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学位論文内容の要旨

博士 (環境科学)

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学位論文題名

Self-assembled structure and magnetism of lanthanoid multinuclear complexes
with lacunary polyoxometalate ligands
(欠損型ポリオキソメタレート配位子を有するランタノイド多核錯体の自己組織化構造と
磁性)

Single-molecule magnets (SMMs) can be applied to ultra-high-density data storage,¹ quantum computing, and spintronics and attracting much attention in recent years. SMMs are paramagnetic metal complexes exhibiting low-frequency molecular magnetization reversal at low temperatures. They are "molecule-sized permanent magnets" that exhibit magnetic hysteresis as ferromagnets, although they have no magnetic long-range order. A number of polynuclear complexes of lanthanides have been developed, due to their large magnetic moments. The spatial isolation of magnetic molecules in crystals is important for the manifestation of SMM properties. The coordination sphere around the magnetic ions also greatly affects the magnetic interactions within the multinuclear complex.

In this thesis I have explored the magnetic properties of multinuclear lanthanide complexes with α -lacunary Keggin POMs as a ligand, which has many active oxygen sites and a clear symmetry, by controlling the arrangement of the complexes using the symmetry and self-organizing ability of the counter cations.

In Chapter 3, I discussed the effect of simple ammonium counter cations on the symmetry of lanthanide trinuclear triangle (Ln_3CO_3) units formed by a μ_3 - η^2 : η^2 : η^2 -carbonate ligand sandwiched by a lacunary Keggin POMs [PW_9O_{34}] with C_{3v} symmetry. Simple ammonium cations, methylammonium, dimethylammonium, trimethylammonium, tetramethylammonium and diprotonated 1,4-diazabicyclo[2.2.2]octane with the symmetry of $C_{\infty v}$, C_{2v} , C_{3v} , T_d and D_{3h} , respectively, were provided. Ten sandwich-type POMs $(\text{CH}_3\text{NH}_3^+)_{10}\text{Na}[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OLn})_3\text{CO}_3]$ ($\text{Ln} = \text{Tb}, \text{Dy}, \text{Er}$ and Y for crystals **1-Tb**, **1-Dy**, **1-Er** and **1-Y**, respectively, MA = methylammonium), $((\text{CH}_3)_2\text{NH}_2^+)_{11}[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OTb})_3\text{CO}_3]$ (2) (DMA = dimethylammonium), $(\text{CH}_3)_3\text{NH}^+)_{8}\text{Na}_3[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OTb})_3\text{CO}_3]$ (3), (TriMA = trimethylammonium), $(\text{CH}_3)_4\text{N}^+)_{6}\text{Na}_5[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OTb})_3\text{CO}_3]$ (4), (TMA = tetramethylammonium), and $(\text{H}_2\text{DABCO}^{2+})_6[(\text{PW}_9\text{O}_{34})_2(\text{H}_2\text{OLn})_3\text{CO}_3](\text{BF}_4)$ ($\text{Ln} = \text{Er}, \text{Dy}$ and Tb for crystals **5-Er**, **5-Dy**

and **5-Tb**, respectively), were synthesized. Crystals **1** and **4** gave space groups with high symmetry, $P6_3/m$ and $R\bar{3}m$, respectively, and an equilateral triangular (Ln_3CO_3) structure was maintained in the complex. The highly symmetric structure of these crystals is induced by the supramolecular structure formed by hydrogen bonding between ammonium derivatives and water molecules. The number of hydrogen-bonding sites is one of the critical parameters that leads to the high symmetry of the crystals. Crystals **2** and **3** take the polar space groups $Pna2_1$ and $Cmc2_1$, respectively, because the DMA^+ and TriMA^+ cations have low symmetry and only two and one hydrogen bonding sites, respectively. In crystal **5**, another highly symmetric space group of $P6_3/mcm$ was achieved by the introduction of a highly symmetric cation, the equilateral triangle Ln was not maintained. Crystals **1-Tb**, **1-Dy**, **1-Er**, **2**, **3** and **4** exhibited a slow relaxation of magnetization typical of single molecular magnets in temperature-dependent ac susceptibility measurements under static magnetic field.

In chapter 4, the supramolecular approach is adopted to isolate SMM structures in crystals. With $(\text{Na}^+)(\text{B18C6})$ (B18C6 = benzo[18]crown-6) as a counter cation, we succeeded in isolating three O^{2-} bridged dinuclear Ln complexes with lacunary Keggin ligands $[(\text{PW}_{11}\text{O}_{39})\text{Ln}(\text{H}_2\text{O})_2]_2\text{O}$ (Ln_2POM) in the crystal, $[(\text{Na}^+)(\text{B18C6})]_2[(\text{Na}^+)(\text{B18C6})(\text{H}_2\text{O})]_4[(\text{Na}^+)(\text{B18C6})(\text{H}_2\text{O})_2]_2[(\text{Na}^+)_2(\text{B18C6})_2(\text{H}_2\text{O})_3][(\text{PW}_{11}\text{O}_{39})\text{Ln}(\text{H}_2\text{O})_2]_2\text{O}$ ($\text{Ln} = \text{Dy}, \text{Er}$ and Tb for **6-Dy**, **6-Er** and **6-Tb** respectively). $(\text{Na}^+)(\text{B18C6})$ was one-dimensionally arranged in the crystal, forming a bamboo-like channel structure. Ln_2POM units were embedded between "bamboo nodes" and completely isolated from neighboring complexes. Thus, it was possible to evaluate the magnetic properties of Ln_2POM as a single molecule. Weak ferromagnetic interactions between Dy^{3+} ions bridged by O^{2-} were observed. Dy_2POM (**6-Dy**) and Er_2POM (**6-Er**) display magnetic relaxation characteristics of SMMs at low temperatures. Magnetic relaxation proceeded via the Orbach process, and the absolute values of the effective energy barrier and relaxation time were estimated. The supramolecular approach is extremely useful for realizing isolated SMM structures in crystals.

In chapter 5, besides the lanthanoid complexes, the effect of supramolecular cation symmetry on POM assembly was investigated using a simple Dawson structure. By introducing two kinds of supramolecular cations with different symmetry, two crystal structures with highly symmetric space group of $P4/ncc$ and low symmetric space group of $Pbca$ are achieved in crystals $[(\text{Na}^+)_2(\text{DB}[24]\text{crown-8})]_2[(\text{W}_{10}\text{O}_{32})]$ (**7**) and $[(\text{Na}^+)(\text{DB}[24]\text{crown-8})]_2[(\text{W}_{10}\text{O}_{32})]$ (**8**) ($\text{DB}[24]\text{crown-8}$ = dibenzo[24]crown-8), respectively. In crystal **7**, the $[(\text{Na}^+)_2(\text{DB}[24]\text{crown-8})]$ supramolecular cation with C_2 symmetry compatible to the C_4 axis of the $[\text{W}_{10}\text{O}_{32}]^{4-}$ anion achieves a highly symmetric crystal structure. However, the $[(\text{Na}^+)(\text{DB}[24]\text{crown-8})]$ supramolecular cation in crystal **8** is distorted, resulting in a crystal structure with low symmetry.