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Cover Profile

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New Path for Polyoxometalates: Controlled Synthesis and Characterization of Metal-Substituted Tungstosulfates


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Invited for the cover of this issue are Tadaharu Ueda, Kochi University, and co-workers from Okayama University and Hiroshima University, Japan. The cover image shows the synthesis of metal-substituted tungstosulfates via $[(S_2W_{14}O_{54})_3]^{32-}$ with a unique cavity structure from $(S_2W_{18}O_{62})^{4-}$].

What is the most significant result of this study?

Development of systematic synthetic procedures for metal-substituted tungstosulfates. Many metal-substituted tungstophosphates and tungstosilicates have been prepared, characterized, and applied to various fields (especially catalysis for water oxidation) because the lacunary species, which have defect parts in the polyoxometalate (POM) framework, can be prepared systematically from the parent POMs or reaction mixtures by a sophisticated pH control. We have synthesized the lacunary tungstosulfates $[(S_2W_{14}O_{54})_3]^{32-}$, which can be reacted with any transition metal ion to form the corresponding metal-substituted tungstosulfates. This finding would advance the chemistry of POMs.

Did you expect a very different outcome? If so, what was your initial guess?

Synthesis of $[(S_2W_{14}O_{54})_3]^{32-}$ with a unique cavity structure. Initially, we surmised that the species after weak-base treatment of $[S_2W_{18}O_{62}]^{4-}$ with a Wells-Dawson type structure was $[S_2W_{17}O_{61}]^{8-}$, like that obtained from the synthesis of $[P_2W_{17}O_{61}]^{10-}$ from $[P_2W_{18}O_{62}]^{6-}$. The structure of $[(S_2W_{14}O_{54})_3]^{32-}$, as determined by X-ray crystallography, was completely different from those of previously reported POMs with a cavity.

Is your current research mainly curiosity-driven or rather applied?

Our group has focused on fundamental studies of the synthesis and electrochemical properties of (novel) polyoxometalates. Numerous POMs give beautiful voltammetric waves that are indicative of excellent catalysis (e.g., water-oxidation) and electron storage (e.g., super capacitors). However, the voltammetric behavior of POMs is too complicated for a complete understanding of all the aspects. We have tried to elucidate the detailed electrochemical reaction mechanism of POMs under various conditions with the help of EPR, NMR, and simulations of voltammograms. We believe that our results provide useful information to many researchers studying the applications of POMs.

What other topics are you working on at the moment?

We have developed an electrochemical method for evaluation of the antioxidant capacity of food and beverages using POMs as electrochemical probes. Well-known spectrophotometric evaluation methods, such as the ORAC and DPPH methods, require expensive apparatus and great skill, whereas the method we developed is low-cost and can easily be used for measuring the antioxidant capacity with high accuracy and precision.

What was the inspiration for this cover design?

POMs have been extensively investigated for almost 200 years since they were first reported. However, many aspects of POMs are still not completely understood by the research community. This cover design highlights a better understanding of POM chemistry, which contributes to significant advances in this field.