

Isolation, characterization, and reactivity of the reaction products of the dimeric, Ti–O–Ti bridged anhydride form of the 1,2-di-titanium(IV)-substituted α -Keggin polyoxometalate with aqueous 30% H_2O_2

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Abstract

The isolation and characterization of the monomeric bis[peroxotitanium(IV)]-substituted α -Keggin polyoxometalate (POM) $\text{K}_7[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiO}_2)_2\text{O}_{38}]\cdot 8\text{H}_2\text{O}$ (**1**) and the monomeric bis[hydroperoxotitanium(IV)]-substituted α -Keggin POM $\text{K}_5[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiOOH})_2\text{O}_{38}]\cdot 5\text{H}_2\text{O}$ (**2**) are described. The orange solution was prepared by adding an excess amount of aqueous 30% H_2O_2 to the in situ-generated monomeric Keggin species $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$ in a neutral aqueous solution derived by the hydrolytic cleavage of the dimeric, Ti–O–Ti bridged anhydride form $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2\cdot 18\text{H}_2\text{O}$. Reprecipitation of the orange solution with MeOH gave a *thermally stable* yellow species containing the peroxo groups (compound **1**) whereas reprecipitation with EtOH yielded a relatively *unstable* orange species that would contain the hydroperoxo groups (compound **2**). The characterization of **1** and **2** was accomplished by a complete elemental analysis, TG/DTA, FTIR, UV–vis, solution (^{31}P and ^{183}W) NMR and ^{31}P CPMAS NMR spectroscopy, and (for **1** only) X-ray crystallography. Complex **1** did not show any activity for 2-propanol oxidation in the absence of 30% H_2O_2 whereas complex **2** showed an effective activity for the oxidation reaction.

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1. Introduction

Polyoxometalates (POMs) are molecular metal-oxide clusters, which are currently of interest as they are soluble metal oxides and have applications in catalysis, medicine, and material sciences [1–12]. The site-selective substitution of the W^{VI} atoms in POMs with Ti^{IV} atoms is particularly interesting due to the formation of multicenter active sites with corner- and/or edge-sharing TiO_6 octahedra and the water-soluble molecular modeling of titanium(IV) oxides, which are good semiconductors and photocatalysts [13–15].

Many H_2O_2 -based oxidation reactions catalyzed by titanium(IV)-substituted POMs have been reported, in which the unstable hydroperoxotitanium(IV) species, rather than the stable peroxotitanium(IV) species, have been regarded as being the active intermediate [16–19]. The synthesis and structural characterization of the peroxotitanium(IV)

and/or hydroperoxotitanium(IV)-substituted POMs would be an intriguing project to undertake in order to investigate the reaction mechanisms for the H_2O_2 -based oxidation catalysis. Hardly any examples of the structural determination of POM-based peroxotitanium(IV) complexes have been reported so far; the two examples reported have been mono-peroxotitanium(IV)-substituted Keggin POM $[\text{PW}_{11}(\text{TiO}_2)\text{O}_{39}]^{5-}$ [20] and tri-peroxotitanium(IV)-substituted Dawson POM $[\alpha\text{-}1,2,3\text{-P}_2\text{W}_{15}(\text{TiO}_2)_3\text{O}_{56}(\text{OH})_3]^{9-}$ with side-on coordination (i.e. η^2 -coordination) of the peroxo groups to the titanium(IV) atoms [21]. These peroxotitanium(IV)-substituted POMs were inactive toward organic substrates. In contrast, Kholdeeva and co-workers [22] recently reported the first example of the isolated protonated peroxotitanium(IV)-substituted Keggin POM $[\text{HPTi}(\text{O}_2)\text{W}_{11}\text{O}_{39}]^{4-}$, which was active toward organic substrates.

Here, we prepared in situ-generated monomeric di-titanium(IV)-substituted Keggin POM $[\text{PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$ in aqueous solution by the hydrolytic cleavage of the dimeric precursor $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2\cdot 18\text{H}_2\text{O}$ [23]; this POM contained corner-sharing Ti–O–Ti bridges in both the inter-Keggin

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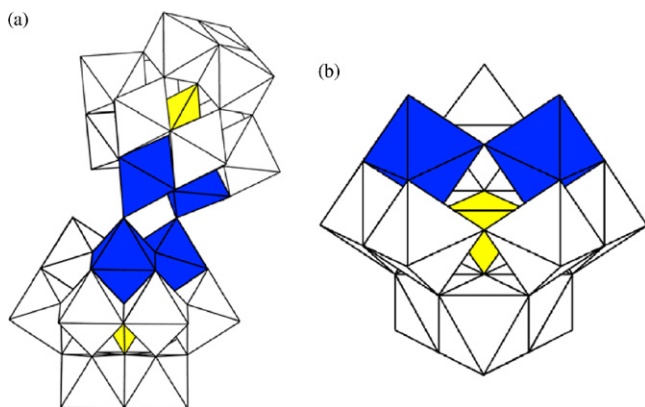


Fig. 1. Polyhedral representations of: (a) $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2^{10-}$ and (b) in situ-generated $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$. The TiO_6 octahedra in the 1,2-positions are represented as the blue octahedra, the WO_6 octahedra are shown as the white octahedra, and the central PO_4 group is shown as the internal yellow tetrahedron.

and intra-Keggin units, as shown in Fig. 1. The orange solution obtained by a reaction of in situ-generated $[\text{PW}_{10}\text{Ti}_2\text{O}_4]^{7-}$ with an excess amount of aqueous 30% H_2O_2 showed a single peak in ^{31}P NMR at -11.77 ppm, assignable to the hydroperoxo group-coordinating species. We found that reprecipitation of the orange solution with alcohols yielded two different colored compounds: reprecipitation with MeOH yielded a thermally stable yellow species (compound **1**) whereas reprecipitation with EtOH yielded a relatively unstable orange species (compound **2**). The yellow and orange species were isolated as analytically pure, all-inorganic compositions of the bis[peroxotitanium(IV)]-substituted α -Keggin POM $\text{K}_7[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiO}_2)_2\text{O}_{38}] \cdot 8\text{H}_2\text{O}$ (**1**) and the bis[hydroperoxotitanium(IV)]-substituted α -Keggin POM $\text{K}_5[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiOOH})_2\text{O}_{38}] \cdot 5\text{H}_2\text{O}$ (**2**), respectively. The characterization of **1** and **2** was accomplished by a complete elemental analysis, TG/DTA, FTIR, UV–vis, solution (^{31}P and ^{183}W) NMR and ^{31}P CPMAS NMR spectroscopy, and X-ray crystallography. We also investigated the NMR tube reaction of 2-propanol to form acetone by the compounds **1** and **2** in the absence of H_2O_2 to confirm that compound **1** was an inactive peroxotitanium(IV) species but that compound **2** was an active hydroperoxotitanium(IV) species for the oxidation reaction.

2. Experimental

2.1. Materials

The following materials were used as received: (1 and 0.1 M) aqueous KOH solutions, MeOH, Et_2O , 30% aqueous H_2O_2 solution (all from Wako); D_2O (Isotec). The synthesis and characterization of the dimeric precursor $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$ was reported elsewhere [23].

2.2. Instrumentation and analytical procedure

A complete elemental analysis was carried out by Mikro-analytisches Labor Pascher (Remagen, Germany). The sample was dried overnight at room temperature under a pressure of

10^{-3} to 10^{-4} torr before analysis. IR spectra were recorded on a Jasco 300 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were performed using a Rigaku TG8101D and a TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of $4^\circ\text{C}/\text{min}$ between 25 and 500°C . ^{31}P NMR (161.70 MHz) spectra in D_2O solution were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and a JEOL EX-400 NMR data-processing system. The ^{31}P NMR spectra were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts were reported on the δ scale with resonances upfield of H_3PO_4 (δ 0) as negative. ^{183}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}W NMR spectra measured in D_2O were referenced to an external standard of saturated $\text{Na}_2\text{WO}_4\text{-D}_2\text{O}$ solution (δ 0). The ^{31}P CPMAS NMR spectra were referenced to an external standard of $(\text{NH}_4)_2\text{HPO}_4$ by a substitution method at 25°C , and their chemical shifts were calibrated indirectly through an external $(\text{NH}_4)_2\text{HPO}_4$ (δ 1.6). UV–vis absorption spectra were recorded on a Jasco V-560 spectrophotometer using a quartz cell.

2.3. Synthesis of $\text{K}_7[\text{PW}_{10}(\text{TiO}_2)_2\text{O}_{38}] \cdot 8\text{H}_2\text{O}$ (**1**) by reprecipitation with MeOH

The dimeric precursor $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$ (0.5 g, 0.085 mmol) was dissolved in 10 mL of water which was adjusted to pH 7 with 1 M aqueous KOH. (The pH of the resulting solution was acidic, i.e. it was less than pH 7.) Furthermore, the pH of the solution was readjusted to pH 7.0 using 0.5 and 0.05 M aqueous KOH solutions. (It took more than 11 h for the pH meter to stabilize.) To the aqueous solution was added 1 mL (12.7 mmol) of 30% aqueous H_2O_2 , followed by stirring for 1 h. The resulting orange-colored solution showed a single peak in ^{31}P NMR at -11.77 ppm. The solution was added dropwise to 300 mL of MeOH, followed by stirring for 1 h. The yellow powder (compound **1**) that was formed was collected on a membrane filter (JG 0.2 μm), washed with MeOH (2×50 mL) and then with Et_2O (2×50 mL), and dried in vacuo for 2 h. (When EtOH was used instead of MeOH, a different species (product **2**) were obtained; see Section 2.5.)

Compound **1**, which was highly soluble in water and insoluble in MeOH and Et_2O , was obtained in 46.3% yield (0.24 g scale). $\text{K}_7[\text{PW}_{10}(\text{TiO}_2)_2\text{O}_{38}] \cdot 3\text{H}_2\text{O} = \text{K}_7\text{H}_6\text{PW}_{10}\text{Ti}_2\text{O}_{45}$ (2964.94): calcd. H, 0.20; K, 9.23; P, 1.04; W, 62.01; Ti, 3.23; O, 24.28%; found H, 0.25; K, 9.36; P, 0.97; W, 62.2; Ti, 3.21; O, 24.1; total 100.09%. Before analysis, a weight loss of 3.25% was observed during the course of overnight drying at room temperature under a pressure of 10^{-3} to 10^{-4} torr, suggesting the presence of five to six weakly solvated or adsorbed water molecules. IR (KBr) (polyoxometalate region, Appendix A Fig. S1b): 1076s [P–O], 1062s [P–O], 1041m, 960vs [W–Ot], 889s [W–Oc], 797vs [W–Oe], 683m, 622m, 594m, 584m, 519m, 483w, 443w cm^{-1} . ^{31}P NMR (D_2O ,

22.5 °C): δ –11.32. ^{183}W NMR (D_2O , 23.7 °C): δ –82.5 (2W), –101.02 (2W), –105.41 (2W), –128.08 (2W), –152.42 (1W), –162.08 (1W). ^{31}P CPMAS NMR (25 °C): δ –11.55. UV–vis spectrum (in water, $5.1 \times 10^{-5} \text{ M}^{-1}$): λ 351 nm (extinction coefficient (ϵ) $3161 \text{ M}^{-1} \text{ cm}^{-1}$). TG/DTA under atmospheric conditions showed a weight loss of 6.50% below 458 °C with endothermic points at 121 and 172 °C. A weight loss of 6.50% observed below 458 °C could be divided into a weight loss (calcd. 2.17%) due to the decomposition of two peroxy ligands ($n=2$) and a weight loss (calcd. 4.77%) due to the dehydration of eight hydrated water molecules ($x=8$) in $\text{K}_7[\text{PW}_{10}(\text{TiO}_2)_n\text{O}_{38}] \cdot x\text{H}_2\text{O}$ (calcd. total 6.94%).

2.4. Iodometric titration of **1**

A suspension of 0.3 g of starch dispersed in 50 mL water was stirred for 30 min and filtered through a filter paper (Whatman no. 5). Separately, a solid of NaHSO_3 (0.0415 g, 0.400 mmol) was added to a solution of **1** (0.40 g, 0.13 mmol) dissolved in 30 mL water; this was followed by overnight stirring. The solution was diluted with water to 100 mL of volume; 20.0 mL of the solution was accurately taken, to which a few drops of the starch solution were added. The resulting solution was titrated with 0.01 M of I_2 aqueous solution in a buret. The end point was defined as the point at which the solution colored pale purple. The average consumption of I_2 solution over four trials was 2.70 mL, i.e. $2.7 \times 10^{-5} \text{ mol}$ ($2.7 \times 10^{-2} \text{ mmol}$). Thus, 2 mol of the peroxy groups contained in **1** were estimated.

2.5. Synthesis of $\text{K}_5[\text{PW}_{10}(\text{TiOOH})_2\text{O}_{38}] \cdot 5\text{H}_2\text{O}$ (**2**) by reprecipitation with EtOH

When EtOH was used for reprecipitation instead of MeOH in the preparation of **1**, an orange powder (compound **2**) that was soluble in water and insoluble in EtOH and Et_2O was obtained in 82.4% (0.41 g scale) yield. The clear orange aqueous solution of **2** changed to a clear yellow solution within 3 days, accompanied by the evolution of gas. $\text{K}_5[\text{PW}_{10}(\text{TiOOH})_2\text{O}_{38}] \cdot 2\text{H}_2\text{O} = \text{K}_5\text{H}_6\text{PW}_{10}\text{Ti}_2\text{O}_{45}$ (2870.75): calcd. H, 0.21; K, 6.81; P, 1.08; W, 64.04; Ti, 3.34; O, 24.52%; found H, 0.18; K, 7.26; P, 1.00; W, 63.5; Ti, 3.49; O, 24.4; total 99.83%. A weight loss of 1.60% was observed during the course of overnight drying at room temperature at 10^{-3} to 10^{-4} torr before analysis, suggesting the presence of two to three weakly solvated or adsorbed water molecules. IR (KBr) (polyoxometalate region, Appendix A Fig. S1c): 1625m, 1076s [P–O], 1062s [P–O], 1044m, 961vs [W–Ot], 891s [W–Oc], 799vs [W–Oe], 686m, 621m, 584m, 517m, 482w cm^{-1} . ^{31}P NMR (D_2O , 23.2 °C, fresh sample): δ –11.24 (minor peak), –11.64 (major peak; the hydroperoxy species), –11.76 (minor peak, due to the dimeric species $[(1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39})_2]^{10-}$ that may be formed by a reaction with EtOH, or are unreacted or contaminated). ^{31}P CPMAS NMR (25 °C): δ –11.68. UV–vis spectrum (in water, $5.1 \times 10^{-5} \text{ M}^{-1}$): λ 368 nm (extinction coefficient (ϵ) $1774 \text{ M}^{-1} \text{ cm}^{-1}$). TG/DTA under atmospheric conditions: a weight loss of 4.94% was observed below 484.1 °C with an endothermic point at 60.8 °C. The weight loss of 4.94%

observed below 484.1 °C could be divided into weight loss (calcd. 2.33%) due to the decomposition of two hydroperoxy ligands ($n=2$) and weight loss (calcd. 3.08%) due to the dehydration of five hydrated water molecules ($x=5$) in $\text{K}_5[\text{PW}_{10}(\text{TiOOH})_n\text{O}_{38}] \cdot x\text{H}_2\text{O}$ (calcd. total 5.41%).

3. Results and discussion

3.1. Reaction of in situ-derived monomeric, di-titanium(IV)-substituted Keggin species with aqueous 30% H_2O_2

The monomeric, di-titanium(IV)-substituted Keggin species was derived in situ in a neutral aqueous solution by a hydrolytic cleavage reaction, i.e. $[\text{P}_2\text{W}_{20}\text{Ti}_4\text{O}_{78}]^{10-} + 4\text{OH}^- \rightarrow 2[\text{PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-} + 2\text{H}_2\text{O}$, from the dimeric precursor $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$, which possessed the corner-sharing Ti–O–Ti bridges in both the inter-Keggin and intra-Keggin units. The dimeric precursor and the in situ-generated monomer showed different ^{31}P NMR signals, at –11.74 and –12.14 ppm, respectively (Fig. 2a and b) [23]. The colorless solution containing the in situ-generated monomer reacted with an excess amount of aqueous H_2O_2 to form an orange solution, which showed a single peak in ^{31}P NMR at –11.77 ppm as shown in Fig. 2c. It is noted that the orange-colored solution was not observed by the direct reaction of the colorless solution of $\text{K}_{10}[\alpha\text{-}$

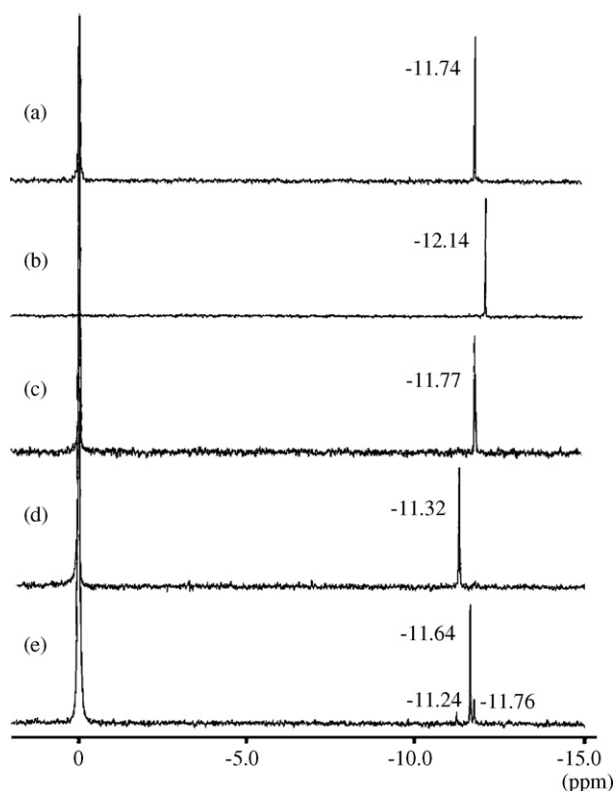


Fig. 2. ^{31}P NMR in D_2O of: (a) $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$; (b) in situ-generated $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$; (c) $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$ after the addition of an excess amount of aqueous H_2O_2 (the orange-colored solution); (d) compound **1**; (e) compound **2**. The resonance at 0.0 ppm is due to the external reference: 25% H_3PO_4 in H_2O .

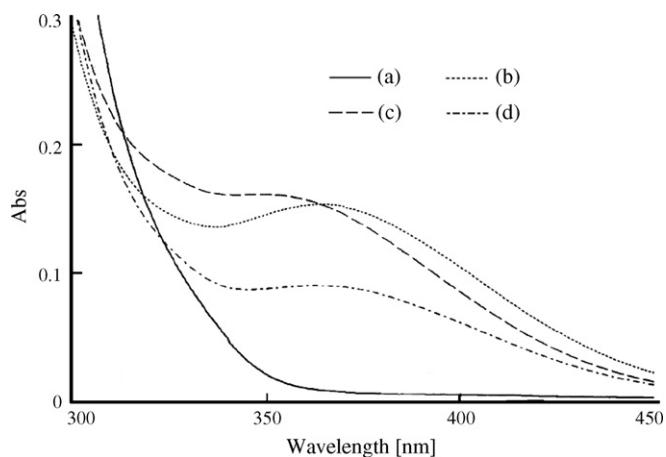


Fig. 3. UV-vis spectra in water of: (a) $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2^{10-}$ ($2.6 \times 10^{-5} \text{ M}^{-1}$); (b) $[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$ after the addition of an excess amount of aqueous H_2O_2 (the orange-colored solution) ($5.1 \times 10^{-5} \text{ M}^{-1}$); (c) compound **1** ($5.1 \times 10^{-5} \text{ M}^{-1}$); (d) compound **2** ($5.1 \times 10^{-5} \text{ M}^{-1}$).

$1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$ with H_2O_2 . Thus, the single peak at -11.77 ppm was due not to $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$ but to the new oxidizing species formed by the reaction of $[\text{PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$ with H_2O_2 , although it was close to -11.74 ppm of $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$. The orange-colored solution was also monitored by UV-vis spectroscopy, as shown in Fig. 3a and b. After the addition of H_2O_2 to the aqueous solution containing in situ-generated monomer, a new band was observed at 364 nm ($\epsilon \sim 3000 \text{ M}^{-1} \text{ cm}^{-1}$), which was assigned to $\text{O} \rightarrow \text{Ti}^{\text{IV}}$ ligand to metal charge transfer (LMCT) band of titanium(IV)-oxidizing species [18,20]. In order to determine whether the orange-colored species is an active hydroperoxotitanium(IV) species or an inactive peroxotitanium(IV) species for oxidation catalysis, its characteristic reaction with 2-propanol was studied as follows: $\text{K}_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$ (0.5 g; 0.085 mmol) was dissolved in 10 mL of water adjusted to pH 7.0 with 1 M aqueous KOH solution. The pH of the solution was readjusted to pH 7.00 using aqueous KOH solution. To the aqueous solution was added 30% H_2O_2 (12.7 mmol), followed by stirring for 1 h. Separately, 0.52 mmol of 2-propanol was diluted in D_2O (10 mL). The 500 μL (0.052 mmol) of 2-propanol- D_2O solution was added to the 1 mL of aqueous solution. After being allowed to stand for 39 h at 50°C , the solution was cooled to room temperature and analyzed using a ^1H NMR spectrometer. Acetone was detected in the orange-colored solution, showing that the orange-colored species that was observed at -11.77 ppm in ^{31}P NMR spectrum was an active hydroperoxotitanium(IV) species for oxidation catalysis [16–19].

3.2. Formation and characterization of **1**

Reprecipitation with MeOH was carried out to isolate the orange-colored hydroperoxotitanium(IV) species. When the orange-colored species was reprecipitated with MeOH, a thermally stable and light-stable compound **1** was obtained as a yellow powder.

However, the ^{31}P NMR in D_2O of **1** showed a single peak at -11.32 ppm , which was different from that of the orange-

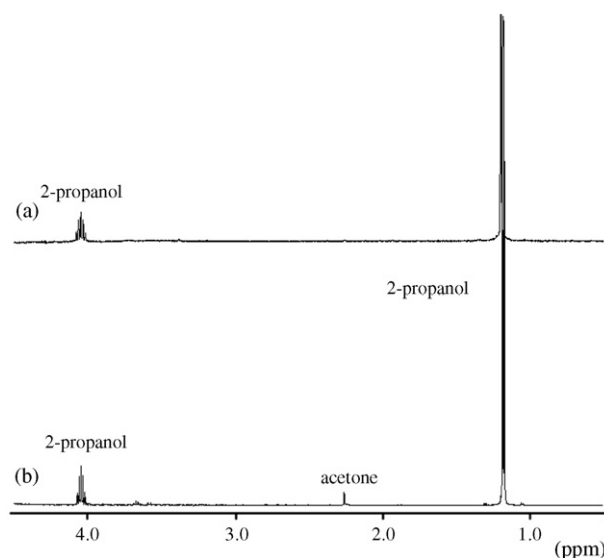


Fig. 4. ^1H NMR in D_2O of: (a) compound **1** after the addition of 2-propanol and (b) compound **2** after the addition of 2-propanol.

colored species (-11.77 ppm), as shown in Fig. 2d. The UV-vis spectrum in water of compound **1** showed a new band at 351 nm ($\epsilon 3161 \text{ M}^{-1} \text{ cm}^{-1}$), which was also different from the $\text{O} \rightarrow \text{Ti}^{\text{IV}}$ LMCT band of the orange-colored species (at 364 nm), as shown in Fig. 3c. To determine whether compound **1** is an active species for oxidation catalysis, a reaction with 2-propanol in a solution of **1** in D_2O in an NMR tube at 20°C , to which 1 equiv. of 2-propanol was added, was also studied. After being allowed to stand for 5 h at 50°C , no acetone was detected for species **1** in the absence of H_2O_2 , showing that compound **1** was not an active hydroperoxotitanium(IV) species but an inactive peroxotitanium(IV) species (Fig. 4a).

The complete elemental analysis data showed that compound **1** was a bis[peroxotitanium(IV)]-substituted α -Keggin POM $\text{K}_7[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiO}_2)_2\text{O}_{39}] \cdot 8\text{H}_2\text{O}$. TG/DTA under atmospheric conditions showed a weight loss of 6.50% below 458°C with endothermic peaks at 121 and 172°C . The endothermic peak at 172°C can be attributed to the decomposition of the coordinating peroxo group because a very similar endothermic peak has been found in the TG/DTA measurement of the tris[peroxotitanium(IV)]-substituted Dawson POM $\text{Na}_9[\alpha\text{-}1,2,3\text{-P}_2\text{W}_{15}(\text{TiO}_2)_3\text{O}_{56}(\text{OH})_3] \cdot 16\text{H}_2\text{O}$ [21]. Thus, a weight loss of 6.50% observed below 458°C could be divided into a weight loss (calcd. 2.17%) due to the decomposition of the two peroxo ligands ($n=2$) and weight loss (calcd. 4.77%) due to the dehydration of the eight hydrated water molecules ($x=8$) in $\text{K}_7[\text{PW}_{10}(\text{TiO}_2)_2\text{O}_{38}] \cdot x\text{H}_2\text{O}$ (calcd. total 6.94%). Iodometric titration experiments showed the presence of 2 mol of the peroxo group per molecule in **1** [see Section 2].

The solid FTIR spectrum of **1**, measured as a KBr disk, showed the characteristic vibrational bands of the Keggin-type POM “ $\text{XW}_{12}\text{O}_{40}^{n-}$ ” framework [24–26]. The lack of bands at around 721 cm^{-1} due to intermolecular $\text{Ti}-\text{O}-\text{Ti}$ bonds suggests that **1** is a monomer and not an oligomer. The $\text{O}-\text{O}$ stretching band, which has been known to appear around 900 cm^{-1} for monoperoxo complexes [27,28] and at 890 cm^{-1} for the

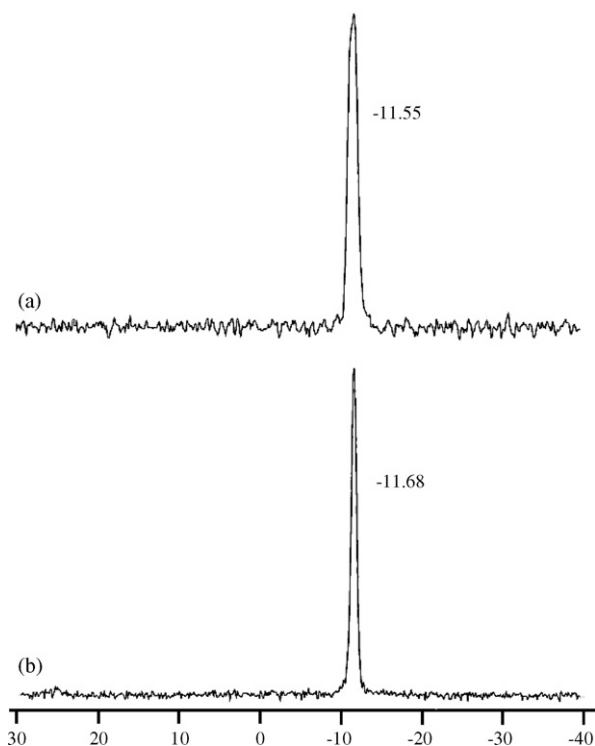


Fig. 5. Solid-state ^{31}P CPMAS NMR of: (a) compound **1** and (b) compound **2**.

tris[peroxotitanium(IV)]-substituted Dawson POM [21], overlapped with the strong W–O–W asymmetric stretch (895 cm^{-1}) of the Keggin unit.

Solid-state ^{31}P CPMAS NMR also showed a single peak at -11.55 ppm , suggesting that compound **1** was stable in a solid state, as shown in Fig. 5a. The ^{183}W NMR in D_2O at $23.7\text{ }^\circ\text{C}$ of **1** showed a six-line spectrum at -82.5 (2W), -101.02 (2W), -105.41 (2W), -128.08 (2W), -152.42 (1W), and -162.08 (1W) with relative intensities of 2:2:2:2:1:1. The six-line ^{183}W NMR spectrum of **1** is consistent with the C_s symmetry structure, as shown in Fig. 6. The solution (^{31}P and ^{183}W) NMR and ^{31}P CPMAS NMR suggest that the solid-state molecular structure is maintained in an aqueous solution. X-ray crystallography revealed that **1** was a monomeric α -Keggin POM, but that the crystal and molecular structures of **1** were not determined Appendix A (Fig. S2), because of the disorder of ten tungsten(VI) atoms due to the highly symmetric space group as in the earlier case of $[\text{PW}_{11}(\text{TiO}_2)\text{O}_{39}]^{5-}$ [20]; this is frequently observed in modified POMs with α -Keggin structure.

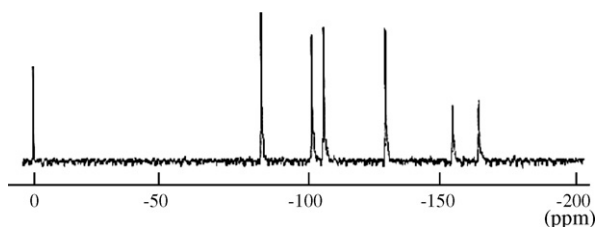


Fig. 6. ^{183}W NMR in D_2O of compound **1**. The resonance at 0.0 ppm is due to the external reference of saturated $\text{Na}_2\text{WO}_4\text{-D}_2\text{O}$ solution.

3.3. Formation and characterization of **2**

Next, we used EtOH instead of MeOH for the reprecipitation of the orange-colored species. Reprecipitation with EtOH gave the relatively *unstable* species **2** in the form of an orange powder. The ^{31}P NMR spectrum of **2** as a fresh sample showed at least three peaks at -11.24 ppm (minor peak), -11.64 ppm (major peak), and -11.76 ppm (minor peak), as shown in Fig. 2e. The major peak at -11.64 ppm gradually decomposed into a dimeric species $[(\text{PW}_{10}\text{Ti}_2\text{O}_{39})_2]^{10-}$ (-11.74 ppm) in solution at room temperature. The major peak at -11.64 ppm would be due to the thermally unstable hydroperoxotitanium(IV) species. The UV–vis spectrum in water of compound **2** showed a new band at 368 nm ($\epsilon\ 1774\text{ M}^{-1}\text{ cm}^{-1}$), which was similar to the $\text{O} \rightarrow \text{Ti}^{\text{IV}}$ LMCT band of the orange-colored species (at 364 nm) but different from that of compound **1** (at 351 nm), as shown in Fig. 3d. The lower ϵ value of compound **2** than that of compound **1** might be due to the partial decomposition of the hydroperoxo ligand in solution at $25\text{ }^\circ\text{C}$. On the other hand, the solid-state ^{31}P CPMAS NMR spectrum of compound **2** showed a singlet at -11.68 ppm at room temperature, showing that compound **2** was unstable in solution but stable in a solid state (Fig. 5b). To confirm if compound **2** is an active species for oxidation catalysis, a reaction with 2-propanol was also studied under the same reaction conditions as those of compound **1**. After being allowed to stand for 22 h at $50\text{ }^\circ\text{C}$, acetone was detected for species **2** in the absence of H_2O_2 (the conversion of 2-propanol to acetone was $\sim 1\%$, which was due to the decomposition of hydroperoxo ligand), showing that compound **2** was an active hydroperoxotitanium(IV) species (Fig. 4b).

The complete elemental analysis data exhibited that compound **2** was the bis[hydroperoxotitanium(IV)]-substituted α -Keggin POM, $\text{K}_5[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiOOH})_2\text{O}_{38}] \cdot 5\text{H}_2\text{O}$. TG/DTA under atmospheric conditions showed a weight loss of 4.94% below $484.1\text{ }^\circ\text{C}$. The weight loss of 4.94% observed below $484.1\text{ }^\circ\text{C}$ could be divided into a weight loss (calcd. 2.33%) due to the decomposition of the two hydroperoxo ligands ($n=2$) and weight loss (calcd. 3.08%) due to the dehydration of the five hydrated water molecules ($x=5$) in $\text{K}_5[\text{PW}_{10}(\text{TiOOH})_n\text{O}_{38}] \cdot x\text{H}_2\text{O}$ (calcd. total 5.41%).

The solid FTIR spectrum of **2**, measured as a KBr disk, showed vibrational bands characteristic of the Keggin-type POM “ $\text{XW}_{12}\text{O}_{40}^{n-}$ ” framework [24–26]. The lack of bands at around 721 cm^{-1} due to intermolecular Ti–O–Ti bonds suggests that **2** is also a monomer and not an oligomer.

Thus, the orange-colored species formed in situ, showing a single peak of ^{31}P NMR at -11.77 ppm due to the active hydroperoxotitanium(IV) species, readily reacted with MeOH to yield the stable peroxotitanium(IV) compound **1**. In contrast, reprecipitation of the in situ orange species with EtOH yielded the unstable hydroperoxotitanium(IV) compound **2**.

4. Conclusions

Neutral aqueous solution containing the monomeric dioxotitanium(IV)-substituted Keggin POM $[\text{PW}_{10}\text{Ti}_2\text{O}_{40}]^{7-}$ derived by a hydrolytic cleavage of the dimeric, Ti–O–Ti bridged anhy-

dride form $K_{10}[\alpha\text{-}1,2\text{-PW}_{10}\text{Ti}_2\text{O}_{39}]_2 \cdot 18\text{H}_2\text{O}$, reacted with aqueous 30% H_2O_2 to form an orange solution. Reprecipitation of the orange solution with MeOH yielded a *thermally stable* yellow species **1**, i.e. the peroxy species of POM, whereas reprecipitation with EtOH yielded a relatively *unstable* orange species **2** that contained the hydroperoxy species of POM. The peroxotitanium(IV) species **1** with a formula of $K_7[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiO}_2)_2\text{O}_{38}] \cdot 8\text{H}_2\text{O}$, which has been isolated as an analytically pure, yellow powder, was inactive for the oxidation of 2-propanol in the absence of aqueous H_2O_2 . The hydroperoxotitanium(IV) species **2** with a formula of $K_5[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiOOH})_2\text{O}_{38}] \cdot 5\text{H}_2\text{O}$, which has also been isolated as an analytically pure, orange powder, was active for the oxidation of 2-propanol in the absence of aqueous H_2O_2 .

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molcata.2006.08.053](https://doi.org/10.1016/j.molcata.2006.08.053).

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