscript{0} → \textsuperscript{7}F\textsubscript{0}) are present, pointing towards the presence of at least two types of Eu\textsuperscript{III} centers with low symmetries in the Eu\textsubscript{12} due to the non-degeneracy of the \textsuperscript{5}D\textsubscript{0} and \textsuperscript{7}F\textsubscript{0} levels. This is in accordance with the distinguished Eu4 and Eu11 sites in the crystal structure. The high intensity of the hypersensitive \textsuperscript{5}D\textsubscript{0} → \textsuperscript{7}F\textsubscript{2} transition (614.7 nm), which is highly influenced by the environment of the Eu\textsuperscript{III}, further suggests the low symmetry of the Eu\textsuperscript{III} centers in this compound.

When the excitation spectrum of Na-Eu\textsubscript{12} dissolved in water was measured, a dominant ligand-to-metal charge transfer (LMCT) band appeared with a maximum intensity at 296.0 nm (Figure 5-18a, dash line). The energy from the photoexcitation of the O → W transition of the POM is transferred to the excited energy levels of the Eu\textsuperscript{III} ion, thereby sensitizing Eu\textsuperscript{III} emission.\[14\] The difference between the excitation spectra of solid Na-Eu\textsubscript{12} and its aqueous solution lies in the diversity of the energy transfer processes. In the solid state, Na-Eu\textsubscript{12} only gives rise to the sharp characteristic Eu\textsuperscript{III} transition peaks without a charge transfer band, which means the excitation in the \{GeW\textsubscript{10}\} group will be followed primarily by non-radiative transitions, due to the delocalization of the d\textsuperscript{1} electron.\[14\] For this reason,
luminescence can only be observed when the Eu\textsuperscript{III} ion is excited directly into its absorption lines. Nevertheless, the energy transfer properties change when Na-Eu\textsubscript{12} is dissolved in water, as the LMCT band dominates the excitation spectrum. Upon dissolution in water, Eu\textsubscript{12} decomposes into smaller 1:1 \{EuGeW\textsubscript{10}\} monomers, as shown by the ESI-mass spectrometry result. Clearly, in this newly formed structure the delocalization of the d\textsuperscript{1} electron is reduced, leading to an efficient energy transfer to the Eu\textsuperscript{III} ion. Accordingly, the optimal excitation of this polyanion in solution is...
established by indirect excitation at 296.0 nm. The emission spectrum of the aqueous solution of Na-Eu$_{12}$ is shown in Figure 5-18c. It shows an intense peak with a maximum intensity at 616.5 nm which can be ascribed to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. In contrast to the emission spectrum of Eu$_{12}$ in the solid state, only one peak can be observed for the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition (579.9 nm), suggesting the presence of only one type of Eu$^{III}$ center in aqueous solution.

Figure 5-19. Time-resolved decay data of Na-Eu$_{12}$ dissolved in (a) H$_2$O and (b) D$_2$O. The calculated concentration of Eu$_{12}$ is 5×10$^{-5}$ M.

Table 5-7. Time-resolved decay data for Eu$_{12}$ in aqueous solution (5×10$^{-5}$ M). Excitation was at 296.0 nm, and the emission was monitored at 616.5 nm.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_1$/ms</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.27918</td>
<td>0.99974(3)</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>1.89861</td>
<td>0.99996(1)</td>
</tr>
</tbody>
</table>

The lifetimes of the excited $^5\text{D}_0$ state of the Eu$^{III}$ ion in the {EuGeW$_{10}$} monomer in H$_2$O were measured by monitoring the emission at 616.5 nm (Figure 5-19 and Table 5-7). From the reasonable mono-exponential decay, we obtained a lifetime value of 0.28 ms. By also measuring the lifetime in D$_2$O (1.90 ms), the number of water molecules coordinated to the Eu$^{III}$ ion, $q$(Eu), can be calculated using the following equation 5-1:$^{[15]}

$q$(Eu) = 1.11[$\tau$(H$_2$O)$^{-1}$ - $\tau$(D$_2$O)$^{-1}$ - 0.31] \tag{5-1}

In the above equation, $\tau$(H$_2$O) and $\tau$(D$_2$O) are the measured lifetimes in ms in water and deuterated water, respectively. The number of coordinated water molecules was found to be 3.03, suggesting that three water molecules are coordinated to the
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Eu\textsuperscript{III} ion of the 1:1 \{EuGeW\textsubscript{10}\} monomer. Given the presence of three quenching water molecules coordinated to Eu\textsuperscript{III}, the lifetime of 0.28 ms for this polyanion lies within the expected range, as compared to other Eu-containing POMs with varying numbers of coordinated waters. For comparison, the polyanion in Na\textsubscript{9}[Eu(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]\cdot32H\textsubscript{2}O is lacking any coordinated water ligands to Eu\textsuperscript{III} and shows a lifetime of 2.8 ms at 300 K, which compares to 1.1 ms for K\textsubscript{15}H\textsubscript{3}[Eu\textsubscript{3}(H\textsubscript{2}O)\textsubscript{3}(SbW\textsubscript{9}O\textsubscript{33})(W\textsubscript{5}O\textsubscript{18})\textsubscript{3}]\cdot25.5H\textsubscript{2}O in which the polyanion contains two coordinated waters per Eu\textsuperscript{III}, and finally 0.20 ms for [NH\textsubscript{4}]\textsubscript{12}H\textsubscript{2}[Eu\textsubscript{4}(H\textsubscript{2}O)\textsubscript{16}(MoO\textsubscript{4})(Mo\textsubscript{7}O\textsubscript{24})\textsubscript{4}]\cdot13H\textsubscript{2}O in which the polyanion contains four coordinated waters per Eu\textsuperscript{III}.\textsuperscript{[16]}

![Figure 5-20.](image)

**Figure 5-20.** (a) Excitation and (b) emission spectra of Na-Dy\textsubscript{12} in the solid state. (c) Excitation and (d) emission spectra of Na-Dy\textsubscript{12} dissolved in water.

The excitation spectrum of solid Na-Dy\textsubscript{12} was taken monitoring the emission at 572.7 nm (Figure 5-20a). Again, no LMCT band was seen for this solid compound in the region between 200 - 350 nm. Here, the direct excitation of Dy\textsuperscript{III} at 365.9 nm ($^4\text{I}_{11/2} \leftarrow ^6\text{H}_{15/2}$) was used for the emission spectrum (Figure 5-20b). When the
emission spectrum was measured, the slits were opened wider to have a decent count number, as the Dy-POM seems to be less luminescent than the Eu one. The peak at 485.1 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$) is less intense than that at 572.7 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$). The latter is the hypersensitive one and is strongly influenced by the environment of Dy$^{III}$. The stronger intensity of the hypersensitive peak over the one at 485.1 nm is again an indication for a low-symmetry environment of the Dy$^{III}$ ions. The weaker peak at 663.0 nm can be attributed to the $^4F_{9/2} \rightarrow ^6H_{11/2}$ transition. The excitation spectrum of Na-Dy$_{12}$ dissolved in H$_2$O is shown in Figure 5-20c. A LMCT band can be identified with a maximum intensity at 296.0 nm, albeit it is not as intense as in the Eu$_{12}$ case. The emission spectrum of a Na-Dy$_{12}$ solution sample was measured by taking the excitation at 296.0 nm (Figure 5-20d), leading to an almost identical spectrum as in the solid state.

5.3.7 Magnetism

Magnetic susceptibility for Na-Dy$_{12}$ and Na-Gd$_{12}$ were measured (2–300 K) in presence of a magnetic dc field of 500 Oe. At room temperature, the value

![Figure 5-21](image_url)

**Figure 5-21.** (a) Magnetization data vs. H $T^{-1}$ at 8 K (•), 5 K (•) and 2 K (•) for Na-Dy$_{12}$. Inset: temperature dependence of the $\chi T$ product. (b) Magnetization data vs. H $T^{-1}$ at 8 K (•), 5 K (•) and 2 K (•) for Na-Gd$_{12}$. Inset: temperature dependence of the $\chi T$ product.
\( \chi_T = 165.5 \text{ cm}^3\text{mol}^{-1}\text{K} \) for Na-Dy\(_{12} \) is consistent with twelve non-interacting Dy\(^{\text{III}} \) ions (ground state \( ^{6}H_{15/2}, \) \( S = 5/2, \) \( L = 5 \) and Landé factor \( g = 4/3 \)).\(^{17}\) This value remains constant with decreasing temperature, down to 100 K. Then \( \chi_T \) decreases smoothly upon reaching a value of \( \chi_T = 138.7 \text{ cm}^3\text{mol}^{-1}\text{K} \) at 2 K (Figure 5-21a, inset). This magnetic behavior is typical for Dy\(^{\text{III}} \) ions, due to the thermal depopulation of the Stark sublevels of the \( ^{6}H_{15/2} \) state. We cannot rule out a contribution from super-exchange interactions between Dy\(^{\text{III}} \) centers. However, these should be very weak since they cannot be distinguished from the single ion anisotropy.

For Na-Gd\(_{12} \), the \( \chi_T \) value \( 97 \text{ cm}^3\text{mol}^{-1}\text{K} \) at room temperature is in good agreement with twelve non-interacting Gd\(^{\text{III}} \) ions (ground state \( ^{8}S_{7/2}, \) \( S = 7/2, \) \( L = 0 \) and \( g \approx 2 \)).\(^{17}\) \( \chi_T \) remains constant when decreasing the temperature down to 5 K, indicating a very good magnetic isolation between spin carriers. At very low temperature the signal suddenly decreases, reaching a value of \( \chi_T = 91 \text{ cm}^3\text{mol}^{-1}\text{K} \) at 2 K, (Figure 5-21b, inset). This decrease should be due to super-exchange antiferromagnetic interactions between Gd\(^{\text{III}} \) centers, although very weak since they only become apparent at such very low temperatures.

The field dependence of the magnetization at low temperature for Na-Dy\(_{12} \) reveals a sharp increase for low fields, and a progressive and linear increase at higher fields (Figure 5-21a). At 2 K and 7 T the magnetization reaches a value equal to 69.65 \( \mu_B \). This value implies a contribution to the magnetization of 5.8 \( \mu_B \) per Dy\(^{\text{III}} \) ion, which is far from the theoretical 10 \( \mu_B \) per Dy\(^{\text{III}} \) ion at saturation. Such an effective magnetic moment has also been observed for other Dy compounds and can be attributed to crystal-field effects and a high magnetic anisotropy which eliminates the 16-fold degeneracy of the ground state. The \( M \) vs \( H/T \) curves at different temperatures are not superimposable, which is also indicative of the high magnetic anisotropy of the Dy\(^{\text{III}} \) ions.

For Na-Gd\(_{12} \), the magnetization at low temperature smoothly increases until reaching a saturation magnetization equal to 85.7 \( \mu_B \) at 2 K and 5 T (Figure 5-21b). This value implies a contribution to the magnetization of 7.1 \( \mu_B \) per Gd\(^{\text{III}} \) ion, in good agreement with the expected theoretical 7 \( \mu_B \) per isolated Gd\(^{\text{III}} \) ion. The master curves \( M \) vs \( H/T \) at different temperatures are superimposable, as expected for a magnetically isotropic center.
Chapter 5 Cage-like Ln$_{12}$-Containing 60-Tungstogermanates

Figure 5-22. Temperature dependence of the in-phase ($\chi'$) and out-of-phase component ($\chi''$) of the ac susceptibility for Na-Dy$_{12}$ at frequencies: 1 Hz (▼), 20 Hz (○), 50 Hz (■), 100 Hz (•), 200 Hz (△), 450 Hz (☆) and 1000 Hz (X). Inset: Frequency dependence of the out-of-phase component ($\chi''$) of the ac susceptibility for Na-Dy$_{12}$ at 1.8 K and field 0 Oe(•), 500 Oe(•) and 1000 Oe(•).

As other Dy-based POMs have shown single molecule magnet (SMM) behavior,$^{[18]}$ we investigated this possibility and carried out ac susceptibility measurements on Dy$_{12}$. A frequency-dependent signal appears below 12 K in zero-dc field (Figure 5-22), showing a decrease in the in-phase contribution ($\chi'$) associated to the appearance of an out-of-phase signal ($\chi''$). $\chi''$ increases with higher frequencies, but no maximum is observed above 2 K. In Dy$^{\text{III}}$ SMMs, these apparently low blocking temperatures are due to effective tunneling, which can be suppress by a dc magnetic field.$^{[19]}$ However, in the case of Na-Dy$_{12}$, a dc magnetic field does not modify the blocking process (Figure 5-22, inset), suggesting that tunneling is not affecting the
observed blocking phenomena. This could be due to the existing super-exchange interactions, which very effectively suppress tunneling even if very weak.

5.4 Conclusion

We have prepared a new family of Ln$_{12}$-containing (Ln = Eu, Gd, Dy) 60-tungstogermanates, synthesized in slightly acidic aqueous solution. The three polyanions Eu$_{12}$, Gd$_{12}$, and Dy$_{12}$ are formed via transformation of the trilacunary POM precursor [$\alpha$-GeW$_9$O$_{34}$]$^{10-}$ to the di-lanthanide-embedded {\beta}(4,11)-GeW$_{10}$ unit in the presence of Ln$^{III}$ ions. Self-assembly of such {Ln$_2$GeW$_{10}$} subunits resulted in a hexameric structure. An interesting incorporation of extra Ge$^{IV}$ centers was observed, as well as encapsulation of a [Na(H$_2$O)$_6$]$^+$ complex or a (H$_2$O)$_6$ cluster, respectively, directly related to the different sizes of the three lanthanide ions. ESI-mass spectrometry and UV-vis studies indicated decomposition of Ln$_{12}$ into stable {LnGeW$_{10}$} monomers in water, which is supported by photoluminescence. Magnetic data on Na-Gd$_{12}$ and Na-Dy$_{12}$ suggested very weak super-exchange interactions in these materials. The latter material was proven to be a SMM, due to single ion anisotropy of the Dy$^{III}$ ions. Our work shows that interaction of lanthanide ions with lacunary heteropolytungstates can result in large and unexpected clusters, with interesting structural features associated with photochemical and magnetic properties. Such materials are mainly of interest in the solid state. It remains a challenge in this chemistry to stabilize large Ln-POMs in aqueous solution or in the gas phase.

5.5 Experimental section

5.5.1 General methods and reagents

The POM precursor salt Na$_{10}$[$\alpha$-GeW$_9$O$_{34}$]-18H$_2$O and Na$_{10}$[$\alpha$-SiW$_9$O$_{34}$]-18H$_2$O was prepared according to the published procedure and characterized by FTIR spectroscopy.$^{[20]}$ The other reagents were used as purchased without further purification. FTIR spectra (KBr pellets) were recorded on a Nicolet-Avatar 370 spectrometer. The UV-vis absorption spectra were recorded on a Varian Cary 100 Bio UV-vis spectrophotometer. Thermogravimetric analyses were carried out on a TA Instruments Q 600 device at a heating rate of 5 °C/min under a nitrogen atmosphere. Elemental analyses were performed at CNRS, Service Central d'Analyse, Solaize, France.
5.5.2 Synthesis

Na\textsubscript{39}[Na(H\textsubscript{2}O)\textsubscript{6}⊂Eu\textsubscript{12}(OH)\textsubscript{12}(H\textsubscript{2}O)\textsubscript{18}Ge\textsubscript{2}(GeW\textsubscript{10}O\textsubscript{38})\textsubscript{6}]·159H\textsubscript{2}O (Na-Eu\textsubscript{12})

EuCl\textsubscript{3}·6H\textsubscript{2}O (0.063 g, 0.17 mmol) was dissolved in 20 mL aqueous solution of sodium chloride (0.25 M) followed by addition of Na\textsubscript{10}[α-GeW\textsubscript{9}O\textsubscript{34}]·18H\textsubscript{2}O (0.48 g, 0.17 mmol). The mixture was then adjusted to pH 5 with 6M HCl dropwise, resulting in a transparent solution. Then the solution was kept at 50 °C for 30 minutes with constant stirring. After cooling down to room temperature, the solution was filtered and allowed to evaporate in an open beaker. Colourless plate-like crystals of Na-Eu\textsubscript{12} started to appear after one week and were collected after approximately two weeks when the final volume of the solution reduced to 12-15 mL. Yield: 0.072 g, 23%, based on EuCl\textsubscript{3}·6H\textsubscript{2}O.

FTIR of Na-Eu\textsubscript{12}: 1627 (m), 932 (m), 793 (s), 637 (w), 523 (w), 446 (w).

Anal. Calcd (Found) for Na-Eu\textsubscript{12}: Na 4.28 (4.22), Eu 8.48 (8.52), Ge 2.70 (2.60), W 51.30 (51.16).

Na\textsubscript{37}[Na(H\textsubscript{2}O)\textsubscript{6}⊂Gd\textsubscript{12}(OH)\textsubscript{6}(H\textsubscript{2}O)\textsubscript{24}Ge(GeW\textsubscript{10}O\textsubscript{38})\textsubscript{6}]·129H\textsubscript{2}O (Na-Gd\textsubscript{12})

The synthetic procedure for Na-Gd\textsubscript{12} is analogues to that for Na-Eu\textsubscript{12}, but the GdCl\textsubscript{3}·6H\textsubscript{2}O (0.063 g, 0.17 mmol) was used as lanthanide salt instead of EuCl\textsubscript{3}·6H\textsubscript{2}O. Colourless plate-like crystals of Na-Gd\textsubscript{12} started to appear after one week and were collected after approximately two weeks when the final volume of the solution reduced to 12-15 mL. Yield: 0.060 g, 20% based on GdCl\textsubscript{3}·6H\textsubscript{2}O.

FTIR of Na-Gd\textsubscript{12}: 1627 (m), 933 (m), 797 (s), 638 (w), 523 (w), 446 (w). Anal. Calcd (Found) for Na-Gd\textsubscript{12}: Na 4.18 (4.20), Gd 9.02 (9.15), Ge 2.43 (2.44), W 52.74 (52.57).

Na\textsubscript{36}[(H\textsubscript{2}O)\textsubscript{6}⊂Dy\textsubscript{12}(H\textsubscript{2}O)\textsubscript{24}Ge(GeW\textsubscript{10}O\textsubscript{38})\textsubscript{6}]·122H\textsubscript{2}O (Na-Dy\textsubscript{12})

The synthetic procedure for Na-Dy\textsubscript{12} is analogous to that of Na-Eu\textsubscript{12}, but the DyCl\textsubscript{3}·6H\textsubscript{2}O (0.064 g, 0.17 mmol) was used as lanthanide salt instead of EuCl\textsubscript{3}·6H\textsubscript{2}O. Colorless needle-like crystals of Na-Dy\textsubscript{12} started to appear after one week and were collected after approximately two weeks when the final volume of the solution reduced to 12-15 mL. Yield: 0.062 g, 21% based on DyCl\textsubscript{3}·6H\textsubscript{2}O.

FTIR of Na-Dy\textsubscript{12}: 1634 (m), 934 (m), 796 (s), 637 (w), 522 (w), 440 (w). Anal. Calcd (Found) for Na-Dy\textsubscript{12}: Na 4.01 (4.09), Dy 9.45 (9.56), Ge 2.11 (2.09), W 53.47 (53.05).

The Tb-containing analogue Na-Tb\textsubscript{12}

The synthetic procedure for Na-Tb\textsubscript{12} is analogous to that of Na-Eu\textsubscript{12}, but TbCl\textsubscript{3}·6H\textsubscript{2}O (0.063 g, 0.17 mmol) was used as lanthanide salt instead of EuCl\textsubscript{3}·6H\textsubscript{2}O. A mixture of needle-like crystals (major phase, isomorphous with Na-Dy\textsubscript{12}) and plate-like crystals
(minor phase, isomorphous with Na-Gd$_{12}$) started to appear after one week, and they were collected after approximately two weeks, when the final volume of the solution had reduced to 12-15 mL. Yield: 0.070 g, ~22% based on TbCl$_3$·6H$_2$O. FTIR of Na-Tb$_{12}$: 1626 (m), 935 (m), 796 (s), 639 (w), 522 (w), 441 (w). Anal. Found for Na-Tb$_{12}$: Na 14.15, Tb 19.25, Ge 12.01, W 53.54 %.

5.5.3 Crystallography

Colorless crystals of Na-Eu$_{12}$, Na-Gd$_{12}$ and Na-Dy$_{12}$ were mounted on a Hampton cryo-loop for indexing and intensity data collection at 100 K on a Bruker D8 APEX II CCD using Mo-Kα radiation ($\lambda$ = 0.71073 Å). Data integration was performed using SAINT.$^{[21]}$ Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.$^{[22]}$ Direct methods (SHELXS) successfully located the tungsten and lanthanide atoms, and successive Fourier syntheses (SHELXL) revealed the remaining atoms.$^{[23]}$ Refinements were full matrix least-squares against $|F|^2$ using all data. The relevant crystallographic data and structure refinement details of Na-Eu$_{12}$, Na-Gd$_{12}$ and Na-Dy$_{12}$ can be found in Table 5-1.

5.5.4 Photoluminescence

Steady state luminescence spectra were recorded on an Edinburgh Instruments FS900 steady state spectrofluorimeter. Time-resolved luminescence spectra were recorded on an Edinburgh Instruments FS920 spectrofluorimeter. Quartz cuvettes with 10.0 mm optical path length were used. Spectra were recorded on the aqueous solution with a concentration of 5×10$^{-5}$ M for the Ln$_{12}$. For the measurements on the solid Na-Eu$_{12}$ and Na-Dy$_{12}$, the slits were opened at 0.37 mm (resolution of 1 nm) for both excitation and emission spectra. For the measurements in solution, the slits were opened at 0.37 mm (resolution of 1 nm) for the Eu$_{12}$, whereas at 0.74 mm (resolution of 2 nm) for Dy$_{12}$.

5.5.5 Magnetic measurements

Magnetic measurements on polycrystalline samples of Na-Gd$_{12}$, and Na-Dy$_{12}$ have been carried out with a Quantum Design MPMS-XL magnetometer. Susceptibility measurements were performed under variable-temperature (2-300 K) and variable magnetic field (0-7 T). The experimental susceptibilities were corrected for the sample holder and diamagnetism of the constituent atoms using Pascal’s tables.
Alternating-current (ac) susceptibility measurements were performed using an oscillating ac field of 3.5 Oe and ac frequencies ranging from 1 to 1000 Hz, under different applied static fields and at different temperatures.

5.6 References


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[21] SAINT, Bruker AXS Inc.: Madison, WI, **2007**.

[22] G. M. Sheldrick, SADABS, University of Göttingen: Göttingen, **1996**.

Chapter 6 Summary and outlook

This thesis comprises two research projects: Titanium(IV)- and Lanthanide(III)-containing heteropolytungstates. A total of 11 compounds were synthesized and characterized by single-crystal X-ray diffraction, elemental analysis, Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) in the solid-state, and multinuclear NMR, ESI-Mass spectroscopy, UV-vis, and electrochemistry in solution. Photoluminescence as well as magnetic properties of some compounds were also investigated.

The main highlights of the thesis are listed as follows:

- Interaction of [TiO]$^{2+}$ with the [$\alpha$-As$^{III}$W$_9$O$_{33}$]$^{6-}$ POM precursor results in two novel the compact (Ti$_r$) or lacunary (Ti$_l$) Ti$^{IV}$-containing tungstoarsenates(III).
- It was demonstrated that Ti$_l$ represents a heterometallic, monolacunary POM host platform for selective incorporation of various main-group and d-block metal-ion guests, allowing for flexible tuning of the physicochemical properties.
- A new class of hexameric Ln$_{12}$-containing 60-tungstogermanates (Ln$_{12}$; Ln = Eu, Gd, Tb, Dy) is introduced, which feature different structural discrepancies depending on the size of the Ln$^{III}$ ion.

These research progresses in the thesis shed light on the design and preparation of polyoxometalates in several promising aspects in the future: (i) extend the scope of lone-pair containing POM precursors to the {Se$^{IV}$W$_9$}, {Te$^{IV}$W$_9$} units, which should probably directed the formation of novel Ti$^{IV}$-containing polanions due to their different charge from those of {As$^{III}$W$_9$}, {Sb$^{III}$W$_9$}; (ii) investigate the reactivity of Ti$_l$ precursor with other electrophiles, e.g. Ln$^{III}$, d$^8$ metals, with a specific focus on the functionalization of the POM host in catalysis and material sciences; (iii) employ large alkali metal ions (K$^+$, Rb$^+$, Cs$^+$) or alkaline earth metal ions (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) as guests to direct novel assemblies of the in situ formed {Ln$_2$GeW$_{10}$} building blocks, contributing to an instructive guest-host relationship for a further structural studies. (iv) Combine the new microwave-assisted synthetic method with the solution analytical techniques such as NMR, ESI-MS to study the mechanism of the POM formation.
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Publications

1. Wang, K.-Y.; Bassil, B. S.; Xing, X.; Keita, B.; Bindra J. K.; Diefenbach K.; Dalal N. S.; Kortz U.* “Incorporation of Transition Metal (Co, Ni, Cu, Zn) Guests into the Ti$_2$-containing 18-Tungsto-2-ArSENate(III) Monolacunary Host” manuscript to be submitted.


**Conferences**


2. Hexameric Assemblies of Di-Ln$^{III}$-Substituted (Ln = Eu, Gd, Dy) Keggin Ions, Koordinationschemie-Tagung, Paderborn, Germany, 2015. (Talk)


6. Metal Ion Guests Embedded in Ti$_2$-containing 18-Tungsto-2-Arsenate(III) Host, Norddeutsches Doktorandenkolloquium (NDDK), Göttingen, Germany, 2015. (Poster)


8. Ti$_7$-Containing, Tetrahedral 36-Tungsto-4-Arsenate(III), Norddeutsches Doktorandenkolloquium (NDDK), Rostock, Germany, 2014. (Poster)