

Abstract

論文の内容の要旨

論文題目 Study on Development of Sequential Synthesis Methods for
Constructing Multinuclear Metal Clusters by Using Multivacant
Lacunary Polyoxometalates
(多欠損型ポリオキソメタレートを用いた金属多核構造
の逐次的合成法開発に関する研究)

氏 名 湊 拓生

1. Introduction

Numerous types of multinuclear metal clusters within organic and inorganic ligands are known to exhibit unique chemical and physical properties that are largely dependent on the types, nuclearities, combinations, and coordination geometries of the constituent metal cations. Therefore, to develop novel molecular materials that possess

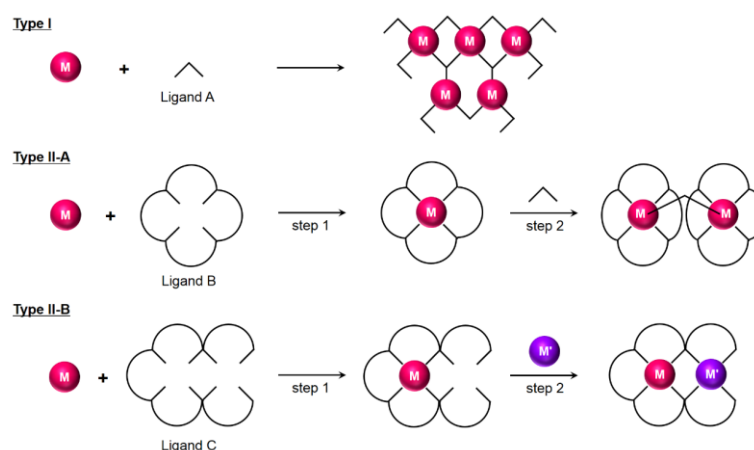


Figure 1. Synthesis methods for multinuclear metal clusters.

excellent catalytic, redox, luminescent, and magnetic properties, it is extremely important to precisely synthesize multinuclear metal clusters as designed at the atomic level and to control their properties by slightly changing the structures and coordination geometries of their metal cations. However, these multinuclear metal clusters have been synthesized mainly by the empirical one-step reactions of metal sources with ligands (type I), thus making it difficult to predict the structures of the final products and to control the structures precisely (Figure 1). Conversely, the synthesis of multinuclear metal clusters by multistep reactions is effective for constructing these structures as designed (type II), and the precise arrangement of metal cations in the proper positions has been partially achieved (Figure 1). However, the synthesis of multinuclear metal clusters of different types and nuclearities is still quite difficult even by using highly designed multidentate organic or inorganic (lacunary polyoxometalate (POM)) ligands through the type II-B sequential synthesis method (Figure 1). Accordingly, several problems must be overcome to achieve the truly rational synthesis of multinuclear metal clusters possessing many cation types and nuclearities: i) difficulties in synthesis and design of

multidentate organic ligands; ii) difficulties in suppressing the undesired type II-A-like condensation of metal-containing units; iii) difficulties in suppressing the decomposition and isomerization of lacunary POMs in aqueous media; iv) low number of interaction sites in organic-solvent-soluble lacunary POMs.

In this thesis, organic-solvent-soluble multivacant lacunary POMs that overcome all of these difficulties are focused. It is expected that they could act as rigid multidentate inorganic ligands that possess more coordination sites than conventional organic ligands and enable the synthesis of multinuclear metal clusters by the type II-B sequential synthesis. In addition, the type II-B sequential introduction of metal cations into the vacant sites of multivacant lacunary POMs in organic media could suppress the undesired decomposition and isomerization reactions of the anion frameworks and allow the stoichiometric sequential multinucleation. Thus, organic-solvent-soluble multivacant lacunary POMs could be synthesized, they could be used as novel rigid inorganic ligands, and the rational synthesis of multinuclear metal clusters with many cation types and nuclearities would be possible. Based on these idea, the development of a rational synthesis method for multinuclear metal clusters of different types and nuclearities was performed using organic-solvent-soluble multivacant lacunary POMs.

2. Synthesis of organic solvent soluble multivacant lacunary polyoxometalates

Three types of organic solvent-soluble trivacant (**XW9**, X = Si, Ge) and hexavacant (**P2W12**) lacunary POMs were successfully synthesized by carefully controlling synthetic conditions, such as amounts of TBABr (TBA = tetra-*n*-butylammonium), types of buffer solutions or acids, pH values, temperatures, and ionic strengths (Figure 2). These multivacant lacunary POMs easily dissolved in various kinds of organic solvents. The dimerization of **SiW9** proceeded just by dissolving it in acetone, dichloromethane, 1,2-dichloroethane, or nitromethane. In order to suppress the dimerization of **SiW9**, several alkoxy groups were introduced into the vacant sites as protecting groups. The reaction of **XW9** (X = Si, Ge) with methanol resulted in the

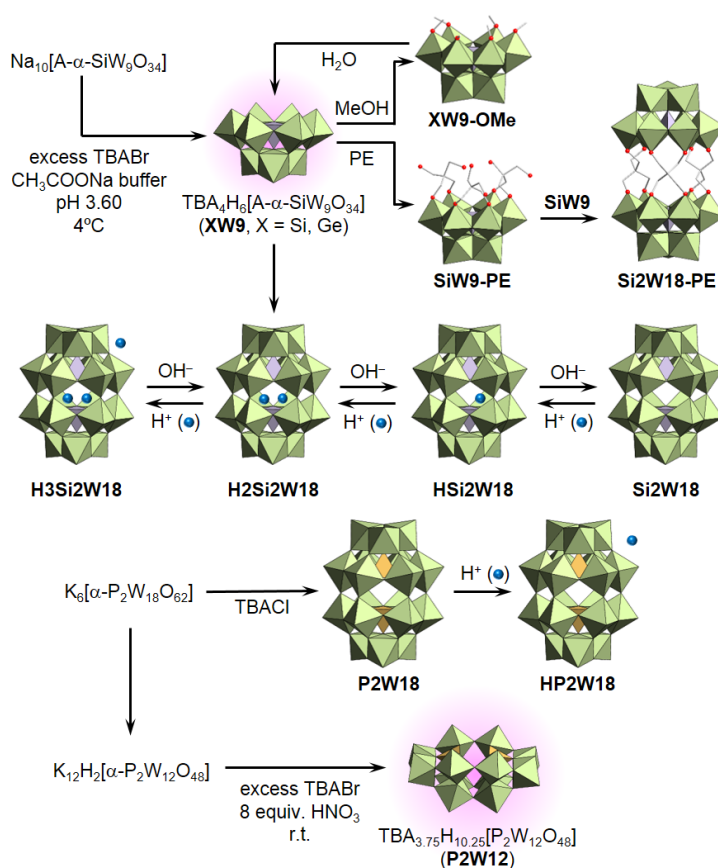


Figure 2. Synthesis of multivacant lacunary POMs.

introduction of six methoxy groups into the vacant sites (**XW9-OMe**). Furthermore, the reaction of **SiW9** with pentaerythritol (PE) resulted in the introduction of bidentate alkoxy groups into

the vacant sites (**SiW9-PE**). The methoxy groups of **SiW9-OMe** were easily dissociated by addition of water, while multidentate alkoxy groups of **SiW9-PE** were hardly dissociated even in the presence of water. Moreover, the dimeric structures **SiXW18-PE** ($X = \text{Si, Ge}$) with the same or different heteroatoms could also be synthesized by reacting **SiW9-PE** with trivacant lacunary Keggin-type POMs. These compounds were the first examples of alkoxides of lacunary POMs. The CSI mass and NMR measurements indicated alkoxy groups could also be introduced into the vacant sites of **P2W12** to stabilize its monomeric structure. It is highly expected that these multivacant lacunary POMs can be utilized as precursors for constructing multinuclear metal clusters.

The dimerization of **SiW9** resulted in the formation of a silicon-centered α -Dawson-type POM (**H2Si2W18**). Interestingly, **H2Si2W18** possessed two protons inside the cage-like anion structure through intramolecular hydrogen bonds. These two protons could reversibly be deprotonated (in the presence of base) and protonated (in the presence of acid) inside the aperture. Conversely, phosphorus-centered α -Dawson-type POM (**P2W18**) could not capture protons inside the aperture. Additionally, non-protonated **Si2W18** showed the excellent base catalysis for the Knoevenagel condensation as compared with other multivacant lacunary POMs (**SiW9**, **GeW9**, **P2W12**) and **P2W18**.

3. Synthesis of multinuclear metal clusters by using trivacant lacunary polyoxometalates

By utilizing organic solvent-soluble trivacant lacunary POMs, various types of multinuclear metal oxo clusters were successfully synthesized through the type II-B sequential synthesis method. By reacting **SiW9** with 0.5 equivalents of metal cations, various types of mononuclear $\{M\}$ in $\text{TBA}_7\text{H}_n[(A-\alpha\text{-SiW}_9\text{O}_{34})M]$ (**I_M**; $M = \text{Cr}^{3+}, \text{V}^{3+}, \text{Mn}^{3+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Ga}^{3+}$) were successfully synthesized (Figure 3). Since $\{M\}$ in **I_M** possessed distorted octahedral

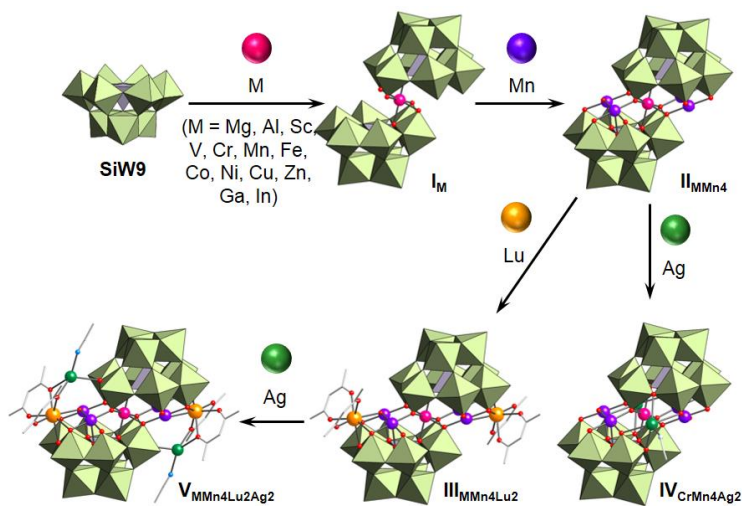


Figure 3. Synthesis of multinuclear metal clusters using trivacant lacunary POMs.

geometry, **I_{Fe}** showed the SMM property. As **I_M** still possessed the vacant sites, further introduction of metal cations could be possible. By reacting **I_M** with 4 equivalents of Mn^{3+} , heteropentanuclear $\{\text{MMn}_4\}$ clusters in $\text{TBA}_7[(A-\alpha\text{-SiW}_9\text{O}_{34})\text{MMn}_4(\text{OH})_2]$ (**II_{MMn4}**) were successfully synthesized. **II_{MMn4}** ($M = \text{Mn, Fe, V}$) showed SMM properties even under the zero external magnetic dc field. Additionally, further installation of metal cations was possible because **II_{MMn4}** still possessed pseudo vacant sites. By installing Ag^+ or Lu^{3+} into **II_{MMn4}**, trimetallic heptanuclear $\{\text{MMn}_4\text{Lu}_2\}$ clusters in $\text{TBA}_7[(A-\alpha\text{-SiW}_9\text{O}_{34})\text{MMn}_4\text{O}_2\{\text{Lu}(\text{acac})_2\}_2]$ (**III_{MMn4Lu2}**) or $\{\text{MMn}_4\text{Ag}_2\}$ clusters in $\text{TBA}_5[(A-\alpha\text{-SiW}_9\text{O}_{34})\text{MMn}_4(\text{OH})_2\{\text{Ag}(\text{CH}_3\text{CN})\}_2]$ (**IV_{MMn4Ag2}**) were successfully synthesized. Furthermore, by installing Ag^+ into **III_{MMn4Lu2}**, tetrametallic nonanuclear $\{\text{MMn}_4\text{Lu}_2\text{Ag}_2\}$ clusters in

TBA₅[(A- α -SiW₉O₃₄)MMn₄O₂{Lu(acac)₂}₂{Ag(CH₃CN)}₂] (**V**_{MMn₄Lu₂Ag₂}) with the widest variety of metal cations (i.e., M, Mn, Lu, Ag, and W) among the discrete multinuclear heterometallic oxo clusters previously reported. Particularly, **V**_{FeMn₄Lu₂Na₂} showed SMM property with the highest energy barrier ($U_{\text{eff}} = 40.3$ K) among the previously reported transition metal-containing POMs. A series of compounds possessing {CrMn₄} paramagnetic metal units with slightly different coordination geometries (**II**_{CrMn₄}, **III**_{CrMn₄Lu₂}, **IV**_{CrMn₄Ag₂}, and **V**_{CrMn₄Lu₂Ag₂}) allowed the investigation of their magneto-structural correlations, resulting in the proportional relation between the Cr–O–Mn bond angles and the corresponding magnetic superexchange interactions.

Based on these results, it was demonstrated that the type II-B synthesis method by using multivacant lacunary POMs was quite effective for constructing multinuclear metal clusters possessing the large number of types and nuclearities of metal cations. By utilizing this sequential synthetic protocol, the precise design of metal cations in multinuclear metal clusters was possible, which leads to the fine and rational control of their chemical and physical properties.

4. Synthesis of multinuclear metal clusters by using hexavacant lacunary polyoxometalates

By using multiple types of interaction sites to imitate the disassembly and reassembly processes in biological systems, structural transformation of the anion of giant ring-shaped POM oligomers has been successfully demonstrated for the first time (Figure 4). Since **P2W12** possess two types of vacant sites, the introduction of Mn cations into the respective vacant sites successfully lead to constructing structurally defined two types of interaction sites. By protecting these interaction sites, a giant ring-shaped hexamer of monomeric {P₂W₁₂O₄₈Mn₄} units (**VI**) was successfully constructed. The hexameric structure of **VI** was disassembled without the undesired decomposition and isomerization reactions simply by dissolving in acetonitrile. Importantly, the removal of protecting capping organic ligands on interaction sites in monomeric {P₂W₁₂O₄₈Mn₄} units were triggered by addition of base, resulting in the successful reassembly into a tetramer **VII**. In **VI** and **VII**, the nuclearities, anion sizes, shapes of the rings, and magnetic properties were drastically changed by a new type of sequential synthesis method “disassembly/reassembly”, which was different from type I and type II synthesis methods for constructing multinuclear metal clusters. Therefore, utilizing multiple types of interaction sites for proceeding disassembly and reassembly processes leads to complicated structural rearrangement and expands the methodology for the synthesis of giant molecules and multinuclear metal clusters in artificial systems.

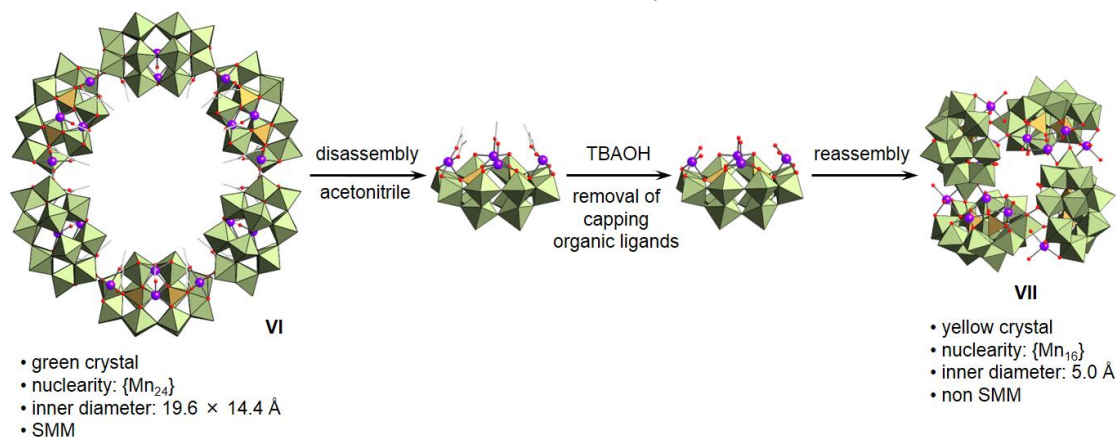


Figure 4. Synthesis of multinuclear metal clusters using hexavacant lacunary POMs.