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Preparation and Characterization of Preyssler-type Phosphotungstic Acid, $H_{15-n}[P_5W_{30}O_{110}M^{n+}]$, with Different Encapsulated Cations (M = Na, Ca, Bi, Eu, Y, or Ce), and their Thermal Stability and Acid Catalyst Properties

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Abstract. Preyssler-type phosphotungstic acid, $H_{15-n}[P_5W_{30}O_{110}M^{n+}]$, with different encapsulated cations (M = Ca^{2+}, Bi^{3+}, Eu^{3+}, Y^{3+}, Ce^{3+}) were prepared and characterized using ^{31}P NMR and IR spectroscopy, acid-base titration, and elemental analyses. The pK_a value of an internal proton of Ca-encapsulated derivative, $[P_5W_{30}O_{110}CaH_{in}]^{12-}$, was estimated to be 5.9. Their thermal stabilities and acid catalyst properties were compared with a parent Na-encapsulated Preyssler-type phoshotungstic acid, $H_{14}[P_5W_{30}O_{110}Na]$. Thermal stability of the Preyssler-type molecule was increased by exchanging the encapsulated Na^+ with Bi^{3+}, Eu^{3+}, or Ce^{3+}, with keeping their high acidic properties.

Introduction

Heteropolyacids (HPAs) are acidic metal-oxygen clusters of early transition metals such as W, Mo, and V with other elements. They show strong acidity,[1,2] and have been utilized as catalysts even in industrial processes, such as hydration of isobutylene to *tert*-butanol and polymerization of tetrahydrofurane.

Among the various HPAs, a Keggin-type phosphotungstic acid, $H_3PW_{12}O_{40}$, is the most widely used acid catalyst, which has a central PO_4 tetrahedron and surrounding 12 WO_6 octahedra with T_d symmetry (Figure 1a).

Preyssler-type phosphotungstate, $[P_5W_{30}O_{110}Na]^{14-}$, which has approximate D_{5v} symmetry and consists of a cyclic assembly of five $[PW_6O_{22}]^{3-}$ units, is another phosphotungstate.[3,4] A Na^+ is encapsulated within a cage of the Preyssler-type phosphotungstate on the fivefold axis with the internal Na^+ shifted off from the center (Figure 1b and c). This anion was isolated as a potassium-sodium mixed salt, and the counter cations are able to be ion-exchanged by protons to give the acidic form.[4]

The research groups of *Heravi*, *Bamoharram*, *Gharib*, *Alizadeh*, *Hekmatshorar*, and *Feizi* have reported acid catalytic activities of the Preyssler-type phosphotungstic acid, $H_{14}[P_5W_{30}O_{110}Na]$, for many organic reactions such as esterification, tetrahydropyranyl (THP) protection of hydroxyl groups, syntheses of dibenzo xanthene derivatives and 2,4,6-triarylpyridines, and alkylation of phenol.[5–12] We also reported that the Preyssler-type phosphotungstic acid is effective for acylation of methyl pyruvate.[13] We furthermore reported that the Preyssler-type phosphotungstic acid were more active than the Keggin-type phosphotungstic acid for hydrolysis of alkyl acetates with small alkyl groups on the basis of catalyst weight.[14] However, the Preyssler-type phosphotungstic acid was thermally less stable than the Keggin-type phosphotungstic acid. The Keggin-type phosphotungstic acid is stable after heating at 673 K, whereas the Preyssler-type phosphotungstic acid started to decompose by heating at 373 K.[14] It is desired to improve thermal stability of the Preyssler-type phosphotungstic acid.

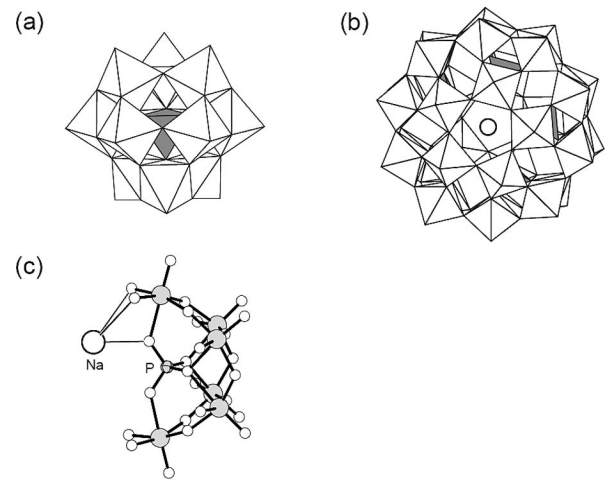

Figure 1. Polyhedral representations of (a) Keggin-type and (b) Preyssler-type phosphotungstates. Dark polyhedra, while octahedra, and a white circle indicate PO_4, WO_6, and encapsulated sodium cation, respectively. (c) Ball-and stick representation of one-fifth of the Preyssler-type phosphotungstate ($[PW_6O_{22}]$ unit) with a encapsulated sodium cation. A grey ball with a cross line, grey balls, and white balls indicate P, W, and O atom, respectively.

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It has been known that the encapsulated Na^+ is exchangeable with other cations such as Ca^{2+}, Y^{3+}, lanthanides, Bi^{3+}, and actinides, and stability was expected to be increased by the exchange.[4,15–17] Herein, we report synthesis and characterization of Preyssler-type phosphotungstic acid with different encapsulated cations of Ca^{2+}, Y^{3+}, Ce^{3+}, Eu^{3+}, and Bi^{3+}, and their thermal stabilities, acidic strength, and catalytic activities for hydrolysis activities of ethyl acetate and cellobiose.

Results and Discussion

Preparation and Characterization of Preyssler-type Phosphotungstic Acid with Different Encapsulated Cations

Potassium salts of Preyssler-type phosphotungstates with different encapsulated cations, $K_{(15-n)}[P_5W_{30}O_{110}M^{n+}]$ [Ca (n = 2), Y (n = 3), Eu (n = 3), Ce (n = 3), and Bi (n = 3), designated as **K-Ca**, **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi**, respectively], were prepared by exchanging encapsulated Na^+ of $K_{14}[P_5W_{30}O_{110}Na]$ (designated as **K-Na**) according to reported literatures[15,16] with slight modifications. Figure 2 (top) shows ^{31}P NMR spectra of **K-Na**, **K-Ca**, **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi** dissolved in D_2O and chemical shifts are summarized in Table 3. In the case of **K-Na**, **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi**, only one singlet was observed and their chemical shifts were close to the reported values.[15] The IR spectrum of **K-Na** had three bands at 1167, 1084, and 1020 cm^{-1}, which were in the P–O stretching region and was consistent with a local *Cs* symmetry for PO_4 caused by the internal Na^+, and four bands at 985, 941, 914, 789, and 744 cm^{-1}, which were in the W–O vibration region (Figure 3). The band at 1084 cm^{-1} for **K-Na** shifted to shorter wavenumber by exchanging the encapsulated Na^+, whereas wavenumber shifts of other bands were small.

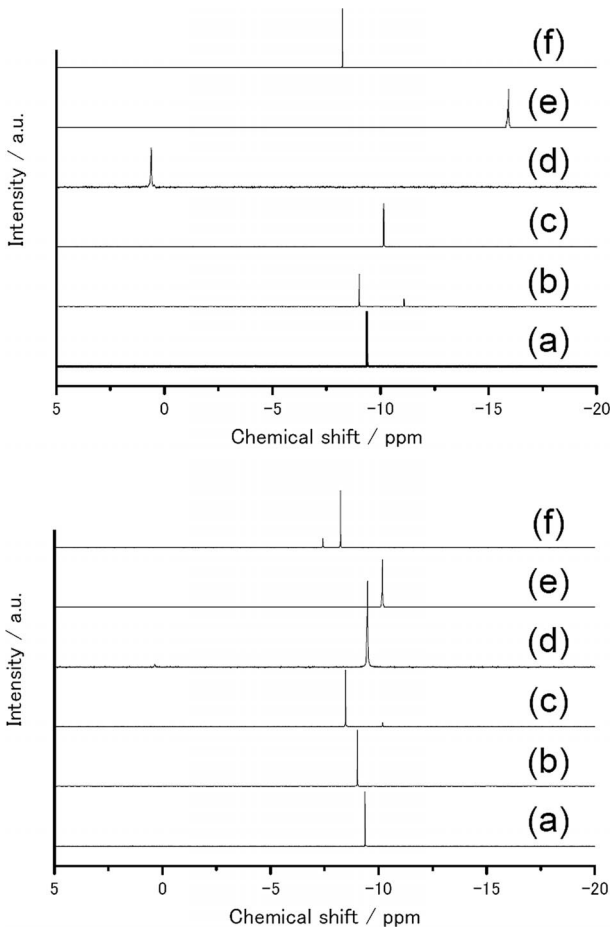

Figure 2. ^{31}P NMR spectra of (top) (a) **K-Na**, (b) **K-Ca**, (c) **K-Y**, (d) **K-Eu**, (e) **K-Ce**, and (f) **K-Bi**, and (bottom) (a) **H-Na**, (b) **H-Ca**, (c) **H-Y**, (d) **H-Eu**, (e) **H-Ce**, and (f) **H-Bi**. Samples (ca. 50 mg) were dissolved in D_2O (1 mL).

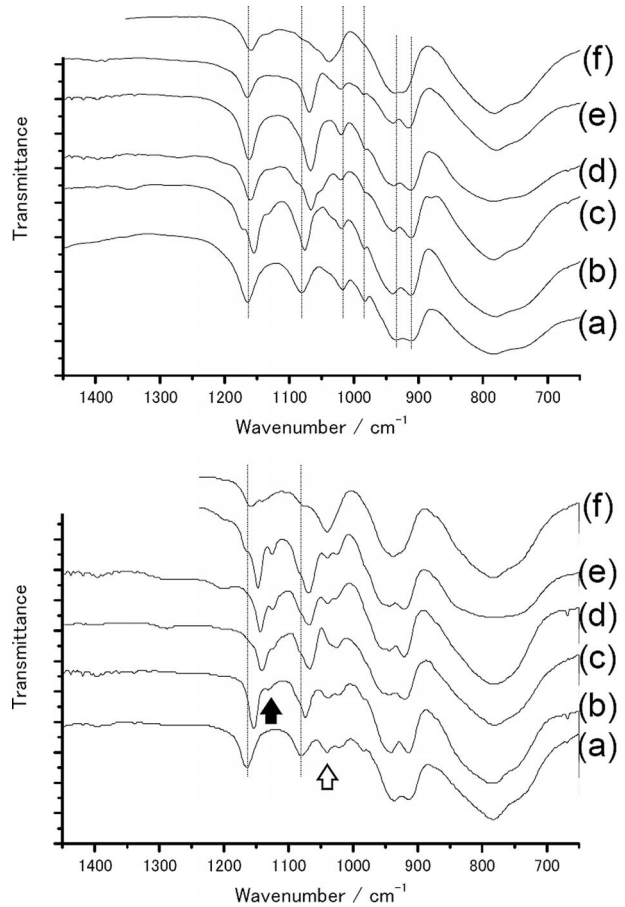

Figure 3. (top) IR spectra of (a) **K-Na**, (b) **K-Ca**, (c) **K-Y**, (d) **K-Eu**, (e) **K-Ce**, and (f) **K-Bi**. Dashed lines indicate bands at 1167, 1084, 1022, 985, 941, and 914 cm^{-1} for **K-Na**. (bottom) IR spectra of (a) **H-Na**, (b) **H-Ca**, (c) **H-Y**, (d) **H-Eu**, (e) **H-Ce**, and (f) **H-Bi**. Dashed lines indicate bands at 1167 and 1084 cm^{-1} for **H-Na**. The white and black arrows indicate new peaks at 1045 and 1126 cm^{-1}.

In the case of the ^{31}P NMR spectrum of **K-Ca** (Figure 2 top, b), two singlet signals were observed at –9.0 and –11.1 ppm, which were close to the reported ^{31}P NMR spectroscopic values of Ca-encapsulated Preyssler-type phosphotungstate in an aqueous solution with different pH values.[16] Pope′s group has reported protonation of inner oxygen in the Preyssler-type phosphotungstates with encapsulated cations of Ca^{2+}, Y^{3+}, Ce^{3+}, Eu^{3+}, or Bi^{3+} under acidic conditions [Equation (1)].[16] The exchange rate of this internal proton

(H_{in}) was slower than NMR time scale, and two ^{31}P NMR singlet signals were observed where one singlet was assignable to the phosphorus of protonated compound, $[P_5W_{30}O_{110}CaH_{in}]^{12-}$, and the other was assigned to the phosphorus of non-protonated compound, $[P_5W_{30}O_{110}Ca]^{13-}$.

$$[P_5W_{30}O_{110}M^{n+}]^{(15-n)-} + H^+ \rightleftarrows [P_5W_{30}O_{110}M^{n+}H_{in}]^{(14-n)-} \quad (1)$$

IR spectrum of **K-Ca** was similar to one of **K-Na**, and there are additional bands near the P–O stretching band at 1160 cm^{-1}, which were also observed for potassium salt of Ca-encapsulated Preyssler-type phosphotungstate prepared by *Pope's* group.[4] Details about these bands are described below. These data and elemental analyses indicated that **K-Y**, **K-Ca**, **K-Eu**, **K-Ce**, and **K-Bi** were prepared in pure forms.

The potassium cations of **K-Na**, **K-Ca**, **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi** were exchanged using a Dowex-50W proton exchange resin to produce Preyssler-type phosphotungstic acids with different encapsulated cations, and they were designated as **H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**, respectively. Elemental analyses of the proton exchanged samples indicated that almost all potassium cations were removed without collapse of cation-encapsulated Preyssler-type phosphotungstates (Table 1).

Table 1. Catalytic activities for hydrolysis of ethyl acetate.

Catalyst [a]	Conv. /%	Rate Per weight / mmol·g^{-1}·min^{-1}	Per acid amount / mmol·(acid-mol)$^{-1}$·min^{-1}
$H_{14}P_5W_{30}O_{110}Na$	46.2	275.7	164.0
$H_{13}P_5W_{30}O_{110}Ca$	48.2	257.0	171.3
$H_{12}P_5W_{30}O_{110}Y$	49.6	255.2	176.2
$H_{12}P_5W_{30}O_{110}Eu$	50.2	258.5	178.5
$H_{12}P_5W_{30}O_{110}Ce$	48.0	247.2	170.7
$H_{12}P_5W_{30}O_{110}Bi$	51.2	254.9	182.1
$H_3PW_{12}O_{40}$	49.1	175.2	174.5
Blank	1.4		

a) Amount of protons: 0.042 mmol, 5 wt% ethyl acetate in D_2O (total volume: 3.0 mL, ethyl acetate: 0.15 g), Reaction temperature: 353 K, Reaction time: 2 h.

Figure 2 (bottom) shows ^{31}P NMR spectra of **H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**. After the exchange of potassium cations with protons, the ^{31}P NMR signals did not shift in the case of **H-Na**. In the case of **H-Ca**, one singlet at –9.0 ppm which corresponded to the Ca-encapsulated Preyssler-type phosphotungstates with internal proton, $[P_5W_{30}O_{110}CaH_{in}]^{12-}$, was observed. However, two peaks appeared in the case of **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**, where the chemical shift of the one peak was similar to the one of **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi** in D_2O,[15,16] and the chemical shift of a new peak was similar to the reported chemical shift of **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi** in aqueous solution with a pH value of 1.[16] These new peaks were assigned to the protonated Preyssler-type compounds, $[P_5W_{30}O_{110}M^{3+}H_{in}]^{11-}$, ($M$ = Y, Eu, Ce, and Bi).

Figure 4 shows acid-base titration curves of **H-Na**, **H-Ca**, **H-Eu**, and **H-Bi**. In the case of **H-Na**, **H-Eu**, and **H-Bi**, pH value suddenly increased when all H^+ were consumed, indicating that all protons were highly acidic. Pope's group has reported that the inner proton of Eu-encapsulated Preyssler-type phosphotungstic acid, $[P_5W_{30}O_{110}Eu^{3+}H]^{11-}$, was highly acidic.[16]

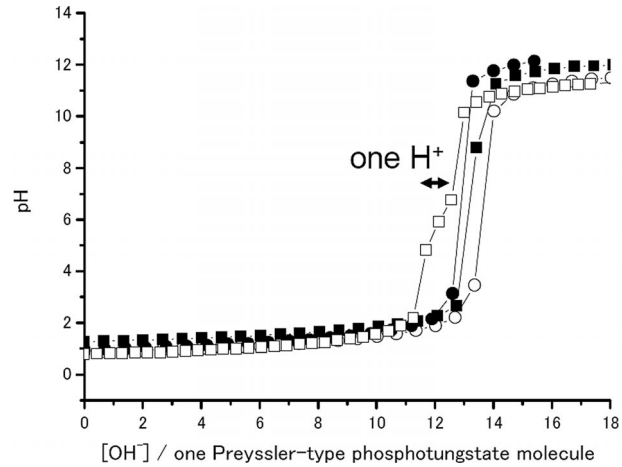

Figure 4. Acid-base titration of (black circles) **H-Na**, (white squares) **H-Ca**, (white circles) **H-Eu**, and (black squares) **H-Bi**. NaOH solution (1.0 M) was added into the solution of **H-Na**, **H-Ca**, **H-Eu**, or **H-Bi**, (H^+ concentration: ca. 0.1 M), and pH values were plotted against amount of added NaOH.

Acid-base titration of **H-Ca** was different from **H-Na**, **H-Eu**, and **H-Bi**, and there was a weak proton with a pK_a value of ca. 6.

The ^{31}P NMR spectrum of Ca-encapsulated Preyssler-type phosphotungstates with different pH values (Figure 5 top) was measured. In a solution with a pH value of 0.8, one singlet at ca. –9.0 ppm was observed, and one singlet at ca. –11.1 ppm was observed in a solution with a pH value of 10.1. In a solution with pH value of 5.9, two singlets were observed with an integration ratio of ca. 50:50. Integration ratios of these two peaks were plotted against the pH values (Figure 5 bottom). The integration ratio change was well simulated by an equation assuming that one proton was included with a pK_a value of 5.9. This result confirmed that two singlets at –9.0 and –11.1 ppm were assigned to be phosphorus of Ca-encapsulated Preyssler-type phosphotungstate with one internal proton, $[P_5W_{30}O_{110}CaH_{in}]^{12-}$, and without the internal proton $[P_5W_{30}O_{110}Ca]^{13-}$.

Pope's group has investigated the ^{31}P NMR spectroscopic behavior of Eu^{3+}-encapsulated Preyssler-type phosphotungstate in aqueous solutions with different pH, however, the pK_a value of the internal proton in Eu-encapsulated Preyssler-type phoshotungstate was not detected because the pK_a value was close to pK_a values of protons on the outside of the Preyssler phosphotungstate.[16] Our presented result is the first pK_a measurement of the inner proton of $[P_5W_{30}O_{110}Ca^{2+}H]^{12-}$.

The ^{31}P NMR spectrum of **K-Ca** in D_2O showed two singlets, whereas ^{31}P NMR of **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi** in D_2O showed one singlet. ^{31}P NMR of **H-Ca** in D_2O showed one singlet signal, whereas the ^{31}P NMR spectrum of **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi** in D_2O showed two singlet signals. From these results and acid-base titration, we propose that the pK_a values of internal proton of Y, Eu, Ce, and Bi-encapsulated

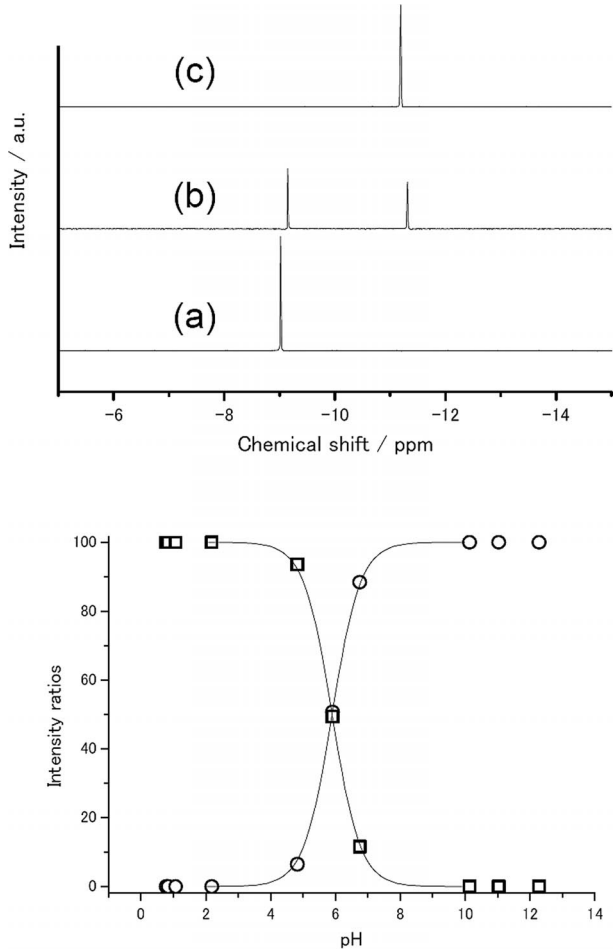

Figure 5. (top) ^{31}P NMR spectra of **H-Ca** in aqueous solutions with different pH values. (a) 0.8, (b) 5.9, and (c) 10.8. (bottom) ^{31}P NMR integration ratio vs. pH value. Solid lines indicate theoretical curves with pK_a value of 5.9. NaOH solution (1.0 M) was added into the solution of **H-Na** (H^+ concentration: ca. 0.1 M) and ^{31}P NMR spectra of solution with different pH values was measured.

Preyssler-type phoshotungstates were close to those of acidic protons.

The IR spectrum of **H-Na** was similar to one of **K-Na**, and there was an additional weak band at 1045 cm^{-1} (Figure 3 bottom, white arrow). IR spectra of **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi** were similar to one of **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi**, but a band at ca. 1167 cm^{-1} shifted to shorter wavenumber, and there are two additional weak bands at ca. 1126 (Figure 3 bottom, black arrow) and ca. 1040 cm^{-1}. When the IR spectra of **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi** were compared with one of **H-Na**, two bands of **H-Na** at 1167 and 1084 cm^{-1} shifted to shorter wavenumber by exchanging the encapsulated cations.

Ca-encapsulated Preyssler-type phosphotungstates were isolated as a cesium salts from solutions of **H-Ca** with different pH values, and the IR spectra of these solids are presented in Figure 6. The IR spectrum of **H-Ca** (Figure 6 a and Figure 3 b) was similar to those of **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**. The IR spectrum of cesium salt of the Ca-encapsulated Preyssler-type phosphotungstates isolated from aqueous solution with pH value of 9.8 (Figure 6 c) was similar to one of **K-Na**. The IR spectrum of cesium salt of the Ca-encapsulated Preyssler-type phosphotungstate isolated from aqueous solution with pH value of 2.0 (Figure 8 b) was a mixture of IR spectra of **H-Ca** and the cesium salt of the Ca-encapsulated Preyssler-type phosphotungstates isolated from aqueous solution with pH value of 9.8. These results confirmed that the presence of internal proton affected IR bands assignable to P–O vibrations, and strong band at 1176 cm^{-1} was assignable to a P–O vibration of the non-protonated Ca-encapsulated Preyssler-type phosphotungstate, $[P_5W_{30}O_{110}Ca]^{13-}$, and a strong band at 1155 cm^{-1} and a weak band at 1134 cm^{-1} were assignable to P–O vibrations of the one-proton protonated Ca-encapsulated Preyssler-type phosphotungstate, $[P_5W_{30}O_{110}CaH_{in}]^{12-}$. There were three band at 1176, 1155, and 1134 cm^{-1} in the IR spectrum of **K-Ca**. Therefore, **K-Ca** was a mixture of Ca-encapsulated Preyssler-type phosphotungstates with one internal proton, $[P_5W_{30}O_{110}CaH_{in}]^{12-}$, and without the internal proton, $[P_5W_{30}O_{110}Ca]^{13-}$.

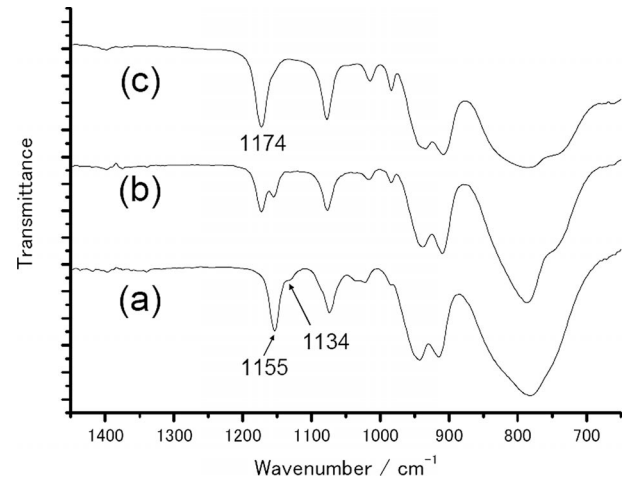

Figure 6. IR spectra of Ca-encapsulated Preyssler-type phosphotungstate isolated from different pH values of (b) 2.0 and (c) 9.8, and **H-Ca** (a). **H-Ca** was dissolved in water (concentration of H^+ was ca. 0.1 M), and pH was adjusted by adding NaOH (1.0 M), and cesium chloride was added to isolate cesium salts of Ca-encapsulated Preyssler-type phosphotungstate.

These results indicated that **H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi** were isolated in pure forms.

Thermal Stability

The obtained cation-encapsulated Preyssler-type phosphotungstic acids, **H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**, and their potassium salts, **K-Na**, **K-Ca**, **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi**, were heated in a muffle oven and analyzed by solution ^{31}P NMR spectroscopic measurements to estimate thermal stability. In the ^{31}P NMR spectrum of **H-Na** heated at 373 K for 1 h, several small peaks together with the peak of **H-Na** were observed, suggesting **H-Na** started to decompose at 373 K.[14] We evaluated thermal stability of cation-encapsulated Preyssler-type phosphotungstic acids and their potassium salts by comparing residual ratio of the Preyssler-type phosphotungstates estimated by ^{31}P NMR spectroscopic measurements after

calcination at different temperatures (Figure 7). **H-Na**, **H-Ca**, and **H-Y** started to decompose in the range of 373–423 K, whereas **H-Eu**, **H-Ce**, and **H-Bi** were stable up to 423 K. Their potassium salts were more stable than their acid. **K-Na** and **K-Ca** started to decompose at 523 K, but **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi** were stable up to 623 K.

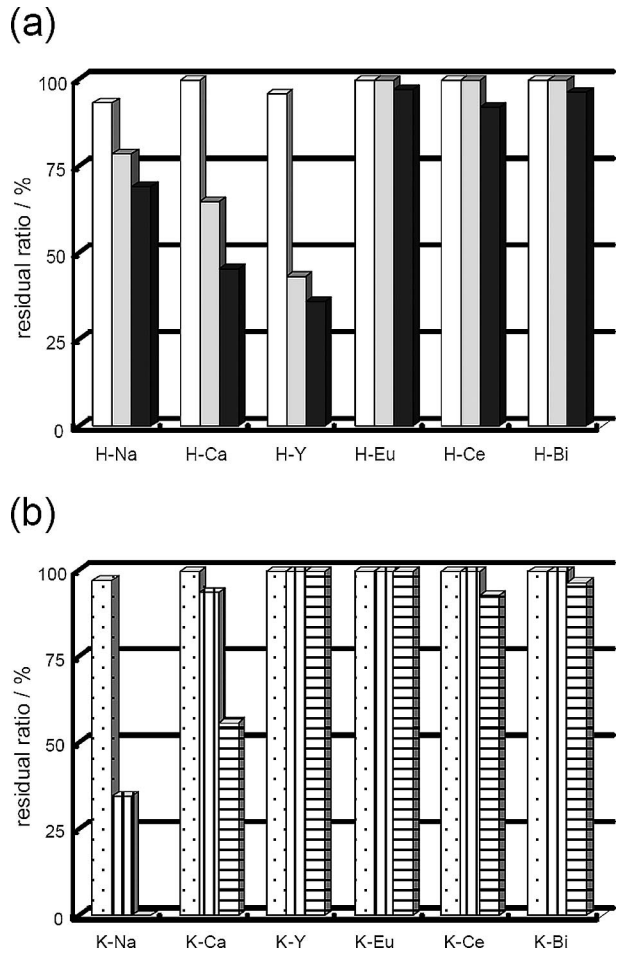

Figure 7. Comparison of the thermal stability of (a) Preyssler-type phsphotungstic acids (**H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**) after heating at (white bars) 373 K, (grey bars) 423 K, and (black bars) 473 K, and (b) their potassium salts, (**K-Na**, **K-Ca**, **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi**) after heating at (dotted bars) 523 K, (bars with vertical stripes) 573 K, and (bars with horizontal stripes) 623 K. After heating the samples, the ^{31}P NMR spectrum of the sample dissolved in D_2O was measured. Residual ratio was calculated by an equation [residual ratio = (integration of ^{31}P NMR signal assignable to the Preyssler-type Phosphotungstate) / (sum of integrations of all ^{31}P NMR peaks)].

Acidic Strength Measurement

Acidic strength of the ion-encapsulated Preyssler-type phosphotungstic acid was compared with those of Keggin-type phosphotungstic acid and sulfuric acid using trimethyl phosphine oxide (Me_3P=O) as a probe molecule. Trialkyl phosphine oxide is known as an acidic strength indicator both in a solid state and in solution.[18–21] Trialkyl phosphine oxide is protonated to form trialkyl phosphine hydroxide cation [Equation (2)]. This reversible reaction is so much faster than the ^{31}P NMR time-scale that only one ^{31}P NMR spectroscopic signal is detected. The peak moves to a more positive chemical shift if the acidic strength and amount of proton increase. Therefore, the acidic strength can be estimated by the peak shift:

$$Me_3P{=}O + H^+ \rightleftarrows Me_3P{-}OH^+ \quad (2)$$

The chemical shift of trimethyl phosphine oxide was plotted against proton-trimethyl phosphine mole ratio (Figure 8). When the amount of acid was increased, the chemical shift moved in a more positive direction. The shift in the presence of **H-Na** was larger than those of Keggin-type phosphotungtic acid and sulfuric acid. The shifts in the presence of **H-Ca**, **H-Y**, **H-Eu**, and **H-Bi** were almost the same except **H-Ce**, indicating that the acidic strengths of **H-Ca**, **H-Y**, **H-Eu**, and **H-Bi** were similar to one of **H-Na**.

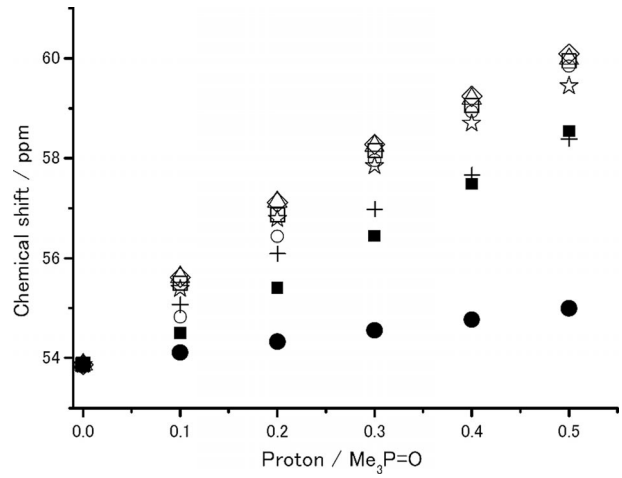

Figure 8. Change in ^{31}P NMR chemical shift of Me_3P=O (1 mM) in D_2O in the presence of the Preyssler-type phosphotungtic acid (open circles) **H-Na**, (open squares) **H-Ca**, (open stars) **H-Y**, (open triangles) **H-Eu**, (crosses) **H-Ce**, and (open diamonds) **H-Bi**, (close squares) Keggin-type phosphotungstic acid and (close circles) sulfuric acid.

Hydrolysis of Ethyl Acetate and Cellobiose

Hydrolysis of ethyl acetate and cellobiose were carried out in the presence of same amount of protons, and their activities are summarized in Table 1 and Table 2.[22] For hydrolysis of ethyl acetate, catalytic activities of **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**,

Table 2. Catalytic activities for hydrolysis of cellobiose.

Catalyst [a]	Cellobiose conv. /%	Glucose yield /%	Sel. /%
$H_{14}P_5W_{30}O_{110}Na$	39.5	39.0	98.7
$H_{13}P_5W_{30}O_{110}Ca$	38.1	35.5	93.2
$H_{12}P_5W_{30}O_{110}Y$	38.9	36.6	94.1
$H_{12}P_5W_{30}O_{110}Eu$	40.9	39.3	95.9
$H_{12}P_5W_{30}O_{110}Ce$	37.4	36.1	96.5
$H_{12}P_5W_{30}O_{110}Bi$	41.9	39.4	94.2
$H_3PW_{12}O_{40}$	39.1	38.1	97.6
H_2SO_4	22.8	22.1	97.0

a) Amount of proton: 0.10 mmol, Cellobiose: 0.20 g, H_2O: 12 mL, Reaction temperature: 373 K, Reaction time: 24 h.

and **H-Bi** were similar to one of **H-Na**, and were much higher than that of sulfuric acid. Catalytic activities of **H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**, were similar to that of the Keggin-type phosphotungtic acid[23] on the basis of acid amount, but became higher on the basis of catalyst amount because acid concentration of the Preyssler-type phosphotungstic acid (14–12 per $[P_5W_{30}O_{110}M]$) is higher than one of the Keggin-type phosphotungstic acid (3 per $[PW_{12}O_{40}]$).

Catalytic activities of **H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**, for the hydrolysis of cellobiose were much higher than one of sulfuric acid, and were similar to one of the Keggin-type phosphotungstic acid on the basis of the acid amount. *Shimizu's* group reported that the Keggin-type phosphotungtic acid was active catalyst for the hydrolysis of cellobiose and their derivatives.[24] Acid concentration of the Preyssler-type phosphotungtic acid is higher than that of the Keggin-type phosphotungtic acid. Therefore, less amount of the Preyssler-type phosphotungtic acid catalyst is enough to achieve the same activity.

Conclusions

Preyssler-type phosphotungstic acid, $H_{15-n}[P_5W_{30}O_{110}M^{n+}]$, with different encapsulated cations ($M = Ca^{2+}$, Bi^{3+}, Eu^{3+}, Y^{3+}, Ce^{3+}) were prepared and fully characterized using ^{31}P NMR and IR spectroscopy, acid-base titration, and elemental analyses. The Ca-encapsulated derivative with a internal proton (H_{in}), $[P_5W_{30}O_{110}CaH_{in}]^{12-}$, and without internal proton, $[P_5W_{30}O_{110}Ca]^{13-}$, were characterized using IR and ^{31}P NMR spectroscopy, and pK_a value of the internal proton was estimated to be 5.9 by acid-base titrations. Thermal stability of the Preyssler-type structure was increased by exchanging Na^+ with Bi^{3+}, Eu^{3+}, or Ce^{3+}, without loosing high acid catalyst activities.

Experimental Section

Materials: All of the chemicals used were of reagent grade, and they were used as supplied. Keggin-type phosphotungstic acid, $H_3PW_{12}O_{40}{\cdot}6H_2O$, was purified by using a published method.[23] $K_{14}[P_5W_{30}O_{110}Na]{\cdot}23H_2O$ and $H_{14}[P_5W_{30}O_{110}Na]{\cdot}44H_2O$ were prepared according to a published method[14] and the purity was confirmed by IR, ^{31}P NMR, and ^{183}W NMR spectroscopy.

Characterizations: FT-IR spectra were recorded with a Nicolet 6700 FT-IR spectrometer with 2 cm^{-1} resolution. ^{183}W NMR spectra were recorded with a Varian System 500 (500 MHz) spectrometer (W resonance frequency of 20.825 MHz) using an external sat. Na_2WO_4 reference. ^{31}P NMR spectra were recorded with a Varian System 500 (500 MHz) spectrometer (P resonance frequency of 202.327 MHz) using an external H_3PO_4 reference. ^1H NMR spectra were recorded with a Varian System 500 (500 MHz) spectrometer (H resonance frequency of 499.827 MHz). Elemental analyses of **K-Na**, **K-Ca**, **K-Y**, **K-Eu**, **K-Ce**, **K-Bi**, and **H-Na**, were performed by Microanalytisches Labor Pascher (Remagen, Germany). Elemental analyse of **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi** were performed with a ICP-AES (SPS-7700, SII).

Preparation of $K_{15-n}[P_5W_{30}O_{110}M^{n+}]{\cdot}nH_2O$. $K_{14}[P_5W_{30}O_{110}Na]{\cdot}23H_2O$ (10 g, ca. 1.21 mmol) was dissolved in H_2O (120 mL) . To this solution were added 1.2–3.0 equivalents of M^{n+} as the chloride or nitrate salt dissolved in H_2O (30 mL), 0.1 M HCl, or 0.1 M HNO_3. The mixture was placed in autoclave and heated to 433–453 K for 2 d. After the solution was cooled down to room temperature, the solution was filtrated. The potassium salts were isolated by the addition of solid KCl (10 g) to the filtrate. The produced precipitates were dissolved with hot water (20 mL) heated by a metal bath at 353 K, and the heater was switched off to produce the desired products (7.0–9.0 g). The potassium salts of Preyssler-type phosphotungstate with different encapsulated metals, Na (n = 1), Ca (n = 2), Y (n = 3), Eu (n = 3), Ce (n = 3), and Bi (n = 3), were designated as **K-Na**, **K-Ca**, **K-Y**, **K-Eu**, **K-Ce**, and **K-Bi**, respectively.

Metal salts, amount of metal salts, reaction conditions, elemental analysis results, IR and ^{31}P NMR spectroscopic data are summarized in Table 3.

Preparation of $H_{15-n}[P_5W_{30}O_{110}M^{n+}]{\cdot}nH_2O$. $K_{15-n}[P_5W_{30}O_{110}M^{n+}]{\cdot}nH_2O$ (10 g) was dissolved in H_2O (200 mL) and passed through 50 g of Dowex 50W × 8 in the proton form packed in a glass tube (inner diameter: 15 mm), and the obtained eluent was evaporated in vacuo at 318 K (Caution: Evaporation at a higher temperature caused slight decomposition. See also Results and Discussion.).

The Preyssler-type phosphotungstic acid with different encapsulated metals, $H_{(15-n)}[P_5W_{30}O_{110}M^{n+}]$, Na ($n$ = 1), Ca (n = 2), Y (n = 3), Eu (n = 3), Ce (n = 3), and Bi (n = 3), were designated as **H-Na**, **H-Ca**, **H-Y**, **H-Eu**, **H-Ce**, and **H-Bi**, respectively.

Elemental analysis results, IR and ^{31}P NMR spectroscopic data are summarized in Table 3.

Hydrolysis of Ethyl Acetate: Hydrolysis of ethyl acetate was carried out at 353 K with 5 wt% ethyl acetate in D_2O (total volume: 3.0 mL, ethyl acetate: 0.15 g) for 2 h.[22] The amount of protons used was kept to be 0.042 mmol.

Conversion and yield were estimated using ^1H NMR spectroscopy. Signals corresponding to ethyl acetate, ethyl alcohol, and acetic acid were observed. No other signal was observed. Therefore, we assumed that selectivity of this hydrolysis was 100%. Since signals of methylene (CH_2O) for ethyl acetate (4.03) and ethyl alcohol (3.52) were well separated, the conversion of ethyl acetate was calculated using the integration ratio of these two signals as follows:

Conversion = (integration of CH_2O of ethyl alcohol) / (integration of CH_2O of ethyl acetate + integration of CH_2O of ethyl alcohol).

^1H NMR of ethyl acetate in D_2O (HOD peak at δ = 4.75 ppm): 1.13 ppm (CH_3CH_2, triplet, 3 H), 1.97 ppm (CH_3CO, singlet, 3 H), 4.03 ppm (CH_2O, quartet, 2 H).

^1H-NMR of ethyl alcohol in D_2O (HOD peak at δ = 4.75 ppm): 1.06 ppm (CH_3CH_2, triplet, 3 H), 3.52 ppm (CH_2O, quartet, 2 H).

^1H NMR of acetic acid in D_2O (HOD peak at δ = 4.75 ppm): 1.97 ppm (CH_3CO, singlet, 3 H).

Hydrolysis of Cellobiose: Hydrolysis of cellobiose was carried out at 373 K with cellobiose (0.20 g) in H_2O (12 mL) for 24 h.[22] The amount of protons used was kept to be 0.1 mmol.

Conversion of cellobiose and yield of glucose was estimated using HPLC with a column (Shodex Sugar SH1011) and RI detector (RID-10A, Shimadzu).

Table 3. Reaction condition for the preparation of $K_{15-n}[P_5W_{30}O_{110}M^{n+}]$ and characterization of $H_{15-n}[P_5W_{30}O_{110}M^{n+}]$.

Encapseled cation	Metal salt (mmol)	Solvent	Temp. /°C	Time /h
Na^{+} [14]				
$K_{14}[P_5W_{30}O_{110}Na]\cdot 23H_2O$ (**K-Na**) Elemental analysis: found: P, 1.83;W, 65.5; Na, 0.28; H, 0.54; Cl, <0.05;K, 6.31 %; calcd: P, 1.84;W, 65.5; Na, 0.27; H, 0.59; Cl, 0;K, 6.48 0 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1167 (s), 1084 (s), 1020 (m), 985 (m), 941 (vs), 914 (vs), 789 (vs), 744 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –9.39 ppm				
$H_{14}[P_5W_{30}O_{110}Na]\cdot 44H_2O$ (**H-Na**) Elemental analysis, found: P, 1.72;W, 67.02; Na, 0.26; H, 1.1; Cl, 0.008;K, <0.002 %; calcd: P, 1.88;W, 66.77; Na, 0.28; H, 1.24; Cl, 0;K, 0 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1167 (s), 1084 (s), 1045 (m), 1024 (m), 987 (m), 936 (vs), 918 (vs), 787 (vs), 746 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –9.39 ppm				
Ca^{2+}	$CaCl_2$ (1.44 mmol)	H_2O	160	48
$K_{12.2}[P_5W_{30}O_{110}CaH_{0.8}]\cdot 25H_2O$ (**K-Ca**) Elemental analysis, found: P, 1.84;W, 65.4; Ca, 0.46; H, 0.6; Cl, <0.05;K, 5.94; Na, <0.01 %; calcd: P, 1.84;W, 65.7; Ca, 0.48; H, 0.61; Cl, 0;K, 5.68; Na, 0 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1176 (m), 1157 (s), 1134 (w), 1078 (s), 1022 (m), 985 (m), 943 (vs), 914 (vs), 784 (vs), 739 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –9.02, –11.1 ppm				
$H_{13}[P_5W_{30}O_{110}Ca]\cdot 85H_2O$ (**H-Ca**) Elemental analysis, found: P, 1.81;W, 61.1; Ca, 0.50;K, 0.04 %; calcd: P, 1.72;W, 61.2; Ca, 0.44;K, 0.00 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1154 (s), 1134 (w), 1074 (s), 1040 (w) 1024 (m), 985 (m), 943 (vs), 916 (vs), 787 (vs), 748 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –9.05 ppm				
Y^{3+}	$Y(NO_3)_3\cdot 6H_2O$ (1.44 mmol)	H_2O	160	48
$K_{12}[P_5W_{30}O_{110}Y]\cdot 25H_2O$ (**K-Y**) Elemental analysis, found: P, 1.84;W, 65.4; Y, 1.04; H, 0.55; Cl, <0.05;K, 5.74; Na, <0.01; N, <0.03 %; calcd: P, 1.84;W, 65.4; Y, 1.05; H, 0.59; Cl, 0;K, 5.78; Na, 0 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1160 (s), 1067 (s), 1020 (m), 984 (m, sh), 939 (vs), 912 (vs), 784 (vs), 742 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –10.1 ppm				
$H_{12}[P_5W_{30}O_{110}Y]\cdot 90H_2O$ (**H-Y**) Elemental analysis, found: P, 1.80;W, 60.0; Y, 1.11;K, 0.04 %; calcd: P, 1.69;W, 60.3; Y, 0.97;K, 0.00 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1143 (s), 1126 (w), 1067 (s), 1038 (m), 1025 (m), 944 (vs), 920 (vs), 780 (vs), 744 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –8.46, –10.1 ppm				
Eu^{3+}	$Eu(NO_3)_3$ (1.44 mmol)	H_2O	160	48
$K_{12}[P_5W_{30}O_{110}Eu]\cdot 25H_2O$ (**K-Eu**) Elemental analysis, found: P, 1.82;W, 64.8; Eu, 1.81; H, 0.53; Cl, <0.05;K, 5.8; Na, <0.01; N, <0.03 %; calcd: P, 1.82;W, 64.9; Eu, 1.79; H, 0.59; Cl, 0;K, 5.74; Na, 0 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1162 (s), 1067 (s), 1020 (m), 981 (m), 939 (vs), 912 (vs), 784 (vs), 739 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = 0.60 ppm				
$H_{12}[P_5W_{30}O_{110}Eu]\cdot 65H_2O$ (**H-Eu**) Elemental analysis, found: P, 1.80;W, 62.8; Eu, 1.77;K, 0.01 %; calcd: P, 1.77;W, 62.9; Eu, 1.73;K, 0.00 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1143 (s), 1125 (m), 1068 (s), 1041 (m), 1028 (m), 944 (vs), 920 (vs), 784 (vs), 748 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = 0.32, –9.51 ppm				
Ce^{3+}	$(NH_4)_2[Ce(NO_3)_6]_2$ (3.6 mmol)	0.1 M HNO_3	180	48
$K_{12}[P_5W_{30}O_{110}Ce]\cdot 25H_2O$ (**K-Ce**) Elemental analysis, found: P, 1.81;W, 64.7; Ce, 1.63; H, 0.6; Cl, <0.05;K, 5.78; Na, <0.01; N, <0.03 %; calcd: P, 1.83;W, 65.0; Ce, 1.65; H, 0.59; Cl, 0;K, 5.74; Na, 0 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1165 (s), 1069 (s), 1020 (m), 985 (m), 940 (vs), 916 (vs), 779 (vs), 744 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –15.9 ppm				
$H_{12}[P_5W_{30}O_{110}Ce]\cdot 120H_2O$ (**H-Ce**) Elemental analysis, found: P, 1.76;W, 56.8; Ce, 1.42;K, 0.00 %; calcd: P, 1.59;W, 56.6; Ce, 1.44;K, 0.00 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1147 (s), 1126 (m), 1070 (s), 1040 (m), 1026 (m), 984 (sh), 945 (vs), 921 (vs), 778 (vs, br) cm^{-1} **^{31}P NMR** (D_2O): δ = –10.1, –15.9 ppm				
Bi^{3+}	$BiCl_3$ (2.4 mmol)	0.1 M HCl	160	48
$K_{12}[P_5W_{30}O_{110}Bi]\cdot 25H_2O$ (**K-Bi**) Elemental analysis, found: P, 1.8;W, 64.6; Bi, 2.41; H, 0.54; Cl, <0.05;K, 5.73; Na, <0.01 %; calcd: P, 1.81;W, 64.5; Bi, 1.65; H, 0.58; Cl, 0;K, 5.70; Na, 0 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1159 (s), 1039 (s), 1024 (sh), 985 (sh), 937 (vs), 924 (vs), 782 (vs), 752 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –8.2 ppm				
$H_{12}[P_5W_{30}O_{110}Bi]\cdot 60H_2O$ (**H-Bi**) Elemental analysis, found: P, 1.86;W, 63.4; Bi, 2.68;K, 0.02 %; calcd: P, 1.78;W, 63.2; Bi, 2.39;K, 0.00 %. **IR**: $\tilde{\nu}$ = >$_{max}$ = 1161 (s), 1140 (sh) 1041 (s), 939 (vs, br), 783 (vs), 746 (sh) cm^{-1} **^{31}P NMR** (D_2O): δ = –7.44, –8.25 ppm				

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