論文の要旨

題　目　Synthesis and Characterization of Novel Preyssler-type Polyoxometalates by Migration of Encapsulated Cation and Substitution of Framework Tungsten
（　内包カチオンの移動と骨格タングステンの置換による新規 Preyssler 型ポリオキソメタレートの合成と構造解析　）

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Abstract

Investigations of Preyssler-type polyoxometalates (POMs) have increased recently due to their interesting properties, such as rigid framework, redox properties, acidic properties, and open cavity for metal cation encapsulation. These properties give Preyssler-type POMs potential applications in catalysis, magnetism, photochemistry, medicine, staining agents, and broader fields. The objectives of this doctoral research were to design novel Preyssler-type POMs and structurally characterize them. Preyssler-type POMs were prepared under hydrothermal conditions and modified based on the goals of this research.

Chapter 1 summarizes the progress and prospects of POMs from platonic solids to diverse applications, the history of Preyssler-type POMs (a large cluster of the POM family), and Pope et al.'s revised structure determined by single-crystal X-ray diffraction. Their structure presented open challenges to numerous researchers worldwide to design novel Preyssler-type POMs related to certain applications, such as catalysis, photochemistry, magnetism, and broader fields. This chapter briefly describes six strategies for designing novel Preyssler-type POMs those are: substitution of metal encapsulated, extending the Preyssler-type framework by organic–inorganic hybrids, mixing the addenda of the Preyssler-type framework, hetero-element replacement in the Preyssler-type framework, shifting the position of encapsulated metal, and reduction of the encapsulated metal and or the framework. The outline and declaration of the problems stated in this chapter motivated the scope of the research presented herein.

Chapter 2 explains the degradation behavior of a Preyssler-type phosphotungstate to a Keggin-type derivative in slightly acidic media. Our group reported the synthesis of a di-potassium encapsulated derivative, $[P_5W_{30}O_{110}K_2]^{13-}$, from the hydrothermal reaction of $[P_5W_{30}O_{110}Bi(H_2O)]^{12-}$ in acetate buffer of pH 4.7 in the presence of potassium chloride (KCl). At the end of this reaction, we detected a side product confirmed as a new compound containing Bi^{3+} and mono-lacunary Keggin-type phosphotungstate $[\alpha\text{-}PW_{11}O_{39}]^{7-}$. A preliminary study of the side product via infrared (IR) spectroscopy identified the similarity bands in phosphotungstate $[PW_{11}O_{39}]^{7-}$, whereas the ^{31}P nuclear magnetic resonance (NMR) measurement revealed a chemical shift. Electrospray ionization–mass

spectroscopy (ESI–MS) measurement detected $[PW_{11}O_{39}Bi]^{4-}$ in the solution, indicating the presence of Bi^{3+} in this new unknown species. Based on this result, I first believed the species to be a Preyssler-type phosphotungstate divided into small pieces and detected as Keggin-type derivatives. This result motivated us to interact Bi^{3+} with mono-lacunary Keggin-type phosphotungstate $[\alpha\text{-}PW_{11}O_{39}]^{7-}$. The ^{31}P NMR spectrum of the solution obtained by mixing $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ and Bi^{3+} with a ratio of 2:1 with time course investigation contained a single signal at -11.38 ppm after 24 h, which was different from those of the $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ species. This indicated that the detected species was new. When the mixing ratio was increased to 1:1, a signal appeared at -11.58 ppm, confirming another new species. I also performed reactions with several different ratios of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ and Bi^{3+}. For the 2:1 complex, structural analysis revealed a sandwich architecture similar to that of the Peacock and Weakley anion in a lanthanide derivative. This finding suggested that Bi^{3+} could imitate the behavior of Ln^{3+} in POMs.

Chapter 3 discusses the migration of a sodium ion in the cavity of a Preyssler-type phosphotungstate. Recently, our group reported that a di-potassium encapsulated derivative, $K_{13}[P_5W_{30}O_{110}K_2]$, could be produced by heating $K_{14}[P_5W_{30}O_{110}K]$ at 300 °C for 1 h under solid-state conditions. This was the first method to insert a counter cation in the Preyssler cavity. I applied this method to $K_{14}[P_5W_{30}O_{110}Na(H_2O)]$ under similar conditions. The ^{31}P NMR spectrum contained four signals corresponding to parent species $[P_5W_{30}O_{110}K]^{14-}$ and $[P_5W_{30}O_{110}K_2]^{13-}$ and a new species. The potassium-encapsulated derivative was obtained by potassium counter cation migration into the cavity. To prevent potassium contamination, I exchanged it with $Na_{14}[P_5W_{30}O_{110}Na(H_2O)]$ and heated it in the range of 200–600 °C for 1 h. The ^{31}P NMR spectra exhibited one signal when $Na_{14}[P_5W_{30}O_{110}Na(H_2O)]$ was heated at 300 °C. At a relatively higher temperature, the Preyssler-type framework began to decompose into smaller classes, such as Keggin and Dawson types. Therefore, 300 °C was the optimal condition to prepare this new species. Structural analysis revealed that the new species was a Preyssler-type phosphotungstate containing one sodium in the central cavity. I also confirmed this structure via elemental analysis, NMR, IR, and ESI–MS techniques.

Chapter 4 explains the solid-state transformation behavior of Preyssler-type phosphotungstate. Motivated by the results presented in Chapter 3, I continued to investigate the transformation of potassium salt and protonic forms of $[P_5W_{30}O_{110}Na(x)]^{14-}$ (x = in the side or center position). I monitored the thermal transformations of $K_{14}[P_5W_{30}O_{110}Na(H_2O)]$, $K_{14}[P_5W_{30}O_{110}Na(center)]$, $H_{14}[P_5W_{30}O_{110}Na(H_2O)]$, and $H_{14}[P_5W_{30}O_{110}Na(center)]$. I also monitored the thermal time course of $K_{14}[P_5W_{30}O_{110}Na(x)]$ (x = in the side or center position). The ^{31}P NMR spectra showed that the thermal behavior of $K_{14}[P_5W_{30}O_{110}Na(x)]$ (x = in the side center position) was similar to that of insertion of potassium counter cations in the Preyssler cavity, and mono-potassium and di-potassium-encapsulated derivatives were detected as the major species in both the compounds with treatment above 400 °C. The $[P_5W_{30}O_{110}Na(center)]^{14-}$ species was present as the major product when $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ was heated at 300 °C for 1 h; increasing the temperature caused the potassium-encapsulated derivative to increase. No potassium-encapsulated derivative was detected in the thermal treatment of $[P_5W_{30}O_{110}Na(x)]^{14-}$ (x = in the side or center position) used in the protonic form. I identified the equilibrium migration behavior of the encapsulated sodium located at the side or center position. Migration from the side to the center position was revealed in $H_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ and vice versa in $H_{14}[P_5W_{30}O_{110}Na(center)]$, where the encapsulated sodium migrated from the center to the side position. A slow conversion of $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$ to $[P_5W_{30}O_{110}K_2]^{13-}$ was also observed when dissolving potassium salts with a H_2O-drying method.

Chapter 5 discusses the incorporation of molybdate $[MoO_4]^{2-}$ into the Preyssler-type framework. In this study, I constructed a new Preyssler-type phosphotungstate, $[P_5W_{30-x}Mo_xO_{110}Na(H_2O)]^{14}$, where Mo was substituted into the framework via the self-assembly reaction of $[WO_4]^{2-}$ and $[MoO_4]^{2-}$ in the presence of phosphoric acid under hydrothermal conditions. I performed this reaction with different ratios of tungstate and molybdate (W:Mo): 11:0, 10;1, 9;2, 8;3, 7;4, 6;5, 3;8, 1;10, and 0;11. Preyssler-type species were detected when the reactions were performed with W:Mo ratios of 11:0, 10:1, 9:2, 8:3, and 7:4. Increasing the number of Mo atoms in the reaction increased the number of substituted Mo atoms in the Preyssler framework. No Preyssler-type species were obtained when Mo:W was higher than 7:4. Structural analysis confirmed the DFT calculation result that the preferred site for Mo substitution was in the belt of the framework or close to the encapsulated Na, rather than both the cap positions. I also confirmed this structure via elemental analysis, NMR, IR, and ESI–MS techniques.

Chapter 6 summarizes the finding of this study and suggest future research concepts.