1. Introduction

Polyoxometalates have attracted much attention in the fields of catalytic chemistry, surface science, and materials science because their acidity, redox property, and solubility in various media can be controlled at molecular levels [1 – 3]. In particular, coordination of metal ions and organometallics to the vacant site(s) of lacunary polyoxometalates is one of the powerful techniques to construct effective and well-defined metal centers. Among the various metals and their derivatives that can be coordinated to the vacant site(s) of lacunary polyoxometalates, magnesium and magnesium derivatives are intriguing because of their efficient properties as catalysts, reagents for organic syntheses, pharmaceutical compounds, and so on [4, 5]. However, magnesium-coordinated polyoxometalates (characterized by X-ray crystallography) are still one of the least reported compounds: Examples that have been reported include 

\[ \text{Mg}_8\text{SiW}_{12}\text{O}_{37} \cdot 24.5\text{H}_2\text{O} \] [6], 
\[ \text{Mg}_8\text{SiW}_{12}\text{O}_{37} \cdot 12\text{H}_2\text{O} \] [6], and 
\[ \text{Mg}_7(\text{MgW}_{12}\text{O}_{42})(\text{OH})_4(\text{H}_2\text{O})_8 \] [7].

In this study, we first report the syntheses and molecular structures of cesium and tetra-\(n\)-butylammonium salts of \(\alpha\)-Keggin–type mono-magnesium–substituted polyoxotungstate, i.e., 

\[ \text{Cs}_{5.25}\text{H}_{1.75}[\alpha\text{-PW}_{11}\text{MgO}_{40}] \cdot 6\text{H}_2\text{O} \] and 
\[ [(\text{CH}_3)_4\text{N}]_{4.25}\text{H}_{2.75}[\alpha\text{-PW}_{11}\text{MgO}_{40}] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CN}, \]

and potassium and dimethylammonium salts of \(\alpha\)-Dawson–type mono-magnesium–substituted polyoxotungstate, i.e., 

\[ \text{K}_8\text{H}_2[\alpha_2\text{-P}_2\text{W}_{17}\text{MgO}_{62}] \cdot 15\text{H}_2\text{O} \] and 
\[ [(\text{CH}_3)_2\text{NH}]_{7.5}\text{H}_{2.5}[\alpha_2\text{-P}_2\text{W}_{17}\text{MgO}_{62}] \cdot 6\text{H}_2\text{O}; \]

these salts were characterized via X-ray crystallography, elemental
analysis, thermogravimetric/differential thermal analysis, Fourier–transform infrared spectroscopy, solution nuclear magnetic resonance spectroscopies, and density-functional-theory (DFT) calculations. The X-ray crystallography results for Cs\textsubscript{5.25}H\textsubscript{1.75}[\alpha-PW\textsubscript{11}MgO\textsubscript{40}]⋅6H\textsubscript{2}O, [(n-C\textsubscript{4}H\textsubscript{9})\textsubscript{4}N]\textsubscript{4.25}H\textsubscript{2.75}[\alpha-PW\textsubscript{11}MgO\textsubscript{40}]⋅H\textsubscript{2}O, and [(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}]\textsubscript{7.5}H\textsubscript{2.5}[\alpha\textsubscript{2}-P\textsubscript{2}W\textsubscript{17}MgO\textsubscript{62}]⋅6H\textsubscript{2}O showed that the mono-magnesium–substituted sites in the \(\alpha\)-Keggin and \(\alpha\)-Dawson structures could not be identified because of the high symmetry of the compounds, as has been observed for mono-metal–substituted polyoxometalates; however, the bonding modes (i.e., bond lengths and angles) were significantly influenced by the insertion of magnesium ions into the vacant sites. The DFT calculation results also showed that coordination of a hydroxyl group and water molecule to the mono-magnesium–substituted site distorted the molecular structures.

2. Experimental section

2.1. Materials

\(K_7[\alpha-PW_{11}O_{39}]\cdot xH_2O\) (\(x = 16\) and 20) [8] and \(K_{10}[\alpha_2-P_2W_{17}O_{61}]\cdot 14H_2O\) [9] were prepared as described in the literature. The number of solvated water molecules was determined by thermogravimetric/differential thermal analyses. All the reagents and solvents were obtained and used as received from commercial sources.

2.2. Instrumentation/analytical procedures

Elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Prior to analysis, the samples were dried overnight at room temperature under pressures of \(10^{-3}\) – \(10^{-4}\) Torr. Infrared spectra of the solid samples were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer in KBr disks at around 25 °C in air. Infrared spectra of the liquid samples were recorded on a Perkin Elmer Frontier FT-IR spectrometer attached to a Universal ATR sampling accessory at around 25 °C in air. Thermogravimetric (TG) and differential thermal analyses (DTA) data were obtained using Rigaku Thermo Plus 2 TG/DTA TG 8120 and Rigaku Thermo Plus EVO2 TG/DTA 81205Z instruments and were performed in air while constantly increasing the temperature from 20 to 500 °C at rates of 1 and 4 °C/min. \(^{1}H\) (600.17 MHz) and \(^{31}P\)-\(^{1}H\) (242.95 MHz) nuclear magnetic resonance (NMR) spectra were recorded in tubes (outer diameter: 5 mm) on a JEOL ECA-600 NMR spectrometer (Shizuoka University). \(^{1}H\) NMR spectra were measured in dimethylsulfoxide-\(d_6\) and referenced to tetramethylsilane (TMS). Chemical shifts were reported as positive for resonances downfield of TMS (δ 0). \(^{31}P\) NMR spectra were referenced to an external standard of 85% H\textsubscript{3}PO\textsubscript{4} in a sealed capillary. Negative chemical shifts were reported on the δ scale for resonances upfield of H\textsubscript{3}PO\textsubscript{4} (δ 0). \(^{183}W\) NMR (25.00 MHz) spectra were recorded in tubes (outer diameter: 10 mm) on a JEOL ECA-600 NMR spectrometer (Kyushu University). The \(^{183}W\) NMR spectrum measured in 2.0 mM Mg(NO\textsubscript{3})\textsubscript{2}-D\textsubscript{2}O was referenced to an external standard of saturated Na\textsubscript{2}WO\textsubscript{4}-D\textsubscript{2}O solution (substitution method). Chemical shifts were reported as negative for resonances upfield of Na\textsubscript{2}WO\textsubscript{4} (δ 0).
2.3. Synthesis of Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O

Solid K$_4$[α-PW$_{11}$O$_{39}$]·20H$_2$O (1.01 g; 0.31 mmol) was added to a solution of MgBr$_2$, 6H$_2$O (0.18 g; 0.62 mmol) in 10 mL of water. After stirring for 10 min at 75 °C, solid CsCl (1.02 g; 6.06 mmol) was added to the solution, which was then stirred at 25 °C for 15 min. The resultant white precipitate was collected using a membrane filter (JG 0.2 μm). At this stage, 0.927 g of crude product was obtained. For purification, the crude product (0.927 g) was dissolved in 7 mL of acetonitrile (5.5 mL). After filtration through a folded filter paper (Whatman No. 5), colorless crystals were obtained by vapor diffusion from methanol at ~25 °C for one week. The obtained crystals weighed 0.384 g (the yield calculated via [mol of Cs]/[mol of K$_4$[α-PW$_{11}$O$_{39}$]·20H$_2$O] × 100% was 35.7%). The elemental analysis results were as follows: H, ≤ 0.1; Cs, 20.5; Mg, 0.65; P, 0.87; W, 58.9; Br, 0.01%. The calculated values for Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O/[mol of K$_4$[α-PW$_{11}$O$_{39}$]·20H$_2$O] × 100% was 35.7%. The calculated values for Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O were as follows: H, 0.05; Cs, 20.42; Mg, 0.71; P, 0.91; W, 59.18; Br, 0%. A weight loss of 3.03% was observed in the product during overnight drying at room temperature at 10$^{-3}$–10$^{-4}$ Torr before the analysis, which suggested that the complex contained six adsorbed water molecules (3.07%). TG/DTA obtained at a heating rate of 4 °C/min under atmospheric conditions showed a weight loss of 3.0% with an endothermic peak at 242 °C in the temperature range of 25 to 500 °C; our calculations indicated the presence of six water molecules (calcd. 3.07%). The results were as follows: IR spectroscopy (KBr disk): 1081s, 1058s, 961s, 888s, 830m, 808m, 769m, 724m cm$^{-1}$; IR spectroscopy (in water): 1079m, 1056s, 957s, 898s, 823m, 779w, 724m cm$^{-1}$; $^{31}$P NMR (27 °C, D$_2$O): δ−10.81.

2.4. Synthesis of [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]·H$_2$O·CH$_3$CN

The tetra-$n$-butylammonium salt of [α-PW$_{11}$MgO$_{40}$]$^{7-}$ was obtained from the reaction of K$_4$[α-PW$_{11}$O$_{39}$]·16H$_2$O (2.00 g; 0.62 mmol) with MgBr$_2$, 6H$_2$O (0.19 g, 0.65 mmol) in 250 mL of water at 70 °C. After stirring for 1 h at 70 °C, solid [(CH$_3$)$_4$N]Br (4.75 g; 30.8 mmol) was added to the solution, which was then stirred at 25 °C for 4 d. The resultant white precipitate was collected using a membrane filter (JG 0.2 μm). The white precipitate (1.708 g) was dissolved in water (350 mL) at 80 °C, [(n-C$_4$H$_9$)$_4$N]Br (16.99 g; 52.7 mmol) was added to the colorless clear solution, and the solution was stirred at 80 °C for 1 h. The resultant white precipitate was collected on a glass frit (G4). At this stage, 1.862 g of the crude product was obtained. The crude product (1.862 g) was dissolved in acetonitrile (5.5 mL). After filtration through a folded filter paper (Whatman No. 5), colorless crystals were obtained by vapor diffusion from methanol at ~25 °C for one week. The obtained crystals weighed 0.765 g (the yield calculated from [mol of [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]·H$_2$O·CH$_3$CN]/[mol of K$_4$[α-PW$_{11}$O$_{39}$]·16H$_2$O] × 100% was 32.5%). The elemental analysis results were as follows: C, 21.5; H, 4.08; N, 1.72; P, 0.83; Mg, 0.63; W, 54.0; K, <0.03%. The calculated values for [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]·H$_2$O = C$_{60}$H$_{157.75}$Mg$_{1.75}$O$_{125.41}$P$_{1.41}$W$_{1.41}$ were as follows: C, 21.67; H, 4.22; N, 1.58; P, 0.82; Mg, 0.64; W, 53.66; K, 0%. A weight loss of 1.44% from the product was observed during overnight drying at room temperature at 10$^{-3}$–10$^{-4}$ Torr before the analysis, which suggested the presence of a weakly solvated or adsorbed acetonitrile molecule (1.08%); this was also supported by the presence of a signal at 2.10 ppm in the $^1$H NMR spectrum (in DMSO-d$_6$) of the sample after drying overnight, which was due to an acetonitrile molecule. TG/DTA results obtained under
atmospheric conditions at a rate of 4 °C/min showed a weight loss of 27.46% with an endothermic peak at 312.2 °C and an exothermic peak at 412.7 °C in the temperature range of 25 to 500 °C; our calculations indicated the presence of 4.25[(C₄H₉)_₄N]^+ ions, a water molecule, and an acetonitrile molecule (calcd. 28.6%). The results were as follows: IR spectroscopy (KBr disk): 1081m, 1060s, 919s, 734s cm⁻¹; IR spectroscopy (in acetonitrile): 1082m, 1059s, 955s, 889s, 811s, 733s cm⁻¹; ³¹P NMR (20.5 °C, acetonitrile-d₃): δ −10.26.

2.5. Synthesis of K₆H₃₂[P₂W₁₇MgO₆₅]·15H₂O

Solid K₁₀[α₂P₂W₁₇MgO₆₅]·14H₂O (2.00 g; 0.42 mmol) was added to a solution of Mg(NO₃)₂·6H₂O (0.32 g; 1.25 mmol) in 50 mL of water. After stirring for 2 h at 25 °C, solid KCl (1.57 g; 21.1 mmol) was added to the solution. The resultant white precipitate was collected using a glass frit (G3) and washed with methanol. At this stage, 1.730 g of a crude product was obtained. For purification, the crude product (1.730 g) was dissolved in 17 mL of a 2.0 mM Mg(NO₃)₂ solution; the resulting solution was filtered through a folded filter paper (Whatman No. 5) and yielded 0.693 g of product. The percent yield calculated using [mol of K₁₀[α₂P₂W₁₇MgO₆₅]·14H₂O]/[mol of K₁₀[α₂P₂W₁₇MgO₆₅]·14H₂O] × 100% was 34.8%. The elemental analysis results were as follows: H, <0.1%; K, 7.17; Mg, 0.52; P, 1.34; W, 68.6; N, <0.1%; the calculated values for K₁₀[α₂P₂W₁₇MgO₆₅]·14H₂O were H, 0.09; K, 6.90; Mg, 0.54; P, 1.37; W, 68.89; N, 0%. A weight loss of 5.30% was observed during overnight drying at room temperature at 10⁻³–10⁻⁴ Torr before analysis, suggesting the presence of 14 weakly solvated or adsorbed water molecules (5.27%). TG/DTA results obtained at a heating rate of 4 °C/min under atmospheric conditions showed a weight loss of 5.62% below 500 °C with an endothermic point at 101.4 °C; calculations showed that 5.64% corresponded to 15 water molecules. The results were as follows: IR spectroscopy (KBr disk): 1084s, 1063m, 1015w, 946s, 914s, 892s, 823s, 786s, 736s cm⁻¹; IR spectroscopy (in water): 1086s, 1064m, 1015w, 946s, 914s, 811s, 788s, 724m cm⁻¹; ¹⁸O NMR (D₂O, 23.9 °C): δ −7.77, −13.77. ¹⁸O NMR (2.0 mM Mg(NO₃)₂·D₂O, 40 °C): δ −57.04, −80.87, −131.47, −176.59, −181.67, −201.40, −207.65, −208.63, −230.51.

2.6. Synthesis of [(CH₃)₂NH₃]₂[(C₃H₇)₂H₂₅[α₂P₂W₁₇MgO₆₅]·6H₂O

The dimethylammonium salt of [(CH₃)₂NH₃]₂[(C₃H₇)₂H₂₅[α₂P₂W₁₇MgO₆₅]·6H₂O was obtained via the reaction of K₁₀[α₂P₂W₁₇MgO₆₅]·14H₂O (2.00 g; 0.42 mmol) with Mg(NO₃)₂·6H₂O (0.11g; 0.43 mmol) in 50 mL of water. After stirring for 1 h at 25 °C, solid (CH₃)₂NH₂Cl (3.44 g; 42.2mmol) was added to the solution. The resultant white precipitate was collected using a glass frit (G4). At this stage, 1.363 g of the crude product was obtained. For purification, the crude product (1.363 g) was dissolved in 32 mL of water. After filtration through a folded filter paper (Whatman No. 5), colorless crystals were obtained by vapor diffusion from ethanol at 25 °C for 4 d. The obtained crystals weighed 0.740 g (the yield calculated from [mol of [(CH₃)₂NH₃]₂[(C₃H₇)₂H₂₅[α₂P₂W₁₇MgO₆₅]·6H₂O]/[mol of K₁₀[α₂P₂W₁₇MgO₆₅]·14H₂O] × 100% was 38.1%). The elemental analysis results were as follows: C, 3.72; H, 1.42; N, 2.50; Mg, 0.42; P, 1.34; W, 68.0; K, <0.1%; the calculated values for [(CH₃)₂NH₃]₂[(C₃H₇)₂H₂₅[α₂P₂W₁₇MgO₆₅]·6H₂O were C, 3.91; H, 1.50; N, 2.28; Mg,
A weight loss of 1.30% was observed during overnight drying at room temperature at 10^{-3}–10^{-4} Torr before analysis, suggesting the presence of three weakly solvated or adsorbed water molecules (1.16%). TG/DTA results obtained at a rate of 1 °C/min under atmospheric conditions showed weight losses of 2.33% and 7.42% without clear endothermic and exothermic points in the temperature ranges of 25 to 200 °C and 200 to 500 °C, respectively; calculations showed that 2.32% and 7.42% corresponded to six water molecules and 7.5 dimethylammonium ions, respectively. The results were as follows: IR spectroscopy (KBr disk): 1087s, 1065m, 1018m, 948s, 919s, 891s, 805s, 777s, 717s cm\(^{-1}\); IR spectroscopy (in water): 1086s, 1065m, 1020w, 945s, 913s, 808s, 790s, 723m cm\(^{-1}\); \(^{31}\)P NMR (D\(_2\)O, 21.7 °C): δ −7.73, −13.74.

2.7. X-Ray crystallography

A colorless prism crystal of Cs\(_{5.25}\)H\(_{1.75}\)\([\alpha\text{-PW}_{11}\text{MgO}_{40}]\)⋅6H\(_2\)O (0.090 × 0.070 × 0.060 mm), colorless platelet crystal of \([(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{-C}_4\text{H}_9\text{H}_{2.75}\text{[\alpha-P}_{2}\text{W}_{17}\text{MgO}_{62}]\)⋅H\(_2\)O (0.200 × 0.100 × 0.020 mm), and colorless block crystal of \([(\text{CH}_3)_2\text{NH}]_7.5\text{H}_2\text{O} \cdot \text{CS}_{2}\text{W}_{17}\text{MgO}_{62}\)⋅6H\(_2\)O (0.200 × 0.100 × 0.100 mm) were mounted on a loop or MicroMount. The measurements for the cesium and tetra-n-butylammonium salts of α-Keggin mono-magnesium–substituted polyoxotungstate were obtained using a Rigaku VariMax with a Saturn diffractometer using multi-layer mirror-monochromated Mo Kα radiation (λ = 0.71075 Å) at 100±1 K. The measurement for the dimethylammonium salt of α-Dawson mono-magnesium–substituted polyoxotungstate was carried out using a Rigaku VariMax with an XtaLAB P200 diffractometer using multi-layer mirror-monochromated Mo Kα radiation (λ = 0.71075 Å) at 153±1 K. Data were collected and processed using CrystalClear, CrystalClear-SM Expert for Windows, and structural analysis was performed using CrystalStructure for Windows. The structure was solved by SHELXS-97, SHELXS-2013, and SIR-2004 (direct methods) and refined by SHELXL-97 and SHELXL2013 [10, 11]. In these magnesium compounds, a magnesium atom was disordered over ten and twelve tungsten atoms in \([\alpha\text{-PW}_{11}\text{MgO}_{40}]\)\(^{7-}\), and six tungsten atoms at B-sites (cap units) in \([\alpha\text{-PW}_{17}\text{MgO}_{62}]\)\(^{10-}\). The occupancies for the magnesium and tungsten atoms were fixed at 1/10 and 9/10, 1/12 and 11/12, and 1/6 and 5/6, respectively. For Cs\(_{5.25}\)H\(_{1.75}\)\([\alpha\text{-PW}_{11}\text{MgO}_{40}]\)⋅6H\(_2\)O, 5.25 cesium ions were disordered at Cs(1) and Cs(2) and the water molecules were disordered. For the structural analysis of \([(\text{CH}_3)_2\text{NH}]_7.5\text{H}_2\text{O} \cdot \text{CS}_{2}\text{W}_{17}\text{MgO}_{62}\)⋅H\(_2\)O⋅CH\(_3\)CN, tetra-n-butylammonium ions, water molecules, and acetonitrile molecules could not be modeled because of disorder of the atoms. Accordingly, the residual electron density was removed using the SQUEEZE routine in PLATON [12]. Disordered counter-cations and solvated molecules are common in polyoxometalate chemistry [13 – 16].

2.8. Crystal data for Cs\(_{5.25}\)H\(_{1.75}\)\([\alpha\text{-PW}_{11}\text{MgO}_{40}]\)⋅6H\(_2\)O

H\(_{13.75}\)Cs\(_{5.25}\)MgO\(_{40}\)PW\(_{11}\); M = 3525.27, tetragonal, space group: P\(_4_2\)ncm (#138), a = 20.859(4) Å, c = 10.387(2) Å, V = 4520(2) Å\(^3\), Z = 4, D\(_c\) = 5.181 g/cm\(^3\), μ(Mo Kα) = 321.99 cm\(^{-1}\), R\(_1\) = 0.0508 [I > 2σ(I)], wR\(_2\) = 0.1070 (for all data). GOF = 1.248 [52491 total reflections and 2703 unique reflections where I > 2σ(I)]. CCDC No. 1020993
2.9. Crystal data for \([n-C_4H_9]_4N[H_2.75[\alpha-PW_{11}MgO_{40}]-H_2O-CH_3CN\]

\[\text{CsH}_{160.75}\text{MgN}_{5.25}\text{O}_{41}\text{PW}_{11}; M = 3809.93, \text{cubic, space group: Im-3m (\#229), } a = 17.650(6) \text{ Å, } V = 5498(3) \text{ Å}^3, Z = 2, D_c = 2.301 \text{ g/cm}^3, \mu(\text{Mo K} \alpha) = 115.627 \text{ cm}^{-1}, R_1 = 0.0578 [I > 2\sigma(I)], wR_2 = 0.1312 (for all data). GOF = 1.181 (44531 total reflections, 653 unique reflections where } I > 2\sigma(I)). \text{CCDC No. 1020994}

2.10. Crystal data for \([(\text{CH}_3)_2\text{NH}_2]_3\text{H}_2.5\text{[\alpha}_2\text{-P}_{17}\text{MgO}_{62}]\cdot3\text{H}_2\text{O}

\[\text{C}_{15}\text{H}_{68.50}\text{MgN}_{7.50}\text{O}_{65}\text{P}_{2.54}\text{W}_{17}; M = 4605.92, \text{orthorhombic, space group: Pnma (\#62), } a = 27.7901(12) \text{ Å, } b = 20.4263(9) \text{ Å, } c = 15.0638(6) \text{ Å, } V = 8550.9(7) \text{ Å}^3, Z = 4, D_c = 3.577 \text{ g/cm}^3, \mu(\text{Mo K} \alpha) = 229.323 \text{ cm}^{-1}, R_1 = 0.0685 [I > 2\sigma(I)], wR_2 = 0.1980 (for all data). GOF = 1.096 (95493 total reflections, 12764 unique reflections where } I > 2\sigma(I)). \text{CCDC No. 1020995}

2.11. Computational details

The optimal geometries of \([\alpha-PW_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) and \([\alpha-PW_{11}\{\text{Mg(OH}_2)\}O_{39}]^{5-}\) were computed using a DFT method. First, we optimized the molecular geometries and then applied single-point calculations with larger basis sets. All calculations were performed using a spin-restricted B3LYP method with the Gaussian09 program package [17]. The solvent effect of acetonitrile was considered using the polarizable continuum model. The basis sets used for geometry optimization were LANL2DZ for the W atoms, 6-31+G* for the P atoms, and 6-31G* for the H, O, and Mg atoms. LANL2DZ and 6-31+G* were used for the W and other atoms, respectively, for the single-point calculations. Geometry optimization was started using the X-ray structure of \([\alpha-PW_{12}O_{40}]^{3-}\) as the initial geometry, and was performed in acetonitrile. The optimized geometries were confirmed to be true minima by frequency analyses. All atomic charges used in this text were obtained from Mulliken population analysis. Zero-point energy-corrected total energies were used to consider the structural stabilities of \([\alpha-PW_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) and \([\alpha-PW_{11}\{\text{Mg(OH}_2)\}O_{39}]^{5-}\).

3. Results and discussion

3.1. Syntheses and molecular structures of cesium and tetra-\(n\)-butylammonium salts of \(\alpha\)-Keggin mono-magnesium-substituted polyoxotungstate \(\text{Cs}_{5.25}\text{H}_{1.75}[\alpha-PW_{11}\text{MgO}_{40}]-6\text{H}_2\text{O}\) and \([n-C_4H_9]_4\text{N}[\alpha-PW_{11}\text{MgO}_{40}]-\text{H}_2\text{O-CH}_3\text{CN}\)

The cesium salt of \([\alpha-PW_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) was formed by the direct reaction of magnesium bromide with \([\alpha-PW_{11}O_{39}]^{5-}\) (at a \(\text{Mg}^{2+}/[\alpha-PW_{11}O_{39}]^{5-}\) ratio of ~2.0) in aqueous solution, followed by the addition of excess cesium chloride. The pure cesium salt was not obtained by a stoichiometric reaction of \(\text{Mg}^{2+}\) with \([\alpha-PW_{11}O_{39}]^{5-}\) in aqueous solution. Crystallization was performed via slow-evaporation from a 3.3 mM \(\text{MgBr}_2\) solution at 70 °C. Here, single crystals suitable for X-ray crystallography could not be obtained in water because a mono-lacunary polyxoanion formed upon the removal of magnesium ions from \([\alpha-PW_{11}\text{MgO}_{40}]^{7-}\) in water at around 70 °C. In contrast, the tetra-\(n\)-butylammonium salt of \([\alpha-PW_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) was formed by a stoichiometric reaction of magnesium bromide with \([\alpha-PW_{11}O_{39}]^{5-}\) in aqueous solution, followed by the
addition of excess tetra-n-butylammonium bromide. Crystallization was performed by vapor diffusion from acetonitrile/methanol at ~25 °C.

Samples for the elemental analyses were dried overnight at room temperature under a vacuum of $10^{-3} - 10^{-4}$ Torr. The elemental analysis results for H, Cs, Mg, P, and W were in good agreement with the calculated values for the formula of [Cs$_{5.25}$H$_{1.75}$]$_2$α-PW$_{11}$MgO$_{40}$]⋅6H$_2$O. Br analysis revealed no contamination of bromide ions from MgBr$_2$. The weight loss observed during the course of drying before the analysis was 3.03% for [Cs$_{5.25}$H$_{1.75}$]α-PW$_{11}$MgO$_{40}$]⋅6H$_2$O; this corresponded to six weakly solvated or adsorbed water molecules. TG/DTA measurements also showed a weight loss of 3.1% in the temperature range of 25 to 500 °C, which corresponded to six water molecules. For the tetra-n-butylammonium salt, the elemental analysis results for C, H, N, P, Mg, and W were in good agreement with the calculated values for the formula of [(n-C$_4$H$_9$)$_4$N]$_2$H$_2$O-[α-PW$_{11}$MgO$_{40}$]⋅H$_2$O. K analysis revealed no contamination of potassium ions from K$_2$[α-PW$_{11}$O$_{40}$]. The weight loss observed during the course of drying before the analysis was 1.44% for [(n-C$_4$H$_9$)$_4$N]$_2$H$_2$O-[α-PW$_{11}$MgO$_{40}$]⋅H$_2$O⋅CH$_3$CN; this corresponded to one weakly solvated or adsorbed acetonitrile molecule. The $^1$H NMR spectrum in DMSO-$d_6$ also showed the presence of an acetonitrile molecule in the sample after drying under vacuum overnight. TG/DTA measurements showed a weight loss of 27.46% in the temperature range of 25 to 500 °C, which corresponded to 4.25 [(C$_4$H$_9$)$_4$N]$^+$ ions, a water molecule, and an acetonitrile molecule.

The molecular structures of cesium and tetra-n-butylammonium salts of [α-PW$_{11}$MgO$_{40}$]$^-$ as determined by X-ray crystallography, are shown in Figs. 1 and 2. The lengths of the bonds involving oxygen atoms in the central PO$_4$ tetrahedron (O$_a$), bridging oxygen atoms between corner-sharing MO$_6$ (M = W and Mg) octahedra (O$_b$), bridging oxygen atoms between edge-sharing MO$_6$ octahedra (O$_c$), and terminal oxygen atoms (O$_t$) are summarized in Table 1. The molecular structures of these magnesium compounds were identical to that of a monomeric, α-Keggin polyoxometalate [α-PW$_{12}$O$_{40}$]$^{5-}$ [18, 19]. Due to the high-symmetry space groups of the structures, the ten or eleven tungsten(VI) atoms were disordered and the mono-magnesium-substituted site was not identified, as previously reported for [α-PW$_{11}$Al(OH)$_2$]O$_{39}$$^{1+}$ [20]. However, it was clear that the average bond lengths of W(Mg)-O$_a$ in Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]⋅6H$_2$O (2.478 Å) and [(n-C$_4$H$_9$)$_4$N]$_2$H$_2$O-[α-PW$_{11}$MgO$_{40}$]⋅H$_2$O CH$_3$CN (2.483 Å) were longer than those of [CH$_3$NH$_3$]$_2$[PW$_{12}$O$_{40}$]⋅2H$_2$O (2.4398 Å), [(CH$_3$)$_3$NH$_3$][PW$_{12}$O$_{40}$] (2.4430 Å), and [(CH$_3$)$_3$NH$_3$][PW$_{12}$O$_{40}$] (2.4313 Å) [19] (Table 1); this suggested that the magnesium ion was coordinated to the mono-lacunary Keggin-type polyoxometalate.

Although a hydroxyl group and/or water molecule should be coordinated to the magnesium site in [α-PW$_{11}$MgO$_{40}$]$^-$, it could not be identified by X-ray crystallography. On the basis of the Cs analysis results, Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]⋅6H$_2$O should contain species with hydroxyl groups in at least 25% of the molecules. To investigate the coordination spheres around the mono-magnesium-substituted sites containing a hydroxyl group and water molecule, optimized geometries of [α-PW$_{11}$Mg(OH)]O$_{39}$$^{6-}$ and [α-PW$_{11}$Mg(OH)$_2$]O$_{39}$$^{5-}$ were computed by means of a DFT method, as shown in Fig. 3. The bond-length ranges, mean bond distances, and Mulliken charges for DFT-optimized [α-PW$_{11}$Mg(OH)]O$_{39}$$^{6-}$ and [α-PW$_{11}$Mg(OH)$_2$]O$_{39}$$^{5-}$ are summarized in Tables 2 and 3. As shown in Fig. 3, the ligands coordinated to the mono-magnesium-substituted site caused remarkable distortion of the α-Keggin molecular structure:
The Mg–P distance of [α-PW₁₁(Mg(OH))O₃₉]⁶⁻ was 3.652 Å, which was longer than that of [α-PW₁₁(Mg(OH₂))O₃₉]⁵⁻ (3.330 Å). The charges of all atoms in [α-PW₁₁(Mg(OH))O₃₉]⁶⁻ and [α-PW₁₁(Mg(OH₂))O₃₉]⁵⁻ were also influenced by the ligands, as shown in Table 3.

Figure 1. The molecular structure (ORTEP drawing) of Cs₅.₂₅H₁.₇₅[α-PW₁₁MgO₄₀]⋅₆H₂O. The corner- and edge-sharing oxygen atoms in the α-Keggin structure were disordered. W(2) was clearly identified; however, a magnesium atom was disordered over ten tungsten sites in [α-PW₁₁MgO₄₀]⁷⁻, and the occupancies for the magnesium and tungsten sites were fixed at 1/10 and 9/10 throughout the refinement.

Figure 2. The molecular structure (ORTEP drawing) of [(n-C₄H₉)₄N]₄.₂₅H₂.₇₅[α-PW₁₁MgO₄₀]⋅H₂O. A magnesium atom was disordered over eleven tungsten sites in [α-PW₁₁MgO₄₀]⁷⁻, and the occupancies for the magnesium and tungsten sites were fixed at 1/12 and 11/12 throughout the refinement.
Here, the sum of the zero-point energy-corrected total energies (Hartree) of \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{6–} + H_2O\) and \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{5–} + H_2O\) was −4377.185183 and −4377.287786, respectively; the thermal energy of \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{6–} + H_2O\) calculated on the basis of zero-point energy was 64.4 kcal/mol lower than that of \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{5–} + H_2O\). Thus, \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{6–}\) was more stable than \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{5–}\). It was noted that the Mg-O and Mg-O bond lengths of the optimized \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{6–}\) structure were longer than those of \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{5–}\), as shown in Table 2. In the X-ray crystal structures of Cs$_{5.25}$H$_{1.75}$[\alpha-PW$_{11}$MgO$_{40}$]\cdot6H$_2$O and [(n-C$_4$H$_9$)$_4$N]$_{12.5}$H$_{2.5}$[\alpha-PW$_{11}$MgO$_{40}$]\cdotH$_2$O\cdotCH$_3$CN, the mean W(Mg)-O and W(Mg)-O bond lengths of the cesium salt were longer than those of the tetra-n-butylammonium salt. The mean P-O bond length of Cs$_{5.25}$H$_{1.75}$[\alpha-PW$_{11}$MgO$_{40}$]\cdot6H$_2$O (1.562 Å) was also longer than that of [(n-C$_4$H$_9$)$_4$N]$_{12.5}$H$_{2.5}$[\alpha-PW$_{11}$MgO$_{40}$]\cdotH$_2$O\cdotCH$_3$CN (1.511 Å); this was consistent with the DFT calculation results. These results suggested that Cs$_{5.25}$H$_{1.75}$[\alpha-PW$_{11}$MgO$_{40}$]\cdot6H$_2$O contained both \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{6–}\) and \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{5–}\); in contrast, the molecular structure of [(n-C$_4$H$_9$)$_4$N]$_{12.5}$H$_{2.5}$[\alpha-PW$_{11}$MgO$_{40}$]\cdotH$_2$O\cdotCH$_3$CN was predominantly \([\alpha-PW_{11}\text{(Mg(OH))O}_{39}]^{5–}\).

The $^{31}$P NMR spectrum in D$_2$O of Cs$_{5.25}$H$_{1.75}$[\alpha-PW$_{11}$MgO$_{40}$]\cdot6H$_2$O showed a signal at −10.8 ppm that corresponded to the internal phosphorus atom; this demonstrated the high purity of
Cs$_{5.23}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]⋅6H$_2$O in water. However, the presence of polyoxoanions possessing Mg–OH and/or Mg–OH$_2$ moieties could not be identified by $^{31}$P NMR spectroscopy in water. For the $^{31}$P NMR spectrum in acetonitrile-d$_3$ of [$(n$-C$_4$H$_9$)$_4$N]$_4$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]⋅H$_2$O⋅CH$_3$CN, a signal was also observed at −10.3 ppm. These signals exhibited a shift from the signals of K$_7$[α-PW$_{11}$O$_{39}$] (δ −10.6) in D$_2$O and the tetra-$n$-butylammonium salt of [α-PW$_{11}$O$_{39}$]$^{7–}$ (δ −12.0) in acetonitrile-d$_3$, respectively. This showed that the magnesium ion was inserted into the vacant site.

**Figure 3.** DFT-optimized geometries of [α-PW$_{11}$]{Mg(OH)}O$_{39}$]$^{6–}$ (top) and [α-PW$_{11}$]{Mg(OH$_2$)}O$_{39}$]$^{5–}$ (bottom). The phosphorus, oxygen, magnesium, tungsten, and hydrogen atoms are represented by orange, red, green, blue, and white balls, respectively.
Table 2. Ranges and mean bond distances (Å) of \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) and \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}_{2}\}O_{39}]^{5-}\) optimized by DFT calculations. The mean values are provided in parentheses.

| Bond          | \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) | \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}_{2}\}O_{39}]^{5-}\) |
|---------------|-------------------------------------------------|-------------------------------------------------|
| W-O_a         | 2.42491 – 2.50502 (2.45747)                     | 2.43078 – 2.49519 (2.46749)                     |
| W-O_c         | 1.77745 – 2.06287 (1.92795)                     | 1.78987 – 2.04292 (1.92730)                     |
| W-O_e         | 1.77336 – 2.06166 (1.92035)                     | 1.78511 – 2.03477 (1.92000)                     |
| P-O           | 1.54748 – 1.56478 (1.55930)                     | 1.55541 – 1.55857 (1.55763)                     |
| Mg-O_a        | 2.52990 (2.52990)                               | 2.18152 (2.18152)                               |
| Mg-O_c        | 2.10554 – 2.11671 (2.11113)                     | 2.04263 – 2.05034 (2.04649)                     |
| Mg-O_e        | 2.08702 – 2.09720 (2.09211)                     | 2.06585 – 2.08177 (2.07381)                     |
| Mg-OH/OH_2    | 1.93732 (1.93732)                               | 2.12343 (2.12343)                               |

Table 3. Mulliken charges computed for \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) and \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}_{2}\}O_{39}]^{5-}\). The mean values are provided in parentheses.

| Charge | \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}\}O_{39}]^{6-}\) | \([\alpha-\text{PW}_{11}\{\text{Mg(OH)}_{2}\}O_{39}]^{5-}\) |
|--------|-------------------------------------------------|-------------------------------------------------|
| O_W    | -0.752 – -0.731 (-0.740)                        | -0.789 – -0.752 (-0.768)                        |
| O_H    | -1.166 – -0.975 (-1.084)                        | -1.170 – -1.009 (-1.095)                        |
| O_t    | -0.774 – -0.725 (-0.748)                        | -0.743 – -0.708 (-0.730)                        |
| P      | 6.849                                           | 7.192                                           |
| W      | 2.105 – 2.474 (2.304)                           | 2.151 – 2.460 (2.313)                           |
| O_mgo  | -0.489                                         | -0.481                                         |
| O_mgo  | -0.694 – -0.680 (-0.687)                        | -0.749 – -0.690 (-0.720)                        |
| O_mgo  | -0.638 – -0.616 (-0.627)                        | -0.674 – -0.636 (-0.655)                        |
| O_mgo  | -0.961                                         | -0.844                                         |
| Mg     | -0.253                                         | -0.274                                         |
| H      | 0.428                                          | 0.556 – 0.564 (0.560)                           |

The FT-IR spectra measured as KBr disks of \(\text{Cs}_{5.25}\text{H}_{1.75}\{\alpha-\text{PW}_{11}\text{MgO}_{40}\} \cdot 6\text{H}_{2}\text{O}\) and \(\{(\text{n-C}_{4}\text{H}_{9})_{4}\text{N}\}_{4.25}\text{H}_{2.75}\{\alpha-\text{PW}_{11}\text{MgO}_{40}\} \cdot \text{H}_{2}\text{O} \cdot \text{CH}_{3}\text{CN}\) are shown in Fig. 4. These spectra showed bands at 1081, 1058, 961, 888, 830, 808, 769, and 724 cm\(^{-1}\) and 1081, 1060, 957, 891, 819, and 734 cm\(^{-1}\), respectively; these bands were different from those of \(\text{K}_{7}\{\alpha-\text{PW}_{11}\text{O}_{39}\}\) (1086, 1043, 953, 903, 862, 810, and 734 cm\(^{-1}\)) [21, 22]. This also supported that the magnesium ion was coordinated to the vacant site in the polyoxometalate.
The spectral pattern of solid Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O was different from that of solid [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]·H$_2$O·CH$_3$CN even though the counter-ions affected their spectra [21, 22]. As shown in Fig. 5, the FT-IR spectral pattern of solid [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]·H$_2$O·CH$_3$CN was the same as that of a liquid sample observed in acetonitrile (1082, 1059, 955, 889, 811, and 733 cm$^{-1}$); this showed that the molecular structure of [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]·H$_2$O·CH$_3$CN observed in a solid was the same as that in acetonitrile solution. In contrast, the spectral pattern of solid Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O was somewhat different from that in water (1079, 1056, 1017, 957, 898, 823, 779, and 724 cm$^{-1}$). Since a single line was observed in the $^{31}$P NMR spectrum of Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O in D$_2$O at around 25 °C, this change was not due to decomposition of the cesium salt in aqueous solution; however, water may have influenced the structure.

![FT-IR spectra](image)

**Figure 4.** FT-IR spectra (as KBr disks) of Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O (top) and [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$[α-PW$_{11}$MgO$_{40}$]·H$_2$O·CH$_3$CN (bottom) in the range of 1800 – 400 cm$^{-1}$.
3.2 Syntheses and molecular structures of potassium and dimethylammonium salts of α-Dawson-type mono-magnesium–substituted polyoxotungstate K$_8$H$_2$[α$_2$-P$_2$W$_{17}$MgO$_{62}$]·15H$_2$O and [(CH$_3$)$_2$NH$_2$]$_{7.5}$H$_{2.5}$[α$_2$-P$_2$W$_{17}$MgO$_{62}$]·6H$_2$O

The potassium salt of [α$_2$-P$_2$W$_{17}$MgO$_{62}$]$^{10-}$ was formed by the direct reaction of magnesium bromide with [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ (at a Mg$^{2+}$/[α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ molar ratio of ~3.0) in aqueous solution, followed by the addition of excess potassium chloride. Pure potassium salt was not obtained by the stoichiometric reaction of magnesium ions with [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ in aqueous solution, as was observed for Cs$_{5.25}$H$_{1.75}$[α-PW$_{11}$MgO$_{40}$]·6H$_2$O. In contrast, the dimethylammonium salt was formed via a stoichiometric reaction of magnesium nitrate with [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$ in aqueous solution, followed by the addition of excess dimethylammonium chloride. Crystallization was performed by vapor diffusion from water/ethanol at around 25 °C.
Figure 6. Molecular structure (ORTEP drawing) of [(CH$_3_2$)NH$_2$]$_{7.5}$H$_2.5$[P$_2$W$_{17}$MgO$_{62}$]⋅6H$_2$O. One magnesium atom was disordered over six tungsten atoms at the B-sites (i.e., cap units) in [P$_2$W$_{17}$MgO$_{62}$]$^{10-}$. The occupancies for the magnesium and tungsten sites were fixed at 1/6 and 5/6 throughout the refinement; however, the populations of these atoms differed.

The elemental analysis results for H, K, Mg, P, and W were in good agreement with the calculated values for K$_8$H$_2$[P$_2$W$_{17}$MgO$_{62}$]⋅H$_2$O. N analysis revealed no contamination of nitrate ions from Mg(NO$_3$)$_2$. The weight loss observed during drying before the analysis was 5.30% for K$_8$H$_2$[P$_2$W$_{17}$MgO$_{62}$]⋅15H$_2$O; this corresponded to 14 weakly solvated or adsorbed water molecules. TG/DTA data also showed a weight loss of 5.62% in the temperature range of 25 to 500 °C, which corresponded to 15 water molecules. For the dimethylammonium salt, the C, H, N, P, Mg, and W elemental analysis results were in good agreement with the calculated values for [(CH$_3_2$)NH$_2$]$_{7.5}$H$_2.5$[P$_2$W$_{17}$MgO$_{62}$]⋅3H$_2$O. The K analysis revealed no contamination of potassium ions from K$_{10}$[P$_2$W$_{17}$O$_{61}$]⋅14H$_2$O. The weight loss observed during drying before the analysis was 1.30% for [(CH$_3_2$)NH$_2$]$_{7.5}$H$_2.5$[P$_2$W$_{17}$MgO$_{62}$]⋅6H$_2$O; this corresponded to three weakly solvated molecules. TG/DTA data showed weight losses of 2.33 and 7.42% observed in the temperature ranges of 25 to 200 °C and 200 to 500 °C, respectively; these values corresponded to six water molecules and 7.5 [(CH$_3_2$)NH$_2$]$^+$ ions, respectively.
The molecular structure of \([\text{[(CH}_3\text{)}_2\text{NH}_2]_2\text{H}_2[\alpha_2\text{-P}_2\text{W}_{17}\text{MgO}_{62}]\cdot6\text{H}_2\text{O}}\) determined by X-ray crystallography is shown in Fig. 6. This molecular structure was identical to that of monomeric \(\alpha\)-Dawson-type polyoxotungstate \([\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]^{6-}\) [23], which was constructed from cap \((\text{W(Mg)} (1), \text{W(Mg)}(2), \text{W(Mg)}(9), \text{W(Mg)}(10))\) and belt \((\text{W}(3 – 8))\) units. The bond lengths are summarized in Table 4. Because of the high symmetry of the space group, the six tungsten(VI) atoms at the two cap units were disordered and the partial structure around the magnesium site in \([\text{[(CH}_3\text{)}_2\text{NH}_2]_2\text{H}_2[\alpha_2\text{-P}_2\text{W}_{17}\text{MgO}_{62}]\cdot6\text{H}_2\text{O}}\) was not identified by X-ray crystallography, as was observed for \(\text{Cs}_5.25\text{H}_1.75[\alpha\text{-PW}_{11}\text{MgO}_{40}]\cdot6\text{H}_2\text{O}\) and \([\text{([n-C}_4\text{H}_9\text{])}_4\text{N}]_4.25\text{H}_2.75[\alpha\text{-PW}_{11}\text{MgO}_{40}]\cdot\text{H}_2\text{O}\cdot\text{CH}_3\text{CN}\); however, the \text{W(Mg)}–O\_t bond lengths in the cap units (average 1.760 Å) were remarkably longer than those of \text{W–O}\_t in the belt units (average 1.717 Å) and \([\alpha\text{-PW}_{11}\text{MgO}_{39}]^{6-}\) \(\sim1.7\) Å [24]. Although it was difficult to discuss that the \text{W(Mg)}–O\_t lengths of \(\text{Cs}_5.25\text{H}_1.75[\alpha\text{-PW}_{11}\text{MgO}_{40}]\cdot6\text{H}_2\text{O}\) and \([\text{([n-C}_4\text{H}_9\text{])}_4\text{N}]_4.25\text{H}_2.75[\alpha\text{-PW}_{11}\text{MgO}_{40}]\cdot\text{H}_2\text{O}\cdot\text{CH}_3\text{CN}\) were longer than those of \(\text{Mg–OH}\) in \([\text{2MgSO}_4\cdot\text{Mg(OH)}_2]\) (2.025 Å) [27]. These results suggested that a water molecule was coordinated to the mono-magnesium-substituted site in \([\text{[(CH}_3\text{)}_2\text{NH}_2]_2\text{H}_2[\alpha_2\text{-P}_2\text{W}_{17}\text{MgO}_{62}]\cdot6\text{H}_2\text{O}}\).
The $^{31}$P NMR spectrum of K$_8$H$_2$[α$_2$-P$_2$W$_{17}$MgO$_{62}$]·15H$_2$O in D$_2$O showed signals at –7.8 and –13.8 ppm, which were the same as those of [(CH$_3$)$_2$NH]$_7$.H$_2$.[(α$_2$-P$_2$W$_{17}$MgO$_{62}$)].6H$_2$O (–7.7 and –13.7 ppm); this was also confirmed by the two-line spectrum observed for a mixture of the potassium and dimethylammonium salts in D$_2$O. These signals were different from those of K$_{10}$[α$_2$-P$_2$W$_{17}$O$_{61}$]·14H$_2$O (δ –6.8 and –13.9), suggesting that a magnesium ion was coordinated to the vacant site of [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$. The $^{183}$W NMR spectrum of K$_8$H$_2$[α$_2$-P$_2$W$_{17}$MgO$_{62}$]·15H$_2$O in 2.0 mM Mg(NO$_3$)$_2$-D$_2$O showed nine signals at –57.0, –80.87, –131.47, –176.59, –181.67, –201.40, –207.65, –208.63, and –230.51, as shown in Fig. 7. These signals were also different from those of K$_{10}$[α$_2$-P$_2$W$_{17}$O$_{61}$]·14H$_2$O (δ –117.1, –140.4, –151.7, –181.0, –183.1, –218.1, –220.5, –224.0, and –242.6) observed in D$_2$O [28]. These results also supported that a magnesium ion was coordinated to the vacant site of [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$, resulting in an overall C$_s$ symmetry.

The FT-IR spectra of K$_8$H$_2$[α$_2$-P$_2$W$_{17}$MgO$_{62}$]·15H$_2$O and [(CH$_3$)$_2$NH]$_7$.H$_2$.[(α$_2$-P$_2$W$_{17}$MgO$_{62}$)].6H$_2$O measured as KBr disks are shown in Fig. 8. The potassium and dimethylammonium salts showed bands at 1084, 1063, 945, 920, 892, 823, 786, and 736 cm$^{-1}$ and 1087, 1065, 1018, 948, 919, 891, 805, 777, and 717 cm$^{-1}$, respectively. These bands were different from those of K$_{10}$[α$_2$-P$_2$W$_{17}$O$_{61}$]·14H$_2$O (1084, 1051, 1016, 940, 918, 887, 811, 740, and 601 cm$^{-1}$), which also supported that a magnesium atom was coordinated in the vacant site of [α$_2$-P$_2$W$_{17}$O$_{61}$]$^{10-}$. The spectral pattern of solid [(CH$_3$)$_2$NH]$_7$.H$_2$.[(α$_2$-P$_2$W$_{17}$MgO$_{62}$)].6H$_2$O was quite similar to that in water (1086, 1065, 1020, 945, 913, 808, 790, and 723 cm$^{-1}$); this suggested that the molecular structure of [(CH$_3$)$_2$NH]$_7$.H$_2$.[(α$_2$-P$_2$W$_{17}$MgO$_{62}$)].6H$_2$O observed in a solid was maintained in an aqueous solution. In addition, the FT-IR spectrum of [(CH$_3$)$_2$NH]$_7$.H$_2$.[(α$_2$-P$_2$W$_{17}$MgO$_{62}$)].6H$_2$O observed in water was the same as that of a liquid sample of K$_8$H$_2$[α$_2$-P$_2$W$_{17}$MgO$_{62}$]·15H$_2$O (1086, 1064, 1015, 946, 914, 811, 788, and 724 cm$^{-1}$). These results showed that the molecular structure of potassium salt was the same as that of the dimethylammonium salt, as suggested by the $^{31}$P NMR spectra of the salts in D$_2$O.
4. Conclusion

In this study, we synthesized α-Keggin-type mono-magnesium-substituted polyoxotungstate Cs$_{5.25}$H$_{1.75}$(α$_z$-PW$_{11}$MgO$_{40}$)·6H$_2$O and [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$(α$_z$-PW$_{11}$MgO$_{40}$)·H$_2$O·CH$_3$CN, and α-Dawson-type mono-magnesium-substituted polyoxotungstate K$_8$H$_2$(α$_z$-P$_2$W$_{17}$MgO$_{62}$)·15H$_2$O and [(CH$_3$)$_2$NH$_2$]$_{7.5}$H$_{2.5}$(α$_z$-P$_2$W$_{17}$MgO$_{62}$)·6H$_2$O by reacting magnesium ions with mono-lacunary α-Keggin and α-Dawson-type phosphotungstates. The compounds were characterized by X-ray crystallography, elemental analysis, thermogravimetric/differential thermal analysis, Fourier-transform infrared spectra, and solution $^{31}$P and $^{183}$W nuclear magnetic resonance spectroscopy. The single-crystal X-ray structure analyses of Cs$_{5.25}$H$_{1.75}$(α$_z$-PW$_{11}$MgO$_{40}$)·6H$_2$O, [(n-C$_4$H$_9$)$_4$N]$_{4.25}$H$_{2.75}$(α$_z$-PW$_{11}$MgO$_{40}$)·H$_2$O·CH$_3$CN, and [(CH$_3$)$_2$NH$_2$]$_{7.5}$H$_{2.5}$(α$_z$-P$_2$W$_{17}$MgO$_{62}$)·6H$_2$O revealed monomeric, α-Keggin, and α-Dawson structures, respectively; the mono-magnesium–substituted sites could not be identified because of the high symmetry of the products. However, the bonding modes (i.e., bond lengths and bond angles) suggested that a hydroxyl group and/or water molecule were coordinated to the mono-magnesium-substituted site in [α$_z$-PW$_{11}$MgO$_{40}$]$^{7-}$ and [α$_z$-P$_2$W$_{17}$MgO$_{62}$]$^{10-}$. The DFT and zero-point energy calculation results also suggested that the molecular structures of [α-
PW$_{11}$[Mg(OH)]O$_{39}$]$^{6-}$ and [α-PW$_{11}$[Mg(OH)$_2$]O$_{39}$]$^{5-}$ were significantly influenced by coordination of a hydroxyl group and water molecule to the magnesium site, and [α-PW$_{11}$[Mg(OH)]O$_{39}$]$^{6-}$ was more stable than [α-PW$_{11}$[Mg(OH)]O$_{39}$]$^{5-}$.

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