学 位 論 文 概 要

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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In Chapter 1, I summarized the fundamental aspect of POMs, which include the timeline discovery of each subclass of POMs. In this part, I chose the Preyssler-type POMs as the main topic in this report. The state of the art of Preyssler-type POMs and its progress inspired me to study these clusters more intensively.

Therefore, in Chapter 2, I studied the degradation of Preyssler-type into Keggin-type POMs when the new unknown solid containing Keggin-type phosphotungstate and bismuth is found under preparation of $[P_5W_{30}O_{110}K_2]^{13-}$ in acetate buffer. The mixing ratio of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ and Bi^{3+} reached 2:1 and 1:1 produced Weakley-type $[(PW_{11}O_{39})_2Bi]^{11-}$ and $[PW_{11}O_{39}Bi]^{4-}$ complexes, respectively. Complexes of $[(PW_{11}O_{39})_2Bi]^{11-}$ were successfully isolated as tetramethyl ammonium and potassium salts and were characterized by single-crystal XRD, IR, and elemental analysis. The sandwich structures of $[(CH_3)_4N]_{11}[(PW_{11}O_{39})_2Bi]$ and $K_{11}[(PW_{11}O_{39})_2Bi]$ were constructed through the eight Bi–O bonds with two $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ units. This confirmed the degradation of $[P_5W_{30}O_{110}Bi(H_2O)]^{12-}$ into $[(PW_{11}O_{39})_2Bi]^{11-}$ during preparation of $[P_5W_{30}O_{110}K_2]^{13-}$ in acetate buffer solution.

In Chapter 3, I investigated sodium ion migration in the cavity of Preyssler-type phosphotungstate. Inspired by our previous work on K^+ counter cation insertion into $[P_5W_{30}O_{110}K]^{14-}$ and forming $[P_5W_{30}O_{110}K_2]^{13-}$ by heat treatment of $K_{14}[P_5W_{30}O_{110}K]$ at 300 °C. I started to heat $K_{14}[P_5W_{30}O_{110}Na(H_2O)]$ at similar temperatures to $K_{14}[P_5W_{30}O_{110}K]$. ^{31}P NMR spectroscopy detected four signals attributable to $[P_5W_{30}O_{110}Na(H_2O)]^{14-}$, $[P_5W_{30}O_{110}K]^{14-}$, $[P_5W_{30}O_{110}K_2]^{13-}$, and a new species, respectively. The single-crystal structural analysis revealed that the sodium ion occupied the central cavity of Preyssler-type phosphotungstate.

In Chapter 4, I continued the investigation of thermal treatment of Preyssler molecules by employing $[P_5W_{30}O_{110}Na(x)]^{14-}$ (x = in the side or center position) as potassium salts and protonic form. Thermal monitoring at 300 °C and 400 °C and characterization by ^{31}P NMR and IR spectroscopy showed the migration of sodium encapsulated inside the Preyssler cavity and insertion of potassium counter cation to the framework.

In Chapter 5, I synthesized the novel Preyssler-type compound designed by molybdate incorporation into the {30 WO_4} framework via self-assembly reaction under hydrothermal conditions. The formation of $[P_5W_{30-x}Mo_xO_{110}Na(H_2O)]^{14-}$ and the number of molybdenum substituting tungsten in the framework depended on the mixing ratio of $[WO_4]^{2-}$ and $[MoO_4]^{2-}$.

In this dissertation, I successfully synthesized several novel Preyssler-type POMs and one Weakley-type compound, $[(PW_{11}O_{39})_2Bi]^{11-}$, which formed due to degradation of a Preyssler molecule in acetate buffer media. The unique behavior of Preyssler-type POMs and their diverse structure mean there are still unexplored paths.