

# Novel Ti–O–Ti Bonding Species Constructed in a Metal–Oxide Cluster: Reaction Products of Bis(oxalato)oxotitanate(IV) with the Dimeric, 1,2-Dititanium(IV)-Substituted Keggin Polyoxotungstate

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The preparation and structural characterization of a novel Ti–O–Ti bonding complex constructed in a dilacunary  $\alpha$ -Keggin polyoxometalate (POM),  $[\{Ti(ox)(H_2O)\}_4(\mu-O)_3](\alpha-PW_{10}O_{37})^{7-}$  ( $H_2ox = oxalic\ acid$ ) (**1a**), are described. The water-soluble, crystalline complex with a formula of  $K_6H[1a] \cdot 0.5KCl \cdot 10H_2O$  (**1p**) was prepared as the bulk sample in 28.0% (0.51 g scale) yield in a 1:4 molar-ratio reaction of the dititanium(IV)-substituted, dimeric form of an  $\alpha$ -Keggin POM,  $K_{10}[(\alpha-1,2-PW_{10}Ti_2O_{39})_2] \cdot 18H_2O$ , with the titanium(IV) source  $K_2[TiO(ox)_2] \cdot 2H_2O$  in HCl-acidic solution (pH 0.08). Prior to formation of **1p**, the KCl-free crystalline compound (**1c**) obtained was characterized with X-ray crystallography. The compound **1p** was unequivocally characterized with complete elemental analysis, thermogravimetric and differential thermal analyses (TG/DTA), FTIR, and solution ( $^{31}P$ ,  $^{183}W$ , and  $^{13}C$ ) NMR spectroscopy. The molecular structure of **1a** was determined. The POM **1a** in the solid state was composed of the four octahedral Ti groups (four guests), i.e., the two Ti–O–Ti groups linked with the  $\mu$ -O atom, incorporated to the two adjacent, octahedral vacant sites (two hosts) in the dilacunary Keggin POM. The formation of **1a**, as well as the recently found POM  $[\{Ti(ox)(H_2O)\}_2(\mu-O)](\alpha-PW_{11}O_{39})^{5-}$  (**2a**), was strongly dependent on the reaction with  $[TiO(ox)_2]^{2-}$ , i.e., the anionic titanium(IV) complex as the titanium(IV) source. The POM **1a** is contrasted to most titanium(IV)-substituted POMs consisting of a combination of a monolacunary site (one host) and an octahedral Ti group (one guest) and also contrasted to **2a** as a combination of a monolacunary site (one host) and two octahedral Ti groups or a Ti–O–Ti group (two guests).

## Introduction

Polyoxometalates (POMs) are molecular metal–oxide clusters, which are of current interest as soluble metal oxides and for their application to catalysis, medicine, and material sciences.<sup>1</sup> Site-selective substitution of the  $W^{VI}$  atoms in POMs with  $Ti^{IV}$  atoms is particularly interesting because of the multicenter active sites formed with corner- or edge-sharing  $TiO_6$  octahedra.<sup>2</sup>

The ionic radius of  $Ti^{IV}$  (0.75 Å) is close to that of  $W^{VI}$  (0.74 Å), suggesting that  $Ti^{IV}$  should fit nicely into the POM framework. However, there is a significant issue of the oligomeric Ti–O–Ti anhydride formation resulting from the substitution by several  $Ti^{IV}$  atoms. The tri- $Ti^{IV}$ -1,2,3- and the di- $Ti^{IV}$ -1,2-substituted Keggin POMs heretofore reported have been isolated as the dimeric, Ti–O–Ti-bridged anhy-

dride forms, e.g.  $[(\beta-1,2,3-SiW_9Ti_3O_{37})_2O_3]^{14-,2c}$ ,  $[(\alpha-1,2,3-GeW_9Ti_3O_{37})_2O_3]^{14-,2f}$ ,  $[(\alpha-1,2,3-PW_9Ti_3O_{37})_2O_3]^{12-,2g}$  and  $[(\alpha-1,2-PW_{10}Ti_2O_{38})_2O_2]^{10-,2h}$ . On the other hand, as to the

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tri-Ti<sup>IV</sup>-substituted Dawson POMs, the tetrameric Ti–O–Ti-bridged anhydride forms such as  $[(\alpha-1,2,3\text{-P}_2\text{W}_{15}\text{Ti}_3\text{O}_{59}(\text{OH})_3)_4\{\mu_3\text{-Ti}(\text{OH})_3\}_4\text{Cl}]^{33-}$ ,<sup>3a,e</sup>  $[(\alpha-1,2,3\text{-P}_2\text{W}_{15}\text{Ti}_3\text{O}_{57,5}(\text{OH})_3)_4\text{Cl}]^{25-}$ ,<sup>3b,d,e</sup> and  $[(\alpha-1,2,3\text{-P}_2\text{W}_{15}\text{Ti}_3\text{O}_{57,5}(\text{OH})_3)_4]^{24-}$ <sup>3c</sup> have been also recently reported. In the viewpoint of a host–guest relationship, all the Ti–O–Ti bridging oligomeric POMs prepared so far have been composed of a combination of one vacant octahedral site (host) and one octahedral Ti group (guest).

On the other hand, a novel Ti–O–Ti bonding species constructed in the monolacunary site of an  $\alpha$ -Keggin POM,  $[\{\text{Ti}(\text{ox})(\text{H}_2\text{O})_2(\mu\text{-O})\}(\alpha\text{-PW}_{11}\text{O}_{39})]^{5-}$  ( $\text{H}_2\text{Ox}$  = oxalic acid) (**2a**),<sup>4a,b</sup> which is considered as the one host–two guests system, was very recently obtained as  $\text{K}_5[\mathbf{2a}] \cdot 13\text{H}_2\text{O}$  (**2**) by the reactions under strongly acidic conditions of the anionic Ti(IV) complex  $[\text{TiO}(\text{ox})_2]^{2-}$  with mono- or trilacunary Keggin POMs,  $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$  or  $[\text{A-PW}_9\text{O}_{34}]^{9-}$ , as POM precursor. It has been found that **2** can act as a precatalyst for the epoxidation of cyclooctene, cyclohexene, and 1-octene with aqueous  $\text{H}_2\text{O}_2$  at 25 °C in a homogeneous system.<sup>4c</sup>

In this work, we have used the dititanium(IV)-substituted, dimeric form of the  $\alpha$ -Keggin POM,  $\text{K}_{10}[(\alpha-1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2] \cdot 18\text{H}_2\text{O}$ ,<sup>2h</sup> as the POM precursor and examined its reaction with  $\text{K}_2[\text{TiO}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$  in HCl-acidic solution. Interestingly, a novel POM,  $[\{\{\text{Ti}(\text{ox})(\text{H}_2\text{O})_4(\mu\text{-O})_3\}(\alpha\text{-PW}_{10}\text{O}_{37})\}^{7-}]$  (**1a**),<sup>4a</sup> composed of the four octahedral Ti(IV) groups incorporated into the two adjacent, octahedral vacant sites in the Keggin POM (two hosts–four guests POM system), was produced.

Formation of **1a** and the recently found POM **2a** is strongly dependent upon the use of the Ti(IV) source, i.e., the anionic bis(oxalato)oxotitanate(IV) complex. Other examples of the one host–two guests POM systems have been reported such as the Si–O–Si bonding species formed in the monolacunary Keggin POM  $[\{\text{RSi}_2\text{O}\}(\text{SiW}_{11}\text{O}_{39})]^{4-}$  ( $\text{R} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{NC}(\text{CH}_2)_3, \text{C}_3\text{H}_5$ )<sup>5a</sup> and  $[(\text{SiR})_2(\mu\text{-O})\text{-}(\text{SiW}_{11}\text{O}_{39})]^{4-}$  ( $\text{R} = \text{Et}, \text{CH}=\text{CH}_2, \text{C}_{10}\text{H}_{21}, \text{Ph}$ ),<sup>5b</sup> the organosilyl-derivatives of the monolacunary Dawson POM  $[\{\text{PhSi}_2\text{O}\}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})]^{6-}$ ,<sup>5c</sup> the rhodium(II) acetate dimer derivatives of the monolacunary Keggin POM  $[\{\text{Rh}_2(\text{OAc})_2\text{-}(\text{PW}_{11}\text{O}_{39})\}^{5-}]$ ,<sup>5d</sup> the Ge–Fe bond derivatives incorporated into the monolacunary Keggin POM  $[\{\text{CpFe}(\text{CO})_2\text{Ge}\}_2(\mu\text{-O})(\text{SiW}_{11}\text{O}_{39})]^{4-}$ ,  $[\{\text{CpFe}(\text{CO})_2\text{Ge}\}_2(\mu\text{-O})(\text{PW}_{11}\text{O}_{39})]^{3-}$ , and  $[\{\text{CpFe}(\text{CO})_2\text{Ge}\}_2(\mu\text{-O})(\text{SiMo}_{11}\text{O}_{39})]^{4-}$ ,<sup>5e</sup> the Ge–Co bond derivatives  $[\{\{\text{OC}\}_3\text{CoGe}_2\}(\mu\text{-O})(\text{SiW}_{11}\text{O}_{39})]^{5-}$ ,<sup>5e</sup> and the functionalized alkylsilane derivatives, i.e., metallo-salen–POM compounds ( $\text{M-salen-POM}$ )  $[\{\text{SiR}_2(\mu\text{-O})\text{-}(\text{SiW}_{11}\text{O}_{39})\}^{4-}]$  ( $\text{R} = \text{CH}_2\text{CH}_2\text{CH}_2\text{N}=\text{CH}(2\text{-OHPh})$ ).<sup>5f</sup>

Herein we report full details of the synthesis of the KCl-containing bulk sample  $\text{K}_6\text{H}[\mathbf{1a}] \cdot 0.5\text{KCl} \cdot 10\text{H}_2\text{O}$  (**1p**) and the KCl-free crystalline compound  $\text{K}_6\text{H}[\mathbf{1a}] \cdot 10\text{H}_2\text{O}$  (**1c**). The compound **1p** was unequivocally characterized with complete elemental analysis, thermogravimetric and differential thermal analyses (TG/DTA), FTIR and solution (<sup>31</sup>P, <sup>183</sup>W, and <sup>13</sup>C) NMR spectroscopy, and the compound **1c** was characterized with X-ray crystallography.

Experimental Section

**Materials.** The following reactants were used as received: KCl, 6 M aqueous HCl solution (quantitative analysis grade) (all from Wako);  $\text{K}_2[\text{TiO}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$  (Kanto);  $\text{D}_2\text{O}$  (Isotec). The POM precursor  $\text{K}_7[(\text{PW}_{11}\text{TiO}_{39})_2\text{OH}] \cdot 14\text{H}_2\text{O}$  was prepared using KCl, instead of  $\text{Bu}_4\text{NBr}$ , in the synthesis of the  $\text{Bu}_4\text{N}$  salt described in the literature<sup>2i</sup> and characterized with FTIR, <sup>31</sup>P NMR, and TG/DTA. The POM precursor  $\text{K}_{10}[(\alpha-1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2] \cdot 18\text{H}_2\text{O}$ <sup>2h</sup> and the one host–two guests POM,  $\text{K}_5[\mathbf{2a}] \cdot 13\text{H}_2\text{O}$  (**2**),<sup>4b</sup> were also prepared according to the literature and identified.

**Instrumentation/Analytical Procedures.** Complete elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature under  $10^{-3}$ – $10^{-4}$  Torr overnight before analysis. Infrared spectra were recorded on a Jasco 300 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TG8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of 4 °C/min between 20 and 500 °C.

<sup>13</sup>C{<sup>1</sup>H} (100.40 MHz) and <sup>31</sup>P{<sup>1</sup>H} NMR (161.70 MHz) spectra in  $\text{D}_2\text{O}$  solution were recorded in 5-mm outer diameter tubes on a

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- (4) (a) In the present formula of  $[\{\{\text{Ti}(\text{ox})(\text{H}_2\text{O})_4(\mu\text{-O})_3\}(\alpha\text{-PW}_{10}\text{O}_{37})\}^{7-}]$  (**1a**), the oxygen atoms (OH, OH, OH, and OH) coordinated to titanium(IV) atoms are assigned to water oxygens rather than OH groups, because their BVS values (0.419, 0.299, 0.398, and 0.487, respectively) are low ( $\sim 1$  is expected for OH). The formula **1a** is concerned with only the solid-state structure, which could be written as a combination of the cationic fragment “ $[\{\{\text{Ti}(\text{ox})(\text{H}_2\text{O})_4(\mu\text{-O})_3\}^{2+}]$ ” and the anionic POM unit “ $[\alpha\text{-PW}_{10}\text{O}_{37}]^{9-}$ ”. On the other hand, a water molecule coordinated to a higher valence atom such as Ti(IV) can act as strong Bronsted acid. In fact, the deprotonated form  $[\{\{\text{Ti}(\text{ox})(\text{OH})_4(\mu\text{-O})_3\}(\alpha\text{-PW}_{10}\text{O}_{37})\}^{11-}]$  (**1b**) is present in solution (see Experimental Section, pH-Varied <sup>31</sup>P NMR), which could be written as a combination of the anionic fragment “ $[\{\{\text{Ti}(\text{ox})(\text{OH})_4(\mu\text{-O})_3\}^{2-}]$ ” and the anionic POM unit “ $[\alpha\text{-PW}_{10}\text{O}_{37}]^{9-}$ ”. This is also the case for the recently found POM, i.e.,  $[\{\{\text{Ti}(\text{ox})(\text{H}_2\text{O})_2(\mu\text{-O})\}(\alpha\text{-PW}_{11}\text{O}_{39})\}^{5-}]$  (**2a**) or  $[\{\{\text{Ti}(\text{ox})(\text{OH})_2(\mu\text{-O})\}(\alpha\text{-PW}_{11}\text{O}_{39})\}^{7-}]$  (**2b**). In ref 4b, the deprotonated form **2b** is described, while, in ref 4c, the same compound is represented with the protonated form **2a**. (b) Hayashi, K.; Takahashi, M.; Nomiya, K. *Dalton Trans.* **2005**, 3751–3756. (c) Kato, C. N.; Hayashi, K.; Negishi, S.; Nomiya, K. *J. Mol. Catal., A: Chem.* **2006**, in press (a special issue devoted to polyoxoanions in catalysis).

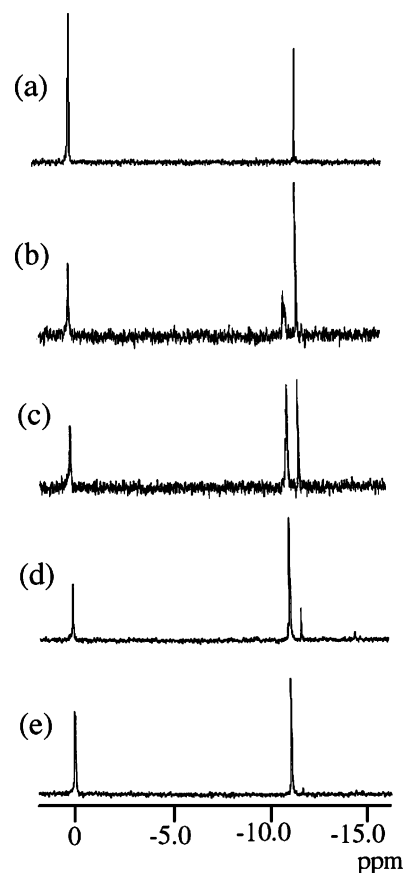
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JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the complexes were measured in  $\text{D}_2\text{O}$  solution with reference to an internal DSS. Chemical shifts are reported as positive for resonances downfield of DSS ( $\delta$  0).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were measured in  $\text{D}_2\text{O}$  solution with reference to an external standard of 25%  $\text{H}_3\text{PO}_4$  in  $\text{H}_2\text{O}$  in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of  $\text{H}_3\text{PO}_4$  ( $\delta$  0).  $^{183}\text{W}$  NMR (16.50 MHz) spectra were recorded in 10-mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe and a JEOL EX-400 NMR data-processing system.  $^{183}\text{W}$  NMR spectra measured in  $\text{D}_2\text{O}$  were referenced to an external standard of saturated  $\text{Na}_2\text{WO}_4\text{-D}_2\text{O}$  solution. Chemical shifts were reported as negative for resonances upfield of  $\text{Na}_2\text{WO}_4$  ( $\delta$  0).

**Preparations.  $\text{K}_6\text{H}\{[\text{Ti}(\text{ox})(\text{H}_2\text{O})_4(\mu\text{-O})_3(\text{PW}_{10}\text{O}_{37})]\cdot 0.5\text{KCl}\cdot 10\text{H}_2\text{O}$  (**1p**) and  $\text{K}_6\text{H}\{[\text{Ti}(\text{ox})(\text{H}_2\text{O})_4(\mu\text{-O})_3(\text{PW}_{10}\text{O}_{37})]\cdot 10\text{H}_2\text{O}$  (**1c**).** To a clear colorless solution of 1.5 g (0.255 mmol) of  $\text{K}_{10}[(\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2]\cdot 18\text{H}_2\text{O}$  dissolved in 20 mL of water was added 5 mL of 6 M aqueous HCl solution. To it was added 0.36 g (1.1 mmol) of  $\text{K}_2[\text{TiO}(\text{ox})_2]\cdot 2\text{H}_2\text{O}$ , followed by stirring for 1 h. To the clear colorless solution was added 1.2 g (16.1 mmol) of solid KCl. After being stirred for 30 min, the solution was filtered through a folded filter paper (Whatman No. 5). The filtrate was placed in a refrigerator at 4 °C. After 2 days the colorless granular KCl-free crystals (**1c**) deposited, which were used for X-ray diffraction measurements. Further on a few days later, from the same mother solution the bulk sample (**1p**) as the KCl-containing crude crystalline compounds was obtained, which was collected on a membrane filter (JG 0.2  $\mu\text{m}$ ) and dried in vacuo for 2 h. The latter was used for characterization with complete elemental analysis, TG/DTA, FTIR, and ( $^{31}\text{P}$ ,  $^{183}\text{W}$ , and  $^{13}\text{C}$ ) NMR spectroscopy. White powder (**1p**) obtained in 28.0% (0.51 g scale) yield was soluble in water but insoluble in EtOH and Et<sub>2</sub>O. Anal. Found (repeat analysis on an independent preparation): H, 0.28 (0.42); C, 2.78 (2.73); Cl, 0.52 (0.32); K, 7.73 (7.97); P, 0.88 (0.79); W, 54.1 (54.3); Ti, 5.73 (5.71); O, 27.1 (26.6); total 99.12 (98.84). Calcd for  $\text{K}_{6.5}\text{H}_{11}\text{Cl}_{0.5}\text{C}_8\text{-PW}_{10}\text{Ti}_4\text{O}_{61}$  or  $\text{K}_6\text{H}\{[\text{Ti}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_4(\mu\text{-O})_3(\text{PW}_{10}\text{O}_{37})]\cdot 0.5\text{KCl}\cdot \text{H}_2\text{O}$ : H, 0.32; C, 2.81; Cl, 0.52; K, 7.44; P, 0.91; W, 53.82; Ti, 5.61; O, 28.57. A weight loss of 4.3% (weakly solvated or adsorbed water) was observed during the course of drying at room temperature at  $10^{-3}\text{-}10^{-4}$  Torr overnight before analysis, suggesting the presence of 8–9 water molecules. TG/DTA under atmospheric conditions: weight loss of 6.1% between 32.2 and 256.5 °C and that of 7.24% between 256.5 and 345.8 °C were observed with endothermic peaks at 99.7 and 268 °C, which could be assigned as calculated weight losses of 5.98% due to dehydration of 12–13 water molecules and those of 6.19% due to decomposition of four oxalato ligands, respectively.

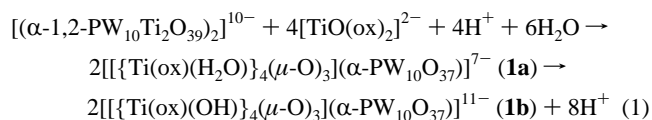
IR (KBr) (polyoxometalate region): 1715 vs, 1688 vs, 1406 m, 1259 w, 1098 m, 1062 m, 1023 w, 966 s, 948 s, 936 s, 870 m (sh), 799 vs, 593 w, 527 m, 495  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR (23.0 °C,  $\text{D}_2\text{O}$ ):  $\delta$  169.8, 170.2. Temperature-dependent  $^{31}\text{P}$  NMR in  $\text{D}_2\text{O}$  (Figure S1, Supporting Information).  $^{31}\text{P}$  NMR (23.2 °C,  $\text{D}_2\text{O}$ ):  $\delta$  -11.2.  $^{31}\text{P}$  NMR (49.7 °C,  $\text{D}_2\text{O}$ ):  $\delta$  -10.9.  $^{31}\text{P}$  NMR (79.7 °C,  $\text{D}_2\text{O}$ ):  $\delta$  -10.7 (main peak) and -11.4, -11.6 (minor peaks).  $^{31}\text{P}$  NMR (23.0 °C,  $\text{D}_2\text{O}$ ), the spectrum remeasured after the sample was cooled from the elevated temperature):  $\delta$  -11.2 (main peak) and -11.8 (minor peak due to  $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2^{10-}$ ).  $^{183}\text{W}$  NMR (22.1 °C,  $\text{D}_2\text{O}$ ):  $\delta$  -131.5 (2W), -141.5 (2W), -156.2 (1W), -248.6 (2W), -303.9 (2W), -403.8 (1W).

**Control Experiment A for Synthesis of 1a.** To a colorless clear solution of  $\text{K}_{10}[(\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2]\cdot 18\text{H}_2\text{O}$  (1.5 g, 0.255 mmol)



**Figure 1.**  $^{31}\text{P}$  NMR of the reaction solutions, in which the molar ratio of the two precursors,  $\text{K}_{10}[(\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2]\cdot 18\text{H}_2\text{O}$  and  $\text{K}_2[\text{TiO}(\text{ox})_2]\cdot 2\text{H}_2\text{O}$ , was changed: (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:4. The solutions (b)–(e) were prepared under HCl-acidic conditions.

in 15 mL of water was added 5 mL of 6 M aqueous HCl. To it was added a solid of  $\text{K}_2[\text{TiO}(\text{ox})_2]\cdot 2\text{H}_2\text{O}$  (0.09 g, 0.255 mmol), the solution was stirred for 30 min, and  $^{31}\text{P}$  NMR was measured. Further addition of a solid of  $\text{K}_2[\text{TiO}(\text{ox})_2]\cdot 2\text{H}_2\text{O}$  (0.09 g, 0.255 mmol) was repeated (up to three times), and the  $^{31}\text{P}$  NMR of the respective solution was measured. Thus, the  $^{31}\text{P}$  NMR spectra in water containing varied molar ratios of the precursor POM and  $[\text{TiO}(\text{ox})_2]^{2-}$  (1:1, 1:2, 1:3, and 1:4) were obtained (Figure 1). By addition of  $[\text{TiO}(\text{ox})_2]^{2-}$ , a new signal appeared at around -11.2 ppm due to a deprotonated species **1b**, and its intensity increased with an increase of  $[\text{TiO}(\text{ox})_2]^{2-}$ . The  $^{31}\text{P}$  NMR spectrum at the 1:4 molar ratio showed a formation of **1b** as a single species (see Experimental Section, pH-Varied  $^{31}\text{P}$  NMR).<sup>4a</sup>

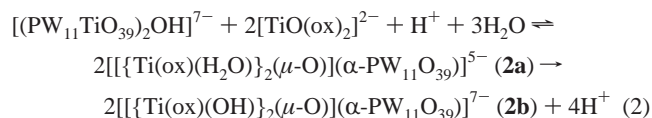


Thus, complex **1p**, and as well as complex **1c**, was synthesized in a 1:4 molar ratio reaction of  $\text{K}_{10}[(\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2]\cdot 18\text{H}_2\text{O}$  with  $\text{K}_2[\text{TiO}(\text{ox})_2]\cdot 2\text{H}_2\text{O}$  in HCl-acidic solution (pH 0.08).

**Control Experiment B for Synthesis of 2a Using the Precursor  $\text{K}_7[(\text{PW}_{11}\text{TiO}_{39})_2\text{OH}]\cdot 14\text{H}_2\text{O}$ .** The recently found POM  $[[\text{Ti}(\text{ox})(\text{H}_2\text{O})_2(\mu\text{-O})](\alpha\text{-PW}_{11}\text{O}_{39})]^{5-}$  (**2a**) has been prepared by reactions of  $[\text{TiO}(\text{ox})_2]^{2-}$  with lacunary Keggin POMs such as  $[\text{A-PW}_9\text{O}_{34}]^{9-}$  and  $[\alpha\text{-PW}_{11}\text{O}_{39}]^{7-}$ .<sup>4b</sup> As a control experiment for synthesis of **2a**, the POM precursor  $[(\text{PW}_{11}\text{TiO}_{39})_2\text{OH}]^{7-}$  was used. This is based on the behavior in solution of **2a**, which has

been exhibited in terms of its dissociation equilibrium to  $[(PW_{11}TiO_{39})_2OH]^{7-}$ ,  $[TiO(ox)_2]^{2-}$ , and  $H^+$ . This equilibrium was consistent with the pH-dependent  $^{31}P$  NMR spectroscopy.<sup>4b</sup>

To a colorless clear solution of  $K_2[TiO(ox)_2] \cdot 2H_2O$  (0.24 g, 0.68 mmol) in 15 mL of water was added  $K_7[(PW_{11}TiO_{39})_2OH] \cdot 14H_2O$  (1.0 g, 0.17 mmol) and then 5 mL of 6 M aqueous HCl. After the sample was stirring for 15 min without heating, the  $^{31}P$  NMR in  $H_2O$  was measured:  $-12.5$  ppm (minor peak) and  $-12.6$  ppm (major peak). The  $^{31}P$  NMR under acidic conditions (pH < 0.5) indicated the formation of a species assignable to **2a** as minor signal and its conjugate base **2b** as a major signal (also see Experimental Section, pH-Varied  $^{31}P$  NMR).<sup>4a</sup>



This control experiment suggests a possibility of formation of novel POMs by reactions of  $K_2[TiO(ox)_2] \cdot 2H_2O$  with various Ti(IV)-substituted Keggin and Dawson POMs as the precursors. Thus, for synthesis of **1a** in this work, we selected the 1,2-dititanium(IV)-substituted  $\alpha$ -Keggin POM  $K_{10}[(\alpha-1,2-PW_{10}Ti_2O_{39})_2] \cdot 18H_2O^{2b}$  as one of such precursors.

**pH-Varied  $^{31}P$  NMR.** A protonated species **1a** is concerned with only the solid-state structure, whereas in aqueous solution it is present as a deprotonated species **1b**. The  $^{31}P$  NMR single peak at  $-11.2$  ppm observed for an aqueous solution of 0.10 g (0.021 mmol) of **1a** dissolved in 10 mL of water (pH = 2.74) is due to **1b**. This chemical shift was unchanged at pH 1.8 and even at pH 0.08. It will be difficult to generate **1a** in aqueous solution. On the other hand, by an increase of the pH of the solution, new signals based on dissociation of the  $ox^{2-}$  ligand and/or decomposition appeared: at pH 4.6 three signals appeared at  $-11.6$  (unknown minor peak),  $-11.9$  (major peak due to the starting, di-Ti(IV)-substituted dimeric POM  $[(\alpha-1,2-PW_{10}Ti_2O_{39})_2]^{10-}$ ),<sup>2b</sup> and  $-12.1$  ppm (major peak due to the monomeric species  $[\alpha-1,2-PW_{10}Ti_2O_{40}]^{7-}$ )<sup>2b</sup> and at pH 7.0 the  $^{31}P$  NMR showed a single peak at  $-12.1$  ppm due to  $[\alpha-1,2-PW_{10}Ti_2O_{40}]^{7-}$ .<sup>2b</sup> Thus, the species **1b** is stable under acidic conditions less than pH ca. 3.

This is the case for protonated species **2a** and deprotonated species **2b** of the one host–two guests POM. The species **2a** is also concerned with only the solid-state structure. An aqueous solution of 1.0 g of **2a** dissolved in 20 mL of water (pH = 1.77) showed two signals of  $^{31}P$  NMR at  $-12.5$  ppm (major) due to **2b** and  $-13.6$  ppm due to the mono-Ti(IV)-substituted dimeric POM  $[(PW_{11}TiO_{39})_2OH]^{7-}$ .<sup>4b</sup> The  $^{31}P$  NMR under much more acidic conditions (pH < 0.5) indicated that a minor peak due to **2a** was observed at  $-12.4$  ppm, in addition to a major peak due to **2b** at  $-12.5$  ppm. The species **2b** was stable under acidic conditions less than pH = 1.5, while, for instance, at pH = 2.5 it completely dissociated to  $[(PW_{11}TiO_{39})_2OH]^{7-}$ ,  $[TiO(ox)_2]^{2-}$ , and  $H^+$ .<sup>4b</sup>

**X-ray Crystallography.** A colorless granular crystal of **1c** ( $0.08 \times 0.06 \times 0.02$  mm<sup>3</sup>) was surrounded by liquid paraffin (Paratone-N) to prevent its degradation. Data collection was done by Bruker SMART APEX CCD diffractometer at 90 K in the range of  $1.10^\circ < 2\theta < 56.56^\circ$ . The intensity data were automatically corrected for Lorentz and polarization effects during integration. The structure was solved by direct methods (program SHELXS-97)<sup>6a</sup> followed by subsequent difference Fourier calculation and refined by full-matrix, least-squares procedure on  $F^2$  (program SHELXL-97).<sup>6b</sup> Absorption correction was performed with SADABS (empirical absorption correction).<sup>6c</sup>

Crystal data for  $C_8H_{29}K_6O_{70}PTi_4W_{10}$ :  $M = 3540.98$ ; triclinic, space group  $P\bar{1}$ ;  $a = 12.638(4)$ ,  $b = 14.219(5)$ ,  $c = 18.992(6)$  Å;  $\alpha = 101.182(4)$ ,  $\beta = 92.160(5)$ ,  $\gamma = 101.480(4)^\circ$ ;  $V = 3270.8(18)$  Å<sup>3</sup>;  $Z = 2$ ;  $D_c = 3.595$  Mg m<sup>-3</sup>;  $\mu(Mo K\alpha) = 18.499$  mm<sup>-1</sup>;  $R1 = 0.0806$ ,  $wR2 = 0.1594$  (for all data);  $R_{int} = 0.0582$ ,  $R1 = 0.0536$ ,  $wR2 = 0.1398$ ; GOF = 1.052 (37 733 total reflections, 15 838 unique reflections where  $I > 2\sigma(I)$ ). The maximum and minimum residual density (8.780 and  $-3.973$  e Å<sup>-3</sup>) holes were located at 0.68 Å from K6 and 0.51 Å from K5, respectively.

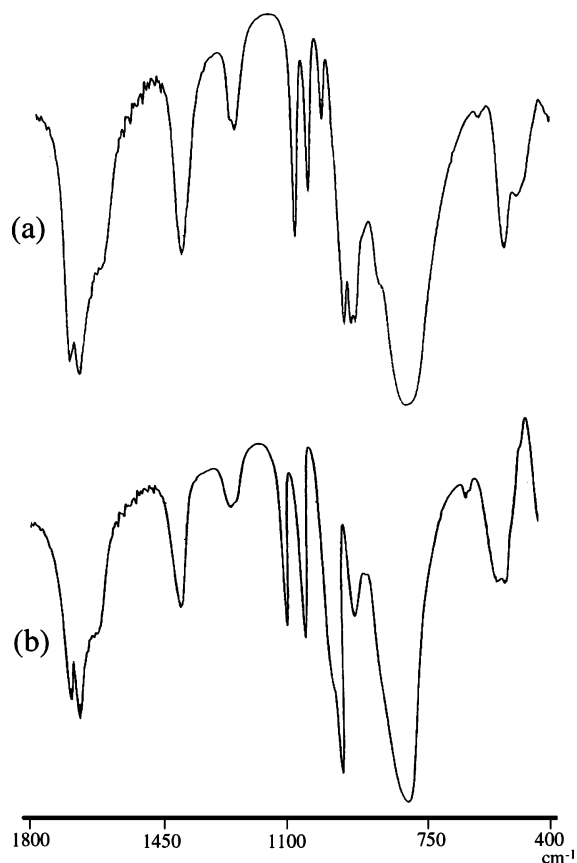
The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (all atoms except solvent water oxygens), and isotropic thermal parameters (some of hydrated water oxygens), converged at  $R = 0.0806$  and  $R_w = 0.1594$ . No hydrogens were included in the refinement. We obtained the best crystallographic refinement results (lowest residual electron density) by assigning 6 potassium counterions (full occupancy for K1–K6). The 10 tungsten atoms, the 4 titanium atoms, and the 1 P atom were clearly identified. Thus, the main features of the molecular structure of the polyoxoanion were clear. However, it is very frequently impossible in POM chemistry due to disorder to locate and assign all counteractions and water molecules of crystallization unequivocally by single-crystal X-ray diffraction. These features are all too common in polyoxoanion crystallography.<sup>2,3,7</sup> CCDC-295994 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax, +44-1223-336-033; e-mail, [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## Results and Discussion

**Compositional Characterization.** The composition and molecular formula of the bulk powder sample (**1p**) were consistent with complete elemental analysis, TG/DTA, FTIR, and ( $^{31}P$ ,  $^{183}W$ , and  $^{13}C$ ) NMR spectroscopy, and those of the crystalline sample (**1c**) without the 0.5 KCl adduct were consistent with X-ray crystallography. In the complete elemental analysis performed on a sample that was dried at room temperature under  $10^{-3}$ – $10^{-4}$  Torr overnight before analysis, all elements including oxygen totaled 99.12% for **1p**, the data of which were consistent with the composition of  $K_6H[1a] \cdot 0.5KCl \cdot H_2O$ . Repeat data for complete elemental analysis carried out on an independently prepared sample also confirmed the composition and formula of **1p** (see Experimental Section).

The weight loss observed during the course of drying before analysis was 4.3%, which corresponded to 8–9 water molecules weakly solvated or adsorbed for **1p**. The number of 10 water molecules in the sample is determined as the sum of the 1 water molecule found in the complete elemental analysis plus the 8–9 water molecules corresponding to the weight loss observed during the course of drying before analysis. Thus, the composition and formula of **1p** as a bulk

- (6) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *A46*, 467–473. (b) Sheldrick, G. M. *SHELXL-97 program for crystal structure refinement*; University of Gottingen: Gottingen, Germany, 1997. (c) Sheldrick, G. M. *SADABS*; University of Gottingen: Gottingen, Germany, 1996.
- (7) (a) Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1235–1241. (b) Sakai, Y.; Kitakoga, Y.; Hayashi, K.; Yoza, K.; Nomiya, K. *Eur. J. Inorg. Chem.* **2004**, 4646–4652. (c) Sakai, Y.; Shinohara, A.; Hayashi, K.; Nomiya, K. *Eur. J. Inorg. Chem.* **2006**, 163–171.



**Figure 2.** FT-IR spectra in the polyoxoanion region (1800–400  $\text{cm}^{-1}$ ), measured as KBr disks, of (a) **1p** and (b) **2**.

sample were determined to be  $\text{K}_6\text{H}[\mathbf{1a}] \cdot 0.5\text{KCl} \cdot 10\text{H}_2\text{O}$ . The adduct of 0.5 KCl in **1p** was found only in the bulk sample for complete elemental analysis and TG/DTA, whereas it was not detected in the crystalline sample **1c** with X-ray crystallography. The contamination of KCl in the bulk sample is dependent on the present experiments for crystallization.

TG/DTA measurements under atmospheric conditions showed a weight loss of 6.1% at under 256.5 °C and that of 7.24% at between 256.5 and 345.8 °C with endothermic peaks at 99.7 and 268 °C, which could be assigned as calculated weight loss of 5.98% due to dehydration of 12–13 water molecules and that of 6.19% due to decomposition of four oxalato ligands.

The solid FTIR spectrum of **1p** showed the characteristic vibrational bands of the Keggin-type “ $\text{XW}_{12}\text{O}_{40}^{n-}$ ” polyoxotungstate framework.<sup>8</sup> The FTIR of **1p** as a powder sample in the 1800–400  $\text{cm}^{-1}$  region (Figure 2) showed the vibrational bands at 1715, 1688, 1406, and 1259  $\text{cm}^{-1}$  originated from the starting compound  $[\text{TiO}(\text{ox})_2]^{2-}$  and the vibrational bands at 1098, 1062, 1023, 966, 948, 936, 870, and 799  $\text{cm}^{-1}$  originated from the “dilacunary  $\alpha$ -Keggin POM unit  $[\alpha\text{-PW}_{10}\text{O}_{37}]^{9-}$ ”.

Bond-valence sum (BVS) calculations<sup>9</sup> of the oxygen atoms in **1a** indicate that the four oxygen atoms (O1H, O2H,

O3H, and O4H), which are bonded to Ti atoms, are protonated. They are assignable to water oxygen atoms rather than the  $\text{OH}^-$  groups, because of lower BVS values (see Molecular Structure of **1a**).<sup>4a</sup>

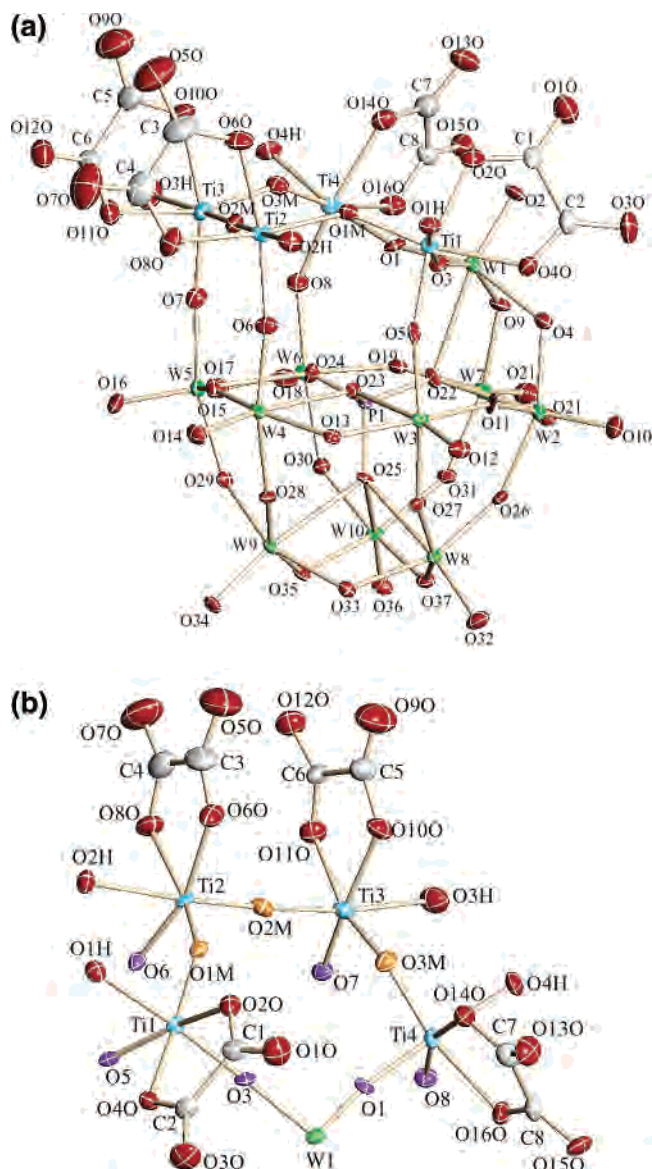
**Molecular Structure of 1a.** The crystal system (triclinic), the space group ( $P\bar{1}$  (No. 2)), and a disorder-free polyoxometalate unit provided a straightforward solution of the structure as well as refinement. Structural analysis revealed the molecular structure of **1a** as shown in Figure 3. The crystals of **1c** contain discrete polyoxoanions, potassium cations, and lattice water molecules, all on general positions in this space group. The 6 potassium cations were identified in the crystal structure of **1c**. The observed electron densities on the Ti and W atoms are quite different, and the data unequivocally distinguish and define the Ti and W atoms.

The molecular structure of **1a** is composed of the “dilacunary  $\alpha$ -Keggin POM unit  $[\alpha\text{-PW}_{10}\text{O}_{37}]^{9-}$ ” and the cationic  $[\{\text{Ti}(\text{ox})(\text{H}_2\text{O})\}_4(\mu\text{-O})_3]^{2+}$  unit that is the two Ti–O–Ti bonding species (–Ti1–O1M–Ti2– unit and –Ti3–O3M–Ti4– unit) linked with the  $\mu\text{-O}$  atom (O2M) (Figure 3). Selected bond distances and angles around the titanium(IV) centers in **1a** are given in Table 1. In the  $[\{\text{Ti}(\text{ox})(\text{H}_2\text{O})\}_4(\mu\text{-O})_3]^{2+}$  unit, there were two nonequivalent groups of 6-coordinate Ti centers (Ti1 and Ti4 are equivalent and Ti2 and Ti3 are also equivalent, whereas Ti1 and Ti2 are nonequivalent and Ti3 and Ti4 are nonequivalent). Each of the four Ti centers was bonded to one chelating oxalato ligand and one monodentate  $\text{H}_2\text{O}$  molecule (O1H, O2H, O3H, O4H),<sup>4a</sup> but the octahedral geometry for the two Ti centers (Ti2 and Ti3) was accomplished by bonding with one oxygen atom (O6 or O7) from the dilacunary Keggin POM and bridging oxygen atoms ( $\mu\text{-O}$ ) (O1M, O2M, O3M) and that for the two Ti centers (Ti1 and Ti4) was attained with two oxygen atoms ((O5 and O3) or (O1 and O8)) from the dilacunary POM and bridging oxygen atom (O1M or O3M), resulting in the overall  $C_s$  symmetry of the polyoxoanion molecule.

The four “ $\{\text{Ti}(\text{ox})(\text{H}_2\text{O})\}$ ” moieties in **1a** can be also considered to be that the two similar Ti–O–Ti units (–Ti1–O1M–Ti2– and –Ti3–O3M–Ti4–) are bridged by one oxygen atom (O2M), because the Ti–O–Ti angles of the intraunits (Ti1–O1M–Ti2 143.3(5)°, Ti3–O3M–Ti4 141.0(5)°) are quite different from that between the two units, i.e., that of interunits (Ti2–O2M–Ti3 176.5(6)°). In **1a**, the Ti–O(bridging) distances in the intraunits (Ti1–O1M 1.798(9) Å, Ti2–O1M 1.853(9) Å, Ti3–O3M 1.817(9) Å, Ti4–O3M 1.810(9) Å) can be compared with those in the interunits (Ti2–O2M 1.755(9) Å, Ti3–O2M 1.850(9) Å). The Ti–O–Ti angles and the Ti–O(bridging) distances of the intraunits are also compared with those in the recently reported POM **2a** (Ti1–O8–Ti2 136.4(3)°, Ti1–O8 1.833(6) Å, Ti2–O8 1.813(6) Å).

(8) (a) Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Franck, R. *Spectrochim. Acta* **1976**, *32A*, 587–597. (b) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R. *Inorg. Chem.* **1983**, *22*, 207–216. (c) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598–605.

(9) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *B41*, 244–247. (b) Brown, I. D.; Shannon, R. D. *Acta Crystallogr., Sect. A* **1973**, *29*, 266–282. (c) Brown, I. D. *Acta Crystallogr., Sect. B* **1992**, *B48*, 553–572. (d) Brown, I. D. *J. Appl. Crystallogr.* **1996**, *29*, 479–480.



**Figure 3.** (a) Molecular structure with 50% probability ellipsoids of **1a**, composed of oxygen (red), carbon (gray), phosphorus (purple), titanium (sky blue), and tungsten (green) atoms, and (b) the partial structure around the two Ti–O–Ti units linked by the  $\mu$ -O (O2M) atom, composed of oxygen (Ti–O–Ti unit (orange), coordinating water and  $ox^{2-}$  ligand (red), and POM unit (purple), carbon (gray), titanium (sky blue), and tungsten (green) atoms. In (b), the Ti1 and Ti4 atoms are equivalent with to each other and as well as the Ti2 and Ti3 atoms, while the (Ti1, Ti4) atoms are inequivalent to the (Ti2, Ti3) atoms. Each 6-coordinate geometry of the two titanium atoms (Ti1 and Ti4) is achieved with the two oxygen atoms (O3, O5) and (O1, O8), respectively, from the “dilacunar POM unit [ $\alpha$ -PW<sub>10</sub>O<sub>37</sub>]<sup>9-</sup>”, a chelating oxalato ligand, one terminal oxygen atom due to H<sub>2</sub>O (O1H and O4H, respectively), and one bridging oxygen atom (O1M and O3M, respectively). On the other hand, each of the other titanium atoms (Ti2 and Ti3) also takes 6-coordinate geometry with one oxygen atom (O6 and O7, respectively) from the “dilacunar POM”, a chelating oxalato ligand, one terminal oxygen atom (O2H and O3H, respectively) and two bridging oxygen atoms (O1M, O2M) and (O3M, O2M), respectively.

Bond distances and angles around the four “{Ti(ox)-(H<sub>2</sub>O)}” moieties in **1a** (C–C 1.49–1.56 Å, O(ox)–Ti–O(ox) 75.9–77.1°, O(ox)–Ti 2.015–2.094 Å, Ti–O(terminal) 2.081–2.262 Å) can be compared with those in **2a** (C–C 1.555–1.563 Å, O(ox)–Ti–O(ox) 77.3–77.5°, O(ox)–Ti 2.018–2.089 Å, Ti–O(terminal) 2.131–2.137 Å). These values can be also compared with those of the precursors

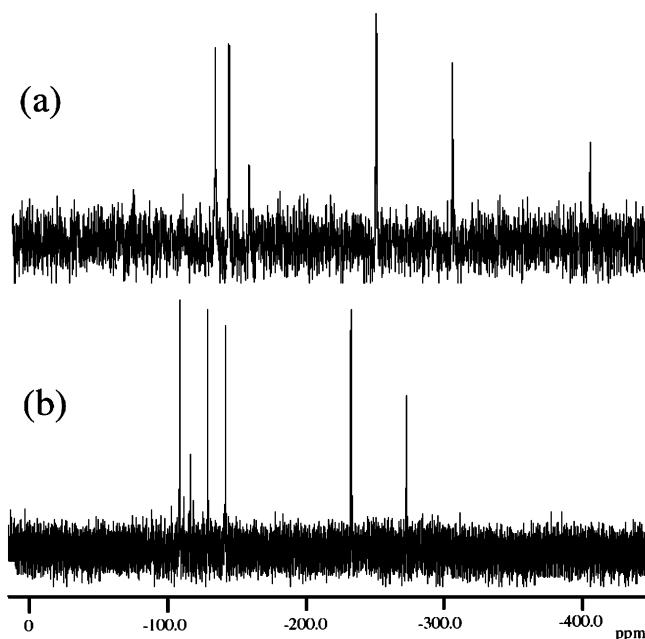
**Table 1.** Selected Bond Distances (Å) and Angles (deg) around the Titanium(IV) Centers in **1a**

| Ti–O Distances and Ti–O–Ti and O–Ti–O Angles around the Ti–O–Ti Bonding Moiety    |           |  |           |
|---|-----------|--|-----------|
| Ti1–O1M   | 1.805(10) | Ti2–O1M                                | 1.763(11) |
| Ti2–O2M   | 1.763(11) | Ti3–O2M                                | 1.843(11) |
| Ti4–O3M   | 1.817(11) | Ti3–O3M                                | 1.814(11) |
| Ti1–O1M–Ti2   | 143.4(6)  | Ti2–O2M–Ti3                            | 176.4(7)  |
| Ti4–O3M–Ti3   | 140.8(7)  |  |           |
| O1M–Ti2–O2 M  | 100.2(5)  | O2M–Ti3–O3 M                           | 96.6(5)   |
| Ti1–O1H   | 2.136(11) | Ti3–O3H                                | 2.163(14) |
| Ti2–O2H   | 2.263(11) | Ti4–O4H                                | 2.073(12) |
| O1M–Ti1–O1H   | 87.8(4)   |  |           |
| O1M–Ti2–O2H   | 81.8(4)   | O2M–Ti2–O2H                            | 176.4(5)  |
| O2M–Ti3–O3H   | 171.2(5)  | O3M–Ti3–O3H                            | 91.3(5)   |
| O3M–Ti4–O4H   | 86.2(5)   |  |           |
| Ti4–O1<br>(A site of POM)   | 1.854(11) | Ti1–O3<br>(A site of POM)              | 1.876(10) |
| Ti1–O5<br>(W <sub>6</sub> belt of POM)  | 1.880(10) | Ti3–O7<br>(W <sub>6</sub> belt of POM) | 1.844(11) |
| Ti2–O6<br>(W <sub>6</sub> belt of POM)  | 1.897(10) | Ti4–O8<br>(W <sub>6</sub> belt of POM) | 1.868(11) |
| O5–Ti1–O1H  | 83.7(4)   | O3–Ti1–O5                              | 97.1(4)   |
| O1M–Ti1–O5  | 103.3(5)  |  |           |
| O1M–Ti2–O6  | 91.7(5)   | O6–Ti2–O2H                             | 84.2(4)   |
| O2M–Ti2–O6  | 93.1(5)   |  |           |
| O7–Ti3–O2M  | 98.2(5)   | O7–Ti3–O3H                             | 83.6(5)   |
| O3M–Ti3–O7  | 103.0(5)  |  |           |
| O8–Ti4–O4H  | 90.7(5)   | O3M–Ti4–O8                             | 104.5(5)  |
| O1–Ti4–O8   | 95.8(5)   |  |           |
| C–C and C–O Distances and O–Ti–O Angles around the Coordinating $ox^{2-}$ Ligands |           |  |           |
| Ti1–O2O(oxalato)  | 2.020(11) | Ti1–O4O(oxalato)                       | 2.092(11) |
| Ti2–O6O(oxalato)  | 2.005(12) | Ti2–O8O(oxalato)                       | 2.053(13) |
| Ti3–O10O(oxalato)   | 2.055(13) | Ti3–O11O(oxalato)                      | 2.064(12) |
| Ti4–O14O(oxalato)   | 2.060(12) | Ti4–O16O(oxalato)                      | 2.090(12) |
| C1–C2   | 1.53(2)   | C5–C6                                  | 1.55(2)   |
| C3–C4   | 1.47(3)   | C7–C8                                  | 1.52(2)   |
| C1–O10  | 1.26(2)   | C5–O90                                 | 1.19(2)   |
| C1–O20  | 1.271(19) | C5–O100                                | 1.30(2)   |
| C2–O30  | 1.26(2)   | C6–O120                                | 1.23(2)   |
| C2–O40  | 1.281(19) | C6–O110                                | 1.272(19) |
| C3–O50  | 1.28(3)   | C7–O130                                | 1.25(2)   |
| C3–O60  | 1.31(2)   | C7–O140                                | 1.30(2)   |
| C4–O70  | 1.28(3)   | C8–O150                                | 1.235(19) |
| C4–O80  | 1.30(2)   | C8–O160                                | 1.272(16) |
| O2O–OTi1–O4O  | 76.7(4)   | O100–Ti3–O110                          | 76.3(5)   |
| O6O–Ti2–O8O   | 76.8(5)   | O140–Ti4–O16O                          | 76.1(5)   |

$M_2[TiO(ox)_2] \cdot nH_2O$  ( $M = K$  and  $NH_4$ ),<sup>10a,b</sup> both of which contained bis( $\mu$ -oxo)tetratitanium anions with an eight-membered –O–Ti–O– ring, i.e.,  $[TiO(ox)_2]_4^{8-}$ : Ti–O(bridging) distances 1.790–1.838 Å, Ti–O(ox) distances 1.977–2.116 Å, and C–C distances 1.530–1.537 Å for  $K_2[TiO(ox)_2] \cdot 2.25H_2O$ <sup>10a</sup> and Ti–O(bridging) distances 1.785–1.855 Å, Ti–O(ox) distances 1.963–2.116 Å, and C–C distances 1.50–1.54 Å for  $(NH_4)_2[TiO(ox)_2] \cdot H_2O$ .<sup>10b</sup>

The bond distances (Ti–O(W)) among the four Ti atoms and the six terminal oxygen atoms of the “dilacunar Keggin POM unit” in **1a** (Ti1–O3 1.875(9) Å, Ti1–O5 1.885(9) Å, Ti2–O6 1.902(8) Å, Ti3–O7 1.846(9) Å, Ti4–O1 1.852(9) Å, Ti4–O8 1.861(9) Å) were close to those among the two Ti atoms and the four terminal oxygen atoms of the

(10) (a) Haddad, M.; Brisse, F. *Can. Mineral.* **1978**, *16*, 379–385. (b) Van de Velde, G. M. H.; Harkema, S.; Gellings, P. J. *Inorg. Chim. Acta* **1974**, *11*, 243–252.



**Figure 4.**  $^{183}\text{W}$  NMR in  $\text{D}_2\text{O}$  of (a) **1p** and (b) **2**. The resonance at 0.0 ppm is due to the external reference of saturated  $\text{Na}_2\text{WO}_4\text{-D}_2\text{O}$  solution.

monolacunary Keggin POM unit in **2a** (Ti1–O2 1.861(6) Å, Ti1–O9 1.885(6) Å, Ti2–O6 1.861(6) Å, Ti2–O14 1.871(6) Å). Several POMs such as the Keggin-type, dimeric, Ti–O–Ti-bridged anhydride forms have shown longer Ti–O(W) distances, e.g. average 1.98 Å (1.92–2.02 Å) in  $[(\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{38})_2\text{O}_2]^{10-2\text{h}}$  and average 2.01 Å (1.98–2.05 Å) in  $[(\alpha\text{-}1,2,3\text{-PW}_9\text{Ti}_3\text{O}_{37})_2\text{O}_3]^{12-2\text{g}}$ .

The W–Ot (Ot: terminal oxygen) [1.696(9)–1.728(8) Å], W–Oc (Oc: corner-sharing oxygen) [1.870(8)–1.986(8) Å], W–Oe (Oe: edge-sharing oxygen) [1.876(8)–1.982(8) Å], and W–Oa (Oa: oxygen coordinated to P atom) [2.333(8)–2.470(8) Å] distances in **1a** are in the normal range (Table S1).<sup>1b</sup> The polyoxoanion contains one central P atom in an almost regular tetrahedral environment of  $\text{PO}_4$  with P–O distances in the range 1.517(9)–1.565(8) Å and O–P–O bond angles of 106.5(4)–111.6(5)°.

The calculated bond valence sum (BVS),<sup>9</sup> based on the observed bond distances in **1a**, at the P heteroatom was 4.899, and those for Ti and W atoms were 4.189–4.262 for the 4 Ti atoms and 6.059–6.321 for the 10 W atoms (Table S2). These data reasonably correspond to the formal valences of  $\text{P}^{5+}$ ,  $\text{Ti}^{4+}$ , and  $\text{W}^{6+}$ , respectively. On the other hand, the BVS values of all 40 oxygen atoms (Table S2), except O1H, O2H, O3H, and O4H atoms, in the polyoxoanion suggest that they are not protonated. The BVS values of the four oxygen atoms O1H (0.419), O2H (0.299), O3H (0.398), and O4H (0.487), which are bonded to Ti atoms as terminal oxygen atoms, suggest that they are doubly protonated; i.e., they exist as the  $\text{H}_2\text{O}$  groups ( $\sim 1$  is expected for the monoprotonated oxygen or OH group).<sup>4a</sup> The BVS values of the  $\mu_2\text{-O}$  atoms, i.e., O1M (1.949), O2M (2.086), and O3M (2.009), in the Ti–O–Ti bonds suggest that they are not protonated.

**Solution ( $^{183}\text{W}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ ) NMR and Behavior in Aqueous Solution.** The  $^{183}\text{W}$  NMR spectrum in  $\text{D}_2\text{O}$  at 22.1

°C of **1p** (Figure 4) showed a six-line spectrum at  $-131.5$  (2W),  $-141.5$  (2W),  $-156.2$  (1W),  $-248.6$  (2W),  $-303.9$  (2W), and  $-403.8$  (1W). The observed spectrum is due to the overall  $C_s$  symmetry and is consistent with the solid-state molecular structure, indicating that the solid-state structure is kept in aqueous solution. Thus, the signals with the relative intensity of 1W at  $-403.8$  and  $-156.2$  ppm would be assignable to the tungsten atom (W1) closest to the Ti atom and to the tungsten atom (W10) far from the Ti atom, respectively.

The  $^{13}\text{C}$  NMR spectrum in  $\text{D}_2\text{O}$  at 23.0 °C of **1p** showed two signals at 169.8 and 170.2 ppm due to the  $\text{ox}^{2-}$  ligands coordinated to the two nonequivalent Ti centers (see Molecular Structure). The  $^{13}\text{C}$  NMR is also consistent with the solid-state molecular structure.

The  $^{31}\text{P}$  NMR spectrum in  $\text{D}_2\text{O}$  at 23.2 °C of **1p** showed a single peak at  $-11.2$  ppm, suggesting that this POM is relatively stable in aqueous solution and does not show the dissociation equilibrium of the  $[\text{TiO}(\text{ox})_2]^{2-}$  anion as observed in  $^{31}\text{P}$  NMR of **2a** dissolved in  $\text{D}_2\text{O}$ .<sup>4b</sup> POM **2a** in aqueous solution has shown a dissociation equilibrium to the monotitanium(IV)-substituted dimeric species  $[(\text{PW}_{11}\text{TiO}_{39})_2\text{OH}]^{7-}$  and the  $[\text{TiO}(\text{ox})_2]^{2-}$  anion. Thus, POM **1a** in aqueous solution is stable in contrast to **2a** (also see Experimental Section, pH-Varied  $^{31}\text{P}$  NMR).

Temperature-dependent  $^{31}\text{P}$  NMR of **1a** in  $\text{D}_2\text{O}$  were also measured (see the Experimental Section and Figure S1). The  $^{31}\text{P}$  NMR at 49.7 °C showing a single peak at  $-10.9$  ppm would be essentially the same spectrum at 23.2 °C. At 79.7 °C, in addition to the main peak at  $-10.7$  ppm, the minor peaks at  $-11.4$  and  $-11.6$  ppm appeared. The  $^{31}\text{P}$  NMR remeasured at 23.0 °C, after cooling, showed the main peak at  $-11.2$  ppm due to **1a** (actually **1b**) and the minor peak at  $-11.8$  ppm due to the precursor  $[(\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2]^{10-}$ . Thus, POM **1a** in aqueous solution is stable at under ca. 50 °C, but at higher temperatures it tends to partially revert to the precursor by dissociating the  $[\text{TiO}(\text{ox})_2]^{2-}$  anion. The temperature-dependent  $^{31}\text{P}$  NMR of **1a** are also in contrast to those of **2a**. The latter showed the temperature-dependent dissociation equilibrium of **2a** to the anions  $[(\text{PW}_{11}\text{TiO}_{39})_2\text{OH}]^{7-}$  and  $[\text{TiO}(\text{ox})_2]^{2-}$ , in which the original  $^{31}\text{P}$  NMR spectrum was recovered after cooling to room temperature.

## Conclusion

Novel POM **1a**, composed of the “dilacunary site (two hosts)” of the  $\alpha$ -Keggin POM unit and the two Ti–O–Ti groups (four guests) linked with the  $\mu\text{-O}$  atom, was produced. The synthesis of **1a** was designed by a reaction of the anionic titanium(IV) complex  $[\text{TiO}(\text{ox})_2]^{2-}$  with the dimeric dititanium(IV)-substituted POM precursor  $[(\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2]^{10-}$  (one host–one guest POM) under HCl-acidic conditions. Solution ( $^{13}\text{C}$  and  $^{183}\text{W}$ ) NMR suggested that the molecular structure of **1a** was also kept in aqueous solution. The pH-varied  $^{31}\text{P}$  NMR showed that **1a** dissolved in aqueous solution was actually present as a deprotonated form **1b** and the latter was stable under acidic conditions less than pH ca. 3. Temperature-varied  $^{31}\text{P}$  NMR also showed that **1a** in aqueous solution was stable at under ca. 50 °C. POM **1a**

### *Novel Ti–O–Ti Bonding Species*

has been extended from the recently prepared, one host–two guests type POM **2a**. The reaction of the bis(oxalato)-oxotitanate(IV) complex with other Ti(IV)-substituted POM precursors would be applicable to formation of novel POMs containing Ti–O–Ti bonding species.

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**Supporting Information Available:** Temperature-dependent  $^{31}\text{P}$  NMR of **1p** in  $\text{D}_2\text{O}$  (Figure S1), X-ray crystallographic files in CIF format, average bond distances ( $\text{\AA}$ ) and angles (deg) (range) for the Keggin POM moiety in **1a** (Table S1), and bond valence sum (BVS) calculations of W(1–10), Ti(1–4), P, and O atoms (Table S2). This material is available free of charge via the Internet at <http://pub.acs.org>.

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