8194 Inorg. Chem. 2010, 49, 8194–8196
DOI: 10.1021/ic101419a

Inorganic Chemistry
Communication

Sandwich-Type Zinc-Containing Polyoxometalates with a Hexaprismane Core $[\{Zn_2W(O)O_3\}_2]^{4+}$ Synthesized by Thermally Induced Isomerization of a Metastable Polyoxometalate

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Received July 16, 2010

Two novel sandwich-type silicotungstates, $TBA_8[\{Zn_2W(O)O_3\}_2H_4\{\alpha\text{-}SiW_9O_{33}\}_2]\cdot 5H_2O$ (**α-Zn4**; TBA = tetra-*n*-butylammonium) and $TBA_8[\{Zn_2W(O)O_3\}_2H_4\{\beta\text{-}SiW_9O_{33}\}_2]\cdot 7H_2O$ (***β*-Zn4**), were synthesized by the solid-state thermally induced isomerization of metastable $TBA_8[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2\{\gamma\text{-}HSiW_{10}O_{36}\}_2]\cdot 9H_2O$ (**γ-Zn4**). Compounds **α-Zn4** and ***β*-Zn4** consisted of two $[SiW_9O_{33}]^{8-}$ subunits sandwiching the unprecedented distorted *hexaprismane* core $[\{Zn_2W(O)O_3\}_2]^{4+}$.

Polyoxometalates (POMs) are attractive compounds and are utilized in many fields, e.g., analytical chemistry, medicine, electrochemistry, photochemistry, and catalysis.[1] Until now, various kinds of metal-substituted POMs have been synthesized by the substitution of metal cations into the vacant site(s) of lacunary POMs and used as catalysts for various functional group transformations because of their unique reactivities depending on their compositions and structures of active sites.[1]

Usually, metal-substituted POMs have been synthesized by the reaction of alkali-metal salts of lacunary POMs and metal salts in (acidic) *aqueous media*.[1] However, isomerization and/or decomposition of lacunary precursors easily proceed in (acidic) aqueous media,[2] and the desired metal-substituted POMs (with retention of the original framework structures of lacunary precursors) cannot be synthesized in some cases.[3] Very recently, we have successfully synthesized a γ-Keggin zinc-containing sandwich-type POM, $TBA_8[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2\{\gamma\text{-}HSiW_{10}O_{36}\}_2]\cdot 9H_2O$ (**γ-Zn4**), by the reaction of $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ with $Zn(acac)_2$ (acac = acetylacetonato) in an *organic medium* (acetone).[3,4] In this case, no isomerization and decomposition of the lacunary precursor proceeded. To date, there are only a few reports on the synthesis of POMs in organic media.[5]

It has been reported that water of crystallization and/or aquo ligands play an important role in the stabilization of metal-substituted POMs and that the removal of water by thermal treatment causes isomerization and/or decomposition of their structures.[6] Compound **γ-Zn4** possessed the tetranuclear zinc−oxygen cluster core $[\{Zn(OH_2)(\mu_3\text{-}OH)\}_2\{Zn(OH_2)_2\}_2]^{6+}$ sandwiched between two $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ subunits (Figure 1).[4] The zinc atoms in **γ-Zn4** possessed one or two aquo ligand(s). The distances between oxygen atoms on zinc atoms (aquo ligands) and nearest-neighbor oxygen atoms from $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ subunits were in the range of 2.91−2.93 Å (Figure 1), showing the existence of *hydrogen-bonding interaction*.[7] Thus, as for **γ-Zn4**, the zinc atoms located *out-of-pocket* of the lacunary site of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ are likely

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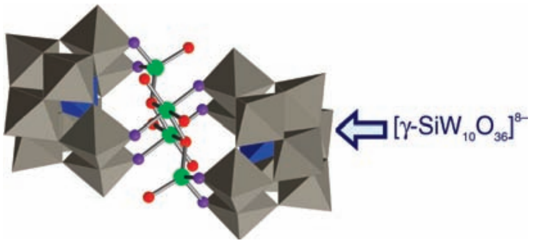

Figure 1. Polyhedral and ball-and-stick representation of the anion part of ***γ*-Zn4**. The $\{WO_6\}$ moieties occupy the gray octahedra, and the $\{SiO_4\}$ groups are shown as internal blue tetrahedra. Green, red, and purple spheres indicate zinc atoms, oxygen atoms coordinating to zinc, and oxygen atoms from $\{WO_6\}$ moieties in $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, respectively.

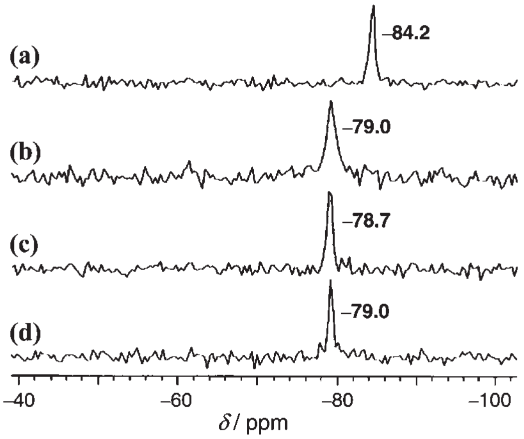

Figure 2. Solid-state MAS ^{29}Si NMR spectra of (a) ***γ*-Zn4**, (b) thermally treated ***γ*-Zn4** (at 150 °C), (c) **α-Zn4**, and (d) ***β*-Zn4**.

stabilized by hydrogen-bonding interaction. If these aquo ligands could be removed, isomerization of ***γ*-Zn4** would take place, resulting in the formation of new zinc-containing POMs. As expected, we found in this study that two novel sandwich-type POMs, $TBA_8[\{Zn_2W(O)O_3\}_2H_4\{\alpha\text{-}SiW_9O_{33}\}_2]\cdot 5H_2O$ (**α-Zn4**) and $TBA_8[\{Zn_2W(O)O_3\}_2H_4\{\beta\text{-}SiW_9O_{33}\}_2]\cdot 7H_2O$ (***β*-Zn4**), could be synthesized by the solid-state thermally induced isomerization of ***γ*-Zn4**.[8]

The IR and thermogravimetric analyses showed that the structure of ***γ*-Zn4** was inherently stable upon solid-state thermal treatment under a vacuum up to 80 °C and that all aquo ligands as well as water of crystallization in ***γ*-Zn4** were removed upon thermal treatment under a vacuum at 150 °C. The IR band positions and intensities of the POM frameworks changed upon treatment at 150 °C (Figure S1 in the Supporting Information). The solid-state magic-angle-spinning (MAS) ^{29}Si NMR spectrum of the thermally treated ***γ*-Zn4** (at 150 °C) showed a broad (overlapped) signal centered at −79.0 ppm (Figure 2b), and the signal position was different from those of the original ***γ*-Zn4** (−84.2 ppm; Figure 2a). The thermally treated ***γ*-Zn4** was dissolved in a mixed solvent of acetone and water (10:1, v/v), and the ^{29}Si NMR spectrum of the solution showed two signals at −78.6 and −79.0 ppm (Figure S2 in the Supporting Information). From this solution, the single crystals of **α-Zn4** were obtained upon standing at room temperature (32% yield based on ***γ*-Zn4**). After **α-Zn4** was completely removed by filtration, the white residue (powder) was obtained by evaporation to dryness. The analytically pure single crystals of ***β*-Zn4** were successfully obtained by recrystallization from a mixed solvent of acetone and acetonitrile (20:1, v/v; 16% yield based on ***γ*-Zn4**). The solid-state MAS ^{29}Si NMR spectra of isolated **α-Zn4** and ***β*-Zn4** showed signals at −78.7 and −79.0 ppm (Figure 2c,d), respectively. The IR spectrum of the thermally treated ***γ*-Zn4** could be well reproduced by using those of **α-Zn4** and ***β*-Zn4** (Figure S3 in the Supporting Information). All of these results show that ***γ*-Zn4** was converted into (at least) two new POMs, **α-Zn4** and ***β*-Zn4**, by solid-state thermal treatment.[8]

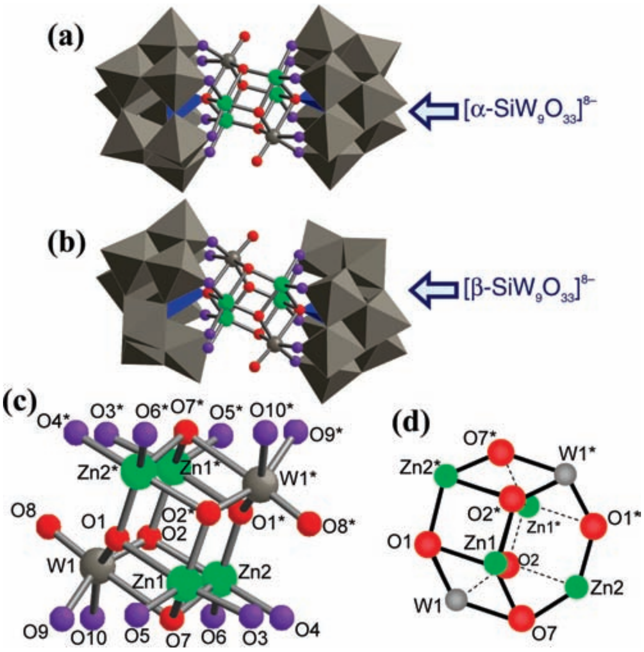

Figure 3. Polyhedral and ball-and-stick representations of the anion parts of (a) **α-Zn4** and (d) ***β*-Zn4**. (c) Ball-and-stick representation and (d) schematic illustration of the *hexaprismane* core $[\{Zn_2W(O)O_3\}_2]^{4+}$. The $\{WO_6\}$ moieties occupy the gray octahedra, and $\{SiO_4\}$ groups are shown by internal blue tetrahedra. Green, gray, red, and purple spheres indicate zinc atoms, tungsten atoms, oxygen atoms from hexaprismane cores, and oxygen atoms from $\{WO_6\}$ moieties in $[SiW_9O_{33}]^{8-}$, respectively.

The molecular structures of **α-Zn4** and ***β*-Zn4** could be determined by X-ray crystallographic analyses. The structures of the anion parts are shown in Figure 3. The crystallographic data and the selected bond lengths and angles in **α-Zn4** and ***β*-Zn4** are summarized in Tables S1 and S2 in the Supporting Information, respectively. The ORTEP representations are shown in Figure S4 in the Supporting Information. As shown in Figure 3, compounds **α-Zn4** and ***β*-Zn4** possessed the distorted *hexaprismane* core $[\{Zn_2W(O)O_3\}_2]^{4+}$ sandwiched between two $[SiW_9O_{33}]^{8-}$ subunits ($[\alpha\text{-}SiW_9O_{33}]^{8-}$ subunits for **α-Zn4**; $[\beta\text{-}SiW_9O_{33}]^{8-}$ subunits for ***β*-Zn4**). Eight TBA cations per each anion (**α-Zn4** and ***β*-Zn4**) could be crystallographically assigned in accordance with the results of the elemental analyses, although they were highly disordered. The bond balance sum (BVS)[9] values of silicon (3.80 for **α-Zn4** and 4.03 for ***β*-Zn4**), tungsten (5.96−6.24 for **α-Zn4** and

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[8] Compounds **α-Zn4** and ***β*-Zn4** could be obtained only by solid-state thermally induced isomerization and could not be synthesized by the reactions of lacunary POMs with zinc precursors in the solution state, e.g., the reactions of (i) $TBA_4H_4[\gamma\text{-}SiW_{10}O_{36}]$ and $Zn(acac)_2$ in organic media, (ii) $K_8[\gamma\text{-}SiW_{10}O_{36}]$, $Zn(NO_3)_2$, and TBABr in aqueous media, and (iii) $Na_{10}[\alpha\text{-}SiW_9O_{34}]$, $Zn(NO_3)_2$, Na_2WO_4, and TBABr in aqueous media. In addition, no isomerization of ***γ*-Zn4** to **α-Zn4** and ***β*-Zn4** took place when ***γ*-Zn4** was heated in acetone (reflux) and *N*,*N*-dimethylformamide (at 150 °C).

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5.94−6.26 for ***β*-Zn4**), and zinc (2.15 and 2.09 for **α-Zn4** and 2.17 and 2.10 for ***β*-Zn4**) atoms indicate that the respective valences in these compounds are 4+, 6+, and 2+. The data of X-ray analyses, elemental analyses, and thermogravimetric analyses show that the formulas of **α-Zn4** and ***β*-Zn4** are $TBA_8[\{Zn_2W(O)O_3\}_2H_4\{\alpha\text{-}SiW_9O_{33}\}_2]\cdot 5H_2O$ and $TBA_8[\{Zn_2W(O)O_3\}_2H_4\{\beta\text{-}SiW_9O_{33}\}_2]\cdot 7H_2O$, respectively. The formations of **α-Zn4** and ***β*-Zn4** anions from ***γ*-Zn4** can be expressed by the following equation (eq 1).

$$[\{Zn(H_2O)(\mu_3\text{-}OH)\}_2\{Zn(H_2O)_2\}_2\{\gamma\text{-}HSiW_{10}O_{36}\}_2]^{8-} \rightarrow [\{Zn_2W(O)O_3\}_2H_4\{SiW_9O_{33}\}_2]^{8-} + 6H_2O \quad (1)$$

Each zinc atom in **α-Zn4** and ***β*-Zn4** was five-coordinated and pyramidally coordinated by three oxygen atoms from the *hexaprismane* cores and two oxygen atoms from the $\{WO_6\}$ moieties in $[SiW_9O_{33}]^{8-}$ subunits. The *hexaprismane* cores were composed of two six-membered puckered rings with the chair conformation ({Zn1−O7−Zn2−O1*−W1*−O2*−} and {O1−W1−O2−Zn1*−O7*−Zn2*−}) (Figure 3). Two puckered rings were essentially located in parallel. The bond lengths Zn−O in the puckered rings (1.937−2.105 Å) were shorter than those of the Zn−O bonds connecting two puckered rings (2.122−2.285 Å) (Table S2 in the Supporting Information). Although complexes with *hexaprismane* cores composed of monometals and oxygen atoms have been reported,[10] *the hexaprismane cores* (*as in* **α-Zn4** *and* ***β*-Zn4**) *composed of multimetals and oxygen atoms have never been reported*, as far as we know.

As for the *hexaprismane* core in **α-Zn4**, the respective BVS values of oxygen atoms O1, O2, and O7* were 1.98, 1.95, and 1.93, showing that these oxygen atoms are μ_3-O ligands bridging two zinc atoms (Zn1 and Zn2* for O1; Zn1* and Zn2 for O2; Zn1* and Zn2* for O7*) and one tungsten atom (W1 for O1 and O2; W1* for O7*). The O8 atom was an oxo ligand (BVS: 1.71). The BVS values of O4 and O6 were 1.17 and 1.25, respectively, suggesting monoprotonation of these oxygen atoms. As for the *hexaprismane* core in ***β*-Zn4**, the respective BVS values of oxygen atoms O2 and O7* were 1.96 and 2.04, showing that O2 and O7* are μ_3-O ligands bridging two zinc atoms (Zn1* and Zn2 for O2; Zn1* and Zn2* for O7*) and one tungsten atom (W1 for O2; W1* for O7*). In contrast, the O1 atom is a μ_3-OH ligand (BVS: 1.18) bridging two zinc atoms (Zn1 and Zn2*) and one tungsten atom (W1). The O8 atom was an oxo ligand (BVS: 1.78). The O4 (BVS: 1.30) and O6 (BVS: 1.90) atoms were μ_2-OH and μ_2-O ligands, respectively. Therefore, the bond lengths and angles in the *hexaprismane* core in ***β*-Zn4** were somewhat different from those in **α-Zn4** (Table S2 in the Supporting Information).

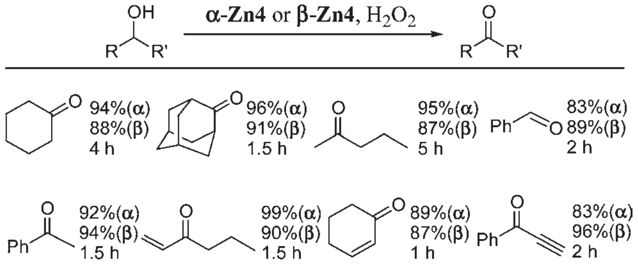

Figure 4. Oxidation of various alcohols. Reaction conditions: **α-Zn4** or ***β*-Zn4** (0.4 mol % with respect to alcohols), alcohol (0.5 mmol), 30% aqueous H_2O_2 (0.25 mmol), acetone (1.5 mL), 56 °C. Yields were determined by gas chromatography analyses and based on H_2O_2 used.

Compounds **α-Zn4** and ***β*-Zn4** showed high catalytic activities for the oxidation of alcohols with H_2O_2, and the catalytic activities of **α-Zn4** and ***β*-Zn4** were intrinsically the same. The scope of alcohol oxidation with **α-Zn4** and ***β*-Zn4** is summarized in Figure 4. The oxidation of various kinds of structurally diverse alcohols including aliphatic, benzylic, allylic, and propargylic ones efficiently proceeded to afford the corresponding carbonyl compounds in high yields. The catalytic activities of **α-Zn4** and ***β*-Zn4** for the oxidation of nonactivated aliphatic alcohols such as cyclohexanol, 2-adamantanol, and 2-pentanol were higher than that of ***γ*-Zn4** (Table S3 in the Supporting Information). For activated alcohols including benzylic and allylic ones, the catalytic activities of three POMs were almost the same (Table S3 in the Supporting Information).

After oxidation was completed, the catalyst could be retrieved by evaporation of acetone, followed by the addition of an excess amount of diethyl ether. The IR spectrum of the used catalyst was intrinsically the same as that of the fresh catalyst (Figure S5 in the Supporting Information), suggesting that the framework structure of the catalyst was preserved even after oxidation. The retrieved catalyst could be reused for alcohol oxidation; for example, oxidation of cyclohexanol with the retrieved ***β*-Zn4** under the same conditions gave cyclohexanone in 91% yield (88% yield with the fresh catalyst).

In summary, the novel POMs **α-Zn4** and ***β*-Zn4** could be obtained by the thermally induced isomerization of ***γ*-Zn4** and showed high catalytic activities for alcohol oxidation.

Acknowledgment. We thank Dr. K. Uehara (The University of Tokyo) for his help with X-ray analyses. This work was supported, in part, by the Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering) and Grants-in-Aid for Scientific Researches from Ministry of Education, Culture, Sports, Science and Technology. Y.K. is grateful for a JSPS Research Fellowship for Young Scientists.

Supporting Information Available: X-ray crystallographic data in CIF format for **α-Zn4** and ***β*-Zn4**, experimental procedures, Tables S1−S3, and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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