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Synthesis and Structural Characterization of a γ-Keggin-Type Dimeric Silicotungstate with a Bis(μ-hydroxo) Dizirconium Core $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\mu\text{-OH})_2]^{10-}$

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A novel dinuclear zirconium sandwich-type silicotungstate cluster of $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\mu\text{-OH})_2]^{10-}$ (**1**) was synthesized by the reaction of a divacant lacunary γ-Keggin silicotungstate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with $\text{ZrOCl}_2\cdot8\text{H}_2\text{O}$. The anion consisted of two $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ units sandwiching a diamond $\text{Zr}_2(\mu\text{-OH})_2$ core, and each zirconium atom in **1** was six-coordinated to two μ-OH ligands and four oxygen atoms of two $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ units. The $\text{Zr}_2(\mu\text{-OH})_2$ core in **1** reacted with methanol to give the corresponding monomethoxo derivative $[(\gamma\text{-SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\mu\text{-OH})(\mu\text{-OCH}_3)]^{10-}$ (**2**).

Zirconium compounds including zirconium oxides have unique chemical and physical properties leading to their applications such as oxygen sensors, fuel cells, catalysts, and catalyst supports.[1] The properties and reactivities are strongly dependent on their structures.[1] Therefore, syntheses of zirconium compounds with structurally well-defined sites and investigation of their reactivities are very important.

Recently, partially metal-substituted polyoxometalates (POMs), which are synthesized by the introduction of substituent metal ions into the vacant site(s) of lacunary POMs, have attracted much attention[2] because POMs can be regarded as discrete fragments of metal oxides. Since Finke and co-workers reported a trinuclear zirconium containing Knoth-type sandwich silicotungstate $[\text{Zr}_3(\mu_2\text{-OH})_3(\text{A-}\beta\text{-SiW}_9\text{O}_{34})_2]^{11-}$ in 1989,[3a] various kinds of zirconium-containing POMs with Keggin (not γ-type)-, Wells−Dawson-, and Lindqvist-type structures have been reported.[3]

In this paper, we report the synthesis and structural characterization of a new complex, a γ-Keggin dimeric silicotungstate with $\text{Zr}_2(\mu\text{-OH})_2$ core (**1**). Further, the reactivity of the $\text{Zr}_2(\mu\text{-OH})_2$ core with methanol was investigated.

The zirconium-containing POM **1** was synthesized by the reaction of a divacant lacunary γ-Keggin silicotungstate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ with $\text{ZrOCl}_2\cdot8\text{H}_2\text{O}$ in an acidic aqueous solution at room temperature (ca. 295 K) as follows. To a suspension of $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot12\text{H}_2\text{O}$[4] (6.0 g, 2.02 mmol) in water (90 mL), $\text{ZrCl}_2\text{O}\cdot8\text{H}_2\text{O}$ (0.33 g, 1.0 mmol) in water (5 mL) was added and the pH of the solution was kept at 3.0 with an aqueous HNO_3 solution (1 M). After 30 min, tetra-*n*-butylammonium bromide (9.00 g, 27.9 mmol) was added to the solution followed by stirring for 30 min with keeping the pH at 3.0. The white precipitate of tetra-*n*-butylammonium salt of **1** (TBA-**1**) was collected by the filtration and washed with an excess amount of water. After being dried, the crude product was purified twice with the precipitation method (addition of water (400 mL) into the acetonitrile solution of crude TBA-**1** (30 mM, 40 mL)).

Complex TBA-**1** was soluble in various organic solvents such as acetonitrile, dichloromethane, 1,2-dichloroethane,

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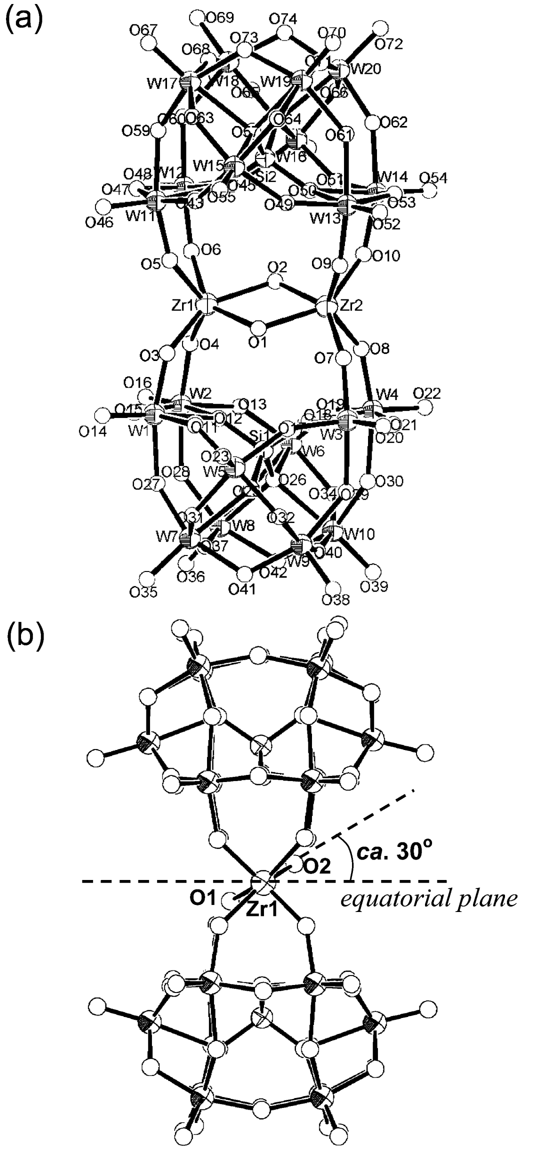

Figure 1. ORTEP representations of the anion part of TBA-**1**; (a) the full numbering scheme and (b) the representative view of the anion along the Zr···Zr axis.

Table 1. Selected Bond Lengths and Angles in **1**

Bond Length (Å)			
Zr(1)−O(1)	2.141(19)	Zr(2)−O(1)	2.171(18)
Zr(1)−O(2)	2.170(16)	Zr(2)−O(2)	2.155(17)
Zr(1)−O(3)	2.066(12)	Zr(2)−O(7)	2.148(11)
Zr(1)−O(4)	2.137(13)	Zr(2)−O(8)	2.090(10)
Zr(1)−O(5)	2.017(10)	Zr(2)−O(9)	2.056(13)
Zr(1)−O(6)	2.074(12)	Zr(2)−O(10)	2.079(11)
Zr(1)···Zr(2)	3.576(2)		
Bond Angle (deg)			
Zr(1)−O(1)−Zr(2)	112.1(7)	O(1)−Zr(1)−O(2)	68.3(6)
Zr(1)−O(2)−Zr(2)	111.6(6)	O(1)−Zr(2)−O(2)	68.1(6)

DMF, and DMSO, and a single crystal suitable for X-ray analysis was successfully obtained by the recrystallization from dichloromethane. The molecular structure of the anion part of TBA-**1** is shown in Figure 1. The selected bond lengths and angles are summarized in Table 1.[5] The anion consisted of two lacunary $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ units sandwiching a diamond $Zr_2(\mu\text{-OH})_2$ core, as shown in Figure 1. Each zirconium atom in **1** was coordinated to two μ-OH ligands and four oxygen atoms of two lacunary $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ units. One axial position of each zirconium center was vacant. Thus, the coordination number of each zirconium center was six and the overall coordination geometry around each zirconium center was distorted trigonal prismatic. The Zr−$O_{hydroxo}$ bonds (average 2.16 Å) were almost equidistant. The Zr(1)−O(1)−Zr(2) and Zr(1)−O(2)−Zr(2) bond angles were 112.1(7)° and 111.6(6)°, respectively. The Zr(1)···Zr(2) distance in **1** was 3.576(2) Å and similar to those of previously reported zirconium-containing POMs such as $[(\alpha\text{-PW}_{11}O_{39})_2Zr_2(\mu\text{-OH})_2]^{8-}$ (3.568 Å)[3c] and $[(W_5O_{18})_2Zr_2(\mu\text{-OH})_2]^{6-}$ (3.633 Å).[3j] The $Zr_2(\mu\text{-OH})_2$ plane in **1** was not placed in the equatorial plane and deviated from the equatorial plane by ca. 30° (Figure 1b).

The bond valence sum (BVS)[6] values of O(1) and O(2) were 1.11 and 1.09, respectively, suggesting that these oxygen atoms are monoprotonated (hydroxo ligands). The BVS values of zirconium (3.72−3.89), tungsten (5.97−6.48), and silicon (4.03) indicate that the respective valences are +4, +6, and +4. These results and elemental and thermogravimetric analyses show that the formula of TBA-**1** is $TBA_7H_3[(\gamma\text{-SiW}_{10}O_{36})_2Zr_2(\mu\text{-OH})_2]\cdot 4H_2O$. The formation of **1** anion can be expressed by the following equation (eq 1).

$$2[\gamma\text{-SiW}_{10}O_{36}]^{8-} + 2ZrOCl_2 + 2H^+ \rightarrow [(\gamma\text{-SiW}_{10}O_{36})_2Zr_2(\mu\text{-OH})_2]^{10-} + 4Cl^- \quad (1)$$

Very recently, the zirconium-containing dimeric and trimeric POMs composed of β-Keggin subunits such as $[(\beta\text{-SiW}_{10}O_{37})_2Zr_4O_2(OH)_2(H_2O)_4]^{10-}$ and $[(\beta\text{-SiW}_{10}O_{37})_3Zr_6O_2(OH)_2(H_2O)_3]^{14-}$ have been synthesized by the reaction of $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ with $ZrCl_4$ in CH_3COOH/CH_3COOK buffer (pH 4.8) at 323 K.[3b] Kortz and co-workers suggested that the γ-Keggin moieties are initially formed as intermediates and that the subsequent rotational isomerization under relatively high reaction temperature proceeds to afford the corresponding β-Keggin subunits of these POMs.[3b,7] Complex **1** is the first structurally characterized zirconium-containing POMs with γ-Keggin structure and has a similar dimeric structure to those of previously reported POMs, in which lacunary subunits are sandwiching zirconium−oxygen cluster cores.[3]

In order to clarify the solution state of **1**, NMR and the cold-spray ionization mass (CSI-MS, cation mode) spectra of TBA-**1** in the solvents were measured. The ^{29}Si NMR spectrum of TBA-**1** in acetonitrile (CD_3CN) showed a signal at −86.4 ppm, suggesting that TBA-**1** is a single species in

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(5) Crystallographic data were collected on a Rigaku AFC-10 Saturn 70 CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 153.1 K. Crystallographic data for TBA-**1**: $C_{114}H_{261}N_7O_{74}Si_2W_{20}Zr_2Cl_4$, M = 6971.8, monoclinic, space group $P2_1/c$ (No. 14), a = 29.4764(7) Å, b = 35.6269(8) Å, c = 19.0523(3) Å, β = 108.7466(8)°, V = 18946.4(7) Å^3, Z = 4, D_{calcd} = 2.444 g·cm^{-3}, μ = 12.346 mm^{-1}, R1 = 0.068 (for 21 331 data, $I > 2\sigma(I)$), wR2 = 0.202 (for all 48 940).

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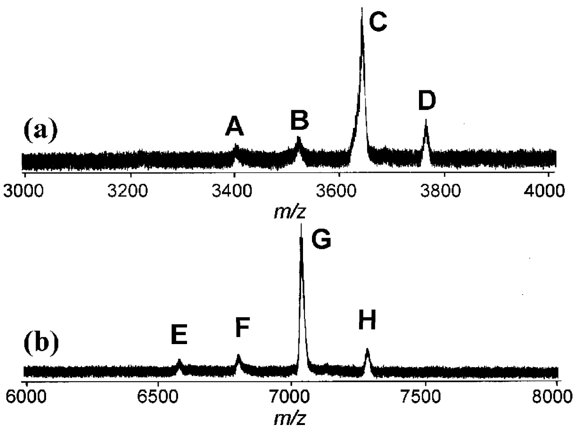

Figure 2. CSI-MS spectra of TBA-**1**: (a) *m/z* 3000−4000 and (c) 6000−8000.

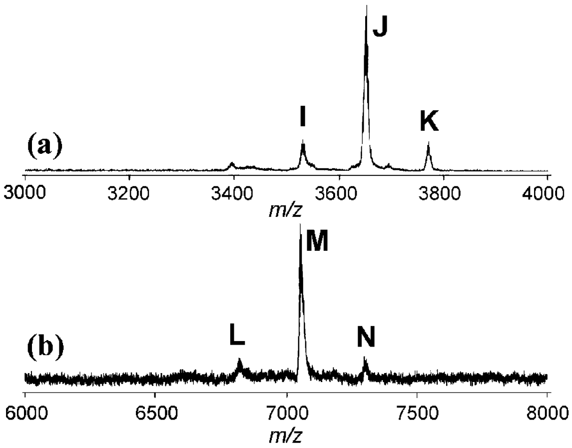

Figure 3. CSI-MS spectra of **2** (the acetonitrile solution of TBA-**1** with 100 equiv of methanol): (a) *m/z* 3000−4000 and (b) 6000−8000.

acetonitrile.[8] The CSI-MS spectrum of TBA-**1** in acetonitrile (Figure 2) exhibited +2-charged signals centered at (**A**) *m/z* = 3402 $\{TBA_7H_5[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{2+}$, (**B**) *m/z* = 3523 $\{TBA_8H_4[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{2+}$, (**C**) *m/z* = 3643 $\{TBA_9H_3[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{2+}$, and (**D**) *m/z* = 3764 $\{TBA_{10}H_2[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{2+}$, and +1-charged signals centered at (**E**) *m/z* = 6579 $\{TBA_6H_5[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{+}$, (**F**) *m/z* = 6803 $\{TBA_7H_4[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{+}$, (**G**) *m/z* = 7044 $\{TBA_8H_3[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{+}$, and (**H**) *m/z* = 7286 $\{TBA_9H_2[(SiW_{10}O_{36})_2Zr_2(OH)_2]\}^{+}$. No signals due to $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ and zirconium-substituted POM monomers were observed. Thus, all signals are assignable to the $[(SiW_{10}O_{36})_2Zr_2(OH)_2]^{10-}$ anion. The CSI-MS spectrum of TBA-**1** in 1,2-dichloroethane and DMF also exhibited the same signals as those in Figure 2. These NMR and CSI-MS data suggest that TBA-**1** exists as a dimer of the di-zirconium-substituted silicotungstate in the solvents and that the structure in the solid state is preserved in solution.

In the presence of methanol ($^{13}CH_3OH$), the ^1H and ^{13}C NMR spectra of the CD_3CN solution of TBA-**1** showed signals at 4.23 (d, $^1J_{CH}$ = 144 Hz, 3H per anion) and 60.4 ppm, respectively, assignable to the methoxo species[9] in addition to the countercation (Figures S1 and S2 in Supporting Information). Further, the CSI-MS spectrum of TBA-**1** in acetonitrile/methanol (Figure 3) exhibited +2-charged signals centered at (**I**) *m/z* = 3530 $\{TBA_8H_4[(SiW_{10}O_{36})_2Zr_2(OH)(OCH_3)]\}^{2+}$, (**J**) *m/z* = 3650 $\{TBA_9H_3[(SiW_{10}O_{36})_2Zr_2(OH)(OCH_3)]\}^{2+}$, and (**K**) *m/z* = 3771 $\{TBA_9H_2[(SiW_{10}O_{36})_2Zr_2(OH)(OCH_3)]\}^{2+}$, and +1-charged signals centered at (**L**) *m/z* = 6817 $\{TBA_7H_4[(SiW_{10}O_{36})_2Zr_2(OH)(OCH_3)]\}^{+}$, (**M**) *m/z* = 7058 $\{TBA_8H_3[(SiW_{10}O_{36})_2Zr_2(OH)(OCH_3)]\}^{+}$, and (**N**) *m/z* = 7300 $\{TBA_{10}H_2[(SiW_{10}O_{36})_2Zr_2(OH)(OCH_3)]\}^{+}$. No signals due to **1** and dimethoxo derivative were observed. All signals are assignable to the $[(SiW_{10}O_{36})_2Zr_2(OH)(OCH_3)]^{10-}$ anion suggesting that the $Zr_2(\mu\text{-}OH)_2$ core in **1** reacts with methanol to give the corresponding monomethoxo derivative $[(\gamma\text{-}SiW_{10}O_{36})_2Zr_2(\mu\text{-}OH)(\mu\text{-}OCH_3)]^{10-}$ (**2**) according to eq 2.[10] The reaction was reversible and the hydrolysis of **2** to **1** proceeded in the presence of water. The formation constant

$$[(\gamma\text{-}SiW_{10}O_{36})_2Zr_2(\mu\text{-}OH)_2]^{10-} + CH_3OH \rightleftarrows [(\gamma\text{-}SiW_{10}O_{36})_2Zr_2(\mu\text{-}OH)(\mu\text{-}OCH_3)]^{10-} + H_2O \quad (2)$$

(K = **[2]**$[H_2O]$/**[1]**$[CH_3OH]$) in acetonitrile at 298 K was determined to be 2.1 ± 0.3 (Figure S3 in Supporting Information), of which the value has not been reported while there have been many reports on the zirconium−alkoxo complexes.[9]

In summary, the novel dinuclear zirconium sandwich-type silicotungstate **1** has been synthesized by the reactions of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with $ZrOCl_2{\cdot}8H_2O$, the molecular structures were successfully determined, and the reactivity with methanol was clarified.

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Supporting Information Available: X-ray crystallography data in CIF format for complex **1** and experimental procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] The measurement of ^{183}W NMR spectrum of TBA-**1** was not successful because of its low solubility in various solvents.

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[10] In the case of $[\gamma\text{-}SiW_{10}V_2(\mu\text{-}OH)_2O_{38}]^{4-}$ and $[(\gamma\text{-}SiW_{10}O_{36})_2\{Ti_2(\mu\text{-}OH)_2(\mu\text{-}O)\}_2]^{8-}$ with similar $M_2(\mu\text{-}OH)_2$ cores, the substitution of methanol proceeded only at the $M_2(\mu\text{-}OH)_2$ core, which was confirmed by the single crystal X-ray diffraction. In the same way, the substitution of methanol in **1** likely proceeds on the $Zr_2(\mu\text{-}OH)_2$ core and the substitution on the γ-Keggin tungstate framework is unlikely. See: (a) Nakagawa, Y.; Uehara, K.; Mizuno, N. *Inorg. Chem.* **2005**, *44*, 14. (b) Nakagawa, Y.; Uehara, K.; Mizuno, N. *Inorg. Chem.* **2005**, *44*, 9068. (c) Nakagawa, Y.; Kamata, K.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 5136. (d) Goto, Y.; Kamata, K.; Yamaguchi, K.; Uehara, K.; Hikichi, S.; Mizuno, N. *Inorg. Chem.* **2006**, *45*, 2347. (e) Nakagawa, Y.; Mizuno, N. *Inorg. Chem.* **2007**, *46*, 1727.