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Chemistry of Group IV Metal Ion-Containing Polyoxometalates

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The chemistry of Group IV metal ion (Ti^{IV}, Zr^{IV} and Hf^{IV})-containing polyoxometalates (POMs) is presented as a sharply focused microreview, introducing an aspect of our own research. The synthesis, structure, and solid/solution state behavior of the POMs, which are prepared by the reactions of various lacunary species of POMs with Ti^{IV}, Zr^{IV} and Hf^{IV} atoms, are described in several sections, classified with Keggin and Dawson POM families. Because of the ionic radius of Ti^{IV} (0.75 Å), close to that of W^{VI} (0.74 Å), the Ti^{IV} atom can fit nicely into the mono-lacunary site of the POM, but Zr^{IV} and Hf^{IV} atoms (0.85–0.86 Å), larger than Ti^{IV} atom, do not fit into the mono-lacunary site of the POM. Thus, the mono-lacunary site of the POM acts as the oxygen-donor pentadentate ligand to the Ti^{IV} atom, whereas it acts as the tetradentate ligand to Zr^{IV} and Hf^{IV} atoms. The Ti^{IV} atom in the POM takes on six-coordinate geometry, whereas the Zr^{IV} and Hf^{IV} atoms have higher coordination numbers (6, 7 and 8) due to their larger ionic radii. Consequently, most Ti-substituted Keggin POMs are isolated as oligomers formed by corner-sharing Ti–O–Ti bonds, whereas Zr/Hf-containing Keggin/Dawson POMs are usually isolated as di-, tri-, tetra-Zr/Hf cluster cations sandwiched between two lacunary POMs, the cluster cations of which are formed by edge-sharing $M(OH)_2M$ (M = Zr, Hf) bonds. These compounds show quite different behavior under pH-dependent conditions. The pH-dependent interconversion between the dimeric and monomeric species of Ti-substituted Dawson POMs is quite an opposite tendency from those of Zr/Hf-containing Dawson POMs. The Ti-substituted Dawson POM oligomers have a tendency to undergo base hydrolysis to give monomers, whereas the Zr/Hf-containing Dawson POM oligomers have a tendency to undergo acid hydrolysis to provide monomers. In the Group IV metal ion-containing POMs, the Zr/Hf atoms function very similarly to each other, but show quite different behavior from the Ti atom.

Introduction

Polyoxometalates (POMs) are molecular metal-oxide clusters, which attract current interest as soluble metal oxides and for their application to homo- and heterogeneous catalysis, surface sciences, material sciences and medicine, since they are often considered as molecular analogues of metal oxides in terms of structure.[1–17] Site-selective lacunary species of W^{VI} atoms in polyoxotungstates can be utilized as an effective reaction space/field or a support for various metal ions and cationic species. Compared with saturated POMs, lacunary POMs have much higher basicity, but they do not have only the empty site as a coordination site. Research on the synthesis, structure and catalytic activities of POMs, which are prepared by reactions of lacunary species of Keggin- and Dawson-type tungstopolyoxoanions with Group IV metal ions such as Ti^{IV}, Zr^{IV} and Hf^{IV}, has been one of our projects. Herein, the chemistry of Group IV metal ion-containing POMs is presented as a sharply focused microreview, the introducing an aspect of our own research and tracing its development, in which several closely related, important works from others are also surveyed.

The ionic radius of Ti^{IV} (0.75 Å) is close to that of W^{VI} (0.74 Å), suggesting that Ti^{IV} should fit nicely into the lacunary sites of the POM framework. Generally, the coordination number of the Ti atom is six, and to the Ti atom the lacunary site of POM acts as an oxygen-donor pentadentate ligand. Therefore, the residual coordination site of the Ti atom substituted in POM is occupied by one water molecule or an OH^- group.

Since the Ti–OH species readily generate Ti–O–Ti anhydride forms by intermolecular dehydration/condensation, most Ti-substituted POMs are isolated as oligomers formed by corner-sharing Ti–O–Ti bonds (Figure 1, a). As a matter of fact, oligomeric Ti–O–Ti formation has been observed resulting from substitution by several Ti^{IV} atoms. For instance, tri-Ti-1,2,3-substituted Keggin POM, $[(\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{37})_2O_3]^{12-}$, has been isolated as a dimeric form composed of two Keggin units linked via three intermolecular Ti–O–Ti bonds (section 1.1).[18] Also, mono-Ti-substituted Dawson POM, $[(\alpha_2\text{-}P_2W_{17}TiO_{61})_2(\mu\text{-}O)]^{14-}$, has been isolated as a dimeric, Ti–O–Ti anhydride form (section 2.1).[19] The tri-Ti-substituted Dawson POM has been formed as a tetrapod-shaped giant tetramer by intermolecular Ti–O–Ti bond formation, and two types of tetra-

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mers, i.e., the non-bridging tetramer and the bridging tetramer, were obtained depending on the reaction conditions (section 2.3).[20–22]

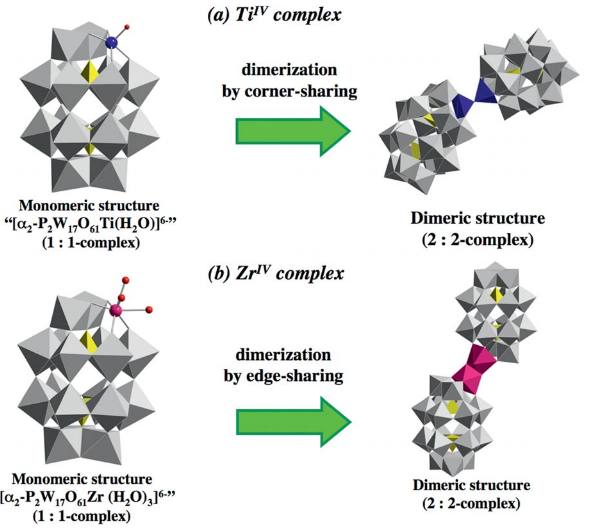

Figure 1. Dimerization by (a) corner-sharing (Ti^{IV}) and (b) edge-sharing (Zr^{IV}) of the monomeric mono-(Zr/Ti)-substituted Dawson POMs.

One of the aspects specific to Ti-substituted POMs is the host-guest relationship observed between the Ti^{IV} atom (guest) and the lacunary site (host) of Keggin POMs. Although the relationship is not necessarily based on the non-covalent interaction, the use of the term is convenient and useful on classifying and understanding the structures in the myriad Ti-substituted POMs. As a matter of fact, in addition to the one host-one guest relationship observed in most Ti-substitutions of Keggin POMs, several examples due to one host- two guest, two host-four guest and three host-four guest relationships are seen (section 1.2).[23–25]

On the other hand, the ionic radii of Zr and Hf atoms in Group IV metals (0.85–0.86 Å) are larger than that of the Ti atom. Zr and Hf atoms do not fit into the size of the mono-lacunary site of POMs and, therefore, to Zr and Hf atoms the mono-lacunary site of POMs acts as the oxygen-donor tetradentate ligand, but not as the pentadentate ligand. Compared with the six-coordinate, octahedral Ti atom, since the Zr and Hf atoms have higher coordination numbers (6, 7 and 8) due to their larger ionic radii, the residual coordination sites of the Zr and Hf atoms inserted into POMs are occupied by 2–4 water molecules or OH^- groups. In contrast to *corner-sharing* octahedra generated in Ti-substituted POMs, dehydration/condensation between the two actual $M(OH)_n$ groups (M = Zr, Hf; n = 2–4) results in the formation of *edge-sharing*, or less possible face-sharing, polyhedra of Zr and Hf centers (Figure 1, b). Therefore, Zr/Hf-containing POMs usually construct sandwich compounds, i.e., di-, tri-, tetra-Zr/Hf cluster cation units, sandwiched between two lacunary POMs (section 3).

Ti-substituted POM oligomers formed by corner-sharing Ti–O–Ti bonds and Zr/Hf-containing POM oligomers formed by edge-sharing $M(\mu\text{-}OH)_2M$ bonds show quite different behavior under pH-dependent conditions. For example, pH-varied ^{31}P NMR spectra in aqueous solutions showed that the mono-Ti-substituted Dawson POM is pres-

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Yoshitaka Sakai was born in Kanagawa, Japan in 1977. He received his Ph.D. degree from Kanagawa University under the supervision of Professor Kenji Nomiya in 2006, where he worked on the syntheses of titanium-substituted Dawson polyoxometalates. He joined Nomiya's group at Kanagawa University in 2007 as a postdoctoral fellow, where he worked until 2010. At present, he works as a researcher at Advantage Science, INC. (Old name: Hitec Corporation), Japan.

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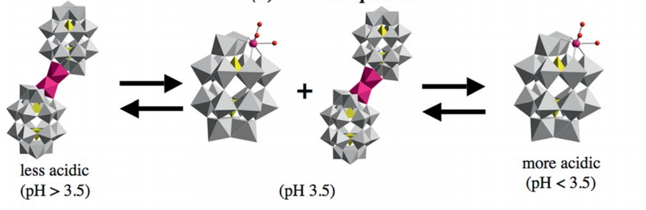
ent as a dimeric form, $[(\alpha_2\text{-}P_2W_{17}TiO_{61})_2(\mu\text{-}O)]^{14-}$ under acidic conditions (at pH 1.0–3.0) and that the mono-protonated species of this dimer predominantly existed at pH 0.5, while the mono-Ti-substituted Dawson POM is present as a monomeric form at pH 7.0 (section 2.1). On the other hand, the Zr/Hf-containing dimeric Dawson POMs (2:2-type complexes), $[\{\alpha_2\text{-}P_2W_{17}O_{61}M(\mu\text{-}OH)(H_2O)\}_2]^{14-}$ (M = Zr and Hf), are predominantly present under less acidic conditions (pH > 3.50), but the monomeric Dawson POMs (1:1-type complexes), $[\alpha_2\text{-}P_2W_{17}O_{61}M(H_2O)_3]^{6-}$, are predominantly formed under more acidic conditions (pH < 3.50). At pH 3.50, both the 2:2- and 1:1-type Dawson POMs were coexistent (section 4.4). Thus, the Ti-substituted Dawson POM oligomers have a tendency to undergo base hydrolysis to give monomers, i.e., a nucleophilic attack on the Ti sites, rather than an electrophilic attack on the μ-O atom in the Ti–O–Ti bonds, readily takes place. On the contrary, Zr/Hf-containing Dawson POM oligomers have a tendency to undergo acid hydrolysis to provide monomers, i.e., the μ-OH groups in the edge-sharing $M(\mu\text{-}OH)_2M$ bonds readily undergo electrophilic attacks by acidic species (Figure 2).

(a) Zr^{IV} complexes



(b) Ti^{IV} complexes

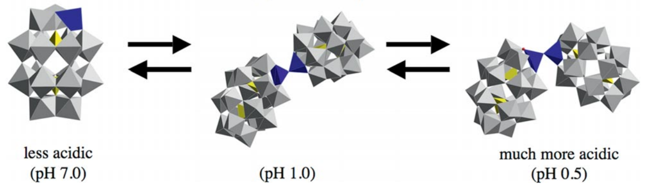


Figure 2. pH dependent interconversion between the monomeric (1:1-type) and dimeric (2:2-type) POMs: (a) Zr^{IV}-containing Dawson POMs and (b) Ti^{IV}-substituted Dawson POMs.

A different catalysis by Group IV metal ion-containing POMs was anticipated. In fact, the Ti-substituted POMs have shown a catalysis for H_2O_2-based epoxidation of olefins, which strongly depended upon the structures around the Ti centers.[26–29] The Zr/Hf-containing POMs have also shown catalytic activities for H_2O_2-based epoxidation of olefins. Many H_2O_2-based catalytic oxidation reactions have been described in which the hydroperoxo species are active species.[30–31] On the other hand, since most Zr/Hf-containing POMs are coordinatively unsaturated complexes of Zr or Hf atoms, their Lewis acid catalysis was also anticipated. Studies in this direction have recently been reported.[32–33]

This microreview includes the syntheses, molecular structures and properties of Group IV metal ion (Ti, Zr and Hf)-containing POMs in sections classified with Keggin and Dawson POM families.

1. Ti^{IV}-Substituted Keggin Polyoxometalates

1.1 Di- and Tri-Ti-Substituted Keggin POM Dimers

Dimeric di-Ti^{IV}-1,2-substituted α-Keggin POM, $[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{38})_2O_2]^{10-}$, was prepared by a 1:2 molar-ratio reaction of tri-lacunary Keggin POM $[A\text{-}PW_9O_{34}]^{9-}$ and $Ti(SO_4)_2\cdot 4H_2O$ in an aqueous solution. Crystalline potassium salt of $[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{38})_2O_2]^{10-}$ was obtained. X-ray structure analysis revealed that this polyoxoanion had a dimeric structure composed of two "$\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}$" Keggin polyoxoanion halves linked via two Ti–O–Ti bonds.[34] Interestingly, ultracentrifugation molecular weight measurements and ^{31}P NMR spectra of this complex in an aqueous solution showed pH-dependent interconversion between the dimer and the monomer (Figure 3). This complex was present as a monomer, $[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$, under neutral conditions (pH ≈ 7), but it was in the dimeric form under acidic conditions. However, the monomer $[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$ readily changed to a dimer and, therefore, isolation of the analytically pure solid of the monomer was difficult.[34]

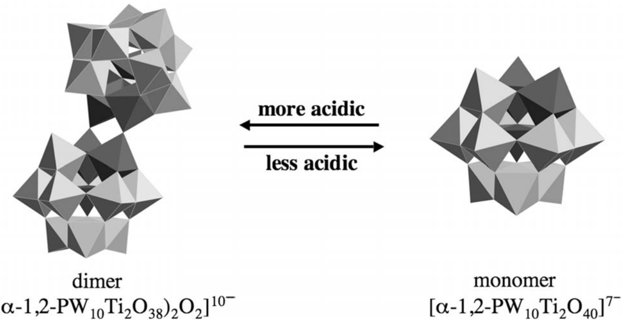


Figure 3. Interconversion between $[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{38})_2O_2]^{10-}$ and $[\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{40}]^{7-}$.

Dimeric tri-Ti^{IV}-1,2,3-substituted α-Keggin POM, $[(\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{37})_2O_3]^{12-}$, was prepared by a 1:3 molar-ratio reaction of tri-lacunary Keggin POM $[A\text{-}PW_9O_{34}]^{9-}$ and $Ti(SO_4)_2\cdot 4H_2O$ in an aqueous solution. Crystalline potassium salt of $[(\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{37})_2O_3]^{12-}$ was isolated. X-ray structure analysis revealed the molecular structure,[18] which had a dimeric structure formed by three Ti–O–Ti bonds linking two tri-Ti^{IV}-1,2,3-substituted Keggin POM $[\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{40}]^{9-}$ units (Figure 4). An isostructural dimeric tri-Ti^{IV}-1,2,3-substituted α-Keggin POM with a heteroatom Si, $[(\alpha\text{-}1,2,3\text{-}SiW_9Ti_3O_{37})_2O_3]^{14-}$, was also obtained. These tri-Ti-substituted POMs were present as dimeric forms in aqueous solution even under less acidic conditions.

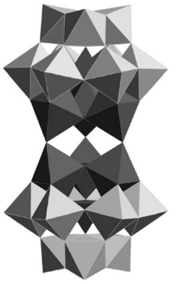


Figure 4. Polyhedral representation of $[(\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{37})_2O_3]^{12-}$.

Several mono-Ti^{IV}-substituted Keggin POMs have been reported so far.[35–37] Hill et al. synthesized the tetrabutylammonium salt of a mono-Ti^{IV}-substituted Keggin POM dimer, $[(PW_{11}TiO_{39})_2OH]^{7-}$, and reported interconversion between the dimer and the monomer,[35] just like our di-Ti^{IV}-1,2-substituted Keggin POM dimer. They concluded that the dimer was linked by a Ti–OH–Ti bond, i.e., the two monomeric units were connected with the μ-OH group, but the molecular structure has not yet been determined by X-ray crystallography.[35,38]

1.2 Host-Guest Chemistry of Ti-Substitution in Keggin POMs: One Host-Two Guest Type POM, Two Host-Four Guest Type POM and Three Host-Four Guest Type POM

Most Ti^{IV}-substituted Keggin POMs consist of a combination of a mono-lacunary site and an octahedral Ti group, e.g., a mono-lacunary site occupied by one Ti group and a di-lacunary site occupied by two Ti groups. From the viewpoint of the host-guest chemistry of Ti-substitution in POM, the lacunary site and the substituted Ti atoms are considered as host and guest, respectively. The above-mentioned di- and tri-Ti-substituted POMs are one host-one guest POMs, which were obtained by a reaction of lacunary POMs with Ti^{IV} sources [$Ti(SO_4)_2$, $TiCl_4$ etc.].

However, an unusual host-guest relationship has been found in some recent POMs. A one host-two guest type POM, $[[\{Ti(ox)(H_2O)\}_2(\mu\text{-}O)](\alpha\text{-}PW_{11}O_{39})]^{5-}$, which was composed of a Ti–O–Ti bonding species, i.e., the $[\{Ti(ox)(H_2O)\}_2(\mu\text{-}O)]^{2+}$ species, and a mono-lacunary α-Keggin POM $[\alpha\text{-}PW_{11}O_{39}]^{7-}$, was obtained by a reaction of the mono- or tri-lacunary species of an α-Keggin POM with the Ti^{IV} source, $[TiO(ox)_2]^{2-}$ (ox = oxalate), in an HCl-acidic solution (Figure 5).[23] This compound was stable in an acidic solution, while it converted into an one host-one guest type mono-Ti-substituted POM under less acidic conditions. This equilibrium can be represented in Equation (1).[23]

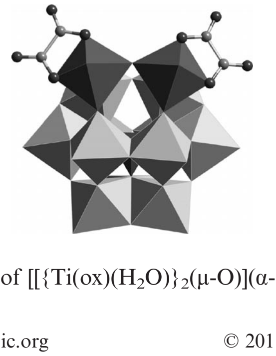


Figure 5. Structure of $[[\{Ti(ox)(H_2O)\}_2(\mu\text{-}O)](\alpha\text{-}PW_{11}O_{39})]^{5-}$.

$$2[[\{Ti(ox)(H_2O)\}_2(\mu\text{-}O)](\alpha\text{-}PW_{11}O_{39})]^{5-} \rightleftarrows [(\alpha\text{-}PW_{11}TiO_{39})_2O]^{8-} + 2[TiO(ox)_2]^{2-} + 2H^+ + 3H_2O \quad (1)$$

This equilibrium indicates that the reaction of one host-one guest type Ti-substituted POMs with Ti^{IV} ions would be applicable to the formation of novel Ti-substituted POMs. In fact, a two host-four guest type POM, $[[\{Ti(ox)(H_2O)\}_4(\mu\text{-}O)_3](\alpha\text{-}PW_{10}O_{37})]^{7-}$ (Figure 6), consisting of a combination of a di-lacunary site (two host sites) and four octahedral Ti groups (four guest atoms), was prepared as crystalline potassium salt by a 1:4 molar-ratio reaction of a dimeric di-Ti^{IV}-1,2-substituted α-Keggin polyoxometalate, $[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{38})_2O_2]^{10-}$, with $[TiO(ox)_2]^{2-}$ under strongly acidic conditions. The formation of this complex can be represented in Equation (2). It should be noted that the dissociation process of the two host-four guest type POM was not observed.[24]

$$[(\alpha\text{-}1,2\text{-}PW_{10}Ti_2O_{38})_2O_2]^{10-} + 4[TiO(ox)_2]^{2-} + 4H^+ + 6H_2O \rightarrow 2[[\{Ti(ox)(H_2O)\}_4(\mu\text{-}O)_3](\alpha\text{-}PW_{10}O_{37})]^{7-} \quad (2)$$

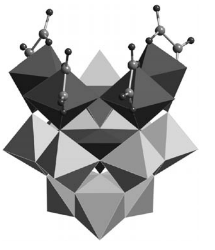


Figure 6. Structure of $[[\{Ti(ox)(H_2O)\}_4(\mu\text{-}O)_3](\alpha\text{-}PW_{10}O_{37})]^{7-}$.

The dimeric tri-Ti^{IV}-1,2,3-substituted α-Keggin polyoxometalate, $[(\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{37})_2O_3]^{12-}$, has been considered as a very stable compound. Nevertheless, this compound reacted with $Ti(SO_4)_2\cdot4H_2O$ under strongly acidic conditions to form two novel Ti^{IV}-substituted POMs, i.e., $[[\{Ti(H_2O)_3\}_2(\mu\text{-}O)](\alpha\text{-}PW_9Ti_2O_{38})]_2^{6-}$ and $[\{Ti_4(\mu\text{-}O)_3(SO_4)_2(H_2O)_8\}(\alpha\text{-}PW_9O_{34})]^{3-}$.[25] Dimeric tetra-Ti^{IV}-substituted POM, $[[\{Ti(H_2O)_3\}_2(\mu\text{-}O)](\alpha\text{-}PW_9Ti_2O_{38})]_2^{6-}$, was obtained as potassium salt by a reaction of $[(\alpha\text{-}1,2,3\text{-}PW_9Ti_3O_{37})_2O_3]^{12-}$ with an excess of $Ti(SO_4)_2\cdot4H_2O$ in an acidic aqueous solution ($pH < 0.1$), followed by stirring the solution at 60 °C for 10 min.[25] The molecular structure of $[[\{Ti(H_2O)_3\}_2(\mu\text{-}O)](\alpha\text{-}PW_9Ti_2O_{38})]_2^{6-}$ is composed of two "$PW_9Ti_4O_{45}$" Keggin POM halves linked via two Ti–O–Ti bonds between them. Each half contains a Ti_4 center consisting of two Ti atoms of a one host (mono-lacunary site)-one guest (one Ti atom) coordination and two Ti atoms of a one host-two guest coordination. In each Keggin POM half unit, six coordinated water molecules shown by bond valence sum (BVS) calculations occupy the six terminal positions of the two Ti atoms of the one host-two guest coordination, which are shown as open circles in Figure 7.[25]

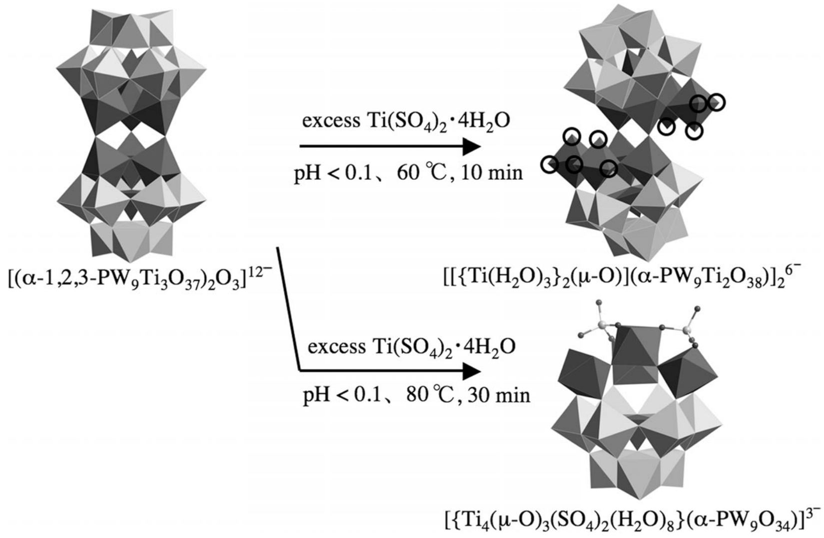


Figure 7. Syntheses using the dimeric tri-Ti-substituted Keggin POM precursor. A total of 12 coordinated water molecules are exhibited in the terminal positions in the four TiO_6 octahedra of $[[\{Ti(H_2O)_3\}_2(\mu\text{-}O)](\alpha\text{-}PW_9Ti_2O_{38})]_2{}^{6-}$.

On the other hand, a three host-four guest type monomeric POM, $[\{Ti_4(\mu\text{-}O)_3(SO_4)_2(H_2O)_8\}(\alpha\text{-}PW_9O_{34})]^{3-}$, was prepared by a 30 min reaction at 80 °C.[25] The molecular structure is a monomeric POM composed of a tetra-Ti cluster unit, $[Ti_4(\mu\text{-}O)_3(SO_4)_2(H_2O)_8]^{6+}$, which is accompanied by two coordinated sulfate ions and eight coordinated water molecules constructed on a tri-lacunary Keggin unit.

1.3 Related Compounds: Ti-Substituted Keggin POM Oligomers

Many Ti^{IV}-substituted Keggin POMs related to this section have been reported. The synthesis and the molecular structure of the di-Ti^{IV}-1,5-substituted α-Keggin POM, $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$, have been reported.[39–40] In contrast to di-Ti^{IV}-1,2-substituted α-Keggin POM, in which two Ti^{IV} atoms were located at positions 1 and 2, two Ti^{IV} atoms of this compound were substituted with W atoms at positions 1 and 5. $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$ was obtained as a single species by a one-pot reaction of $Na_2WO_4\cdot 4H_2O$, NaH_2PO_4 and $TiCl_4$ in an aqueous solution under heating, and was present as a monomer. The reason why $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$ can be obtained as a single species by this one-pot reaction (even if the corresponding lacunary precursor is not used) is not yet understood. Kortz et al. have reported the synthesis of di-Ti^{IV}-1,5-substituted β-Keggin POM with a heteroatom Si, $[\{\beta\text{-}Ti_2SiW_{10}O_{39}\}_4]^{24-}$,[41] which was composed of four $\{\beta\text{-}Ti_2SiW_{10}O_{39}\}$ subunits linked via four Ti–O–Ti bonds leading to a cyclic assembly (Figure 8).

Dimeric di-Ti^{IV}-substituted γ-Keggin POMs with heteroatoms Si and Ge, i.e., $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$[42] and $[\{\gamma\text{-}GeTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$,[43] were synthesized by reactions of di-lacunary γ-Keggin POMs with Ti^{IV} salt (Figure 9).

A dimeric tri-Ti^{IV}-substituted Keggin POM, $[(\alpha\text{-}1,2,3\text{-}GeW_9Ti_3O_{37})_2O_3]^{14-}$, was prepared from a reaction of tri-lacunary Keggin POM with a heteroatom Ge precursor, and the molecular structure was determined.[44] Furthermore, dimeric tri-Ti^{IV}-substituted Keggin POMs with heteroatoms Si and Ge, i.e., $[(\beta\text{-}1,2,3\text{-}SiW_9Ti_3O_{37})_2O_3]^{14-}$,[45] and $[(\beta\text{-}1,2,3\text{-}GeW_9Ti_3O_{37})_2O_3]^{14-}$[46] were also reported.

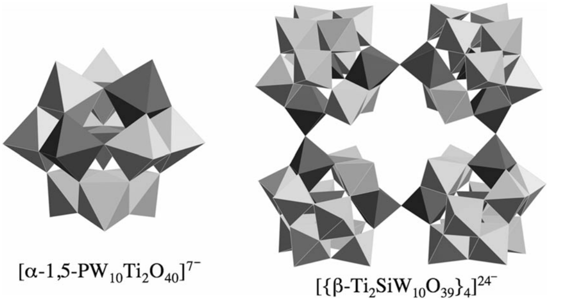

$[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$ $[\{\beta\text{-}Ti_2SiW_{10}O_{39}\}_4]^{24-}$

Figure 8. Structures of $[\alpha\text{-}1,5\text{-}PW_{10}Ti_2O_{40}]^{7-}$[39–40] and $[\{\beta\text{-}Ti_2SiW_{10}O_{39}\}_4]^{24-}$.[41]

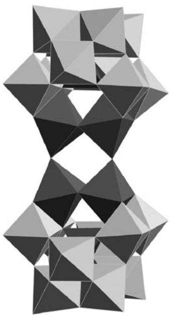


Figure 9. Polyhedral representation of $[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]^{8-}$.[42]

In addition to dimeric POMs, trimeric tri-Ti^{IV}-substituted Keggin POMs have been reported. Kortz et al. synthesized a cyclic trimer, $[(\alpha\text{-}Ti_3PW_9O_{38})_3(PO_4)]^{18-}$, which was composed of three tri-Ti-substituted α-Keggin POM units linked via three Ti–O–Ti bonds and a capping group of the tetrahedral $PO_4{}^{3-}$ ion (Figure 10).[47] This cyclic trimer was prepared by a reaction of $[P_2W_{19}O_{69}(H_2O)]^{14-}$ with $TiO(SO_4)$. Kortz et al. also reported an analogous compound, $[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]^{17-}$ (Figure 10), from a reaction of $[\{K(H_2O)_2\}\alpha\text{-}Si_2W_{18}O_{66}]^{15-}$ and $TiO(SO_4)$ in an aqueous solution.[47] Similar compounds, i.e., $\{K\subset[(Ge(OH)O_3)(GeW_9Ti_3O_{38}H_2)_3]\}^{14-}$ and $\{K\subset[(SO_4)(GeW_9Ti_3O_{38}H_3)_3]\}^{10-}$, were reported by a Chinese group.[48]

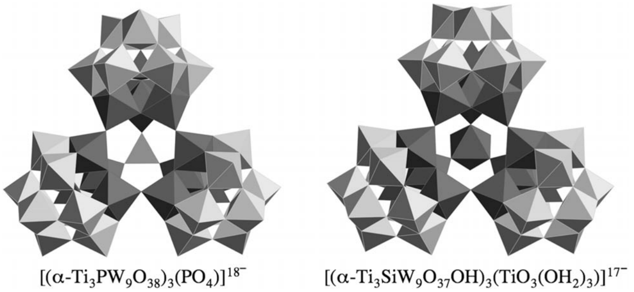


Figure 10. Polyhedral representations of $[(\alpha\text{-}Ti_3PW_9O_{38})_3(PO_4)]^{18-}$ and $[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]^{17-}$.[47]

Finally, the bridge between the lab and the environment has been found in the fundamental building block of the mineral murataite, which contains the α-Keggin structure of $[ZnTi_{12}O_{40}]^{30-}$ with Zn^{2+} as a heteroatom.[49] This may be one of ultimate forms of Ti-substitution in α-Keggin POM, although we are not sure whether it can be synthesized or not.

2. Ti^{IV}-Substituted Dawson Polyoxometalates

2.1 Mono-Ti^{IV}-Substituted Dawson POMs: Monomer and Dimer

A dimeric mono-Ti^{IV}-substituted Dawson POM, $K_{14}[(\alpha_2\text{-}P_2W_{17}TiO_{61})_2(\mu\text{-}O)]\cdot 17H_2O$ (**DK**), was prepared by 1:1-molar ratio reactions of an α_2-mono-lacunary Dawson POM, $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, with $Ti(SO_4)_2\cdot 4H_2O$ in an aqueous solution, followed by recrystallization from an aqueous HCl solution (pH 1.0).[19] Here, the abbreviations **D**, **M**, **K** and **H** stand for dimer, monomer, potassium salt and free-acid form, respectively. The free-acid form, i.e., $H_{13}[(\alpha_2\text{-}P_2W_{17}TiO_{61})(\alpha_2\text{-}P_2W_{17}TiO_{61}H)(\mu\text{-}O)]\cdot 55H_2O$ (**DH**), was prepared by passing an aqueous solution containing **DK** through a cation-exchange resin column. The monomeric form, $K_7[\alpha_2\text{-}P_2W_{17}TiO_{61}]\cdot 18H_2O$ (**MK**), was derived by adjusting an aqueous solution containing **DK** to pH 9.0 with Na_2CO_3 and was isolated as a powder by adding the aqueous solution to an excess amount of EtOH.[19] X-ray structure analysis revealed that **DK** and **DH** were composed of a dimer connected by $\mu\text{-}O^{2-}$ atom through one Ti–O–Ti bond between two α_2-mono-Ti^{IV}-substituted Dawson POM subunits. Although both **DK** and **DH** had the dimeric structure, the orientations of two Dawson subunits were slightly different. In the case of **DH**, BVS. (bond valence sum) calculation showed that one oxygen atom in one of the two Dawson subunits was protonated, therefore the two subunits were inequivalent. On the other hand, the molecular structure of **DK** was a Ti–O–Ti bonding dimer of two equivalent Dawson subunits. This difference in symmetry was also confirmed by ^{31}P NMR spectroscopy. The protonation was found in the bridging O atom of the surface Ti–O–W bond within one Dawson POM unit, but not the bridging O^{2-} atom of the Ti–O–Ti bond.

Intriguingly, the pH-varied ^{31}P NMR spectra of **DK** and **DH** in aqueous solutions showed that the monomer at pH 7.0, the dimer at pH 1.0–3.0, and the mono-protonated species of the dimer at pH 0.5 were the predominant species in the solutions. Thus, interconversion between the monomer and the dimer can be controlled by pH adjustment of the solutions (Figure 2, b).

As examples of mono-Ti^{IV}-substituted Dawson POMs, $\alpha_2\text{-}M_aH_b[P_2W_{17}TiO_{62}]\cdot xH_2O$ and $\alpha_2\text{-}M_aH_b[P_2W_{17}Ti(O)_2O_{61}]\cdot xH_2O$ (M = K, NEt_4, or NBu_4; $a + b = 8$) were reported.[50] However, single-crystal X-ray diffraction measurements were not carried out.

2.2 Sandwich Compound of a Mono-Ti^{IV}-Substituted Di-Lacunary Dawson POM Unit

The compound $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot 26H_2O$ was prepared by 1:1 molar-ratio reactions of tri-lacunary Dawson POM $[B\text{–}P_2W_{15}O_{56}]^{12-}$ with $Ti(SO_4)_2\cdot 4H_2O$ in an aqueous solution, followed by addition of an excess amount of KCl.[51] An aqueous solution of $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot 26H_2O$ was passed through a cation-exchange resin column, and then the free-acid form, $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$, was obtained. X-ray crystallography revealed that two octahedral Ti^{IV} sites were sandwiched between two tri-lacunary Dawson POMs $[P_2W_{15}O_{56}]^{12-}$. Thus, the POM, $[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]^{8-}$, was a di-lacunary species of a saturated sandwich complex of POMs. No observation of a K^+ countercation was confirmed, suggesting that this complex was a free-acid form. The results of BVS calculation showed that four terminal oxygen atoms at the two lacunary sites of the sandwich structure were completely protonated, i.e., all of the terminal oxygen atoms in the lacunary site of $[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]^{8-}$ were doubly protonated in the solid state.

The free-acid form $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$ has also been synthesized by two other methods, in addition to the method by a cation-exchange column (Method 1) mentioned above (Figure 11). In Method 2, a traditional ether-extraction method was applied to a separately prepared precursor, i.e., tetrameric Dawson POM $K_{25}[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl]\cdot 55H_2O$ (section 2.3). In Method 3, an ether-extraction method was applied to an in situ-generated tetrameric Dawson POM derived from $Na_{12}[P_2W_{15}O_{56}]\cdot 21H_2O$ and $Ti(SO_4)_2\cdot 4H_2O$. All three methods gave the free-acid form of the di-lacunary species of the sandwich compound containing Ti atoms, $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$. The free-acid form was obtained by Method 1 in 82.7% yield, whereas the yields by Methods 2 and 3 were 27.4% and 20.0%, respectively. Thus, Method 1 was superior to the other methods.

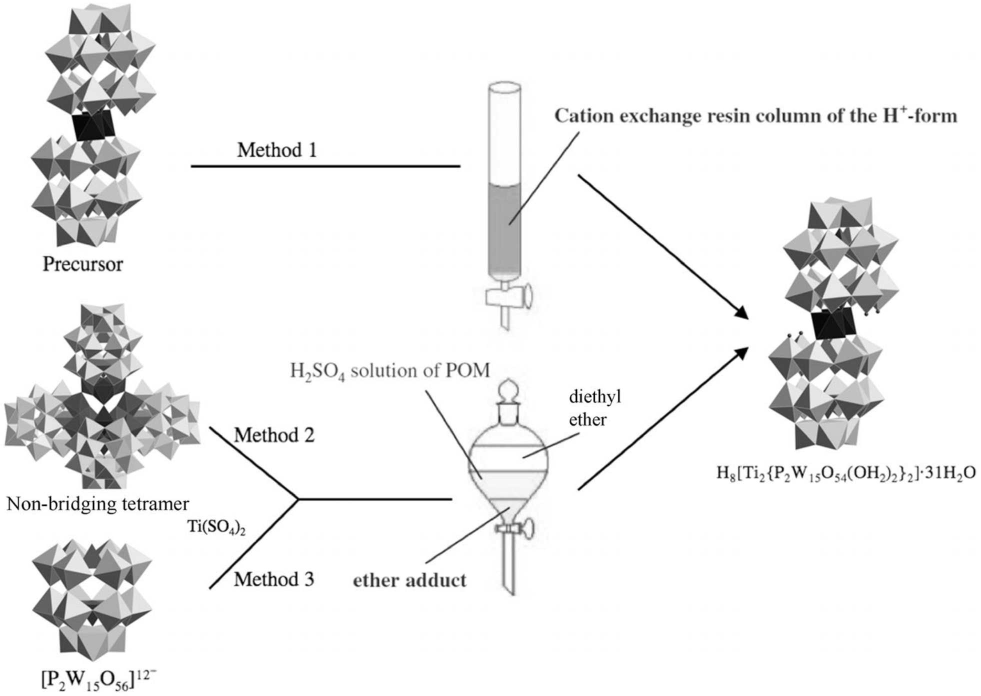


Figure 11. Scheme of the three methods for synthesis of $[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]^{8-}$ (reprinted with permission from ref.[51]; copyright 2007, The Chemical Society of Japan).

The degree of protonation of the oxygen atoms in the lacunary sites in the sandwich complex anion was found to be pH-dependent, in accordance with ^{31}P NMR observations. With regard to the oxygen atoms in the lacunary sites, the non-protonated species $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot 26H_2O$, partially protonated species $Na_5H_9[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]\cdot 38H_2O$ and completely protonated species $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$ were isolated in this work. The partially protonated species, $[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]^{14-}$, obtained as a sodium salt may be substantially similar to the ammonium salt $(NH_4)_{14}[TiP_2W_{15}O_{55}OH]_2\cdot nH_2O$ reported by Kortz's group.[21]

A Hammett acidity constant, H_0, of the free-acid form $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$ in CH_3CN (–2.72) was estimated to be almost the same as that of the homo-Dawson heteropolyacid $H_6[P_2W_{18}O_{62}]\cdot 17H_2O$ known as a super strong acid (–2.77).

2.3 Tetrapod-Shaped Dawson Tri-Ti^{IV}-Substituted POMs as Giant Tetramers: the Non-Bridging Tetramer and the Bridging Tetramer

Although a 1:3 molar-ratio reaction of tri-lacunary Dawson POM $[B\text{-}P_2W_{15}O_{56}]^{12-}$ with $Ti(SO_4)_2\cdot 4H_2O$ in an aqueous HCl solution results in the formation of a tri-Ti^{IV}-substituted POM unit, "$[\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62}]^{12-}$", the tetrapod-shaped tetramer of Dawson POM is *actually* generated by its self-condensation due to rapid formation of Ti–O–Ti bonds. This giant tetramer, $[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl]^{25-}$

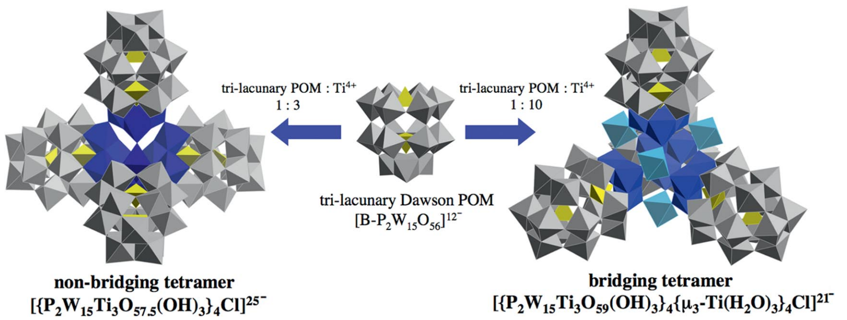


Figure 12. Polyhedral representation of non-bridging tetamer $[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl]^{25-}$ (left) and bridging tetramer $[\{P_2W_{15}Ti_3O_{59}(OH)_3\}_4\{\mu_3\text{-}Ti(H_2O)_3\}_4Cl]^{21-}$ (right). The bridging tetramer was composed of four tri-substituted Dawson POM units linked via four $Ti(H_2O)_3$ groups. Formation of the non-bridging tetramer and the bridging tetramer depended upon the starting molar ratio of the reaction of the tri-lacunary Dawson POM and Ti^{4+} ion.

(here called the non-bridging tetramer, i.e., the tetramer without the bridging Ti groups) was composed of four Dawson units, which were linked through intermolecular Ti–O–Ti bonds and arranged in approximately T_d symmetry (Figure 12).[20] In the central cavity of the non-bridging tetramer, one Cl^- ion was encapsulated. The μ-O atoms of Ti–O–Ti bonds within the Dawson units were protonated, i.e., Ti–(OH)–Ti bonds. This giant tetrapod-shaped non-bridging tetramer contains 72 metal atoms ($W_{60}Ti_{12}$ nuclei), and may be described as a sphere with a diameter of ca. 31.2 Å (a longitudinal distance of one Dawson unit ca. 12.7 Å). Kortz et al. have also reported a similar Ti^{IV}-substituted POMs tetramer, $K_4(NH_4)_{20}[(P_2W_{15}Ti_3O_{57.5}(OH)_3)_4]\cdot 77H_2O$.[21]

Meanwhile, a reaction of tri-lacunary Dawson POM $[B–P_2W_{15}O_{56}]^{12-}$ with an excess amount of $TiCl_4$ (10 equiv.) in an aqueous solution led to the formation of a novel tri-Ti^{IV}-substituted POM tetramer, $[\{P_2W_{15}Ti_3O_{59}(OH)_3\}_4\{\mu_3\text{-}Ti(H_2O)_3\}_4Cl]^{21-}$, composed of four $[\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62}]^{12-}$ subunits, four μ_3-$Ti(H_2O)_3$ groups and one encapsulated Cl^- ion (Figure 12).[22] In this giant tetramer (here called the bridging tetramer, i.e., the tetramer with bridging Ti groups), the μ-O atoms of Ti–O–Ti bonds within the Dawson units were also protonated. The molecular size of the bridging tetramer (inscribed to a sphere with a diameter of ca. 32 Å) is larger than that of the non-bridging tetramer, and the molecular weight of the bridging tetramer, which contains 76 metal atoms ($W_{60}Ti_{16}$ nuclei), was more than 16000.

The bridging tetramers encapsulating various anions (Br^-, I^- and NO_3^-) were synthesized by using in situ-generated TiX_4 (X = Br^-, I^- and NO_3^-), which were prepared by reactions of $Ti(SO_4)_2$ with BaX_2 in aqueous solutions.[52] The fact that encapsulation of different anions was achieved in the central cavity of the bridging tetramer shows the cationic character of the central framework consisting of protonated Ti–O–Ti bonds, i.e., Ti–OH–Ti bonds. The formation of the non-bridging tetramer and the bridging tetramer significantly depended upon the starting molar ratio of the reaction of the tri-lacunary Dawson POM and the Ti^{IV} ion. In the 1:3 molar-ratio reaction, only the non-bridging tetramer was formed. As the ratio of the Ti^{IV} ion was increased, the bridging tetramer began to form, and in the 1:10 molar-ratio reaction, only the bridging tetramer was formed.

2.4 Reactivity of the Non-Bridging Tetramer and the Bridging Tetramer: Formation of Tri-Ti^{IV}-Substituted Peroxo-Coordinating Monomer

The reactivity of the non-bridging and bridging tetramers with hydrogen peroxide (H_2O_2) was quite different. To a colorless solution of the bridging tetramer was added 30% *aq*. H_2O_2 and then the color of the solution changed from colorless to red. Adding an excess amount of NaCl to this solution, monomeric tri-peroxo- Ti^{IV}-substituted α-Dawson POM $[\alpha\text{-}1,2,3\text{-}P_2W_{15}(TiO_2)_3O_{56}(OH)_3]^{9-}$ was obtained. X-ray structure analysis revealed that the peroxo groups on the Ti^{IV} atoms were attached by side-on coordination, i.e., η^2-coordination (Figure 13).[53] This complex is the first example of structurally characterized peroxo-Ti-substituted Dawson POM. In contrast, this POM cannot be obtained from a reaction of the non-bridging tetramer with H_2O_2.

The coordinated peroxo groups of $[P_2W_{15}(TiO_2)_3O_{56}(OH)_3]^{9-}$ were easily decomposed by a heating or reducing agent. The resulting species is expected to be a building block for the synthesis of novel POM-based inorganic giant molecules or nano-devices. In fact, the reaction of $[P_2W_{15}(TiO_2)_3O_{56}(OH)_3]^{9-}$ with a reducing agent such as Na_2SO_3 or thermal decomposition of the peroxo-coordinating POM in aqueous solutions led to the formation of the non-bridging tetramer. Furthermore, the bridging tetramer was also re-generated by thermal decomposition of the peroxo-coordinating POM in the presence of Ti^{IV} ions in an aqueous HCl solution (Figure 13).

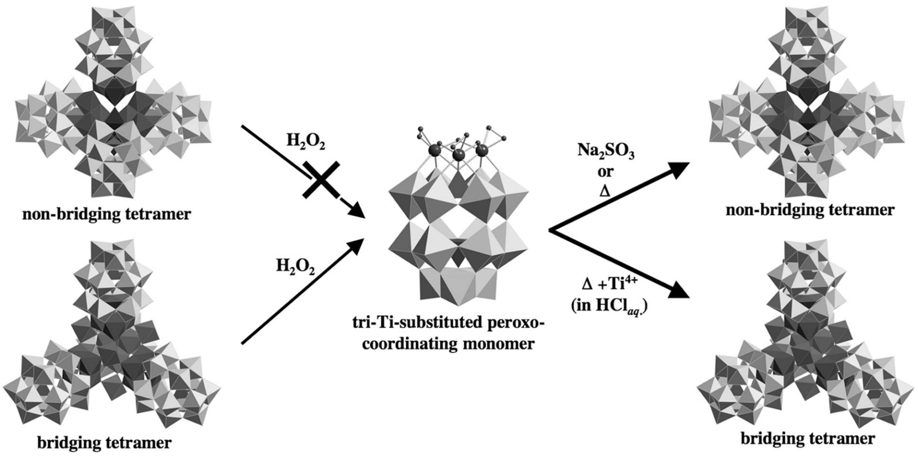


Figure 13. Monomeric tris-peroxo-Ti-substituted α-Dawson POM (middle) which was prepared by the reaction of the bridging tetramer (lower left) with H_2O_2 *aq*. The non-bridging tetramer and the bridging tetramer (right-hand) were re-generated under appropriate conditions.

2.5 Non-Bridging Tetramer Encapsulating Ammonium Cation: Exchange of Encapsulated Ion

All ions so far encapsulated in the central cavity of two tri-Ti^{IV}-substituted POM-based giant tetramers (the non-bridging tetramer and the bridging tetramer) were anions, i.e., Cl$^–$, Br$^–$, I$^–$ and $NO_3^–$ ions.[52] However, the non-bridging tetramer encapsulating the NH_4^+ cation, $(NH_4)_{27}Na_8[(P_2W_{15}Ti_3O_{60.5})_4(NH_4)]\cdot 90H_2O$, was obtained by thermal decomposition of the monomeric tri-peroxo-Ti^{IV}-substituted Dawson POM $[P_2W_{15}(TiO_2)_3O_{56}(OH)_3]^{9–}$ in the solid state, followed by a reaction with NH_4Cl in an aqueous solution.[54] X-ray crystallography revealed that the structure of the non-bridging tetramer encapsulating the NH_4^+ cation was very similar to that of the non-bridging tetramer encapsulating the Cl$^–$ anion. The Cl$^–$ anion was replaced with the NH_4^+ cation, and the edge-sharing oxygen atoms of Ti–O–Ti bonds within the Dawson units were not protonated. The encapsulated NH_4^+ cation was confirmed by ^{15}N NMR measurement of the non-bridging tetramer encapsulating the $^{15}NH_4^+$ cation prepared using $^{15}NH_4Cl$, and the Cl$^–$ ion-free sample was supported by complete elemental analysis. The factor determining whether the encapsulated ion in the central cavity is an anion or a cation, depends on whether the edge-sharing oxygen atoms of Ti–O–Ti bonds are protonated or not. In the non-bridging tetramer encapsulating the Cl$^–$ anion, 12 H$^+$ are appended to the edge-sharing oxygen atoms of the Ti–O–Ti bonds. The resulting central cavity, which is constructed with a total of 12 TiO_6 octahedra, becomes highly cationic, and an anion such as Cl$^–$ is encapsulated. On the other hand, by neutralizing the protons, which are attached to the edge-sharing oxygen atoms, the central cavity becomes highly anionic, and the cation such as NH_4^+ is encapsulated.

In fact, by neutralizing the 12 H$^+$ of the non-bridging tetramer encapsulating the Cl$^–$ anion with aqueous NH_3 in an aqueous solution, the encapsulated Cl$^–$ anion was readily exchanged with the NH_4^+ cation (Figure 14). Replacement of the Cl$^–$ anion encapsulated in the central cavity with NH_4^+ cation was confirmed by elemental analysis and ^{31}P NMR measurements. Conversely, when the non-bridging tetramer encapsulating the NH_4^+ cation was dissolved in an HCl-acidic aqueous solution, the non-bridging tetramer encapsulating the Cl$^–$ anion was re-generated. These results reveal that the encapsulated ion of the non-bridging tetramer can be exchanged, strongly depending on the pH of the solution, without any change in the basic tetrameric structure.

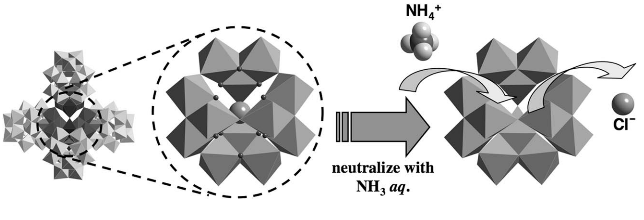


Figure 14. Replacement of the Cl$^–$ anion encapsulated in the central cavity with the NH_4^+ cation. The central cavity becomes highly anionic by neutralizing protons, which are attached to the oxygen atoms of the Ti–O–Ti bonds, and NH_4^+ is encapsulated.

2.6 Related Compounds: Di-Ti^{IV}-Substituted Dawson POM Dimer

Ti^{IV}-substituted Dawson POMs related to this section are scarce. Fox et al. have reported the dimeric POM $[\{P_2W_{16}Ti_2O_{62}\}_2\{Ti(ox)_2\}_2]^{28–}$, which was prepared by a reaction of tri-lacunary Dawson POM $[B–P_2W_{15}O_{56}]^{12–}$ with $[TiO(ox)_2]^{2–}$ in an aqueous HCl solution.[55] The water-soluble potassium salt and the organic solvent-soluble Bu_4N salt were isolated. X-ray structure analysis revealed that two di-Ti^{IV}-substituted Dawson POM units were linked with two bridging $Ti(ox)_2$ units through two inter-unit Ti–O–Ti bonds. This complex demonstrated the photocatalytic activities of the oxidation of alcohol. However, the synthesis described in the literature[55] was not reproduced in our group.[56]

3. Zirconium(IV)/Hafnium(IV) Cluster Cations Sandwiched between Keggin Lacunary Polyoxometalates

3.1 Mononuclear Zirconium(IV) and Hafnium(IV) Complexes: Keggin 1:2-Type Complexes

Diethylammonium salts (1:2-type complexes) of mono-zirconium(IV) and mono-hafnium(IV) ions sandwiched between two mono-lacunary Keggin POMs, $(Et_2NH_2)_{10}[Zr(\alpha\text{-}PW_{11}O_{39})_2]\cdot 7H_2O$ and $(Et_2NH_2)_{10}[Hf(\alpha\text{-}PW_{11}O_{39})_2]\cdot 2H_2O$ as crystalline samples, were obtained in 10.2% and 11.8% yields, respectively.[57] The 1:2-type complexes were prepared by reactions of in situ-generated mono-lacunary Keggin POM $[\alpha\text{-}PW_{11}O_{39}]^{7–}$, generated by a reaction of a saturated Keggin POM, $[\alpha\text{-}PW_{12}O_{40}]^{3–}$, and Na_2CO_3, with $MCl_2O\cdot 8H_2O$ (M = Zr, Hf) in an aqueous solution. X-ray structure analysis revealed that the Zr^{IV} and Hf^{IV} cations were in a square antiprismatic coordination environment with eight oxygen atoms, four of them being provided from each of the two mono-lacunary POM ligands with C_2 symmetry (Figure 15). The polyoxoanions, $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10–}$, were detected as two sets of enantiomeric pairs of two different units in the unit cell.

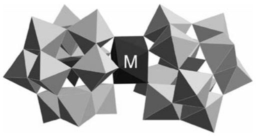


Figure 15. Polyhedral representation of $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10–}$ (M = Zr^{IV}, Hf^{IV}).

At around the same time as we reported, Hill et al. reported the spontaneous resolution of the Me_2NH_2 salt of $[Hf(\alpha\text{-}PW_{11}O_{39})_2]^{10–}$.[58] Further, in 2009, Liu et al. also reported the spontaneous resolution of the Me_2NH_2 salt of the corresponding Zr^{IV} complex.[59] Xue et al. synthesized the potassium salt of $[Zr(\alpha\text{-}BW_{11}O_{39})_2]^{14-}$, and determined its molecular structure by single-crystal X-ray structure analysis. This complex did not show spontaneous resolution.[60]

3.2 Dinuclear Zirconium(IV) and Hafnium(IV) Complexes: Keggin 2:2-Type Complexes

Diethylammonium salts (2:2-type complexes) of di-zirconium(IV) and di-hafnium(IV) cluster cations sandwiched between two mono-lacunary α-Keggin POMs, i.e., $(Et_2NH_2)_8[\{\alpha\text{-}PW_{11}O_{39}M(\mu\text{-}OH)(H_2O)\}_2]\cdot 7H_2O$ (M = Zr and Hf) as crystalline samples, were prepared by a 1:1 molar-ratio reactions of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ with $MCl_2O\cdot 8H_2O$ (M = Zr, Hf) in an aqueous solution and their molecular structures were successfully determined (Figure 16).[61] The central $[M_2(\mu\text{-}OH)_2(H_2O)_2]^{6+}$ (M = Zr, Hf) cation cluster unit was composed of two edge-sharing polyhedral M units, which were linked through two μ-OH groups and contained one water molecule coordinated to each metal center. Since the mono-lacunary Keggin POM acts as an oxygen-donor tetradentate ligand, the Zr and Hf centers are seven-coordinate. Interestingly, the 2:2-type complexes $[\{\alpha\text{-}PW_{11}O_{39}M(\mu\text{-}OH)(H_2O)\}_2]^{8-}$ undergo a reversible conversion to the 1:2-type complexes $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ in solution under appropriate conditions.[61] The reaction of the 1:2-type complex $[Zr(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ with $ZrCl_4\cdot 8H_2O$ (one molar equivalent) generated the 2:2-type complex $[\{\alpha\text{-}PW_{11}O_{39}Zr(\mu\text{-}OH)(H_2O)\}_2]^{8-}$. On the other hand, the reaction of the 2:2-type complex with mono-lacunary Keggin POM $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ (two molar equivalents) generated the 1:2-type complex (Figure 17). A similar interconversion relation was also observed for the hafnium(IV) analogues. The interconversion between the 2:2-type complex and the 1:2-type complex has been confirmed with ^{31}P NMR measurements.[61]

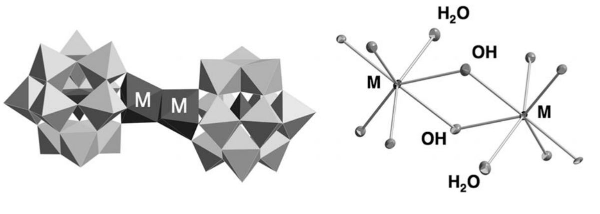


Figure 16. Polyhedral representation of $[\{\alpha\text{-}PW_{11}O_{39}M(\mu\text{-}OH)(H_2O)\}_2]^{8-}$ (M = Zr^{IV}, Hf^{IV}) and the structure of the dinuclear cluster moiety.

The 2:2-type Zr^{IV}-containing Keggin POMs related to this section, a di-zirconium(IV) cation species sandwiched between two mono-lacunary Keggin POMs $[PW_{11}O_{39}]^{7-}$, i.e., the 2:2-type complex $[\{\alpha\text{-}PW_{11}O_{39}Zr(\mu\text{-}OH)\}_2]^{8-}$ has been reported by Kholdeeva and co-workers.[30] The coordination environment around the Zr center in such a 2:2-type complex was different from those of our 2:2-type complexes.[61] The six-coordinate geometry around the Zr center in the former was accomplished by bonding with two bridging μ-O and four terminal oxygen atoms in the mono-lacunary site of the Keggin POM, and without any coordinating water molecules (Figure 18). Mizuno et al. have reported the 2:2-type complexes, $[(\gamma\text{-}SiW_{10}O_{36})_2\{M(H_2O)\}_2(\mu\text{-}OH)_2]^{10-}$ (M = Zr, Hf), consisting of di-Zi and -Hf cation units sandwiched between two γ-Keggin mono-lacunary species.[33,62]

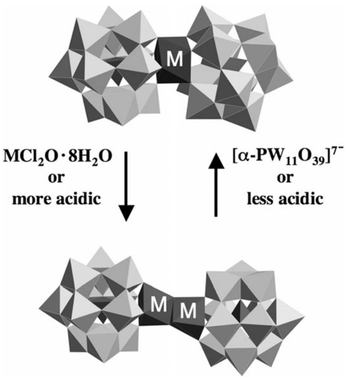


Figure 17. Interconversion between $[M(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ and $[\{\alpha\text{-}PW_{11}O_{39}M(\mu\text{-}OH)(H_2O)\}_2]^{8-}$ (M = Zr, Hf).

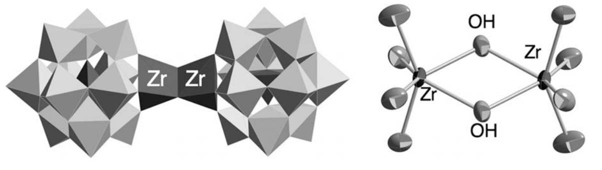


Figure 18. Polyhedral representation $[\{PW_{11}O_{39}Zr(\mu\text{-}OH)\}_2]^{8-}$ and the structure of the dinuclear Zr^{IV} cluster moiety.[30]

3.3 Trinuclear Zirconium(IV) and Hafnium(IV) Complexes Sandwiched between Two A-Site Tri-Lacunary Keggin POMs: Keggin 3:2-Type Complexes (α,α-Junction and α,β-Junction)

3:2-type complexes, which consisted of tri-Zr^{IV} and -Hf^{IV} cation cluster units $[M_3(\mu\text{-}OH)_3]^{9+}$ sandwiched between two tri-lacunary Keggin POMs $[A\text{-}PW_9O_{34}]^{9-}$, were obtained by reactions of the tri-lacunary Keggin POMs with M^{4+} (M = Zr, Hf).

In fact, the crude products of the 3:2-type complexes, were first obtained by a 1:3 molar-ratio reaction under acidic conditions (pH 1.2) of tri-lacunary Keggin POM $[A\text{-}PW_9O_{34}]^{9-}$ with $M(SO_4)_2\cdot nH_2O$ (M = Zr, Hf).[63] ^{31}P NMR in D_2O of the products showed a 7:3 mixture of an α,α-junction sandwich complex, $[M_3(\mu\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (M = Zr^{IV}, Hf^{IV}) (Figure 19(a)), and an α,β-junction sandwich complex, $[M_3(\mu\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})(A\text{-}\beta\text{-}PW_9O_{34})]^{9-}$ (M = Zr^{IV}, Hf^{IV}) (Figure 19, b). Here, the α,α-and α,β-junctions are based on combination of geometries of the two Keggin POM units constituting the sandwich POMs, the terms of which have been first used by C. L. Hill et al.[64]

These crude products were first refluxed for 1 h in an aqueous HCl solution at pH 1.0, and subsequently evaporated to give only an α,α-junction sandwich complex.[63] During the process of heating, a part of the α,β-junction species that was first isolated as a 7:3 mixture of α,α- and

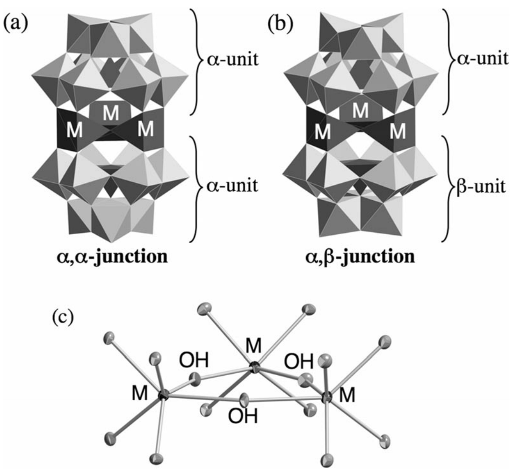


Figure 19. Polyhedral representation of (a) $[M_3(\mu\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (α,α-junction) and (b) $[M_3(\mu\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})(A\text{-}\beta\text{-}PW_9O_{34})]^{9-}$ (α,β-junction); (c) the structure of the trinuclear cluster cation moiety of $[M_3(\mu\text{-}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ (M = Zr^{IV}, Hf^{IV}).

α,β-forms changed to a pure α,α-species, but some of the α,β-junction species decomposed or changed to other unknown species. The central $[M(\mu\text{-}OH)_3]^{9+}$ cluster cation was composed of three Zr^{IV} or Hf^{IV} atoms in a six-coordinate trigonal prismatic coordination environment linked with three bridging OH groups. These compounds are coordinatively unsaturated complexes of Hf or Zr atoms (Figure 19, c).

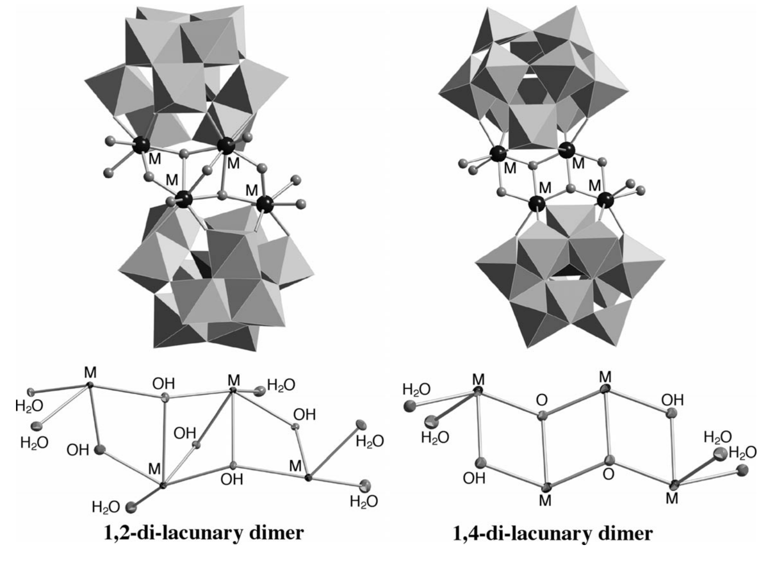
As related compounds, the β,β-junction-sandwiched tungstosilicate $[Zr_3(\mu\text{-}OH)_3(A\text{-}\beta\text{-}SiW_9O_{34})_2]^{11-}$, containing two tri-lacunary β-Keggin POMs, was synthesized and its molecular structure was reported by Finke et al. in 1989.[65] The α,α-junction-sandwiched tungstosilicate $[Zr_3(\mu\text{-}O)(OH)_2(\alpha\text{-}SiW_9O_{34})_2]^{12-}$[66] and the α,β-junction-sandwiched tungstogermanate $[Zr_3(\mu\text{-}O)(OH)_2(\alpha\text{-}GeW_9O_{34})(\beta\text{-}GeW_9O_{34})]^{12-}$[67] were also synthesized and their molecular structures have been determined.

3.4 Tetranuclear Zirconium(IV) and Hafnium(IV) Complexes Sandwiched between Two 1,2- and 1,4-Dilacunary Keggin POMs: Keggin 4:2-Type Complexes

The 4:2-type complexes of tetra-Zr^{IV} and -Hf^{IV} cluster cations with two 1,2-di-lacunary α-Keggin POM units, i.e., $[[\{M(H_2O)\}_2\{M(H_2O)_2\}_2(\mu\text{-}OH)_3(\mu_3\text{-}OH)_2](\alpha\text{-}1,2\text{-}PW_{10}O_{37})_2]^{7-}$ (M = Zr^{IV}, Hf^{IV}), which are simply termed 1,2-dilacunary dimer, were obtained.[68]

The cluster cations, $[\{M(H_2O)\}_2\{M(H_2O)_2\}_2(\mu\text{-}OH)_3(\mu_3\text{-}OH)_2]^{11+}$ (M = Zr^{IV}, Hf^{IV}), were sandwiched between two 1,2-di-lacunary α-Keggin POM units "$[\alpha\text{-}1,2\text{-}PW_{10}O_{37}]^{9-}$". The 4:2-type complexes were prepared by a 1:2 (M = Zr) or 1:4 (Hf) molar-ratio reaction of A-site tri-lacunary Keggin POM $[A\text{-}PW_9O_{34}]^{9-}$ with $Zr(SO_4)_2$ or $HfCl_4$, respectively, in aqueous HCl solutions (pH ≈ 0). X-ray structure analyses of the Cs salts revealed that the molecular structures of the Zr- and Hf- complexes were isostructural with each other. Two seven-coordinate and two eight-coordinate Zr/Hf ions were contained in the central tetranuclear-cluster cation units. Although these complexes were chiral with the overall C_2 symmetry of the polyoxoanion molecule, racemic forms in the crystals were obtained in the present synthesis.

On the other hand, other 4:2-type complexes of tetra-Zr^{IV} and -Hf^{IV} cluster cations with two 1,4-di-lacunary α-Keggin POM units, i.e., $[\{M_4(\mu\text{-}OH)_2(\mu\text{-}O)_2(H_2O)_4\}(\alpha\text{-}1,4\text{-}PW_{10}O_{37})_2]^{8-}$ (M = Zr^{IV}, Hf^{IV}), which are simply called 1,4-di-lacunary dimer, were obtained by 1:3 molar-ratio reactions of B-site tri-lacunary Keggin POM $[B\text{-}PW_9O_{34}]^{9-}$ with $M(SO_4)_2$ (M = Zr, Hf) in aqueous HCl solutions (pH = 1.4–1.5).[68] Structure analysis of the Me_2NH_2 salts revealed that the polyoxoanions were composed of tetranuclear cluster units, $[M_4(\mu\text{-}OH)_2(\mu\text{-}O)_2(H_2O)_4]^{10+}$, sandwiched between two 1,4-di-lacunary α-Keggin POM units "$[\alpha\text{-}1,4\text{-}PW_{10}O_{37}]^{9-}$". The structures of the central tetranuclear cations in the 1,2- and 1,4-di-lacunary dimer, were slightly dif-



1,2-di-lacunary dimer
1,4-di-lacunary dimer

Figure 20. Structures of $[[\{M(H_2O)\}_2\{M(H_2O)_2\}_2(\mu\text{-}OH)_3(\mu_3\text{-}OH)_2](\alpha\text{-}1,2\text{-}PW_{10}O_{37})_2]^{7-}$ (1,2-di-lacunary dimer: left) and $[\{M_4(\mu\text{-}OH)_2(\mu_3\text{-}O)_2(H_2O)_4\}(\alpha\text{-}1,4\text{-}PW_{10}O_{37})_2]^{8-}$ (1,4-di-lacunary dimer: right) (M = Zr, Hf).

ferent. The central tetranuclear cation in the 1,2-di-lacunary dimer was constructed with five bridging OH^- groups (Figure 20 left), whereas that in the 1,4-di-lacunary dimer was composed of two bridging OH^- groups and two bridging O^{2-} atoms (Figure 20 right). All M (M = Zr, Hf) centers in the 1,4-di-lacunary dimer were seven-coordinate, and the polyoxoanion molecule had overall C_i symmetry. The structures of the central $[M_4(\mu\text{-}OH)_2(\mu\text{-}O)_2(H_2O)_4]^{10+}$ cations in the 1,4-di-lacunary dimer were very similar to those of the 4:2-type Dawson complexes, $[M_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$ (M = Zr^{IV},[69] Hf^{IV}[70]) (section 4.5), which were obtained by reactions of tri-lacunary Dawson POMs with Zr^{4+}/Hf^{4+} ions. We have evaluated the catalytic activities of the 1,2-di-lacunary dimer as a Lewis acid catalyst for Mukaiyama aldol reactions.[68]

Kortz et al. have reported the 4:2-type sandwich complex, $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$, which consists of a tetra-Zr^{IV} cluster cation unit sandwiched between two di-lacunary β-Keggin tungstosilicate units, $[\beta\text{-}SiW_{10}O_{37}]^{10-}$.[71] The structure of the tetra-Zr^{IV} cluster cation was very similar to that of the 1,4-di-lacunary dimers described above. Although this complex was synthesized using a di-lacunary γ-Keggin POM, $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, as precursor, the resulting molecular structure consisted of di-lacunary β-Keggin units, $[\beta\text{-}SiW_{10}O_{37}]^{10-}$. Thus, the di-lacunary β-Keggin tungstosilicate $[\beta\text{-}SiW_{10}O_{37}]^{10-}$ may be the metastable state of the di-lacunary γ-Keggin tungstosilicate $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ in aqueous solution containing transition-metal ions.[71]

Mizuno et al. reported the 4:2-type complexes, i.e., $[(\gamma\text{-}SiW_{10}O_{36})_2\{M(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]^{8-}$ (M = Zr, Hf).[33] These POMs consisted of distorted adamantanoid clusters containing the μ_4-O atom in the center, $[\{M(H_2O)\}_4(\mu_4\text{-}O)(\mu\text{-}OH)_6]^{8+}$, sandwiched between two di-lacunary γ-Keggin POM $[\gamma\text{-}SiW_{10}O_{36}]$ units. These 4:2-type complexes showed high catalytic activities with regard to the intramolecular cyclization of (+)-citronellal to isopulegols.[33]

3.5 Related Compounds: Zr- and Hf-Containing Keggin Oligomers

As Zr^{IV}-containing Keggin POMs related to this section, Kortz et al. reported the synthesis and molecular structure of the 6:3-type complex, $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$, which was prepared by a reaction of di-lacunary γ-Keggin POM, $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, with $ZrCl_4$ in a potassium acetate buffer.[71] The 6:3-type complex consisted of a hexa-Zr^{IV} cluster cation $[Zr_6O_2(OH)_6(H_2O)_3]^{16+}$ connected with three di-lacunary β-Keggin POM $[\beta\text{-}SiW_{10}O_{37}]^{10-}$ units. Furthermore, Kortz et al. also reported the peroxo species $[M_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (M = Zr, Hf) (Figure 21).[72] The synthetic procedure of the peroxo species was substantially the same as that of the 6:3-type complex, except for the use of an aqueous 30% H_2O_2 solution. This is the first report on the structures of these peroxo-containing Zr^{IV} and Hf^{IV} POM complexes. Recently, Kortz et al. also reported the peroxo species of di-nuclear Zr^{IV}/Hf^{IV} Keggin POMs, $[M_2(O_2)_2(XW_{11}O_{39})_2]^{12-}$ (M = Zr^{IV}, X = Si, Ge; M = Hf^{IV}, X = Si).[73]

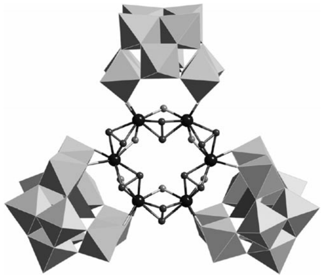


Figure 21. Peroxo species $[M_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (M = Zr, Hf).[72]

May et al. synthesized 1:2-type Zr/Hf complexes sandwiched between saturated Keggin and mono-lacunary Keggin molybdo-POM units, $[M(PMo_{12}O_{40})(PMo_{11}O_{39})]^{6-}$ (M = Zr,[74] Hf[75]). They also reported a Zr complex sandwiched between $[AsW_{10}O_{36}]^{9-}$ and $[AsW_7O_{28}]^{11-}$ units, i.e., $[Zr_2(\mu\text{-}OH)(H_2O)_2(AsOH)_2(AsW_7O_{28})(AsW_{10}O_{36})]^{9-}$, which was prepared using the precursor POM $[NaAs_4W_{40}O_{140}]^{27-}$.[76]

4. Zirconium(IV)/Hafnium(IV) Cluster Cations Sandwiched between Two Dawson Lacunary Polyoxometalates

4.1 Mononuclear Zirconium(IV) and Hafnium(IV) Complexes: Dawson 1:2-Type Complexes (M = Zr and Hf)

Potassium salts (Dawson 1:2-type complexes) of the zirconium(IV) and hafnium(IV) complexes sandwiched between two mono-lacunary α_2-Dawson POMs $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, i.e., $K_{15}H[Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2]\cdot 25H_2O$ and $K_{16}[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]\cdot 19H_2O$ with C_2 symmetry, were obtained in 64.0% and 39.2% yields, respectively.[57] These compounds were prepared by 1:1 (M = Zr) and 1:0.75 (M = Hf) molar-ratio reactions of $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ and $MCl_2O\cdot 8H_2O$ (M = Zr, Hf) in an aqueous solution. Unreacted zirconium and hafnium species were completely removed from the water by crystallization. The formation of $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ can be shown in the ionic balance in Equation (3).

$$2\,[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-} + MCl_2O + 2\,H_3O^+ \rightarrow [M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}\ (M = Zr, Hf) + 2\,Cl^- + 2\,H_2O \quad (3)$$

X-ray crystallography of these complexes demonstrated that the Zr^{IV} and Hf^{IV} ions were coordinated to the oxygen atoms of the mono-vacant site in the "cap" moiety of α_2-mono-lacunary Dawson POM, $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$; the structures were identical to that of the reported POM $[Lu(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$.[77] The two POM "lobes" are oriented in a *syn* fashion. The polyoxoanions were detected as a set of an enantiomeric pair of units in the unit cell. The Zr^{IV} and Hf^{IV} ions are located in a square antiprismatic coordination environment with eight oxygen atoms, four of them being provided from each of the two $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ligands (Figure 22). The Zr–O and Hf–O bond lengths were in the range of 2.172–2.229 Å (average 2.203 Å) and 2.158–2.219 Å (average 2.186 Å), respectively. The Zr–O and Hf–O bond lengths are shorter than those of the lanthanide and actinide atoms containing Dawson POMs $[X(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-/17-}$ (X = Lu^{3+}, Pu^{4+}, Np^{4+}, Th^{4+}, Eu^{3+}, Am^{3+}, Sm^{3+}, Pu^{3+}, Np^{3+}, and Ce^{3+}; 2.31–2.52 Å), and the bond lengths increased with an increase in the ionic radii of the rare-earth elements.[77–79]

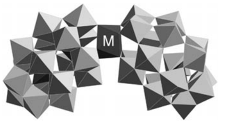


Figure 22. Molecular structure of $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (M = Zr, Hf).

4.2 Dinuclear Zirconium(IV) and Hafnium(IV) Complexes: Dawson 2:2-Type Complexes (M = Zr and Hf)

Dimethylammonium salts (Dawson 2:2-type complexes) of di-hafnium(IV) and di-zirconium(IV) cluster cations sandwiched between two mono-lacunary α_2-Dawson POMs, i.e., $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Zr(\mu\text{-}OH)(H_2O)\}_2]\cdot 16H_2O$ and $(Me_2NH_2)_{14}[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-}OH)(H_2O)\}_2]\cdot 17H_2O$ as crystalline samples, were obtained in 44.7% and 47.0% yields, respectively.[80] The 2:2-type complexes were prepared by 1:1-molar ratio reactions of the mono-lacunary α_2-Dawson POM $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ with $MCl_2O\cdot 8H_2O$ (M = Zr, Hf) at pH = 2.0 in an aqueous HCl solution, followed by stirring the solution at > 90 °C. It should be noted that the 1:2 complexes, $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (M = Zr, Hf), were prepared under almost the same conditions.[57] The only difference is the pH adjustment carried out in the synthesis of the 2:2-type complexes. The Me_2NH_2 salts were dissolved in an HCl acidic solution at pH 2.0 and crystallized by slow evaporation at room temperature. The formation of two 2:2-type complexes can be represented in Equation (4).

$$2\,[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-} + 2\,MCl_2O + 2\,H_3O^+ \rightarrow [\{\alpha_2\text{-}P_2W_{17}O_{61}M(\mu\text{-}OH)(H_2O)\}_2]^{14-}\ (M = Zr\ and\ Hf) + 4\,Cl^- \quad (4)$$

X-ray crystallography revealed that the central dinuclear $[M_2(\mu\text{-}OH)_2(H_2O)_2]^{6+}$ (M = Zr, Hf) cation unit in the 2:2-type complex, composed of two polyhedral M units with one coordinated water molecule linked through two μ-OH groups, was sandwiched between two mono-lacunary α_2-Dawson POM units $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ (Figure 23). Since the mono-lacunary Dawson POM acts as an oxygen-donor tetradentate ligand, the Zr and Hf centers are seven-coordinate. The structure of the central $[M_2(\mu\text{-}OH)_2(H_2O)_2]^{6+}$ cation unit was very similar to that of the α-Keggin analogue $[\{\alpha\text{-}PW_{11}O_{39}M(\mu\text{-}OH)(H_2O)\}_2]^{8-}$ (M = Zr, Hf).[61] The reactivities of the mono-lacunary Keggin and mono-lacunary α_2-Dawson were very similar to each other.

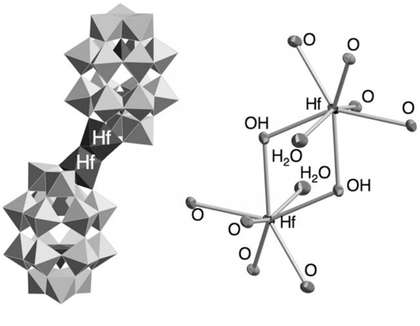


Figure 23. Polyhedral representation of the polyoxoanion $[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-}OH)(H_2O)\}_2]^{14-}$ and partial structure around the Hf_2 center.

4.3 Interconversion between Dawson 2:2- and 1:2-Type Complexes

The Dawson 2:2-type complexes $[\{\alpha_2\text{-}P_2W_{17}O_{61}M(\mu\text{-}OH)(H_2O)\}_2]^{14-}$ (M = Hf and Zr) were converted to Dawson 1:2-type complexes $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$, or vice versa, in solution under appropriate conditions.[80]

To a solution (pH 4.78) of the Dawson 2:2-type complex was added a solid form of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 22H_2O$ (two molar equivalents). After stirring for 30 min, the ^{31}P NMR spectra were measured. The formation of the Dawson 1:2-type POM $[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ was confirmed as ^{31}P resonances at δ –9.23, –13.84. The stoichiometry of the reaction is shown in Equation (5).

$$[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-}OH)(H_2O)\}_2]^{14-} + 2\,[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-} \rightarrow 2\,[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-} + 2\,H_2O + 2\,OH^- \quad (5)$$

To a solution (pH 5.71) of a separately prepared 1:2-type complex, $[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$, was added a solid form of an equimolar amount of $HfCl_2O\cdot 8H_2O$. After stirring for 30 min, the ^{31}P NMR spectra were measured. The formation of the 2:2-type complexes, $[\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-}OH)(H_2O)\}_2]^{14-}$, was confirmed as ^{31}P resonances at δ –9.81, –13.74. The reaction is represented in Equation (6).

$$[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-} + HfCl_2O + 3\,H_2O \rightarrow [\{\alpha_2\text{-}P_2W_{17}O_{61}Hf(\mu\text{-}OH)(H_2O)\}_2]^{14-} + 2\,Cl^- \quad (6)$$

The same relation was also observed for the zirconium(IV) analogues.

By decreasing the pH of the solution containing the 1:2-type complex $[M(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$, the 2:2-type complex was generated together with the saturated Dawson POM $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ and the mono-lacunary Dawson POM $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, whereas the 1:2-type complex was re-generated by increasing the pH of the final solution containing the in situ-generated 2:2-type complex. Such an interconversion has also been recently observed between the 2:2- and 1:2-type Keggin POMs.[61]

4.4 Isolation of the Geometrical Isomer of Dawson 2:2-Type Complex (2:2-Type Complex-Isomer) and Relation Among 2:2- and 1:1-Type Complexes and 2:2-Type Complex-Isomer in the Solid-State and in Solution

The relation between the 1:2- and the 2:2-type complexes derived from mono-lacunary α_2-Dawson POM is shown in

Figure 24. The relation among the 2:2- and 1:1-type complexes and the geometrical isomer of the Dawson 2:2-type complex, the last of which is here called the 2:2-type complex-isomer, in the solid-state and in solution is also summarized in Figure 24.

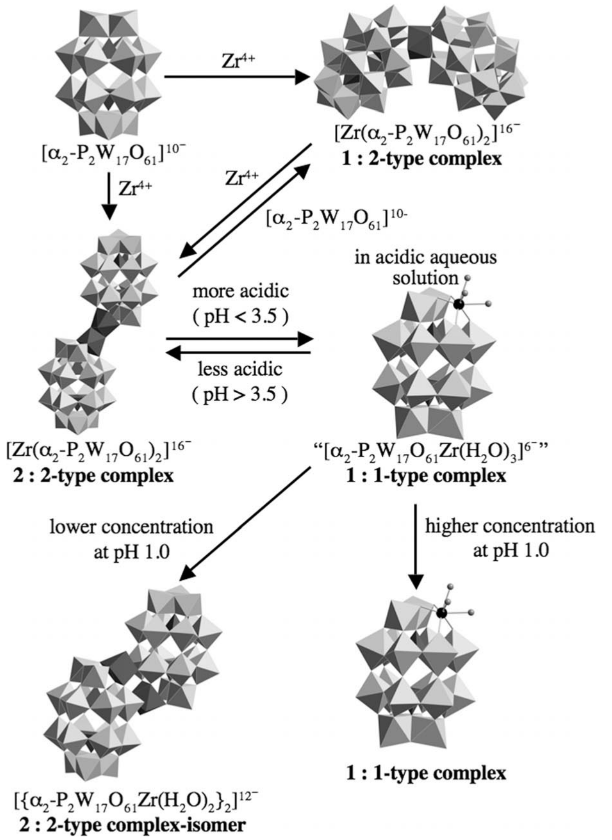


Figure 24. Relation among Dawson 2:2- and 1:1-type complexes and Dawson 2:2-type complex-isomer in the solid state and in solution.

The 1:1-type complex and 2:2-type complex-isomer were isolated by slow evaporation of an HCl-acidic solution (pH 1.0) containing the 1:1-type complex.[81] Even at pH 1.0, the formation of these two complexes was dependent upon the concentration of the complex contained in the solution. From the lower molar concentration, the 2:2-type complex-isomer was isolated, while from the higher molar concentration the 1:1-type complex was deposited.

X-ray crystallography revealed the molecular structures of the 2:2-type complex-isomer and the 1:1-type complex (Figure 24). The 2:2-type complex-isomer, $[\{\alpha_2\text{-}P_2W_{17}O_{61}Zr(H_2O)_2\}_2]^{12-}$, consists of two mono-zirconium(IV)-substituted Dawson units, "$[\alpha_2\text{-}P_2W_{17}O_{61}Zr(H_2O)_2]^{6-}$", linked through a Zr–O–W bond, in which each Zr atom is a seven-coordinate containing two terminal water molecules. The monomeric 1:1-type complex, $[\alpha_2\text{-}P_2W_{17}O_{61}Zr(H_2O)_3]^{6-}$, was isolated and its monomeric structure was confirmed, although the Zr site was disordered. The Zr atom is a seven-coordinate containing three terminal water molecules or OH^- groups. Fedin et al. have reported the structure of the 1:1-type complex as a polymeric chain structure through a Zr–O–W bond among the POMs.[82]

The solid-state ^{31}P NMR of the 2:2-type complex (as a two-line spectrum at –9.66 and –13.33 ppm), the 2:2-type complex-isomer (as a two-line spectrum at –9.45 and –13.12 ppm) and the 1:1-type complex (as a two-line spectrum at –9.74 and –13.80 ppm), all different from each other, correspond to their different crystal structures. However, their solutions, dissolved in an acidic aqueous solution, showed the same ^{31}P NMR chemical shifts at –9.97 and –13.74 ppm. Probably, these complexes would exist as the 1:1-type complex in an acidic solution.

^{31}P NMR spectra in 0.1 M aqueous HCl solutions (actually pH ≈ 1) showed a clean two-line spectrum at –9.97 and –13.71 ppm for the Dawson 2:2-type complex of Zr and at –10.08 and –13.72 ppm for the Hf analogue, both of which were slightly shifted to a higher field (ca. 0.2 ppm) than those in D_2O. Recently, Fedin et al. reported that 2:2 complexes in 1–2 M HCl undergo cleavage of the hydroxo bridges with the formation of the 1:1 complex (acidified to pH 0; an upfield displacement of 0.2 ppm of the peak attributable to the P in the hemisphere closest to the heteroatom is observed), i.e., the monomeric species $[(H_2O)_3M(P_2W_{17}O_{61})]^{6-}$ (at –10.09 and –13.83 for the Dawson 1:1-type Zr POM, and –10.23, –13.84 for the Dawson 1:1-type Hf POM).[82]

The dimeric Dawson 2:2-type complexes for Zr and Hf atoms can be reversibly converted to monomeric (1:1-type) complexes under pH-varied conditions.[80] In fact, the pH-dependent ^{31}P NMR of the dimeric 2:2-type POM of Hf in the pH range of 7.00–0.50 was examined. Under less acidic conditions (pH >3.50), the 2:2-type complex predominantly existed. At pH 3.50, both the 2:2- and 1:1-type complexes were coexistent, indicating a breaking point in the formation of the dimeric and monomeric species.[80] Under more acidic conditions (pH <3.50), the 1:1-type complex was predominantly formed. The ^{31}P NMR in a 0.1 M HCl solution (actually pH ≈ 1) is probably due to monomeric 1:1-type POMs. For the Zr analogue, similar processes were also observed.

4.5 Tetranuclear Zirconium(IV) and Hafnium(IV) Complexes: Dawson 4:2-Type Complexes (M = Zr and Hf)

The dimethylammonium salt and sodium salt (Dawson 4:2 complex) of a tetra-hafnium(IV) cluster cation species, $[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4]^{10+}$, sandwiched between two dilacunary Dawson POMs $[P_2W_{16}O_{59}]^{12-}$, i.e., $(Me_2NH_2)_{12}H_2[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]\cdot 22H_2O$ and $Na_{14}[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]\cdot 30H_2O$ were prepared and their molecular structures were successfully determined.[70] The polyoxoanion $[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$ was formed by a 1:2 molar-ratio reaction of tri-lacunary Dawson POM $[B\text{–}P_2W_{15}O_{56}]^{12-}$ with Hf^{4+} ions in an aqueous solution at pH 1.2–1.6. Dimethylammonium salt and sodium salt as crystalline solids were obtained by slow evaporation in 30.0% and 39.0% yields, respectively.

Structure analysis revealed that the polyoxoanion $[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$ was composed of a centrosymmetric assembly of a tetra-Hf^{IV} cluster cation species, $[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4]^{10+}$, sandwiched between two di-lacunary Dawson POMs, $[P_2W_{16}O_{59}]^{12-}$(Figure 25).

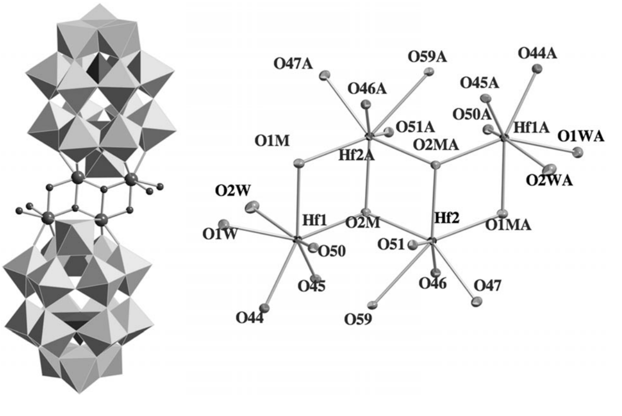


Figure 25. Polyhedral representation of the polyoxoanion $[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$ in Me_2NH_2 salt and Na salt, and partial structure around the Hf_4 center.

The coordination geometries of Hf(1) and Hf(2) are quite different. The seven-coordinate geometry around the Hf(1) center was accomplished by bonding with two bridging oxygen atoms (O1M (μ-OH), O2M (μ_3-O)), two coordinating water molecules (O1W, O2W) and three terminal oxygen atoms (O50, O45, O44) in the lacunary site of the Dawson POM. On the other hand, the seven-coordinate geometry around the Hf(2) center was composed of three bridging oxygen atoms (O1MA (μ-OH), O2M and O2MA (μ_3-O)), and four oxygen atoms (O51, O46, O47 and O59) in the lacunary site without coordinating water molecules. There is no interaction between Hf(1) and Hf(2A) nor between Hf(2) and Hf(2A). The results of bond valence sum (BVS) calculations confirm that the two "unshared" oxygen atoms (O1W, O2W: BVS. 0.398, 0.510, respectively) attached to Hf(1) correspond to water molecules. The μ_3-O atoms (O2M, O2MA; BVS. 2.117) are unprotonated, and the μ_2-O atoms (O1M, O1MA, BVS. 1.201) are OH groups. The BVS. values (1.566–2.068) of the oxygen atoms (O50, O45, O44, O51, O46, O47, O59) in the lacunary site show that they are unprotonated. The two Dawson units are equivalent, resulting in the overall C_i symmetry of the polyoxoanion molecule.

The molecular structures of the polyoxoanion $[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$ in the Me_2NH_2 salt and Na salt were isostructural with each other, and also isostructural with $[Zr_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4]^{10+}$ in the zirconium(IV) analogue reported by Pope et al.[69]

4.6 Related Compounds: Dawson 1:2-Type Complexes

As Zr^{IV}-containing Dawson POMs related to this section, Hill et al. synthesized two POMs, i.e., $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$ (Figure 26, left) and $[\{P_2W_{15}O_{54}(H_2O)_2\}Zr\{P_2W_{17}O_{61}\}]^{14-}$ (Figure 26, right), which exhibit extensive dynamic structural changes induced by completely reversible multiple protonation behavior.[83] The pH titration of $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$ indicates a dissociation of all eight protons, in agreement with structural and spectroscopic studies. These compounds were prepared as Me_2NH_2 salts from a tri-lacunary Dawson POM precursor $[P_2W_{15}O_{56}]^{12-}$ and their solid-state structures were established by single-crystal X-ray diffraction.

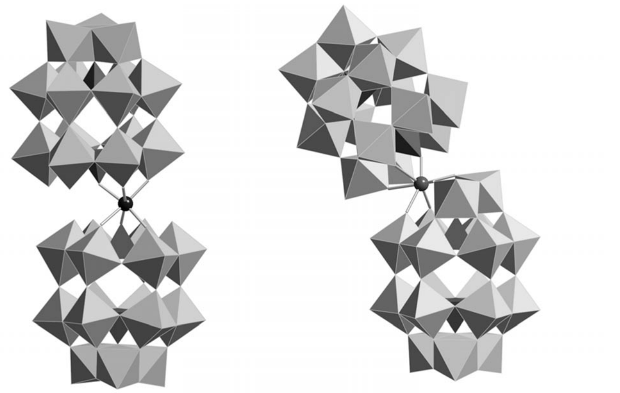

$[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$ $[\{P_2W_{15}O_{54}(H_2O)_2\}Zr\{P_2W_{17}O_{61}\}]^{14-}$

Figure 26. Polyhedral representations of $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$ (left) and $[\{P_2W_{15}O_{54}(H_2O)_2\}Zr\{P_2W_{17}O_{61}\}]^{14-}$ (right).[83]

The POM $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$ is composed of two tri-lacunary Dawson subunits $\{P_2W_{15}\}$ on either side of a single six-coordinate Zr^{IV} center. This POM possesses approximate C_2 symmetry with a twofold axis running through the Zr atom in the lacunary "pocket" that relates the two $\{P_2W_{15}\}$ units, which are slightly offset from each other. Among the four non-coordinating terminal oxo groups in each $\{P_2W_{15}\}$ unit, every second position is diprotonated. The W–OH_2 bond lengths, averaging 2.20(2) Å, are significantly longer than those of their unprotonated counterparts, averaging 1.72(2) Å. Within the lacunary pocket of this POM, the distances between the aqua oxygen atoms (diprotonated) and their neighboring oxo (non-protonated) groups [from the same and adjacent (P_2W_{15}) units] range from 2.61(3) to 3.20(3) Å, indicating the formation of a complex network of intra-POM hydrogen bonds. A similar unprotonated–diprotonated hydrogen-bonding configuration is also found in the POM $[\{P_2W_{15}O_{54}(H_2O)_2\}Zr\{P_2W_{17}O_{61}\}]^{14-}$, where a seven-coordinate Zr^{IV} atom joins two different polyoxoanion ligands: a tri-lacunary, protonated $[\alpha\text{-}P_2W_{15}O_{54}(H_2O)_2]^{8-}$ ion and a mono-vacant, unprotonated $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ion. This polyoxoanion, $[\{P_2W_{15}O_{54}(H_2O)_2\}Zr\{P_2W_{17}O_{61}\}]^{14-}$, decomposed by the addition of a 2.5 equiv. NaOD.

Hill et al. also reported the stereoselective synthesis of Zr^{IV}-containing Dawson POMs using chiral ligands, i.e., $\{[\alpha\text{-}P_2W_{15}O_{55}(H_2O)]Zr_3(\mu_3\text{-}O)(H_2O)(\text{L- or D-tartH})[\alpha\text{-}P_2W_{16}O_{59}]\}^{15-}$. The D- or L-tartrate ligand was coordinated to the tri-Zr^{IV} cluster cation, $\{Zr_3(\mu_3\text{-}O)(H_2O)\}$, sandwiched between the di-lacunary and tri-lacunary Dawson POMs (Figure 27, left).[84] In these complexes, circular dichroism (CD) spectra were observed in the absorption region of the POM chromophore. This indicated that the carbon-centered tetrahedral chirality of the L- or D-tartrate unit was transmitted to the large POM. In a similar manner, other chiral POMs, i.e., $\{[\alpha\text{-}P_2W_{16}O_{59}]_2[Zr_4(\mu_3\text{-}O)_2(\text{L- or D-malate})_2]\}^{18-}$ containing L- or D-malate as the chiral ligand, were synthesized and their crystal structures were determined (Figure 27, right).[85] Structure analysis revealed that the POMs, $\{[\alpha\text{-}P_2W_{16}O_{59}]_2[Zr_4(\mu_3\text{-}O)_2(\text{L- or D-malate})_2]\}^{18-}$, were composed of a tetra-Zr^{IV} cluster cation species, $[Zr_4(\mu_3\text{-}O)_2(\text{L- or D-malate})_2]$, sandwiched between two dilacunary Dawson POMs. The two (L- or D-malate) ligands were coordinated to the central cation unit as chiral sources. Although L,L- and D,D-form complexes were configurationally stable in solution, two *meso* complexes (i.e., L,D- and D,L-forms) were generated due to a cross-over of the malate ligands, upon mixing L,L- and D,D-forms in a 1:1 molar ratio.[85]

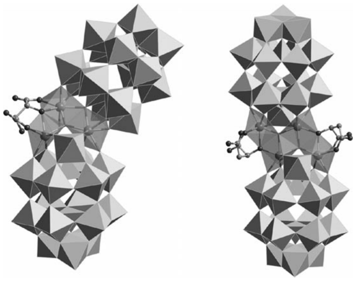


Figure 27. Polyhedral representations of $\{[\alpha\text{-}P_2W_{15}O_{55}(H_2O)]\text{-}Zr_3(\mu_3\text{-}O)(H_2O)(\text{tartH})[\alpha\text{-}P_2W_{16}O_{59}]\}^{15-}$[84] (left) and $\{[\alpha\text{-}P_2W_{16}O_{59}]_2[Zr_4(\mu_3\text{-}O)_2(\text{malate})_2]\}^{18-}$[85] (right).

Conclusions

In this microreview, we have described the chemistry of Group IV metal ion-containing POMs mainly focused on our recent research.

In the synthesis, structure and behavior in the solid state and in solution of the Group IV metal ion-containing POMs, it has been elucidated that the Zr/Hf atoms are very similar to each other, but they are quite different from the Ti atom.

Ti^{IV}-substituted Keggin POMs, derived from Keggin lacunary species such as α-mono-, γ-di-, A-tri- and B-tri-lacunary species as precursors, form oligomeric complexes in the solid state, i.e., dimers, trimers and tetramers, linked via intermolecular corner-sharing Ti–O–Ti bonds. Also, Ti^{IV}-substituted POMs, derived from Dawson lacunary species such as α_2-mono- and B-tri-lacunary species as precursors, form oligomers or sandwich complexes linked via Ti–O–Ti bonds in the solid state. Two tetrapod-shaped Dawson POM tetramers (the non-bridging tetramer and the bridging tetramer), composed of four tri-Ti-substituted Dawson POM subunits linked by intermolecular Ti–O–Ti bonds, are nano-size giant molecules, and their syntheses, molecular structures, and properties are expanding to the chemistry of Dawson tetramers. Of particular note is the fact that the encapsulated ions in the central cavity of the non-bridging tetramer can be exchanged among the anions, and even between the anion and cation by controlling the pH of the solution. Such an exchange of encapsulated ions may be considered as a biomimetic-inorganic model of ion channel structures in biological systems.

In contrast to corner-sharing polyhedral Ti-substituted units, the structures of Zr^{IV}/Hf^{IV}-containing POMs are composed of cluster cations of edge-sharing Zr/Hf polyhedra sandwiched between two lacunary Dawson POMs. The Zr/Hf centers in the POMs show higher coordination numbers (6, 7 and 8), compared with the six-coordinate Ti atom. The pH-dependent interconversion between the dimeric and monomeric species of the Zr/Hf-containing POMs is quite opposite to that of the Ti-substituted POMs.

As far as Ti-substitution in α-Keggin structure is concerned, the bridge between the lab and the environment has been found in the fundamental building block of the mineral murataite, which contains the α-Keggin structure of $[ZnTi_{12}O_{40}]^{30-}$ containing Zn^{2+} as a heteroatom and 12 Ti^{4+} atoms as metals constituting the framework.[49] This unique and highly-charged molecular anion, $[ZnTi_{12}O_{40}]^{30-}$, may be one of ultimate forms of Ti-substitution in α-Keggin POM. Isolation of $[ZnTi_{12}O_{40}]^{30-}$ is one of challenging issue in the synthetic POM chemistry, although we are not sure whether it can be synthesized or not.

From the viewpoint of catalysis, Group IV metal ion-containing POMs have also attracted much attention. We have evaluated the catalytic activities of mono-, di-, tri- and one host-two guest type Ti^{IV}-substituted Keggin POMs in regard to aqueous H_2O_2-based epoxidation of olefin.[26–28] The structures around the Ti centers had a strong influence on the catalytic activities. We also reported that the giant tetramers of Dawson POMs can function as photocatalysts, under irradiation with UV/Vis light, to generate H_2 based on the reduction of H^+ from aqueous glycerin in the presence of H_2SO_4, without requiring any co-catalyst.[86] This photocatalytic reaction using Ti^{IV}-substituted Dawson POM oligomers is very promising, especially from the viewpoint of a clean energy system and/or green chemistry. At present, studies in this direction are in progress. Studies on oxidation catalysis and Lewis acid catalysis by Zr/Hf-containing POMs are also in progress. The multiple structures found in Group IV metal ion-containing POMs in our research will be useful for the design of various catalysts. Those data will be reported in due course.

The discussion in the present microreview has been strictly limited to species based on Keggin and Dawson POMs. However, the expansion of Group IV metal ion-containing POM chemistry in the future may involve other heteropolyanion or even isopolyanion ligands that are not discussed here or not yet discovered.

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