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Syntheses and Molecular Structures of Monomeric and Hydrogen-Bonded Dimeric Dawson-Type Trialuminum-Substituted Polyoxotungstates Derived under Acidic and Basic Conditions

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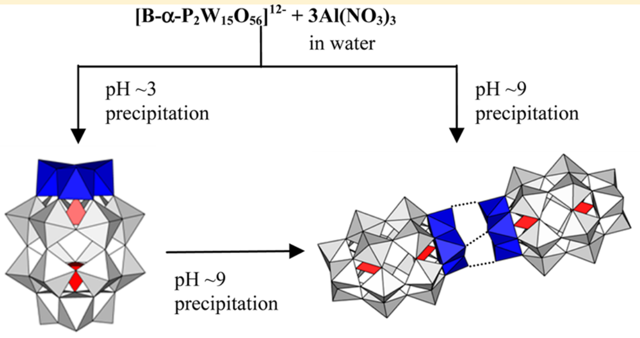
S *Supporting Information*

ABSTRACT: The syntheses and molecular structures of the two types of α-Dawson-type trialuminum-substituted polyoxometalates, $[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]^{6-}$ (**1**) and $[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2^{16-}$ (**2**), are described herein. The potassium and cesium salts of **1**, $K_6[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]\cdot 14H_2O$ (**K-1**), and $Cs_6[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]\cdot 13H_2O$ (**Cs-1**) were formed by a stoichiometric reaction in water of trilacunary α-Dawson polyoxotungstate with aluminum nitrate under acidic conditions (pH ~3). The potassium/sodium and tetramethylammonium/sodium salts of **2**, $K_{14}Na_2[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2\cdot 30H_2O$ (**KNa-2**) and $[(CH_3)_4N]_{14}Na_2[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2\cdot 39H_2O$ (**TMANa-2**) were obtained under basic conditions (pH ~9). These compounds were characterized by X-ray structure analyses, elemental analyses, thermogravimetric/differential thermal analyses, Fourier transform infrared, and solution ^{31}P, ^{27}Al, and ^{183}W NMR spectroscopy. The polyoxoanion **1** is a monomeric, α-Dawson-type structure, resulting in an overall C_{3v} symmetry, while the polyoxoanion **2** is a hydrogen-bonded dimeric structure, resulting in an overall S_3 symmetry in the solid state. The pH dependence of polyoxoanions **1** and **2** in aqueous solution was also investigated by ^{31}P NMR spectroscopy.



INTRODUCTION

Aluminum and its derivatives such as alloys, oxides, organometallics, and inorganic compounds have attracted considerable attention because of their extreme versatility and unique range of properties, including acidity, hardness, and electroconductivity.[1] Because the properties and activities of an aluminum species are strongly dependent on the structures of the aluminum sites, the syntheses of aluminum compounds with structurally well-defined aluminum sites are considerably significant for the development of novel and efficient aluminum-based materials. However, the use of these well-defined aluminum sites is slightly limited by the conditions resulting from hydrolysis of the aluminum species by water.[2]

Polyoxometalates (POMs) have been of particular interest in the fields of catalytic chemistry, surface science, and materials science because their chemical properties such as redox potentials, acidities, and solubilities in various media can be finely tuned by choosing appropriate constituent elements and countercations.[3] In particular, the coordination of metal ions to the vacant site(s) of lacunary POMs is one of the most effective techniques used for constructing efficient and well-defined active metal centers. Over several decades, various types of aluminum-coordinated POMs, e.g., $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$,[4] $(Bu_4N)_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]$,[5] $Cs_4[\alpha\text{-}PW_{11}\{Al(OH_2)\}O_{39}]\cdot 8H_2O$,[6] $K_7[\alpha_2\text{-}P_2W_{17}\{Al(OH_2)\}O_{61}]\cdot 14H_2O$,[6,7] $(Bu_4N)_3H[\gamma\text{-}SiW_{10}O_{36}\{Al(OH_2)\}_2(\mu\text{-}OH)_2]\cdot 4H_2O$,[8] $K_6H_3[ZnW_{11}O_{40}Al]\cdot 9.5H_2O$,[9] $K_6Na[(A\text{-}PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu\text{-}OH)(OH_2)_2\}_2]\cdot 19H_2O$,[10] $Rb_2Na_2[Al_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33}H)_2]\cdot 20H_2O$,[11] and $(NH_4)_2Na_2[Al_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33}H)_2]\cdot 20H_2O$,[11] have been reported, and some of them used as Lewis acid[8] and oxidation catalysts.[6,11] Furthermore, the monoaluminum-substituted site in the Keggin structure can be used as an atomic-level support for the grafting reaction with a bis(cyclopentadienyl)zirconium(IV) compound.[12] However, POMs possessing the multi-aluminum-coordinated sites (trialuminum- or more aluminum-coordinated sites) were still one of the least reported compounds.

In this study, we successfully synthesized monomeric and dimeric trialuminum-substituted α-Dawoson polyoxomataltes $[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]^{6-}$ (**1**) and $[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2^{16-}$ (**2**) by pH control of the aqueous solution dissolving α-Dawson trilacunary poly-

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oxotungstate and aluminum nitrate. Interestingly, the dimeric structure of polyoxoanion **2** was constructed through hydrogen bonds between the two trialuminum-substituted sites in α-Dawson units. In this paper, we report complete details of the syntheses and molecular structures of complexes **1** and **2**. The pH dependence of these polyoxoanions was also investigated in aqueous solution.

■ EXPERIMENTAL SECTION

Materials and Methods. $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot xH_2O$ (x = 24−35) was prepared as described in the literature.[13] The numbers of solvated water molecules were determined by thermogravimetric/differential thermal analyses (TG/DTA). All reagents and solvents were obtained and used as received from commercial sources. Elemental analysis was carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The sample was dried overnight at room temperature under 10^{-3}−10^{-4} Torr before analysis. IR spectra were recorded on a PerkinElmer Spectrum100 Fourier transform infrared (FTIR) spectrometer using KBr disks at room temperature. TG and DTA data were obtained using a Rigaku Thermo Plus 2 series TG/DTA TG 8120 analyzer. TG/DTA measurements were performed in air with a temperature increase of 4 °C/min between 20 and 500 °C. The $^{31}P\{^1H\}$ NMR (242.95 MHz) spectra in solutions were recorded in 5-mm-outer-diameter tubes on a JEOL ECA-600 NMR spectrometer. The ^{31}P NMR spectra were measured in D_2O and $Al(NO_3)_3/D_2O$ with reference to an external standard of 85% H_3PO_4 in a sealed capillary. Chemical shifts were reported as negative on the δ scale for resonances upfield of H_3PO_4 (δ 0). The ^{27}Al NMR (156.36 MHz) spectra in D_2O and $Al(NO_3)_3/D_2O$ were recorded in tubes (outer diameter: 5 mm) on a JEOL ECA-600 NMR spectrometer. The ^{27}Al NMR spectra were referenced to an external standard of a saturated $AlCl_3/D_2O$ solution (substitution method). Chemical shifts were reported as positive on the δ scale for resonances downfield of $AlCl_3$ (δ 0). To determine the half-widths, the ^{27}Al NMR signals were treated with waveform processing. The ^{183}W NMR (25.00 MHz) spectra were recorded in tubes (outer diameter: 10 mm) on a JEOL ECA-600 NMR spectrometer. The ^{183}W NMR spectra measured in D_2O and $Al(NO_3)_3/D_2O$ were referenced to an external standard of a saturated Na_2WO_4/D_2O solution (substitution method). Chemical shifts were reported as negative for resonances upfield of Na_2WO_4 (δ 0).

Synthesis of $K_6[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]\cdot 14H_2O$ (K-1). Solid $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 25H_2O$ (8.884 g, 2.00 mmol) was added to a solution of $Al(NO_3)_3\cdot 9H_2O$ (2.251 g, 6.00 mmol) dissolved in 60 mL of water in a single step. At this stage, the pH was ca. 3.0. The mixture was stirred for 3 h at 25 °C and then for 1 h at 90 °C. After filtration through a folded filter paper (Whatman No. 5), solid KCl (1.491 g; 20.0 mmol) was added to the filtrate. The mixture was stirred overnight at 25 °C, and a white precipitate was collected by a membrane filter (JG 0.2 μm). The crude product was obtained in 4.228 g yield. For purification, the crude product (4.228 g) was dissolved in 35 mL of H_2O at 90 °C, followed by filtration through a folded filter paper (Whatman No. 5). After standing in a refrigerator overnight, a white precipitate was collected by a membrane filter (JG 0.2 μm). The obtained product was 2.550 g (the yield calculated on the basis of [mol of **K-1**]/[mol of $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 25H_2O$] × 100 was 29.1%). The obtained product was soluble in water, slightly soluble in ethanol and dimethyl sulfoxide (DMSO), and insoluble in acetone and acetonitrile. Elem. anal. Found: H, 0.32; Al, 1.94; P, 1.47; W, 66.3; K, 5.58; Na, <0.02; N, <0.1. Calcd for $K_6[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]\cdot xH_2O$ (x = 3; $H_{15}Al_3K_6O_{65}P_2W_{15}$): H, 0.36; Al, 1.93; P, 1.48; W, 65.8; K, 5.60; Na, 0; N, 0. A weight loss of 4.62% was observed during overnight drying at room temperature under 10^{-3}−10^{-4} Torr before analysis, suggesting the presence of 11 weakly solvated or adsorbed water molecules (4.52%). TG/DTA under atmospheric conditions showed a weight loss of 6.64% with endothermic points at 85 °C observed below 500 °C; calculations showed 6.98% for 17 water molecules. IR (KBr disk) results in the 1300−400 cm^{-1} region (POM region): 1100s, 1015m, 948s, 906s, 820s, 739s, 605m, 526m cm^{-1}. ^{31}P NMR (D_2O, 25.9 °C): δ −8.4, −14.1. ^{27}Al NMR [$Al(NO_3)_3/D_2O$, 22.2 °C]: δ 1.294. ^{183}W NMR [$Al(NO_3)_3\text{-}D_2O$, 40 °C]: δ −156.6 (3W), −228.0 (6W), −243.2 (6W).

Synthesis of $Cs_6[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]\cdot 13H_2O$ (Cs-1). Compound **Cs-1** was also synthesized by the reaction of solid $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 30H_2O$ (2.267 g, 0.50 mmol) with $Al(NO_3)_3\cdot 9H_2O$ (0.570 g, 1.52 mmol) in 15 mL of water, followed by the addition of solid CsCl (0.843 g, 5.01 mmol). The crude product was purified by precipitation from 430 mL of H_2O at 90 °C. The obtained product was 1.174 g (the yield calculated on the basis of [mol of **Cs-1**]/[mol of $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 30H_2O$] × 100 was 47.6%). To obtain single crystals for X-ray crystallography, the crude product (50 mg) was dissolved in approximately 25 mL of hot water at 90 °C and evaporated slowly at 25 °C for a few weeks. The obtained product was soluble in water; however, the solubility was much lower than that of **K-1**. Elem anal. Found: H, 0.26; Al, 1.66; P, 1.24; W, 58.3; Cs, 17.1; Na, <0.02. Calcd for $Cs_6[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{56}\{Al(OH_2)\}_3]\cdot xH_2O$ (x = 3; $H_{15}Al_3Cs_6O_{65}P_2W_{15}$): H, 0.32; Al, 1.70; P, 1.30; W, 58.0; Cs, 16.8; Na, 0. A weight loss of 3.58% was observed during overnight drying at room temperature under 10^{-3}−10^{-4} Torr before analysis, suggesting the presence of 10 weakly solvated or adsorbed water molecules (3.65%). TG/DTA under atmospheric conditions showed a weight loss of 6.10% with an endothermic point at 108.2 °C observed below 500 °C; calculations showed 5.84% for 16 water molecules. IR (KBr disk) results in the 1300−400 cm^{-1} region (POM region): 1096s, 1013m, 947s, 904s, 816s, 738s, 599m, 530m cm^{-1}. ^{31}P NMR (D_2O, 25.4 °C): δ −8.4, −14.1.

Synthesis of $K_{14}Na_2[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2\cdot 30H_2O$ (KNa-2). The polyoxoanion **2** was obtained by two methods, i.e., conversion of **1** to **2** by the addition of a base (method I) and a one-pot synthesis of $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ with $Al(NO_3)_3\cdot 9H_2O$ under basic conditions (method II). Here, compound **KNa-2** was synthesized using method I as follows: compound **K-1** (2.493 g, 0.57 mmol) was dissolved in 100 mL of water at 50 °C. After cooling to 25 °C, the pH of the solution was adjusted to 9.00 ± 0.05 by the addition of a 1 M Na_2CO_3 aqueous solution. After the solution was stirred for 24 h at 25 °C, 100 mL of ethanol was added. A white precipitate was collected by a membrane filter (JG 0.2 μm). The crude product was dissolved in 60 mL of water, followed by stirring for 40 min at 90 °C. After filtration through a folded filter paper (Whatman No. 5), the filtrate was allowed to stand in a refrigerator overnight. The obtained white product was 1.168 g (the yield calculated on the basis of 2[mol of **KNa-2**]/[mol of **K-1**] × 100 was 45.9%). The obtained product was soluble in hot water (∼90 °C) and DMSO and insoluble in acetone and acetonitrile. Elem anal. Found: H, 0.35; Al, 1.82; P, 1.47; W, 64.9; K, 6.17; Na, 0.55. Calcd for $K_{14}Na_2[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2\cdot xH_2O$ (x = 6; $H_{26}Al_6K_{14}Na_2O_{130}P_4W_{30}$): H, 0.31; Al, 1.90; P, 1.46; W, 64.88; K, 6.44; Na, 0.54. A weight loss of 4.80% was observed during overnight drying at room temperature under 10^{-3}−10^{-4} Torr before analysis, suggesting the presence of 24 weakly solvated or adsorbed water molecules (4.84%). TG/DTA under atmospheric conditions showed a weight loss of 6.63% with an endothermic point at 62.3 °C observed below 340 °C; calculations showed 6.66% for 33 water molecules. IR (KBr disk) results in the 1300−400 cm^{-1} region (POM region): 1089s, 1013m, 944s, 915s, 825s, 740s, 598m, 528m cm^{-1}. ^{31}P NMR (D_2O, 25.1 °C): δ −6.9, −14.1. ^{27}Al NMR (D_2O, 40 °C): δ 22.1.

Synthesis of $[(CH_3)_4N]_{14}Na_2[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2\cdot 39H_2O$ (TMANa-2). A tetramethylammonium/sodium salt of **2** was synthesized using method II, as follows: The pH of the aqueous solution containing $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ (2.212 g, 0.50 mmol) and $Al(NO_3)_3\cdot 9H_2O$ (0.564 g, 1.50 mmol) in 20 mL of water was adjusted by the addition of a 1 M Na_2CO_3 aqueous solution to 9.00 ± 0.05, followed by stirring for 2 h at 25 °C. After filtration through a folded filter paper (Whatman No. 5), solid tetramethylammonium chloride (5.754 g, 52.5 mmol) was added to the filtrate. After the mixture was stirred for 2 days at 25 °C, a white precipitate was collected by a membrane filter (JG 0.2 μm). The crude product was obtained in 1.933 g yield. For purification, the crude product was dissolved in 80 mL of water, followed by stirring for 15 min at 70 °C. After filtration through a folded filter paper (Whatman No. 5), the colorless crystals were obtained by vapor diffusion from acetonitrile at around 25 °C for 1 month. The obtained white product was 1.071 g (the yield calculated on the basis of 2[mol of **TMANa-2**]/[mol of $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$] × 100 was 44.7%). The obtained product was soluble in water, slightly soluble in ethanol and DMSO, and insoluble in acetone and acetonitrile. Elem anal. Found: C, 7.21; H, 1.98; N, 2.10; Al, 1.82; P, 1.38; W, 61.5; Na, 0.50. Calcd for $[(CH_3)_4N]_{14}Na_2[B\text{-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2\cdot xH_2O$ (x = 7; $C_{56}H_{196}N_{14}Al_6Na_2O_{131}P_4W_{30}$): C, 7.47; H, 2.19; N, 2.18; Al, 1.80; P, 1.38; W, 61.22; Na, 0.51. A weight loss of 6.05% was observed during overnight drying at room temperature under 10^{-3}–10^{-4} Torr before analysis, suggesting the presence of 32 weakly solvated or adsorbed water molecules (6.01%). TG/DTA under atmospheric conditions showed a weight loss of 7.79% with an endothermic point at 58.4 °C observed below 127.7 °C (7.89% corresponds to 42 water molecules, based on calculations). Additionally, a weight loss of 10.4% with an exothermic peak at 386.5 °C was observed in the temperature range from 169.0 to 497.5 °C corresponding to 14 tetramethylammonium ions (calcd 10.83%). IR (KBr disk) results in the 1300–400 cm^{-1} region (POM region): 1090s, 1011m, 949s, 911s, 817s, 743s, 600m, 528m cm^{-1}. ^{31}P NMR (D_2O, 25.1 °C): δ −6.9, −14.1. ^{27}Al NMR (D_2O, 40 °C): δ 22.4.

X-ray Crystallography. A colorless platelet-shaped crystal of **TMANa-2** (0.040 × 0.020 × 0.010 mm) was mounted on a MicroMount. Data were collected on a Rigaku VariMax instrument with Saturn connected to a multilayer mirror using monochromated Mo Kα radiation (λ = 0.71075 Å) at 100 ± 1 K. Data were collected and processed using the software *CrystalClear* for Windows. Structural analysis was performed using the software *CrystalStructure* for Windows. All structures were solved using *SIR-2004* (direct methods) and refined using *SHELXL-97*.[14] For polyoxoanion **2**, 15 tungsten atoms, 3 aluminum atoms, 2 phosphorus atoms, 62 oxygen atoms, 1 sodium ion, and 7 tetramethylammonium ions were clearly identified. Thus, the main features of the molecular structure of the POM were clarified. The bond lengths and angles of the tetramethaylammonium ions were restrained. The water molecules could not be modeled because of disorder of the atoms. Accordingly, the residual electron densities were removed using the *SQUEEZE* routine in *PLATON*.[15] This feature is commonly observed in polyoxoanion crystallography.[16]

Crystal Data for TMANa-2: $C_{28}H_{91}Al_3N_7NaO_{62}P_2W_{15}$; M = 4441.67, monoclinic, space group $C2/c$ (No. 15), a = 58.56(3) Å, b = 14.871(7) Å, c = 25.739(13) Å, β = 114.237(6)°, V = 20439(17) Å^3, Z = 8, D_c = 2.887 g/cm^3, μ(Mo Kα) = 169.738 cm^{-1}, R1 = 0.0921 [$I > 2\sigma(I)$], wR2 = 0.1913 (for all data), GOF = 1.243 [200721 total reflections and 23451 unique reflections where $I > 2\sigma(I)$]. CCDC 980460 contains the supplementary crystallographic data for this paper. The crystallographic data without *SQUEEZE* is also deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44-1223-336-033; e-mail deposite@ccdc.cam.ac.uk).

■ RESULTS AND DISCUSSION

As preliminary experiments, ^{31}P NMR spectroscopy was used to monitor the pH dependence of the reaction of $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ with $Al(NO_3)_3\cdot 9H_2O$ by first adding solid $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 26H_2O$ (2.23 g, 0.5 mmol) to a solution of $Al(NO_3)_3\cdot 9H_2O$ (0.566 g, 1.5 mmol) dissolved in 20 mL of water in a single step. The pH was then adjusted to 3 ± 0.2–9 ± 0.2 by the addition of a 1 M Na_2CO_3 aqueous solution with subsequent stirring for 1 h at 25 °C. Solid KCl (0.376 g, 5.0 mmol) was added to the mixture, followed by collection of the white precipitate using a membrane filter (JG 0.2 μm). The obtained precipitate was analyzed via ^{31}P NMR in D_2O, as shown in Figure 1. All of the spectra obtained in the pH ranges of 3–9 showed two signals with 1:1 integrated intensities due to the two internal phosphorus atoms. The signal at δ −8.4, observed for the product obtained by adjusting the pH to 3, shifted to lower field as the pH was increased. In particular, there was an evident transformation of the species observed in the pH range of 3–6 relative to that observed at pH 6 and above. Thus, attempts were made to isolate the two species by adjusting the pH to 3 and 9 because the chemical shifts of these species were distinctly different at these pH values.

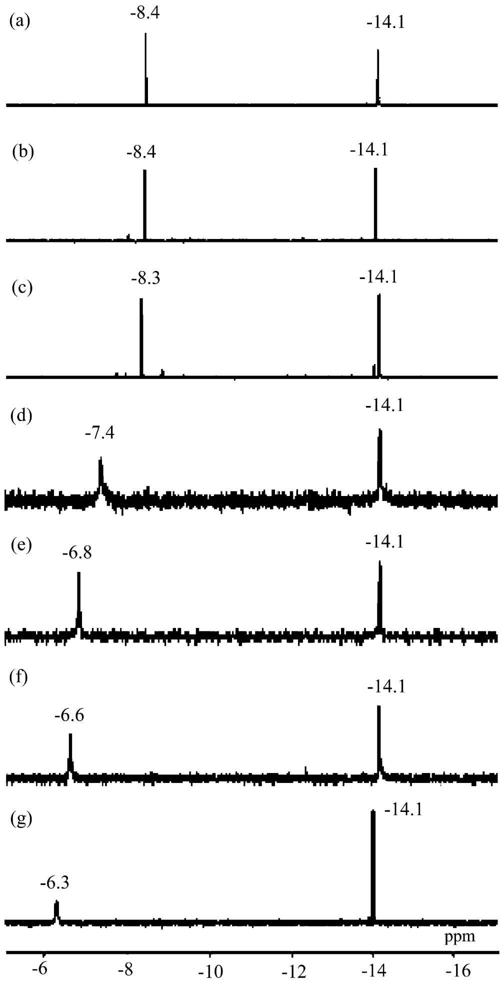

Figure 1. ^{31}P NMR spectra in D_2O of the products obtained by adjusting the pH of a mixture of $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ and $Al(NO_3)_3\cdot 9H_2O$ to (a) 3, (b) 4, (c) 5, (d) 6, (e) 7, (f) 8, and (g) 9 by the addition of a 1 M Na_2CO_3 aqueous solution, followed by the addition of solid KCl. The molar ratio of $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ and $Al(NO_3)_3\cdot 9H_2O$ was 1:3. The error of the pH was ±0.2.

The polyoxoanion **1** was formed by the 3:1 stoichiometric reaction of $Al(NO_3)_3\cdot 9H_2O$ with trilacunary Dawson POM $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ in an aqueous solution, at 25 °C, in air, followed by precipitation from water. When solid $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 30H_2O$ was added to the $Al(NO_3)_3\cdot 9H_2O$ aqueous solution, the pH was around 3. Compounds **K-1** and **Cs-1** were eventually isolated as analytically pure, white powders in 29.1% and 47.6% yield, respectively. The formation of polyoxoanion **1** can be shown by the ionic balance equation (1). For polyoxoanion **2**, it was obtained by two methods (methods I and II). Method I involved conversion of **1** to **2** by adjusting the pH to 9, as shown by the ionic balance equation (2). Polyoxoanion **2** was also obtained from the 3:1 stoichiometric

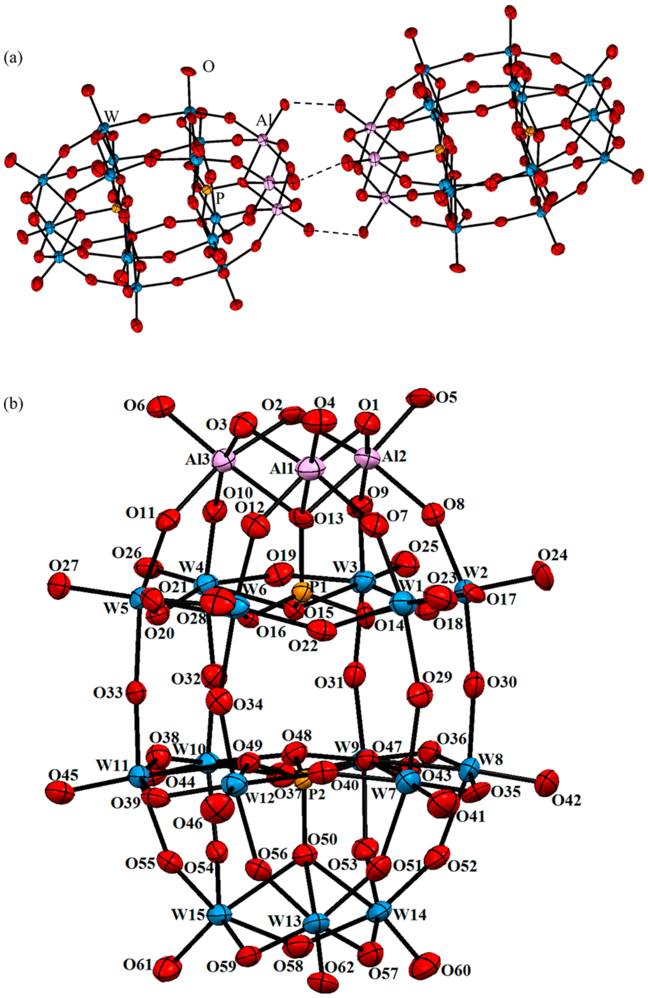

Figure 2. (a) Molecular structure of polyoxoanion **2** and (b) a Dawson unit with atom numbering.

Table 1. Selected Bond Distances (Å) around Trialuminum-Substituted Sites in TMANa-2

Distances (Å)			
Al1−O1	1.883(18)	Al3−O3	1.884(15)
Al1−O4	1.832(16)	Al3−O10	1.918(14)
Al1−O12	1.861(18)	Al3−O13	2.144(15)
Al1−O3	1.863(16)	Al3−O2	1.912(17)
Al1−O7	1.881(16)	Al3−O6	1.814(16)
Al1−O13	2.140(14)	Al3−O11	1.891(17)
Al2−O1	1.908(15)	Al1···Al2	3.087
Al2−O5	1.839(17)	Al1···Al3	3.074
Al2−O9	1.871(14)	Al2···Al3	3.075
Al2−O2	1.871(16)	O4···O4′	2.464
Al2−O8	1.902(15)	O5···O6′	2.457
Al2−O13	2.128(16)	O6···O5′	2.457

reaction of $Al(NO_3)_3{\cdot}9H_2O$ with $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ in aqueous solution, followed by adjustment of the pH of the mixture to 9 [method II; ionic balance equation (3)]. Compounds **KNa-2** and **TMANa-2** were eventually isolated as analytically pure, white powders in 45.9% and 44.7% yield, respectively.

Table 2. Selected Bond Angles (deg) around Trialuminum-Substituted Sites in TMANa-2

Angles (deg)			
O1−Al1−O4	97.3(8)	O1−Al1−O3	90.1(8)
O1−Al1−O12	168.5(7)	O1−Al1−O7	90.3(8)
O3−Al1−O4	99.2(7)	O1−Al1−O13	79.3(6)
O3−Al1−O12	91.8(8)	O3−Al1−O7	167.8(7)
O4−Al1−O7	92.8(7)	O3−Al1−O13	79.3(6)
O4−Al1−O13	176.3(7)	O4−Al1−O12	93.6(8)
O7−Al1−O13	88.8(6)	O7−Al1−O12	85.4(7)
O1−Al2−O2	90.4(7)	O12−Al1−O13	89.9(6)
O1−Al2−O8	90.7(7)	O1−Al2−O5	94.5(7)
O1−Al2−O13	79.1(7)	O1−Al2−O9	168.6(7)
O2−Al2−O8	169.4(7)	O2−Al2−O5	96.0(7)
O2−Al2−O13	80.2(6)	O2−Al2−O9	91.1(7)
O5−Al2−O9	96.5(8)	O5−Al2−O8	94.4(8)
O8−Al2−O9	85.8(6)	O5−Al2−O13	172.5(7)
O9−Al2−O13	90.1(7)	O8−Al2−O13	89.7(6)
O2−Al3−O6	98.2(7)	O2−Al3−O3	89.2(7)
O2−Al3−O11	167.3(6)	O2−Al3−O10	91.2(7)
O3−Al3−O6	98.1(7)	O2−Al3−O13	78.9(6)
O3−Al3−O11	92.5(7)	O3−Al3−O10	167.7(7)
O6−Al3−O10	94.0(7)	O3−Al3−O13	78.8(6)
O6−Al3−O13	175.7(7)	O6−Al3−O11	94.0(8)
O10−Al3−O13	89.3(6)	O10−Al3−O11	84.4(7)
Al1−O1−Al2	109.0(8)	O11−Al3−O13	89.1(6)
Al1−O3−Al3	110.2(7)	Al2−O2−Al3	108.7(7)
Al1−O13−Al2	92.6(6)	Al1−O13−Al3	91.7(6)
Al2−O13−Al3	92.1(5)		

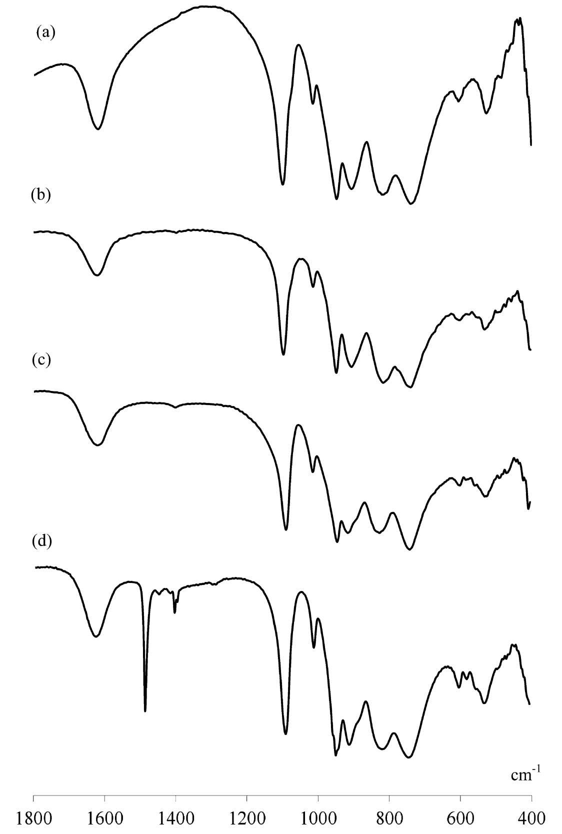

Figure 3. FTIR spectra in the polyoxoanion region (1800−400 cm^{-1}), measured as KBr disks, of (a) **K-1**, (b) **Cs-1**, (c) **KNa-2**, and (d) **TMANa-2**.

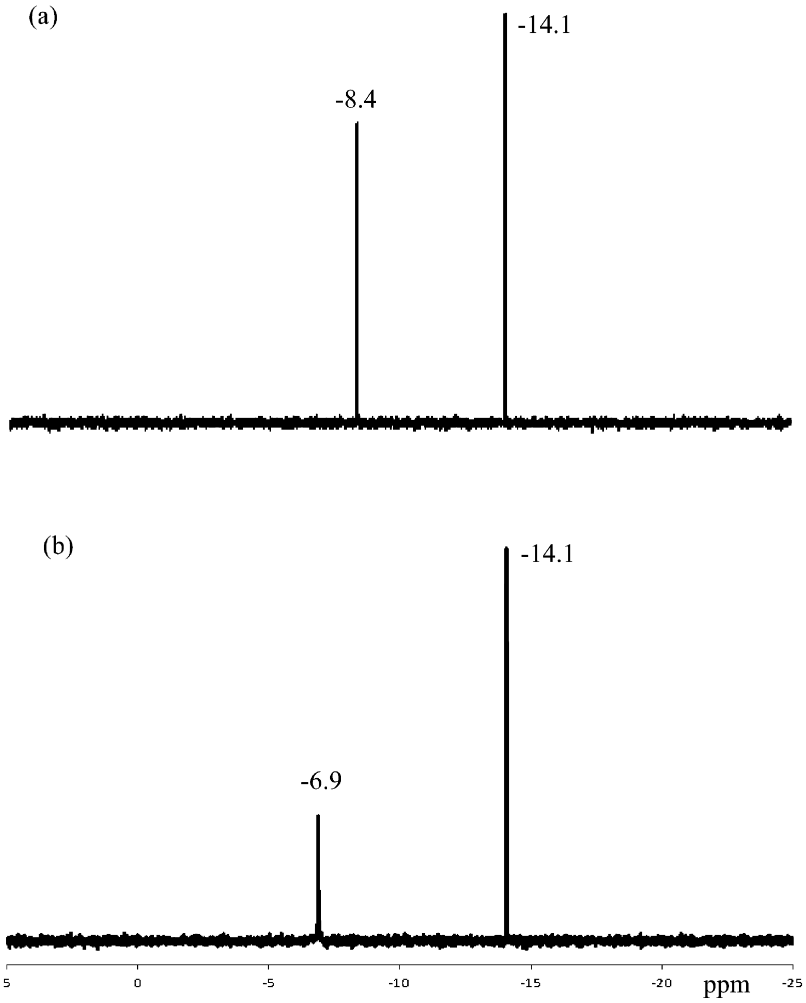

Figure 4. ^{31}P NMR spectra in D_2O of (a) **K-1** and (b) **TMANa-2**. The spectra were referenced to an external standard of 85% H_3PO_4 in a sealed capillary.

$$[\text{B-}\alpha\text{-}P_2W_{15}O_{56}]^{12-} + 3Al(NO_3)_3 + 6H_2O \rightarrow [\text{B-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]^{6-} + 9NO_3^- + 3H^+ \quad (1)$$

$$2[\text{B-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH_2)\}_3]^{6-} + 4OH^- \rightarrow [\text{B-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2^{16-} + 4H_2O \quad (2)$$

$$2[\text{B-}\alpha\text{-}P_2W_{15}O_{56}]^{12-} + 6Al(NO_3)_3 + 10OH^- + 2H_2O \rightarrow [\text{B-}\alpha\text{-}H_3P_2W_{15}O_{59}\{Al(OH)\}_2\{Al(OH_2)\}]_2^{16-} + 18NO_3^- \quad (3)$$

Samples of **K-1**, **Cs-1**, **KNa-2**, and **TMANa-2** were dried overnight at room temperature under a vacuum of 10^{-3}–10^{-4} Torr for elemental analyses; the results were in good agreement with the calculated values for the chemical formulas of these four compounds with three, three, six, and seven hydrated water molecules, respectively (see the Experimental Section). Notably, nitrogen analyses of **K-1** and **Cs-1** revealed no contamination with nitrate ions from the precursor. Weight losses of 4.62% for **K-1** and 3.58% for **Cs-1** were observed during the drying process prior to the analyses, corresponding to the loss of 11 and 10 weakly solvated or adsorbed water molecules, respectively. On the other hand, weight losses of 6.64% for **K-1** and 6.10% for **Cs-1** were observed during the TG/DTA analyses below 500 °C, under atmospheric conditions, corresponding to 17 and 16 water molecules, respectively. Therefore, the total number of water molecules, 17 for **K-1** and 16 for **Cs-1**, observed in the TG/DTA analyses under atmospheric conditions was consistent with the sum of the water molecules (3) coordinated to the three aluminum atoms, the hydrated water molecules (3) indicated by elemental analyses, and the number of water molecules (11 and 10) corresponding to the weight loss observed during drying before analyses, respectively. With regard to **KNa-2** and **TMANa-2**, the weight losses observed during drying before analyses were 4.80% and 6.05% corresponding to 24 and 32 weakly solvated or adsorbed water molecules; thus, the number of water molecules (33 and 42) observed by TG/DTA under atmospheric conditions was consistent with the sum of the water molecules (3) coordinated to the six aluminum atoms in the two α-Dawson units, the hydrated water molecules (6 and 7) indicated by elemental analyses, and the number of water molecules (24 and 32) corresponding to the weight loss observed during drying before analyses, respectively. In addition, 10.4% weight loss was observed in the temperature range of 169.0–497.5 °C for **TMANa-2**, which corresponded

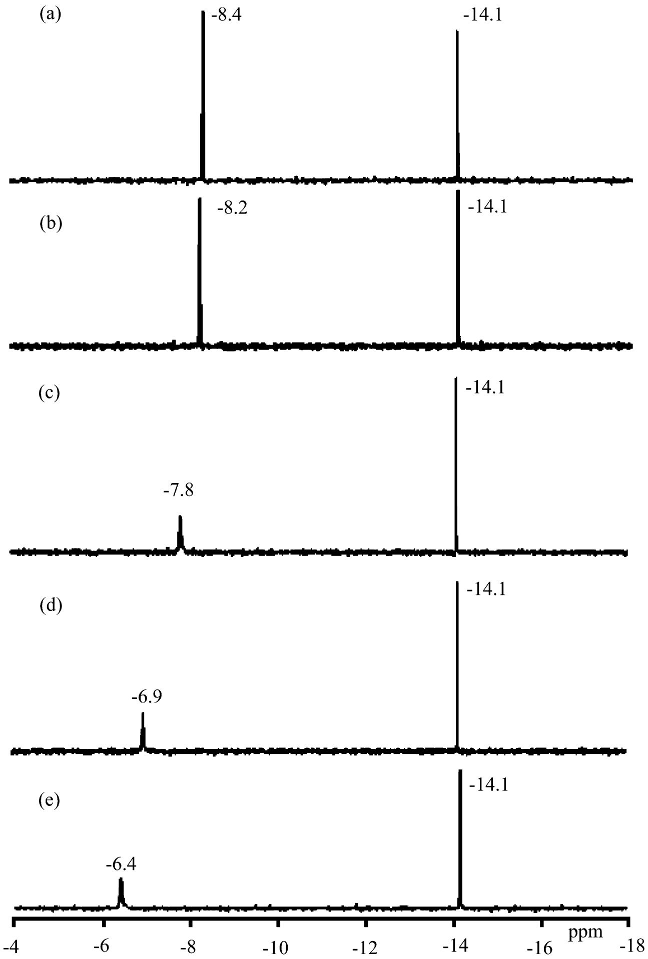

Figure 5. ^{31}P NMR spectra in D_2O of **K-1** at pD values of (a) 5.85, (b) 6.49, (c) 7.34, (d) 8.53, and (e) 9.39 by the addition of a 1 M Na_2CO_3/D_2O solution. The error of the pH was ±0.2.

to 14 tetramethylammonium ions. The ^{1}H NMR spectrum in D_2O of **TMANa-2** indicated the absence of solvated acetonitrile molecules in the sample.

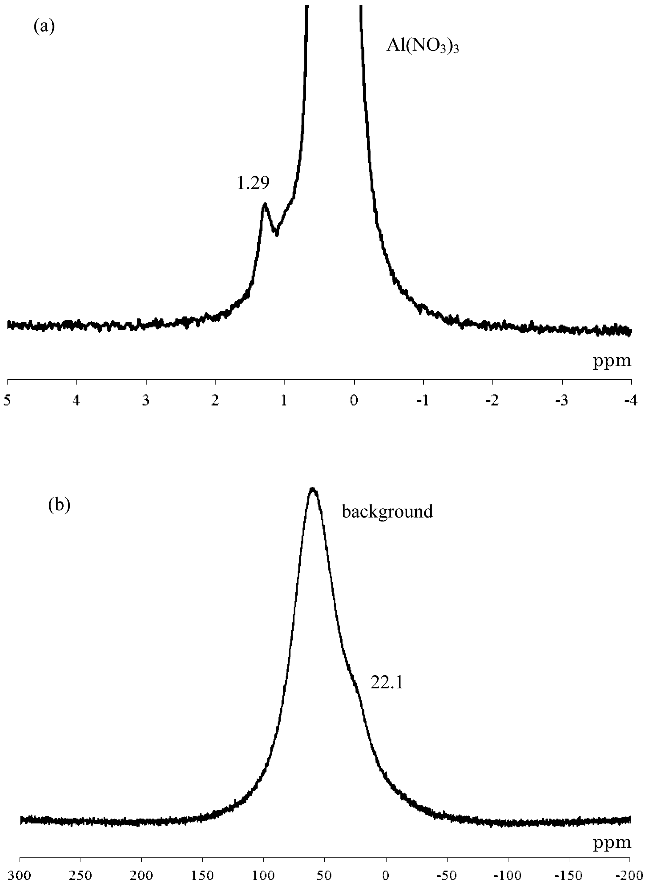

Figure 6. ^{27}Al NMR spectra of (a) **K-1** in a $Al(NO_3)_3/D_2O$ solution and (b) **KNa-2** in D_2O. The spectrum was referenced to an external standard of a saturated $AlCl_3/D_2O$ solution (substitution method).

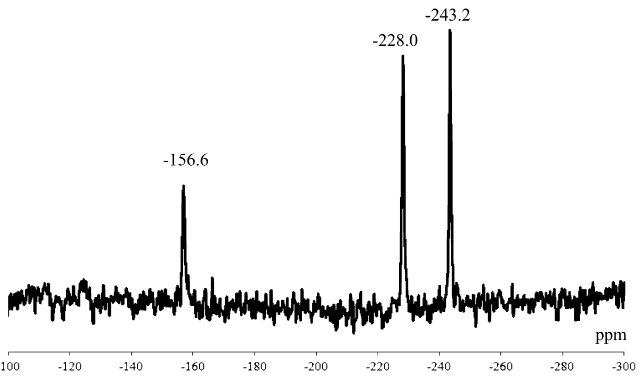

Figure 7. ^{183}W NMR spectrum of **K-1** in a $Al(NO_3)_3/D_2O$ solution. The spectrum was referenced to an external standard of a saturated Na_2WO_4/D_2O solution (substitution method).

Single crystals of **TMANa-2** that were suitable for X-ray crystallography could be obtained by crystallization via vapor diffusion from water/acetonitrile. Structural analysis revealed that the molecular structure of **2** was composed of the two Dawson units, linked through hydrogen bonds and arranged with S_3 symmetry, as shown in Figure 2. The crystallographic details are shown in Table S1 in the Supporting Information (SI). The observed electron densities of the aluminum and tungsten atoms were quite different, and the data unequivocally distinguished and defined the aluminum and tungsten atoms. Thus, the main features of the molecular structure of the polyoxoanion were clear. In addition, seven tetramethylammonium ions and a sodium ion were observed for a Dawson unit, as shown in Figure S1 in the SI. Selected bond distances and angles around the aluminum center for the Dawson–polyoxoanion unit are provided in Tables 1 and 2. As expected, the three AlO_6 octahedra (Al_3 cap) in each "$P_2W_{15}Al_3$" Dawson unit were substituted by the three edge-sharing WO_6 octahedra (W_3 cap) of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. The two Al_3O_6 faces were confronted with each other through several hydrogen bonds. In the Al_3 cap (Al1, Al2, and Al3), the Al···Al distances were in the range of 3.074–3.087 Å (average 3.079 Å); these distances were shorter than the following distances: the W···W distances (3.398–3.416 Å; average 3.408 Å) of the W_3 caps (W13, W14, and W15), the Ti···Ti distances (3.198–3.391 Å; average 3.314 Å) of the Ti_3 caps for the tetrameric Dawson-type trititanium(IV)-substituted polyoxotungstates $Na_xH_{45-x}[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]\cdot yH_2O$ ($x = 16$–19 and $y = 60$–70)[17] and $Na_xH_{33-x}K_4[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{60.5})_4Cl]\cdot yH_2O$ ($x = 21$–26 and $y = 60$–70),[18] and the Nb···Nb distances (3.362–3.390 Å; average 3.374 Å) of the Nb_3 caps for the tetrameric Dawson-type triniobium(V)-substituted polyoxotungstates $K_6Na_4H_8[Eu_6(H_2O)_{38}(P_2W_{15}Nb_3O_{62})_4]\cdot 45H_2O$ and $K_6Na_4H_8[Ce_6(H_2O)_{38}(P_2W_{15}Nb_3O_{62})_4]\cdot 56H_2O$.[19] This was due to the smaller ionic radius of Al^{3+} (0.675 Å) than those of W^{6+} (0.74 Å), Ti^{4+} (0.745 Å), and Nb^{5+} (0.78 Å).[20]

The bond valence sums (BVSs),[21] that were calculated on the basis of the observed bond lengths for **TMANa-2** were in the range of 5.944−6.365 (average 6.212) for the 15 tungsten atoms, 4.758−4.823 (average 4.791) for the two phosphorus atoms, 1.558−2.128 (average 1.900) for the 56 oxygen atoms (excluding O1−O6), and 2.706−2.834 (average 2.762) for the three aluminum atoms in the Dawson unit. These values were reasonably consistent with the formal valences of W^{6+}, P^{5+}, O^{2-}, and Al^{3+}, respectively. The calculated BVS values of the edge-sharing oxygen atoms of the trialuminum-substituted sites were as follows: O1, 0.950; O2, 0.962; O3, 1.008. These BVS values of the oxygen atoms suggested that a proton was bound to each of the edge-sharing oxygen atoms of the Al_3 cap. In contrast, the BVS values of O4, O5, and O6 were 0.564, 0.553, and 0.592, which were larger than those of the water molecules (0.404−0.457) coordinated to the aluminum atoms but smaller than those of the hydroxyl groups coordinated to the aluminum atoms (0.887−1.010) for $K_6Na[(A\text{-}PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu\text{-}OH)(OH_2)_2\}_2]\cdot 19H_2O$.[10] Thus, the elemental analysis and BVS calculation results suggested that three hydrogen bonds were present between the two neighboring Al_3 caps with two hydroxyl groups and a water molecule coordinated to the three aluminum atoms in a Dawson unit. The terminal O···O distances between the two neighboring polyoxoanion units, O4···O4′, O5···O6′, and O6···O5′ were in the range of 2.457−2.464 Å, which were similar to those [2.526(8)−2.761(8) Å] for $[H_9(PtMo_6O_{24})_2]^{7-}$ constructed by seven hydrogen bonds between two $PtMo_6O_{24}$ units.[22] This also supported the presence of hydrogen bonds between the two "$P_2W_{15}Al_3$" units.

With regard to X-ray crystallography of **Cs-1**, single crystals were obtained by slow evaporation of an aqueous solution containing low concentrations of **1** at the precipitation step (see the Experimental Section). However, cracking of the **Cs-1** crystals was observed during the X-ray diffraction measurements in the lower temperature range of 93 ± 1−153 ± 1 K. At 293 K, the quality of the data was still poor [$R1 = 0.158$ for $I > 2\sigma(I)$]; however, on the basis of the reproducibility of the data over a few dozen repetitions, it could be concluded that the crystals of the tetramethylammonium salt of **1** had a molecular structure similar to that of **Cs-1** with comparable quality. The tetra-*n*-butylammonium salt of **1** was not obtained as a single species by the addition of excess tetra-*n*-butylammonium ions to the aqueous solution of **1**. The X-ray crystallography and crystal data for **Cs-1** are shown in the SI. The molecular structure of **Cs-1** is shown in Figure S2 in the SI. X-ray crystallography revealed that polyoxoanion **1** was a monomeric, *α*-Dawson polyoxotungstate with overall C_{3v} symmetry, which was the same as that observed for the Dawson unit of polyoxoanion **2**. The average Al···Al distance was ca. 3.1 Å, which was similar to that of polyoxoanion **2**. The lengths of the bonds between the aluminum and terminal oxygen atoms were in the range of 1.91−1.95 Å, which were quite similar to those of the $AlOH_2$ groups in $[(A\text{-}PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu\text{-}OH)(OH_2)_2\}_2]^{7-}$ (1.910−1.955 Å).[10]

The FTIR spectra of **K-1**, **Cs-1**, **KNa-2**, and **TMANa-2** measured as KBr disks are shown in Figure 3. The bands at 1100, 1015, 948, 906, 820, 739, 605, and 526 cm^{-1} was observed for compound **K-1**, which were the same as those of **Cs-1** (1096, 1013, 947, 904, 816, 738, 599, and 530 cm^{-1}). Compound **KNa-2** showed the bands at 1089, 1013, 944, 915, 825, 740, 598, and 528 cm^{-1}, which were also the same as those of **TMANa-2** (1090, 1011, 949, 911, 817, 743, 600, and 528 cm^{-1}). Furthermore, these spectra were different from that of $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 33H_2O$ (1132, 1087, 1009, 978, 937, 915, 876, 826, 744, and 526 cm^{-1}),[13] suggesting that the aluminum ions were coordinated to the trilacunary site of $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$. Notabley, the spectral patterns (in the range of 1200−400 cm^{-1}) of **K-1** and **Cs-1** were quite similar to those of **KNa-2** and **TMANa-2** with the exception that the band at ca. 1100 cm^{-1}, assigned to the P−O vibration for **K-1** and **Cs-1**, shifted to ca. 1090 cm^{-1} for **KNa-2** and **TMANa-2**; these data also suggested that the Dawson framework structure of polyoxoanion **1** was the same as that of polyoxoanion **2**. The band due to the NO_3^- ions was not observed at 1385 cm^{-1}, indicating that nitrate ion contamination was not present in compounds **K-1**, **Cs-1**, and **KNa-2**, as was also confirmed by elemental analyses.

The ^{31}P NMR spectra of **K-1** and **TMANa-2** in D_2O showed two signals at (δ −8.4 and −14.1) and (δ −6.9 and −14.1) with 1:1 integrated intensities, confirming the purity and homogeneity of the samples (Figure 4). These signals were consistent with those of **Cs-1** (δ −8.4 and −14.1) and **KNa-2** (δ −6.9 and −14.1), respectively, as was also confirmed by the two-line spectra observed for the mixtures of **K-1** and **Cs-1** and of **TMANa-2** and **KNa-2** in D_2O. Thus, the molecular structures of **K-1** and **TMANa-2** were the same as those of **Cs-1** and **KNa-2**, respectively. In addition, these signals were different from those of $Na_{12}[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]\cdot 35H_2O$ (δ −0.49 and −15.0), suggesting that the aluminum ions were coordinated to the trilacunary site of $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$. For compounds **K-1** and **Cs-1**, the two signals were consistent with those of their crude products (both showed two signals at δ −8.4 and −14.1), as shown in Figure 1a. In contrast, the two signals observed for **KNa-2** were slightly shifted from those of its crude product (δ −6.3 and −14.1), as shown in Figure 1g; however, a two-line spectrum was observed for the mixture of **KNa-2** and its crude product. For compound **TMANa-2**, its crude product showed two signals at δ −6.9 and −14.1, which were consistent with those of **TMANa-2**. These results suggested that the molecular structures of **1** and **2** were not changed under the precipitation and crystallization conditions.

Here, pH dependence of polyoxoanion **1** was monitored by in situ ^{31}P NMR spectroscopy in D_2O with varying pH. When **K-1** (100 mg) was dissolved in D_2O (10 mL), the pD was 5.85 (the pH was 6.25).[23] The signal at δ −8.4 was not shifted to lower filed even at pH 6.25, and it was gradually shifted to lower field by adjusting of the pD from 5.85 to 9.39 ± 0.2 (the pH from 6.25 to 9.79 ± 0.2) with a 1 M Na_2CO_3-D_2O solution, as shown in Figure 5. In each spectrum, only two signals were observed with 1:1 integrated intensities; this suggested that a different single species was formed at each pH value. At a pD of 8.53 ± 0.2 (a pH of 8.93 ± 0.2), the two signals at δ −6.9 and −14.1 were observed, which were consistent with those for **KNa-2** and **TMANa-2**. When the pH of the aqueous solution created by dissolving **KNa-2** (450 mg) in water (16 mL) was adjusted to 3.0 ± 0.2, followed by stirring for 5 h at 25 °C, the ^{31}P NMR spectrum in 1:1 H_2O/D_2O of the solution showed two sets of signals at δ−8.4 and −14.1 and at δ −7.0 and −13.8, as shown in Figure S3 in the SI. The signals at δ −8.4 and −14.1 were consistent with those of polyoxoanion **1**; however, the signals at δ −7.0 and −13.8 could not be assigned. Thus, the pH dependence of polyoxoanions **1** and **2** was remarkably different from that for the mixture of trilacunary polyoxoanion and aluminum nitrate in aqueous solution.

Evaluation of the stability of polyoxoanions **1** and **2** in water demonstrated that, for polyoxoanion **1**, a new ^{31}P NMR signal appeared at δ −7.7 when the spectrum was acquired in D_2O after heating for 3 h at 90 °C (Figure S4 in the SI); however, this signal disappeared when $Al(NO_3)_3 \cdot 9H_2O$ was added to the solution [the concentration of the $Al(NO_3)_3/D_2O$ solution was 0.11 M], which suggested that polyoxoanion **1** was stabilized in the aqueous solution containing dissolved aluminum ions. Thus, ^{27}Al and ^{183}W NMR spectra of polyoxoanion **1** were acquired in an $Al(NO_3)_3/D_2O$ solution. In contrast, polyoxoanion **2** was quite stable in water even after heat treatment at 90 °C for 3 h without any additives.

The ^{27}Al NMR spectrum (Figure 6a) of **K-1** in a $Al(NO_3)_3/D_2O$ solution at ~40 °C showed a signal at δ 1.294 ($\Delta\nu_{1/2}$ was 33.6 Hz) arising from the trialuminum-substituted site. In comparison, a broad signal was observed at δ 22.1 ($\Delta\nu_{1/2}$ was 5417 Hz) for compound **KNa-2** in D_2O at ~25 °C, as shown in Figure 6b. Compound **TMANa-2** also showed a broad signal at δ 22.4 ($\Delta\nu_{1/2}$ was 6480 Hz). These chemical shifts were different from that of the counter aluminum ion of $AlHSiW_{12}O_{40}$ (δ 0.2; $\Delta\nu_{1/2}$ was less than 40 Hz),[24] suggesting that the aluminum ions were coordinated to the trilacunary site. It was surprising that the half-widths of the signals for **KNa-2** and **TMANa-2** were 2 orders of magnitude larger than that of **K-1**; however, such a broad ^{27}Al NMR signal was observed for α-Keggin-type monoaluminum-substituted polyoxoanion $[\alpha\text{-}PW_{11}O_{39}Al(OH_2)]^{4-}$ (δ 16.1; $\Delta\nu_{1/2}$ was 5226 Hz)[5] and its zirconocene derivative $[\alpha\text{-}PW_{11}Al(OH)O_{39}ZrCp_2]_2^{6-}$ (Cp = $C_5H_5^-$; δ 17.5; $\Delta\nu_{1/2}$ was 2753 Hz)[12] in acetonitrile-d_3. In addition, the polyoxoanion $[(A\text{-}PW_9O_{34})_2\{W(OH)(OH_2)\}\{Al(OH)(OH_2)\}\{Al(\mu\text{-}OH)(OH_2)_2\}_2]^{7-}$ showed two broad signals at δ 12.5 ($\Delta\nu_{1/2}$ was 618 Hz) and δ 7.8 ($\Delta\nu_{1/2}$ was 375 Hz) in D_2O.[10] The sharp signal for **K-1** suggested that the aluminum ions coordinated to the trilacunary site in $[B\text{-}\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ were in equilibrium with Al^{3+}; however, this could not be confirmed because no signals were observed for **K-1** in D_2O.

The ^{183}W NMR spectrum (Figure 7) of **K-1** in a $Al(NO_3)_3 \cdot 9H_2O/D_2O$ solution at ~40 °C showed a three-line spectrum of δ −156.6, −228.0, and −243.2 with 1:2:2 intensities. The three lines in the spectrum corresponded to the 3W:6W: 6W atoms. This result clearly demonstrates that the three aluminum ions in the polyoxoanion **1** structure were equivalent, possessing C_{3v} symmetry. The ^{183}W NMR spectra of **KNa-2** and **TMANa-2** could not be obtained because of their low solubility in D_2O.

■ CONCLUSION

In this study, we first demonstrated the syntheses and molecular structures of two types of α-Dawson-type trialuminum-substituted POMs, **1** and **2**, by pH control. The potassium and cesium salts of **1**, **K-1**, and **Cs-1** were formed by a stoichiometric reaction in water of trilacunary α-Dawson polyoxotungstate with aluminum nitrate under acidic conditions (pH ~3). The potassium/sodium and tetramethylammonium/sodium salts of **2**, **KNa-2**, and **TMANa-2** were obtained under basic conditions (pH ~9). The characterization of these compounds was accomplished by X-ray structure analysis, elemental analysis, TG/DTA, FTIR, and ^{31}P, ^{27}Al, and ^{183}W NMR spectroscopy. The X-ray structural analyses showed that polyoxoanion **1** was a monomeric α-Dawson structure with an overall C_{3v} symmetry, while polyoxoanion **2** was a hydrogen-bonded dimeric structure with an overall S_3 symmetry in the solid state. The products obtained by the reaction of trilacunary Dawson polyoxotungstate with aluminum nitrate in aqueous solution significantly depended on the pH, and different single species were formed in aqueous solution at each pH value. In addition, the stability and pH dependence of polyoxoanion **1** were remarkably different from those of **2** in aqueous solution. Further studies on the isolation of other species formed at different pH values and applications to catalysts and molecular supports for grafting reactions with organometallic compounds are in progress. These results will be reported elsewhere.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for **Cs-1** and **TMANa-2** in CIF format, crystal data and structural refinement details, and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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