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Relation	

Synthesis of Preyssler-Type Phosphotungstate with Sodium Cation in the Central Cavity through Migration of the Ion

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Abstract

Thermal migration of the sodium cation in the cavity of Preyssler-type phosphotungstate is reported here. Heating of a Preyssler-type compound—$[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$—in which a sodium cation occupies one of the two side cavities, at 300 °C forms a new compound—$[P_5W_{30}O_{110}Na(center)]^{14-}$—in which the sodium cation is encapsulated in the central cavity. Characterization by single crystal X-ray structure analysis, NMR technique, elemental analysis, IR, and ESI-MS confirmed the structure of the compound. The thermal displacement ellipsoid of the central sodium, estimated by the crystallographic study, is elongated along the direction perpendicular to the equatorial plane of the Preyssler molecule. These results confirmed prediction using DFT calculation by López and Poblet (ref. 21, *J. Am. Chem. Soc.* **2007**, *129*, 12244.) that the most stable site for sodium is the central cavity with a slight shift from the center of the molecule.

Keywords: Polyoxometalate, Thermal Migration, Preyssler-type Phosphotungstate

1. Introduction

Polyoxometalates (POMs) are anionic metal oxide clusters of W, Mo, V, and Nb with unique properties such as acidic behavior, multielectron redox activity, magnetism, and photochemistry, which make them a promising candidate for diverse applications in functional materials, magnetic devices, and catalysis.[1,2,3] Among the diverse range of reported POMs, Preyssler-type phosphotungstates have received special attention because of their ability to encapsulate metal ions and serve as a host. The Preyssler-type phosphotungstate was first reported by Preyssler in 1970, and it's structure was later revealed by Pope and Jeannin.[4] A Preyssler-type phosphotungstate, $[P_5W_{30}O_{110}Na(H_2O)]^{14-}$, framework has five PO_4 tetrahedra surrounded by 30 WO_6 octahedra, creating a doughnut-shaped architecture with internal cavities (Fig. 1). There are two types of cavities: two side cavities enclosed by five oxygen atoms (O_a) attached to phosphorus atoms and five bridging oxygen atoms (O_b) attached to tungsten atoms and one central cavity surrounded by ten O_a attached to phosphorus atoms (Fig. 1b).

Preyssler-type compounds can encase different cations such as Ca^{2+},[5–8] Bi^{3+},[5,6,8] Ag^{+},[9–11] Y^{3+},[5–7] lanthanide cations,[5,6,12–14] actinide cations,[5,7,12,13,15] and K^{+}[16–18] in these cavities. In most cases, the cation occupies one of the side cavities and coordinates with a water molecule. (Fig. 1c)[4]. We have already reported a compound, $[P_5W_{30}O_{110}K_2]^{13-}$, in which two K^+ are placed in the two side cavities.[19] There are only a few examples of Preyssler-type compounds in which an encapsulated cation occupies the central cavity. One such compound wherein K^+ is located at the central cavity in the Preyssler-type phosphotungstate ($[P_5W_{30}O_{110}K(center)]^{14-}$) was synthesized previously by our group [16](Fig. 1d), and Wang's group has reported that one K^+ or Na^+ could be encased in the central cavity in

Preyssler-type sulfotungstates such as $[S_5W_{30}O_{110}K(center)]^{9-}$ or $[S_5W_{30}O_{110}Na(center)]^{9-}$, respectively.[20]

Recently, mobility of the encapsulated metal ion was studied in $[P_5W_{30}O_{110}Tb]^{12-}$, wherein Tb^{3+} was observed to migrate randomly between the two side cavities even at room temperature under an electric field which caused single-molecule electric polarization switching property.[14] This finding may open new avenues for ultrahigh-density memory and other molecular-level electronic devices using Preyssler-type phosphotungstates. It is important to understand the migration behavior of metal ions encapsulated in Preyssler molecules because the migration not only causes the single-molecule electric polarization switching property but also produces new Preyssler-type compounds.

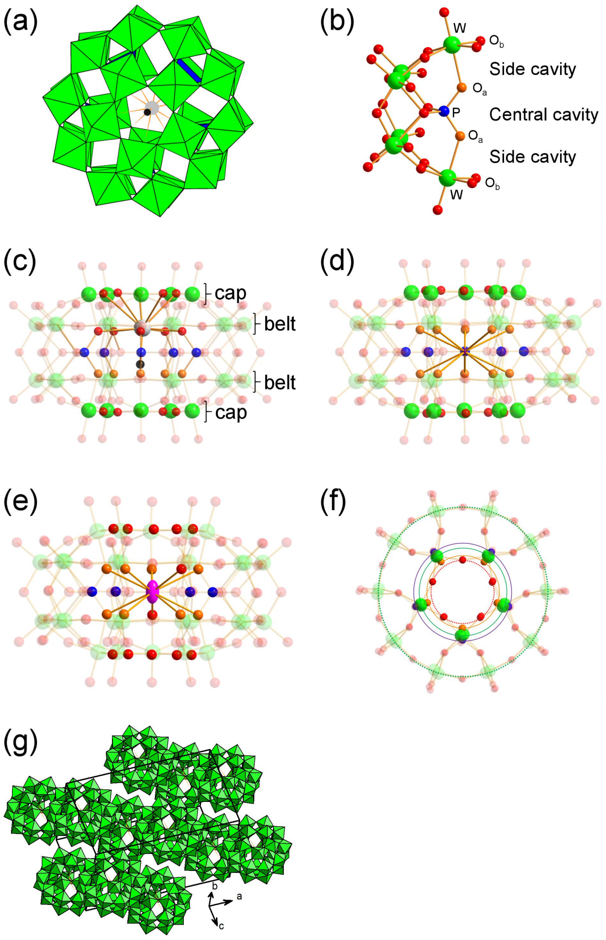
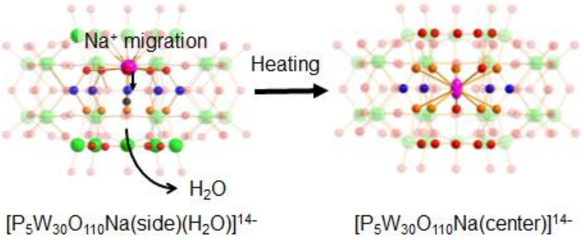


Figure 1. (a) Polyhedral representation of Preyssler-type phosphotungstate with one encapsulated cation, (b) Ball-and-stick representation of one-fifth of the Preyssler-type phosphotungstate $[PW_6O_{22}]$ unit. Ball-and-stick representation of a (c) mono-cation-encapsulated Preyssler-type molecule, (d) mono-K^+-encapsulated Preyssler-type molecule, $[P_5W_{30}O_{110}K(center)]^{14-}$, (e) mono-$Na^+$-encapsulated Preyssler-type molecule, $[P_5W_{30}O_{110}Na(center)]^{14-}$, and (f) concentric circles on the oxygen, tungsten, and phosphorous atoms. (g) Polyhedral presentation of packing of $K_{14}[P_5W_{30}O_{110}Na(center)]$ in the unit cell. Green, blue, red, orange, gray, black, pink, and violet balls represent tungsten, phosphorous, oxygen, oxygen surrounding the central cavity, mono-encapsulated cation, water molecule oxygen coordinated to the cation, thermal ellipsoid of encapsulated Na^+, and thermal ellipsoid of encapsulated K^+, respectively.

López and Poblet have applied the DFT calculations to propose the energy profile for the Preyssler-type phosphotungstate with one encapsulated Na^+, which is not coordinated with water, where Na^+ moves from the center of the molecule to the outside of the molecule perpendicular to the equatorial plane through the cavities.[21] They reported that the most stable site for Na^+ encapsulation is shifted by ~0.5 Å from the center of the molecule that still lies in the center cavity. However, the synthesis of such Preyssler-type phosphotungstate with Na^+ encapsulated in the central cavity has not been reported till date.

In our previous report,[16] we observed the migration of K^+ ions on heating of $K_{14}[P_5W_{30}O_{110}K]$ in the solid state: one K^+, which is the counter cation, enters into the side cavity and the other K^+ encased in the central cavity migrated to the side position to form di-K^+ encapsulated compound, $K_{13}[P_5W_{30}O_{110}K_2]$. This finding inspired us to study the migration of the encapsulated Na^+ from the side cavity to the central cavity and compare the findings with the prediction by DFT calculations.[21]

Herein, we report that the migration of Na^+ from the side cavity to the central cavity is possible through heating the solid form of the compound, which results in the generation of a novel Preyssler-type phosphotungstate, $[P_5W_{30}O_{110}Na(center)]^{14-}$ (Scheme 1).



Scheme 1. Migration of Na^+ from the side cavity to the central cavity of the Preyssler molecule to form $[P_5W_{30}O_{110}Na(center)]^{14-}$. Green, blue, red, orange, pink, and black balls represent tungsten, phosphorous, oxygen, oxygen surrounding the central cavity, Na^+, water molecule oxygen coordinated to Na^+, respectively.

2. Experimental

Materials: Deionized water (Millipore, Elix) was used throughout the experiments. The compounds $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$-$23H_2O$ and $H_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$-$43H_2O$ were prepared according to the published procedure[4,5,22] and analyzed by 31-P NMR and IR. All chemicals were reagent-grade and used without further purification.

Preparation of $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(side)(H_2O)]$-$40H_2O$.

$H_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$-$43H_2O$ (3.036 g, 0.368 mmol) was dissolved in water (40 mL) and then neutralized by titration using 0.1 M NaOH. The neutral solution was then evaporated at 70 °C overnight to obtain the desired solid (3.029 g, 0.362 mmol). IR (KBr): ν = 1598.7 (m), 1163.7 (s), 1076.6 (s), 1019.7 (w), 912.4 (m), 785.7 (m) cm^{-1}. ^{31}P NMR (D_2O): δ = -9.34 ppm. Anal.

Calcd. (%) for $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(side)(H_2O)]$-$40H_2O$: H, 0.80; P, 1.87; W, 66.59; Na, 3.75. found: H, 0.95; P, 1.93; W, 66.80; Na, 3.77.

Preparation of $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(center)]$. $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(side)(H_2O)]$ (3.029 g, 0.362 mmol) was heated to 300 °C in air at a heating rate of 10°C/min in a furnace and was kept for 1 h to form $Na_{14}[P_5W_{30}O_{110}Na(center)]$ (3.010 g, 0.365 mmol). IR (KBr): ν = 1630.3 (m), 1165.2 (vs), 1079.2 (vs), 933.6 (w), 904.2 (s), 792.3 (m) cm^{-1}. ^{31}P NMR (D_2O): δ = -8.97 ppm. ^{183}W NMR (D_2O): δ = -209.7 and -272.1 ppm. Negative ion MS (CH_3CN-H_2O): calculated for $H_8[P_5W_{30}O_{110}Na]^{6-}$ 1243.4834; found 1243.4817.

Preparation of $K_{14}[P_5W_{30}O_{110}Na(center)]$-$20H_2O$. $Na_{14}[P_5W_{30}O_{110}Na(center)]$ (3.010 g, 0.365 mmol) was dissolved in H_2O (40 mL), and KCl (5 g) was added to the solution. The precipitate formed was filtered off and dried at 70 °C to obtain white solid (3.103 g, 0.371 mmol). The white solid was recrystallized from hot water (95 °C, 25 ml) twice to form $K_{14}[P_5W_{30}O_{110}Na(center)]$ (2.746 g, 0.328 mmol, 88 % based on W). IR (KBr): ν = 1166.9 (vs), 1078.7 (vs), 1012.7 (w), 980.6 (w), 931.8 (vs), 900.5 (vs), 790.0 (m) cm^{-1}. ^{31}P NMR (D_2O): δ = -8.97 ppm. Negative ion MS (CH_3CN-H_2O): calculated for $H_8[P_5W_{30}O_{110}Na]^{6-}$ 1243.4834; found 1243.4813. Anal. Calcd. (%) for $K_{14}[P_5W_{30}O_{110}Na(center)]$-$20H_2O$: H, 0.55; P, 1.85; W, 65.97; Na, 0.27; K, 6.55. found: H, 0.47; P, 1.89; W, 66.00; Na, 0.27; K 6.68.

X-ray crystallography. A colorless crystal of the dimension 0.24×0.03×0.01 mm was mounted on a Rigaku VariMax Saturn724R diffractometer and the diffraction images were collected using Mo*K*α radiation (λ = 0.71073 Å). Crystallographic data is summarized in Table S2. CSD 1952522 contains the supplementary crystallographic data. The data may be also obtained from the joint CCDC/FIZ Karlsruhe online deposition service at https://www.ccdc.cam.ac.uk/structures/.

Other analytical techniques. Infrared (IR) spectra were recorded on a NICOLET 6700 FT-IR spectrometer (Thermo Fisher Scientific) using KBr pellets. ^{31}P NMR and ^{23}Na NMR spectra were recorded on a Varian system 500 (500 MHz) spectrometer (Agilent) (P resonance frequency: 202.378 MHz, Na resonance frequency: 132.240 MHz). The spectra were referenced to external 85% H_3PO_4 (0 ppm) and saturated NaCl (0 ppm). ^{23}Na NMR was measured using Quartz NMR sample tube. ^{183}W NMR spectra were recorded on an ECA500 (500 MHz) spectrometer (JEOL) (W resonance frequency 20.839 MHz). The spectrum was referenced to external saturated Na_2WO_4 (0 ppm). Elemental analyses were carried out on a Mikroanalytisches Labor Pascher (Remagen, Germany). High-resolution ESI-MS spectra were recorded on a LTQ Orbitrap XL (Thermo Fisher Scientific) with an accuracy of 3 ppm. Each sample (5 mg) was dissolved in 5 ml of H_2O, and the solutions were diluted by CH_3CN (final concentration: ~10 µg/ml). TG-DTA was measured using TG/DTA7300 (SII, Japan) under N_2 flow of 50 $ml \cdot s^{-1}$.

3. Results and Discussion

Heating of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$

Figure 2 shows ^{31}P NMR of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ and the solid obtained by heating of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ at 300 °C. Heating of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ produces a new species that shows peak at -8.97 ppm, mono-K-encapsulated species ($[P_5W_{30}O_{110}K(center)]^{14-}$) corresponds to -10.17 ppm, and di-K-encapsulated species ($[P_5W_{30}O_{110}K_2]^{13-}$) at -10.98 ppm. Formation of the two K^+ encapsulated species can be explained by insertion of K^+ counter cation into the Preyssler molecule.

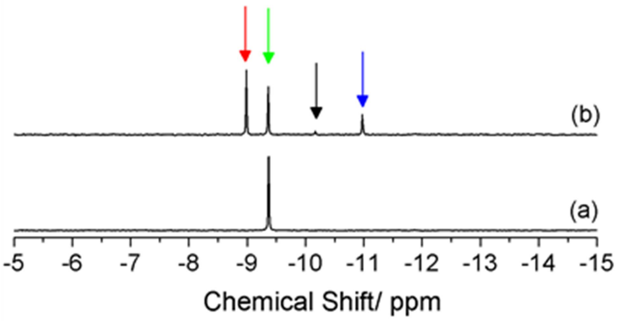


Figure 2. ^{31}P NMR of (a) $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ and (b) solid obtained by heating of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ at 300 °C. Sample was heated with a heating rate of 10 °C min^{-1} until 300 °C, and the temperature was maintained at 300 °C for 1 h. Samples (~30 mg) was dissolved in D_2O (1 mL). Red, green, black, and blue arrows indicate ^{31}P NMR corresponding to new compounds, $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$, $[P_5W_{30}O_{110}K(center)]^{14-}$, and $[P_5W_{30}O_{110}K_2]^{13-}$, respectively.

Heating of $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(side)(H_2O)]$; Preparation and Structural Characterization of $[P_5W_{30}O_{110}Na(center)]^{14-}$

To avoid the formation of K^+ encapsulated species, we exchanged K^+ counter cation with Na^+ cation. In the first step, K^+ counter cation was exchanged with a proton by reacting with H^+-resin (Equation 1), then the H^+ was replaced with Na^+ upon treating with NaOH (Equation 2). The structure and the formula were confirmed by ^{31}P NMR, IR, and elemental analysis. It should be noted that the ^{31}P NMR chemical shift is independent of the counter cations, K^+, H^+ or Na^+.

$$K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)] + 14\ H^+\text{-resin} \rightarrow H_{14}[P_5W_{30}O_{110}Na(side)(H_2O)] + 14\ K^+\text{-resin} \quad \text{(Equation 1)}$$

$$H_{14}[P_5W_{30}O_{110}Na(side)(H_2O)] + 12.5\ NaOH \rightarrow Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(side)(H_2O)] + 12.5\ H_2O \quad \text{(Equation 2)}$$

^{31}P NMR and IR of solid obtained after heating of $Na_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ at 200–600 °C for 1 h are shown in Figure 3 and Figure S1. Heating at 200 °C produced small amount of a new species with peak at -8.97 ppm that was also observed upon heating of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ at 300 °C with $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$. After heating at 300 °C, only one signal at −8.97 ppm of the new species appeared and the disappearance of the peak at -9.34 ppm was observed. After heating at 400 °C, the signal at −8.97 ppm still existed along with other several signals. Signal at ~0.8 ppm can be assigned to phosphate derivatives, which indicated the Preyssler framework had started to decompose. After heating at 500 °C, the signal at -12.3 ppm corresponding to Dawson type phosphotungstate, $[P_2W_{18}O_{62}]^{6-}$,[8] (Fig. S2) and other decomposed phosphate species at ~1.02 ppm were observed along with the peak of new species at -8.97 ppm. Further heating at 600°C produces only two peaks present at -1.78 ppm and -10.10 ppm indicating the presence of decomposed phosphate species and other unknown new species. IR spectra of the solid obtained after heating at up to 400 °C showed bands characteristic for Preyssler-type phosphotungstate (Fig. S1). Upon heating at 500 °C (Fig. S1e), the intensity of characteristic bands for Preyssler-type phosphotungstate was slightly diminished due to decomposition of Preyssler framework and at 600 °C (Fig. S1f), no IR bands characteristic for the Preyssler framework were observed, which confirmed the decomposition of the Preyssler complex at 600 °C. Thus, it can be concluded that 300 °C is the optimal temperature required to prepare the new Preyssler species at -8.97 ppm.

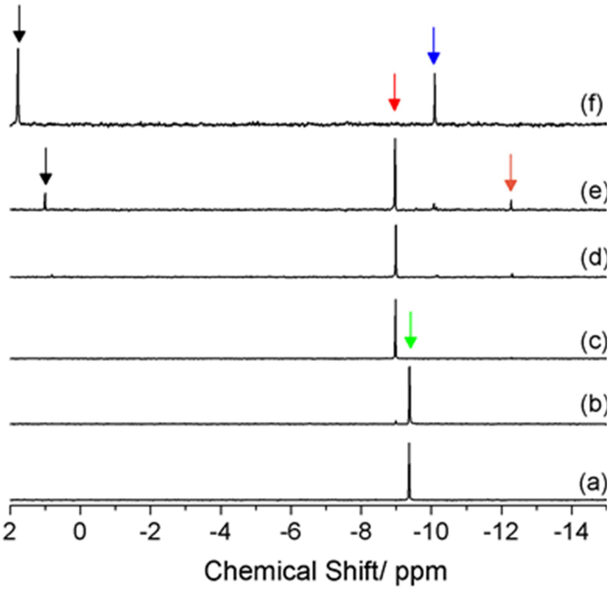


Figure 3. (a) ^{31}P NMR spectrum of $Na_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$. ^{31}P NMR spectra of $Na_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ after heating at (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C and (f) 600 °C for 1 h. The green (δ = -9.34 ppm), the red (δ = -8.97 ppm), the brown (δ = -12.30 ppm) the blue (δ = -10.10 ppm) and the black (δ = +0.74 ppm, + 0.98 ppm, and +1.78 ppm) arrows indicate the signals corresponding to $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$, the new species, $[P_2W_{18}O_{62}]^{6-}$, other unknown species and $[PO_4]^{3-}$ species.

We isolated the new species as a potassium salt by addition of KCl to aqueous solution of the new species. Recrystallization provided crystals suitable for single crystal structure analysis, which revealed that the new species is a Preyssler-type phosphotungstate with one encapsulated Na^+ (Fig. 1e and 1g, Fig. S3(a)). The encapsulated Na^+ was located in the center of the central cavity surrounded by ten O_a with Na-O bond lengths in the range of 2.93-2.95 Å. No water coordinating to the encapsulated Na^+ was observed by single crystal structure analysis. The molecular size of $K_{14}[P_5W_{30}O_{110}Na(center)]$ is similar to that of $K_{14}[P_5W_{30}O_{110}K(center)]$[16] (Table 1).

The thermal displacement ellipsoid of the central Na^+ extends in the direction perpendicular to the equatorial plane of the Preyssler molecule (Fig. 1e and Fig. S3(a)) while that of K^+ in $K_{14}[P_5W_{30}O_{110}K(center)]$ is placed in the center (Fig. 1d and Fig. S3(b)). This result confirmed the DFT prediction that the most stable position of Na^+ in the central cavity is slightly (~0.5 Å) shifted from the center of cavity to one set of five O_a oxygen side of ten O_a oxygens. Average K-O distance in the $K_{14}[P_5W_{30}O_{110}K(center)]$ is 2.95 Å, which is close to sum of ionic radii of K^+ (1.59 Å with 10 coordination) and O^{2-} (1.35 Å with 2 coordination). The Preyssler framework size and the central cavity size did not change upon replacement of K^+ with Na^+ (Table 1). The smaller Na^+ (1.24 Å with 9 coordination and 1.39 Å with 12 coordination) prefers site close to five O_a oxygen side as predicted by DFT calculation. Single crystal X-ray diffraction could not distinguish whether Na^+ is located at the center of the molecule with a large vibration amplitude or Na^+ is delocalized over two sites.

Table 1. Comparison of the NMR Chemical Shift, Wavenumber, and Size of Sodium and Potassium Encapsulated Preyssler-type Phosphotungstate compounds.

	$K_{14}[P_5W_{30}O_{110}Na_{(center)}]$	$K_{14}[P_5W_{30}O_{110}K_{(center)}]$
^{31}P	-8.97	-10.15
^{183}W	-209.7 (20W), -272.1 (10W)	-208.2 (20W), -302.1 (10W)
IR bands (cm^{-1})	1166, 1078, 1012, 980, 931, 900, 789	1173, 1088, 1012, 985, 930, 906, 794
Diameter (Å) of the circle going through the given atoms		
O_b	4.59	4.58
O_a	5.31	5.34
Cap W	6.34	6.34
P	7.01	7.04
Belt W	12.27	12.27
Thickness (Å): distance between belt or cap tungsten atoms		
O_a	2.52	2.51
O_b	6.97	6.95
Belt W	3.32	3.32
Cap W	6.70	6.69
Average bond distance (Å)		
	Na-O : 2.94	**K-O:** 2.95

The IR spectra of new species shows characteristic band for Preyssler-type phosphotungstate (Fig. 4). The elemental analyses of the potassium salt revealed that ratio of K : Na : P : W = 14 : 1 : 5 : 30 confirming the presence of one Na in the compound.

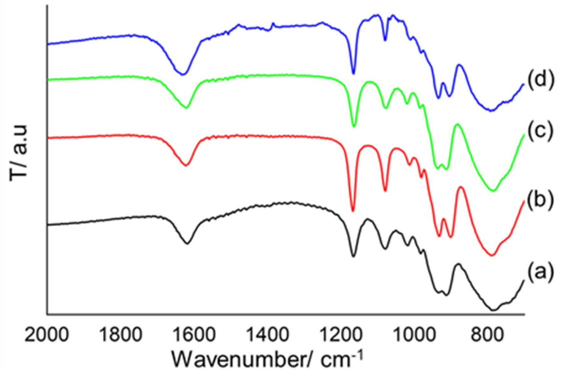


Figure 4 IR Spectra of (a) $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$, (b) $K_{14}[P_5W_{30}O_{110}Na(center)]$, (c) $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(side)(H_2O)]$ and (d) $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(center)]$.

TG-DTA of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$, $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(side)(H_2O)]$, and $K_{14}[P_5W_{30}O_{110}Na(center)]$ (Fig. S4) showed exothermal peaks between 500 and 600 °C which may correspond to decomposition of these molecule. On the other hand, no clear DTA peak for migration of Na^+ in the cavity was observed.

$K_{14}[P_5W_{30}O_{110}Na(center)]$ and $Na_{14}[P_5W_{30}O_{110}Na(center)]$ were dissolved in a H_2O-CH_3CN mixed solution and subjected to characterization by high resolution ESI-MS (Fig. S5 and S6). In both cases, the signals assignable to $H_8[P_5W_{30}O_{110}Na]^{6-}$ were found. The signals corresponding to $H_6KNa[P_5W_{30}O_{110}Na]^{6-}$ were only found in $K_{14}[P_5W_{30}O_{110}Na(center)]$ (Fig. S5a). In the case of $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(center)]$, ESI-MS spectra showed several signals assignable to $H_8[P_5W_{30}O_{110}Na]^{6-}$, $H_7Na[P_5W_{30}O_{110}Na]^{6-}$, $H_6Na_2[P_5W_{30}O_{110}Na]^{6-}$, and $H_5Na_3[P_5W_{30}O_{110}Na]^{6-}$ (Fig. S6). These results indicated that Preyssler-type phosphotungstate with one central Na^+ cation is stable in aqueous solution. On the other hand, ESI-MS of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ showed peaks assignable to $H_8[P_5W_{30}O_{110}Na(H_2O)]^{6-}$ and $H_7K[P_5W_{30}O_{110}Na(H_2O)]^{6-}$, which indicate the presence of a coordinating water molecule in the Preyssler structure. In addition, several peaks assignable to $H_6K_3[P_5W_{30}O_{110}]^{6-}$, $H_5K_3[P_5W_{30}O_{110}Na]^{6-}$, $H_5K_4[P_5W_{30}O_{110}]^{6-}$, $H_4K_4[P_5W_{30}O_{110}Na]^{6-}$, and $H_4K_5[P_5W_{30}O_{110}]^{6-}$ which are produced under ionization condition (Fig. S7 and S8) were observed.

^{183}W NMR of $Na_{14}[P_5W_{30}O_{110}Na(center)]$ dissolved in D_2O showed two sharp singlets at -209.7 and -272.1 ppm with 2:1 integration ratio (Fig 5(b)). The presence of two singlets indicates that $[P_5W_{30}O_{110}Na(center)]^{14-}$ has D_{5h} symmetry similar to $[P_5W_{30}O_{110}K_2]^{13-}$ and $[P_5W_{30}O_{110}K(center)]^{14-}$ (Fig. 5(c) and (d)). On the other hand, Preyssler compounds containing encapsulated cation in one of the side cavities with C_{5v} symmetry, such as $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$, show four singlets with 2:2:1:1 integration ratio (Fig. 5(a)). Presence of two sharp singlets possibly indicates that Na^+ vibrates in the central cavity faster than ^{183}W NMR time scale at room temperature because slight shift of Na^+ in a direction perpendicular to the equatorial plane from the center of the molecules would have caused splitting of ^{183}W NMR signals.

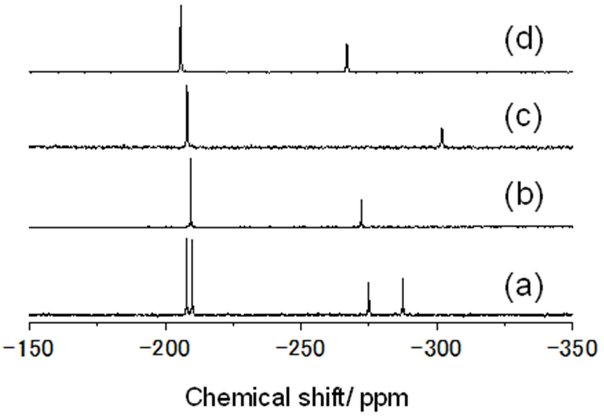


Figure 5. ^{183}W NMR spectra of (a) Lithium salt of $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$, (b) $Na_{14}[P_5W_{30}O_{110}Na(center)]$, (c) Lithium salt of $[P_5W_{30}O_{110}K(center)]^{14-}$, and (d) Lithium salt of $[P_5W_{30}O_{110}K_2]^{13-}$. Each sample (~0.5 g for $K_{14}[P_5W_{30}O_{110}K(center)]$ and 1.0 g for $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ and $K_{13}[P_5W_{30}O_{110}K_2]$) was dissolved in ~2.5 mL of D_2O using a Li-resin. $Na_{14}[P_5W_{30}O_{110}Na(center)]$ (1.0 g) dissolved without the use of Li-resin.

^{23}Na NMR of $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$ showed one broad peak at -18.7 ppm and a sharp peak at +0.15 ppm corresponding to the encapsulated Na^+ and Na^+ counter cation, respectively, as also reported by Pope and Jeannin (Fig. 6a).[4] ^{23}Na NMR of $K_{14}[P_5W_{30}O_{110}Na(center)]$ under same conditions showed a very broad peak from -20 to -50 ppm at room temperature (Fig. 6b). ^{23}Na is quadrupolar, and the signal width increases with asymmetry of the environment. Hence, the peak of Na^+ in the side cavity of $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$ becomes broader[4] while the peak of Na^+ counter cation and standard NaCl in D_2O is sharp. The peak assignable to Na^+ in the central cavity of $[P_5W_{30}O_{110}Na(center)]^{14-}$ coordinated by 10 Oa atoms (Fig. S3(a) and Fig. 1(e)) is broader than the peak assignable to Na^+ in the side cavity of $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$, which is coordinated by 5 Oa atoms, 5 Ob atoms, and one coordinating water (Fig. S3(c) and Fig. 1(c)). The broader peak may be due to the vibration of the Na^+ in the central cavity which is also predicted by the ^{183}W NMR. Further investigation is now underway in our laboratory.

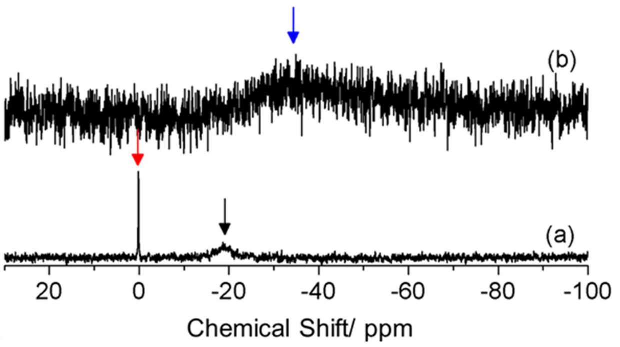


Figure 6. ^{23}Na NMR spectra of (a) $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ and (b) $K_{14}[P_5W_{30}O_{110}Na(center)]$.

4. Conclusion

The new Preyssler-type phosphotungstate with one sodium encapsulated in the central cavity, $[P_5W_{30}O_{110}Na(center)]^{14-}$ has been successfully prepared through thermal treatment of $[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$ at 300 °C. Sodium cation migrated from side cavities to central position upon thermal treatment (Scheme 1). Single-crystal X-ray diffraction analysis of $[P_5W_{30}O_{110}Na(center)]^{14-}$ revealed the thermal displacement ellipsoid of the central sodium is extended from the center of the molecule to the direction perpendicular to the equatorial plane of Preyssler molecule. Our findings confirm the theoretically studies by DFT calculation that the most stable site of sodium in the Preyssler framework is in the central cavity with a slight shifted of 0.5 Å from the molecular center. Further investigation on the vibration of encapsulated sodium cation are being carried.

Acknowledgement

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PhD scholarship (PRJ-36/ LPDP.3/2017). We thank Ms. T. Amimoto, Ms. N. Kawata, and Mr. Fujitaka at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University, for the ESI-MS measurements, the initial single-crystal X-ray structure analysis, and ^{183}W NMR measurements, respectively.

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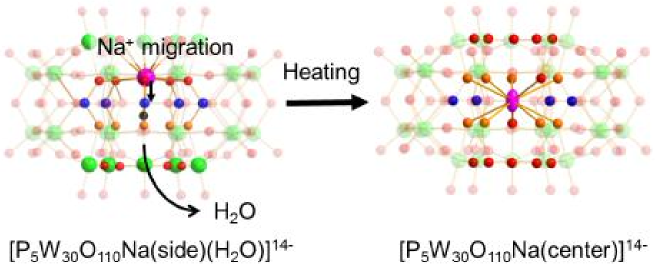
Graphical Abstract

Synthesis of Preyssler-Type Phosphotungstate with Sodium Cation in the Central Cavity through Migration of the Ion

MNK Wihadi, A Hayashi, T Ozeki, K Ichihashi, H Ota, M Fujibayashi, S Nishihara, K Inoue, N Tsunoji, T Sano, and M Sadakane

<Summary>

Heating of a Preyssler-type compound—$[P_5W_{30}O_{110}Na(side)(H_2O)]^{14-}$—in which a sodium cation occupies one of the two side cavities, at 300 °C forms a new compound—$[P_5W_{30}O_{110}Na(center)]^{14-}$—in which the sodium cation is encapsulated in the central cavity. These results confirmed prediction using DFT calculation by López and Poblet (*J. Am. Chem. Soc*. **2007**, *129*, 12244.) that the most stable site for sodium is the central cavity with a slight shift from the center of the molecule.



Synthesis of Preyssler-Type Phosphotungstate with Sodium Cation in the Central Cavity through Migration of the Ion

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Table S1. Peak Assignment of ESI-MS spectra of $[P_5W_{30}O_{110}Na_{(center)}]^{14-}$ with Different Counter Cations.

Table 2. Crystal data of $K_{14}[P_5W_{30}O_{110}Na(center)]$.

Figure S1. IR Spectra of (a) $Na_{14}[P_5W_{30}O_{110}Na(H_2O)(side)]$ and solids after heating at (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, and (f) 600 °C.

Figure S2. (a) ^{31}P NMR spectrum of $Na_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ after heated at 500 °C for 1 h, (b) ^{31}P NMR spectrum of $Na_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ after heated at 500 °C for 1 h and Additional of 10 mg $K_6P_2W_{18}O_{62}$ to solution (a) and (c) ^{31}P NMR spectrum of $K_6P_2W_{18}O_{62}$. The red (δ = -8.97 ppm), the brown (δ = -12.30 ppm), the blue (δ = -10.10 ppm) and the green (δ = +0.98 ppm) arrows indicate the signals correspond to $[P_5W_{30}O_{110}Na(center)]^{14-}$, $[P_2W_{18}O_{62}]^{6-}$, others unknown species and $[PO_4]^{3-}$ derivative detected species as indication the decomposition product of $[P_5W_{30}O_{110}Na(side)]^{14-}$.

Figure S3. Ball-and-stick representation of a (a) mono-K^+-encapsulated Preyssler-type molecule, $[P_5W_{30}O_{110}K(center)]^{14-}$, (e) mono-$Na^+$-encapsulated Preyssler-type molecule, $[P_5W_{30}O_{110}Na(center)]^{14-}$. Green, blue, red, orange, gray, black, pink, and violet balls represent tungsten, phosphorous, oxygen, oxygen surrounding the central cavity, mono-encapsulated cation, water molecule oxygen coordinated to the cation, thermal ellipsoid of encapsulated Na^+, and thermal ellipsoid of encapsulated K^+, respectively.

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Figure S6. ESI-MS profile of $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(center)]$ dissolved in H_2O/CH_3CN.

Figure S7. ESI-MS profile of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ dissolved in H_2O/CH_3CN. (a) m/z 300 – 2000, (b) enlarged profiles (m/z = 1240 – 1290).

Figure S8. Enlarge ESI-MS profile of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ dissolved in H_2O/CH_3CN together with simulated pattern for $H_8[P_5W_{30}O_{110}Na(H_2O)]^{6-}$, $H_7K[P_5W_{30}O_{110}Na(H_2O)]^{6-}$ and $H_6K_3[P_5W_{30}O_{110}]^{6-}$.

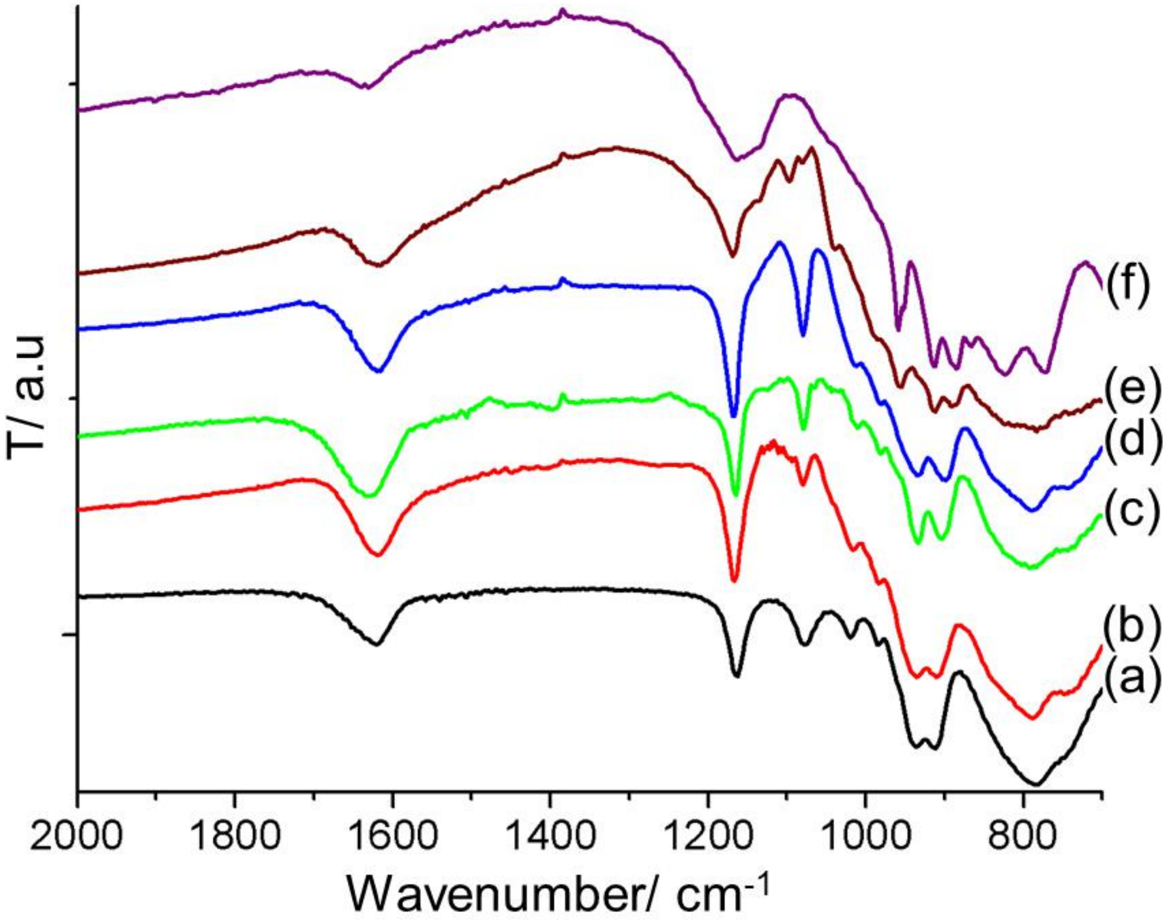
Table S1. Peak Assignment of ESI-MS spectra of $[P_5W_{30}O_{110}Na_{(center)}]^{14-}$ with Different Counter Cations.

Compounds	**Solution**	**Peak Assignment**	**m/z Value (Observed)**	**m/z Value (Simulated)**
$K_{14}[P_5W_{30}O_{110}Na(center)]$	CH_3CN/H_2O	$H_8[P_5W_{30}O_{110}Na]^{6-}$	1243.4813	1243.4834
		$H_6KNa[P_5W_{30}O_{110}Na]^{6-}$	1253.6396	1253.6396
$Na_{14}[P_5W_{30}O_{110}Na(center)]$	CH_3CN/H_2O	$H_8[P_5W_{30}O_{110}Na]^{6-}$	1243.4817	1243.4834
		$H_7Na[P_5W_{30}O_{110}Na]^{6-}$	1247.1438	1247.1466
		$H_6Na_2[P_5W_{30}O_{110}Na]^{6-}$	1250.8080	1250.8105
		$H_5Na_3[P_5W_{30}O_{110}Na]^{6-}$	1254.4716	1254.4743

Table 2. Crystal data of $K_{14}[P_5W_{30}O_{110}Na(center)]$.

Compound identity	$K_{14}[P_5W_{30}O_{110}Na(center)]$
Empirical formula	$K_{14}[P_5W_{30}O_{110}Na(center)]\text{-}20H_2O$
Molecular weight / g·mol^{-1}	8487.18
Crystal color and shape	Colorless, plate
Temperature [°C]	-150
Crystal system	Orthorhombic
Space group (no.)	*P n n a* (52)
a [Å]	32.8620(3)
b [Å]	21.5093(3)
c [Å]	19.1413(2)
Volume [Å^3]	13529.8(3)
Z	4
Data / parameters	21159/865
R(int)	0.0539
Density (calcd) [g·cm^{-1}]	4.167
Abs coefficient [mm^{-1}]	25.997
R_1 (I > 2 s(I)) [a]	0.0424
wR_2 (all data) [b]	0.1053

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$



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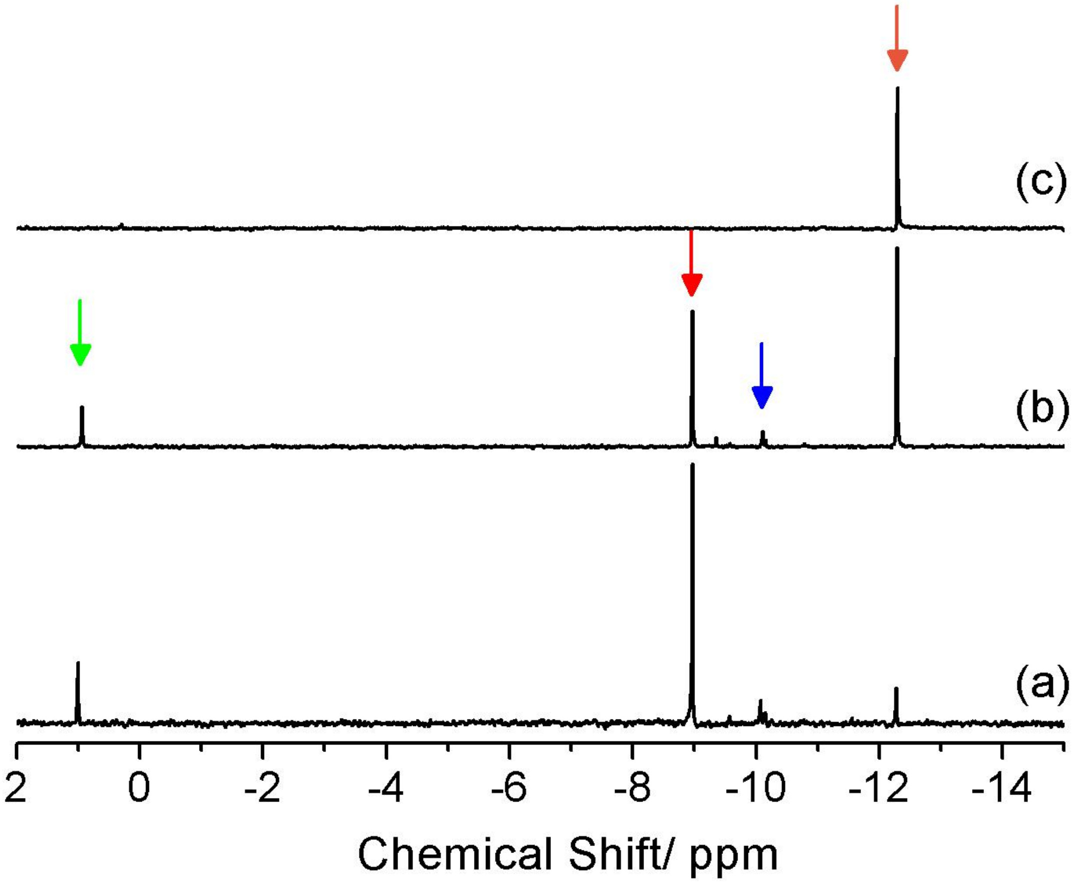

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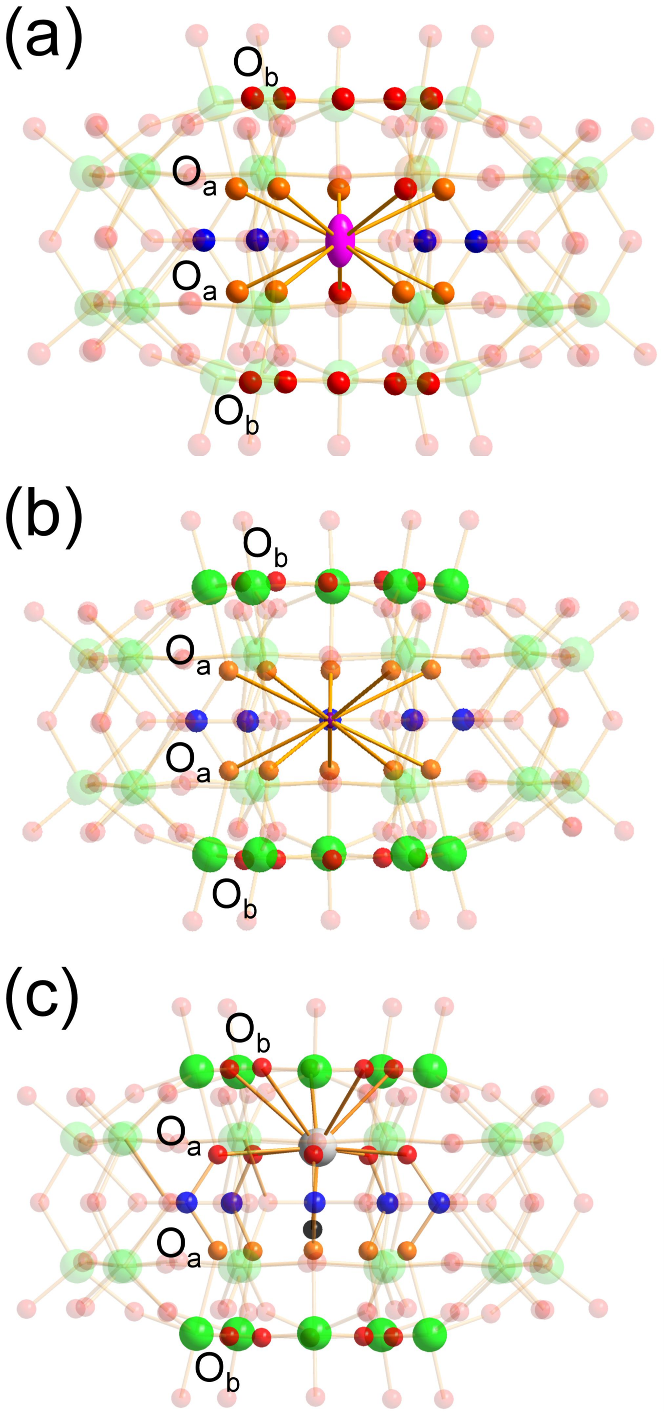

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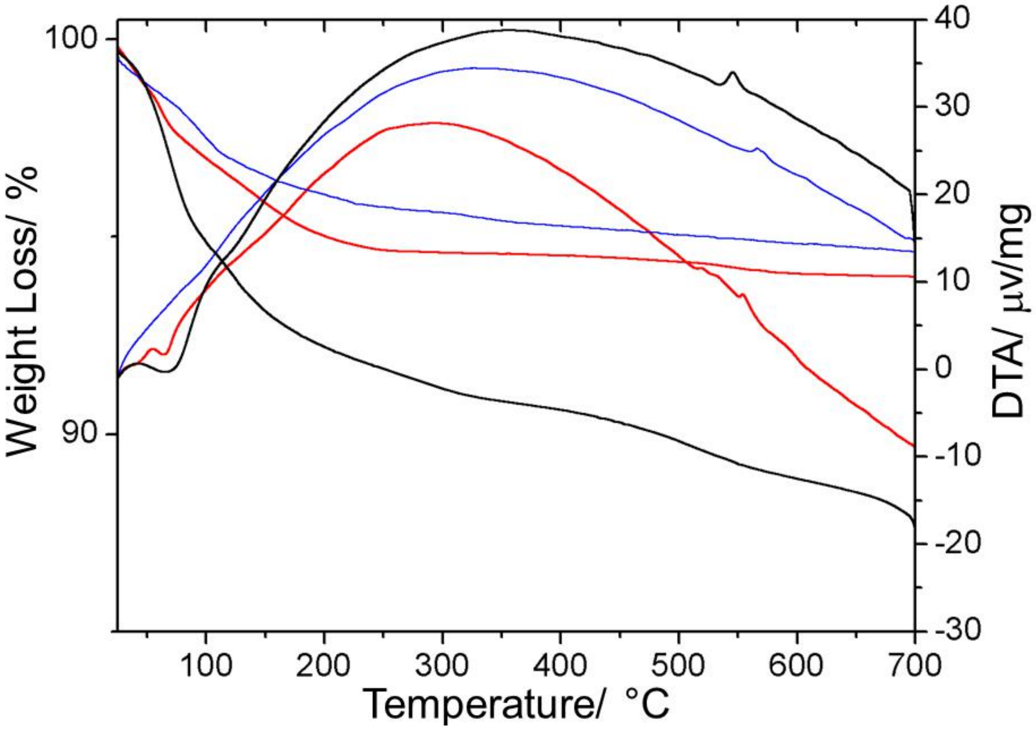

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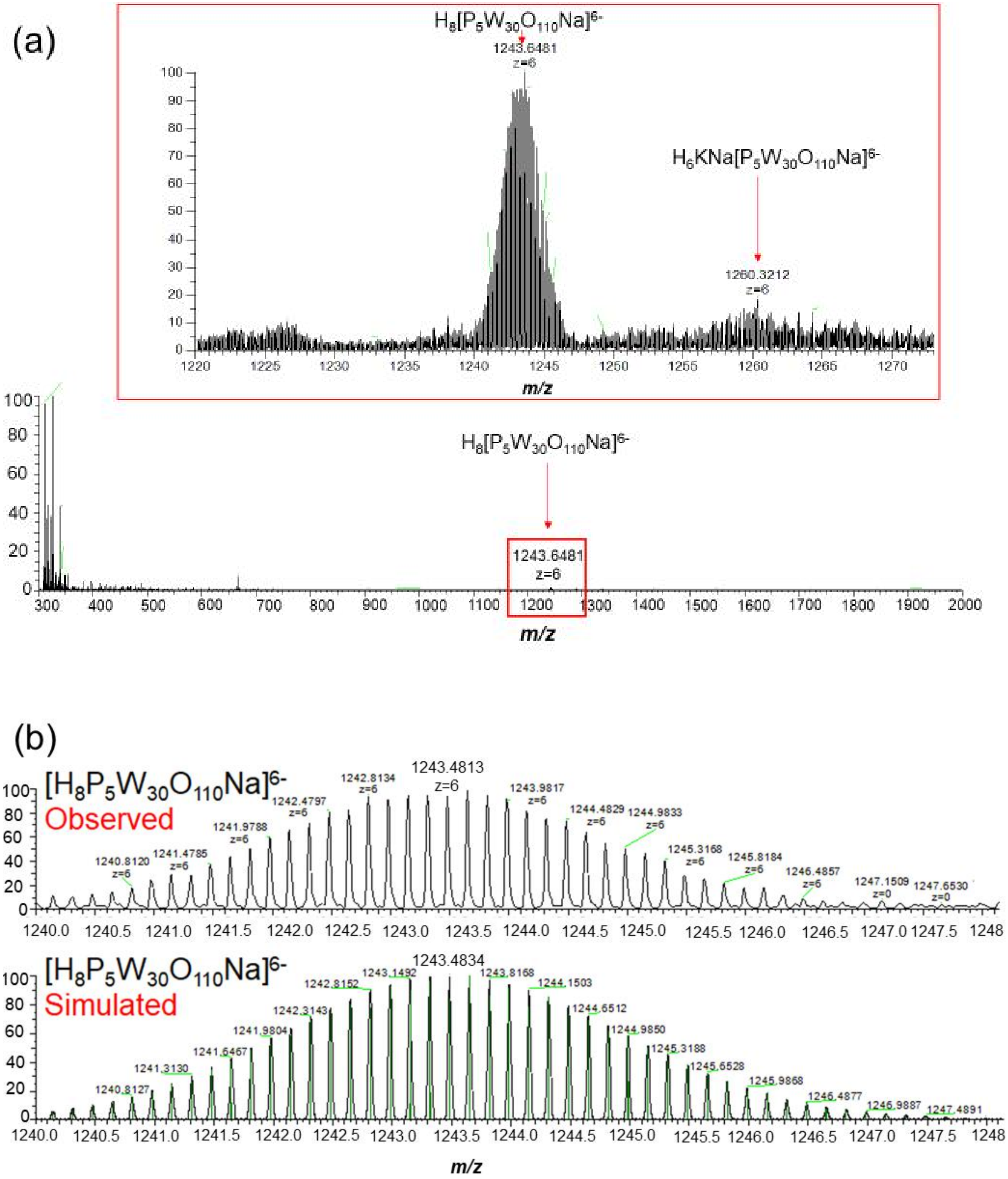

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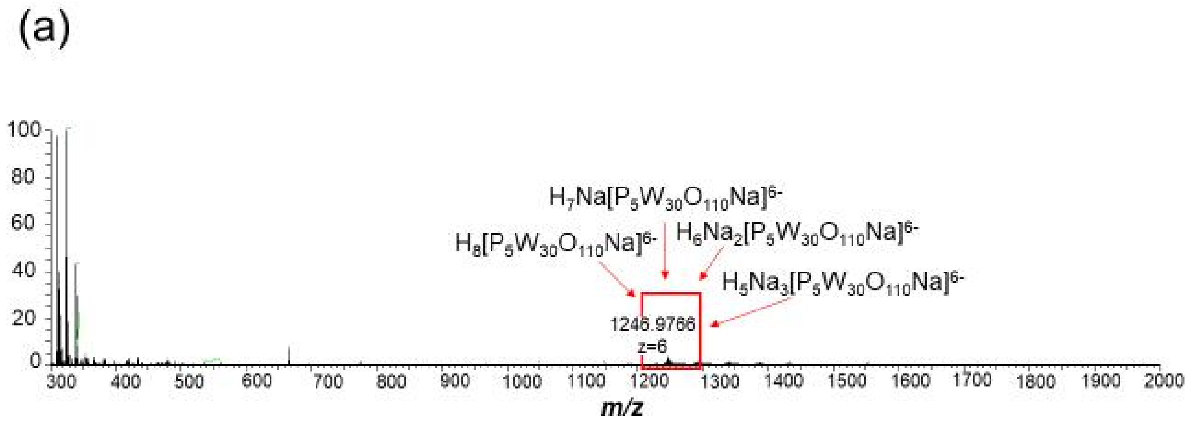
(a)
100
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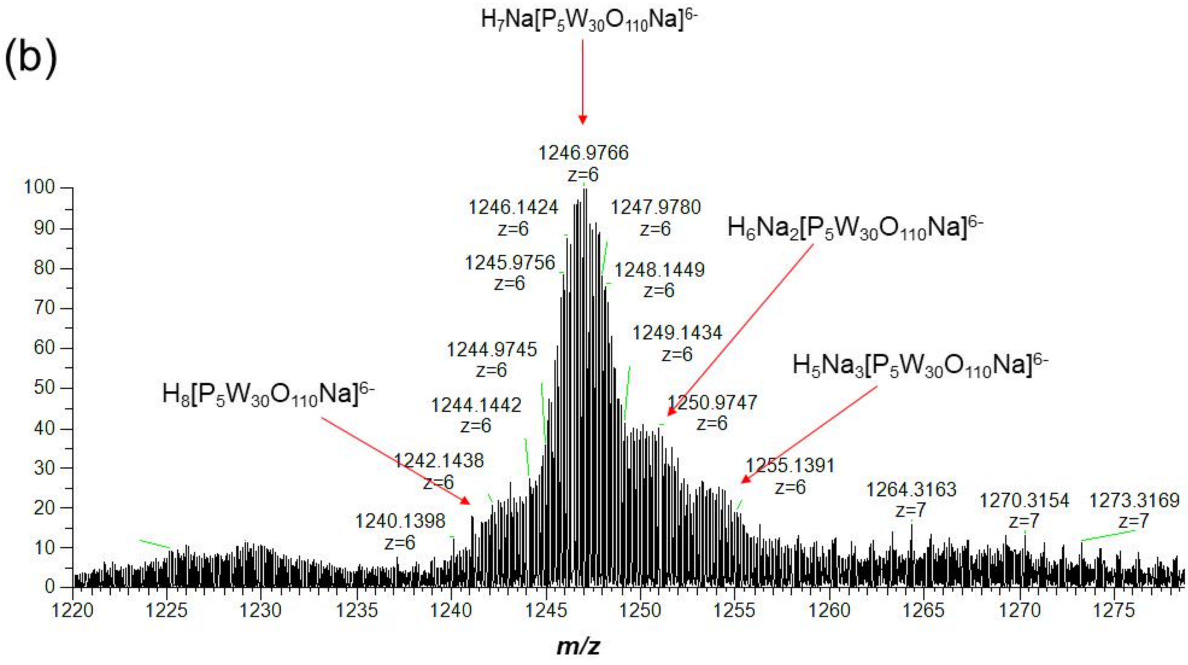
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
m/z
$H_7Na[P_5W_{30}O_{110}Na]^{6-}$
$H_8[P_5W_{30}O_{110}Na]^{6-}$
$H_6Na_2[P_5W_{30}O_{110}Na]^{6-}$
$H_5Na_3[P_5W_{30}O_{110}Na]^{6-}$
1246.9766
z=6


(b)
$H_7Na[P_5W_{30}O_{110}Na]^{6-}$
1246.9766
z=6
1246.1424
z=6
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z=6
1245.9756
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1248.1449
z=6
$H_6Na_2[P_5W_{30}O_{110}Na]^{6-}$
1249.1434
z=6
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1275
m/z

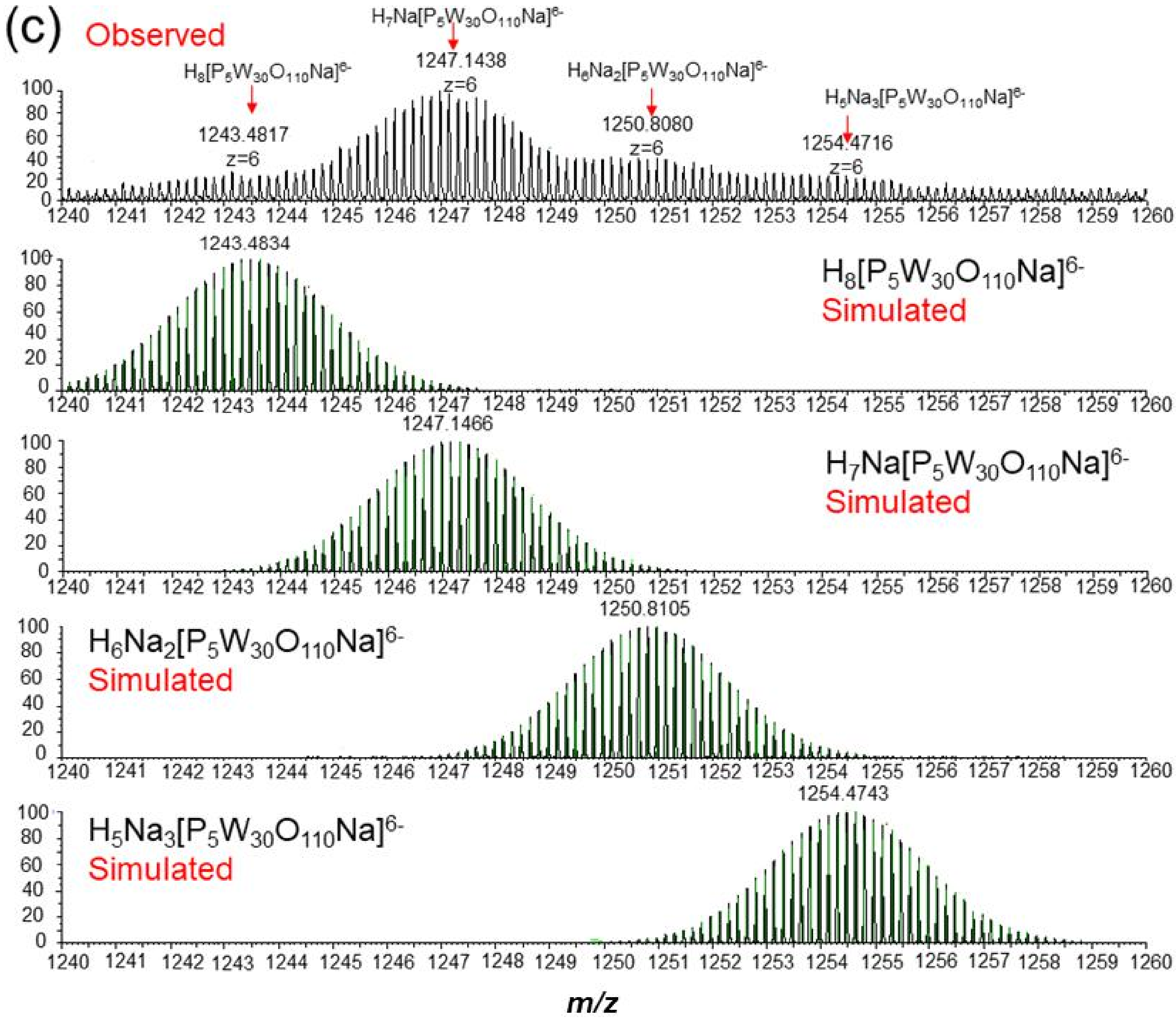

Figure S6. ESI-MS profile of $Na_{12.5}H_{1.5}[P_5W_{30}O_{110}Na(center)]$ dissolved in H_2O/CH_3CN. (a) m/z 300 – 2000, (b) enlarged profiles (m/z = 1220 – 1280) and (c) enlarged profile (1240 – 1248) together with simulated profile for for $H_8[P_5W_{30}O_{110}Na]^{6-}$, $H_7Na[P_5W_{30}O_{110}Na]^{6-}$, $H_6Na_2[P_5W_{30}O_{110}Na]^{6-}$ and $H_5Na_3[P_5W_{30}O_{110}Na]^{6-}$.

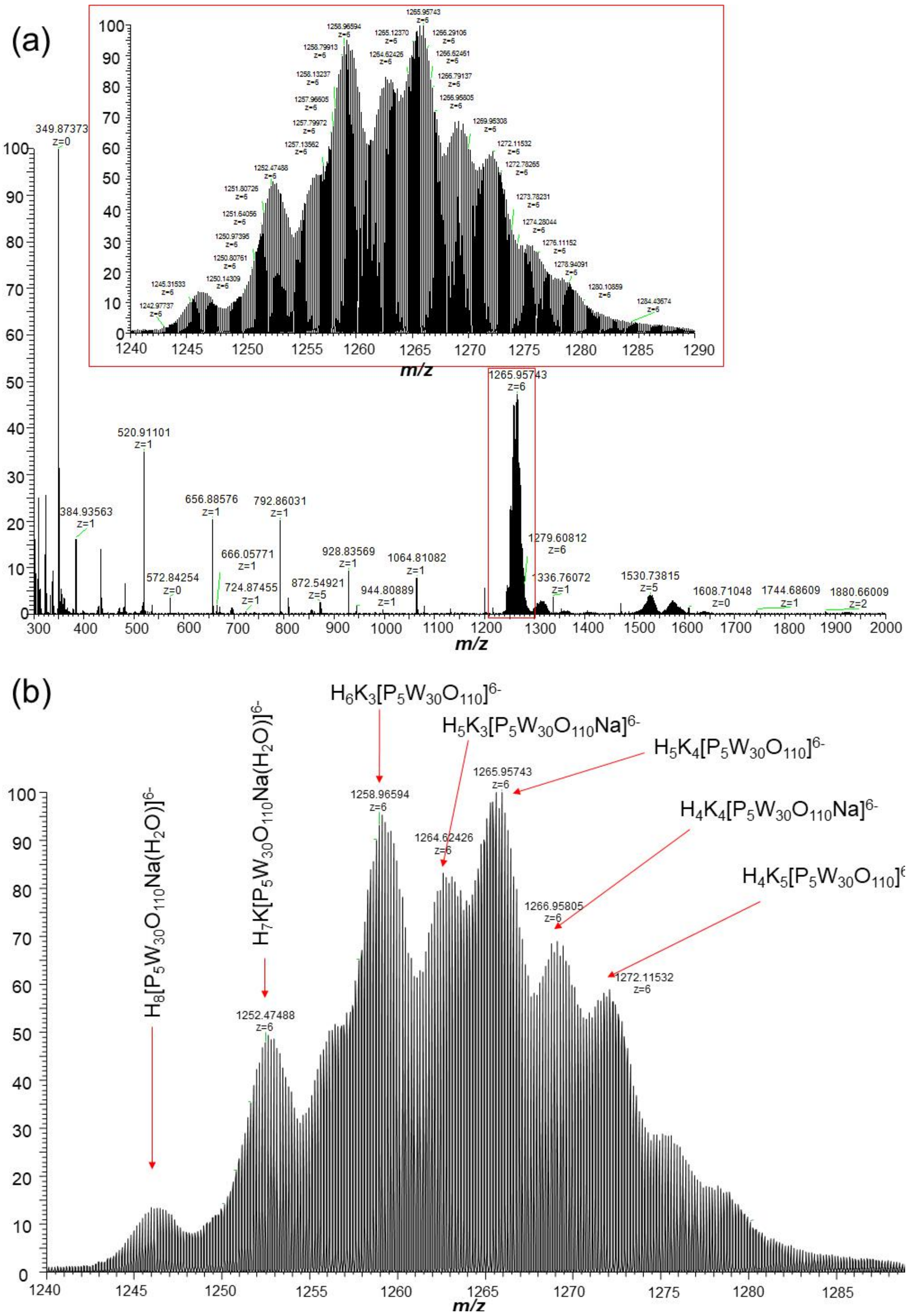

Figure S7. ESI-MS profile of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ dissolved in H_2O/CH_3CN. (a) m/z 300 – 2000, (b) enlarged profiles (m/z = 1240 – 1290).

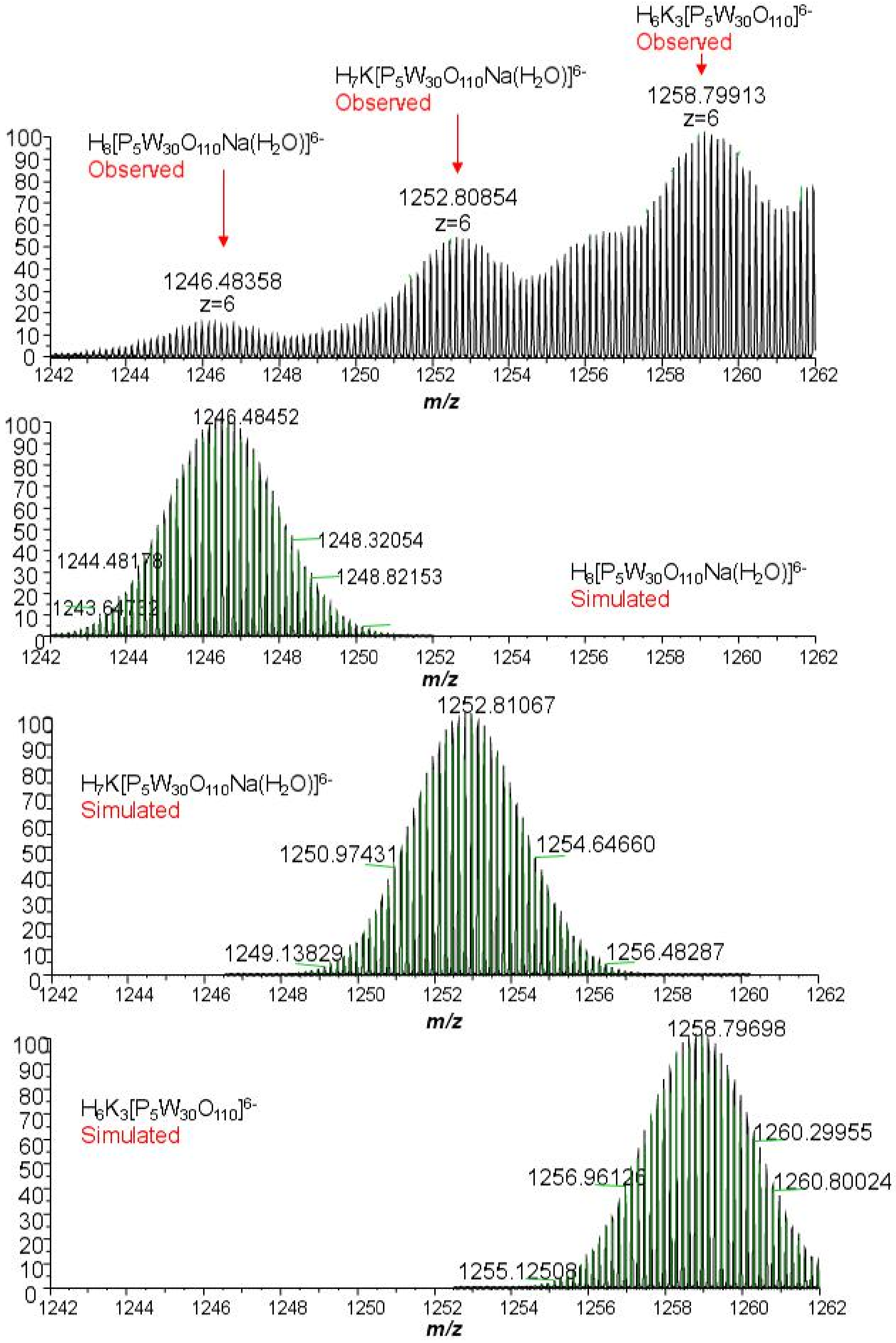

Figure S8. Enlarge ESI-MS profile of $K_{14}[P_5W_{30}O_{110}Na(side)(H_2O)]$ dissolved in H_2O/CH_3CN together with simulated pattern for $H_8[P_5W_{30}O_{110}Na(H_2O)]^{6-}$, $H_7K[P_5W_{30}O_{110}Na(H_2O)]^{6-}$ and $H_6K_3[P_5W_{30}O_{110}]^{6-}$.