**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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Experimental Section

General. IR spectra were measured on Jasco FT/IR-460 Plus using KBr disks. CSI-MS spectra were recorded on JEOL JMS-T100CS. Typical measurements were as follows: Orifice voltage (−90 V), spray temp. (263 K), ion source temp (room temp.). Liquid-state NMR spectra were recorded on JEOL JNM-EX-270. ¹H and ¹³C NMR spectra were measured at 270 and 67.8 MHz, respectively, with TMS as an internal standard. ²⁹Si NMR spectra were measured at 53.5 MHz with TMS as an external standard. Na₂WO₄·2H₂O and zirconium salts were obtained from Wako or Kanto (reagent grade) and used as received. The dilacunary precursor of K₈[γ -SiW₁₀O₃₆]·12H₂O was synthesized according to ref. S1.

Synthesis of TBA-1. ZrCl₂O·8H₂O (0.33 g, 1.0 mmol) in water (5 mL) was added to a suspension of K₈[γ -SiW₁₀O₃₆]·12H₂O (6.0 g, 2.02 mmol) in water (90 mL) and the pH of the solution was kept at 3.0 with an aqueous HNO₃ solution (1 M). After 30 min, [(*n*-C₄H₉)₄N]Br (9.00 g, 27.9 mmol) was added to the solution followed by the stirring for 30 min with keeping the pH at 3.0. The white precipitate of **1** was collected by the filtration and washed with an excess amount of water. After the dryness, the

crude product was purified twice with the precipitation method (1.46 g, 21% yield based on $K_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$). The white needle-like crystals of TBA-1 suitable for the X-ray crystallographic analysis were obtained by the recrystallization from dichloromethane. Anal. Calcd for $[(\text{C}_4\text{H}_9)_4\text{N}]_7\text{H}_3[(\text{SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\text{OH})_2]\cdot 4\text{H}_2\text{O}$: C, 19.67; H, 3.85; N, 1.43; Si, 0.82; W, 53.77; Zr, 2.67. Found: C, 19.67; H, 3.89; N, 1.44; Si 0.94; W, 55.02; Zr, 2.53. IR (KBr pellet, ν): 3447, 2962, 2935, 2874, 1636, 1483, 1462, 1381, 1170, 1152, 1106, 1090, 1063, 1019, 1000, 961, 929, 903, 875, 809, 727, 685, 563, 541, 476, 458, 387, 360, 333, 316 cm^{-1} . CSI-MS (CH_3CN ; spray temperature, 263 K): $m/z = 3643$ $\{[(\text{C}_4\text{H}_9)_4\text{N}]_9\text{H}_3[(\text{SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\text{OH})_2]\}^{2+}$, 7044 $\{[(\text{C}_4\text{H}_9)_4\text{N}]_8\text{H}_3[(\text{SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\text{OH})_2]\}^+$. ^{29}Si NMR (CD_3CN): δ -86.4 ppm.

The CSI-MS spectrum of the acetonitrile solution of TBA-1 in the presence of water (~500 equiv. with respect to TBA-1) also exhibited +2- and +1-charged signals assignable to the $[(\text{SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\text{OH})_2]^{10-}$ anion and no signals of $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and zirconium-substituted POM monomers were observed. In addition, no changes in the UV-vis spectrum of the acetonitrile solution of TBA-1 in the presence of water were observed, suggesting that the γ -Keggin structure is preserved in the presence of water. Further, the acetonitrile solution of TBA-1 (0.1 mM) was heated to 323 K for 1 h, and then the UV-vis and CSI-MS spectra were measured. No changes in the UV-vis spectrum were observed after the thermal treatment. The CSI-MS spectrum of the solution after the treatment also exhibited +2- and +1-charged signals assignable to the $[(\text{SiW}_{10}\text{O}_{36})_2\text{Zr}_2(\text{OH})_2]^{10-}$ anion and no signals due to $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and zirconium-substituted POM monomers were observed. All these results suggest that the γ -Keggin dimeric structure of **1** was hydrolytically (in the presence of water, ~500 equiv. with respect to TBA-1) and thermally (~323 K) stable in acetonitrile.

X-ray Crystallography. Diffraction measurements were made on a Rigaku AFC-10 Saturn 70 CCD detector with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) at 153.1 K. Data were collected and processed using CrystalClear^{S2} for Windows software and HKL2000^{S3} for Linux

software. Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. The structural analysis was performed using the CrystalStructure crystallographic structure-solving program package and Win-GX for Windows software.^{S4} All structures were solved by SHELXS-97 (direct methods) and SHELXH-97 (Fourier synthesis and least-squares refinement).^{S5} Zirconium, tungsten, and silicon atoms were anisotropically, and all atoms except hydrogen were refined isotropically.^{S6}

Substitution of a Methoxy Group for a Hydroxy Group on the $\text{Zr}_2(\mu\text{-OH})_2$ Core. TBA-1 (5 μmol), H_2O (0.2–3.3 mmol), and methanol (0.2–1.1 mmol) were dissolved in CD_3CN (1 mL), and the reaction was traced by ^1H NMR spectroscopy at 298 K. The spectra were recorded every 10 min until no changes were observed in the signal intensity of methoxy protons observed at 4.22 ppm. The data are summarized in Figure S3. Our attempts to obtain crystallographic quality single crystals of compound **2** in various solvents together with vapor diffusion of poor solvents have yet been unsuccessful. Attempts with the other cations and solvents are in progress.

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Figure S1. The ^1H NMR spectra of the CD_3CN solutions of (a) $^{13}\text{CH}_3\text{OH}$ (0.5 M) and (b) TBA-1 (5 mM) in the presence of $^{13}\text{CH}_3\text{OH}$ (0.5 M).

Figure S2. The ^{13}C NMR spectrum of the CD_3CN solution of TBA-1 (5 mM) in the presence of $^{13}\text{CH}_3\text{OH}$ (0.5 M).

Figure S3. Data for determination of the formation constant (K) of **2**.

Figure S4 CSI-MS spectra of TBA-1 (m/z 3620–3680) in (a) a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution (TBA-1: 0.082 mM, H_2O : 0.14 M), (b) a $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution (TBA-1: 0.082 mM, CH_3OH : 0.067 M, H_2O : 0.14 M), and (c) a $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ solution (TBA-1: 0.082 mM, CH_3OH : 0.067 M). No signals due to other species such as $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and zirconium-substituted POM monomers were observed. In the solution, an equimolar mixture of **1** and **2** are present, which is estimated by the formation constant ($K = [\text{2}][\text{H}_2\text{O}]/[\text{1}][\text{CH}_3\text{OH}] = 2.1 \pm 0.3$). The lines in (b') are the calculated patterns of an equimolar mixture of **1** and **2**.