Novel Solid-State 8H$^+$-Heteropolyacid. Synthesis and Molecular Structure of a Free-Acid Form of a Dawson-Type Sandwich Complex, $[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]^{8-}$

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The preparation and structural characterization of a novel molecular solid Brønsted acid based on the Dawson-type sandwich polyoxometalate (POM) are described. The free-acid form of POM, i.e., 8H$^+$-heteropolyacid with the formula $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot31H_2O$ (**1**) ($H_8[\mathbf{1a}]\cdot31H_2O$), was prepared by using three different methods: In Method 1, a cation-exchange resin column was used to separate precursor $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot26H_2O$ (**2**), and in Methods 2 and 3, a traditional ether-extraction method was applied for the other precursors, i.e., isolated or in situ generated compound of the tetrameric Ti–O–Ti anhydride species of trititanium(IV)-substituted Dawson POM, $K_{25}[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl]\cdot55H_2O$ (**3**). Compound **1** was characterized by using complete elemental analysis, thermogravimetric (TG) and differential thermal analysis (DTA), Fourier transform infrared (FT-IR) spectroscopy, (^{31}P, ^{183}W) nuclear magnetic resonance (NMR) spectroscopy, X-ray crystallography, and potentiometric titration with *n*-butylamine. The molecular structure of **1a** indicated it to be a di-lacunary species of the saturated sandwich complex, $[M_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]^{n-}$ (M = transition-metal ions). From the pH-varied ^{31}P NMR spectra of **2** in water, the degree of protonation of the oxygen atoms at the lacunary sites significantly affects the ^{31}P NMR chemical shift. A Hammett acidity constant H_0 of **1** in CH_3CN (−2.72) was estimated to be almost the same as that of the homo-Dawson heteropolyacid $H_6[P_2W_{18}O_{62}]\cdot17H_2O$ (−2.77).

Polyoxometalates (POMs) are molecular metal-oxide clusters and have attracted interest recently because they are soluble metal oxides with applications in the fields of catalysis, medicine, and material sciences.[1] Homogeneous and heterogeneous reactions catalyzed by heteropolyacids, i.e., free-acid forms of POM, are of particular interest.[2] Saturated POMs, such as homo-Keggin POM $[PW_{12}O_{40}]^{3-}$ and homo-Dawson POM $[P_2W_{18}O_{62}]^{6-}$, have lower basicity on the surface oxygen atoms; as a result, their free-acid forms, namely, $H_3[PW_{12}O_{40}]\cdot nH_2O$ and $H_6[P_2W_{18}O_{62}]\cdot nH_2O$ (abbreviated as H_3PW_{12} and $H_6P_2W_{18}$, respectively), become stronger Brønsted acids. Many studies have demonstrated their usefulness as acid catalysts that are more effective than ordinary protonic acids.[1,2]

The acidities of heteropolyacids in solutions have been studied using Brønsted basicity measurements,[3a–c] Hammett acidity constants,[3d,e] ^{13}C shift of mesityl oxide,[3f] temperature-programmed desorption (TPD) and microcalorimetry of gaseous bases,[3g] calorimetric adsorption (Cal-ad) method,[3h] calorimetric tritration,[3i] high-temperature X-ray diffraction (XRD), and thermogravimetry (TG) measurements.[3j] In all instances, the reported studies indicate that the acidity of H_3PW_{12} is greater than that of sulfuric acid.[3,4] However, most studies conducted so far have been concerned with Keggin-type heteropolyacids.

H_3PW_{12} is known to possess primary and secondary structures.[1e,5] The primary structure comprises P, W, and O atoms that are used for constructing the parts of the heteropolyanion skeleton, such as the Keggin and Dawson fragments. The secondary structure is associated with the crystal structures of H_3PW_{12} and depends upon the degree of hydration since the polyoxoanion units are connected with H$^+$ and H_2O molecules. As a matter of fact, the crystal structure of $H_3[PW_{12}O_{40}]\cdot6H_2O$ is comprised of four polyoxoanions of $[PW_{12}O_{40}]^{3-}$ connected by $H^+(H_2O)_2$ bridges by hydrogen bonding at the terminal oxygen atoms of the anions. Thus, it is a reasonable assumption that heteropolyacids are hydronium cations stabilized by heteropolyanions.[5]

On the other hand, limited reports exist on the X-ray crystallography of the free-acid forms of POM, because it is difficult to obtain single crystals suitable for X-ray diffraction measurements. In fact, X-ray crystallography and/or neutron diffraction analysis have been successfully conducted for only limited types of heteropolyacids (regarded as solid-state Brønsted acids), such as Keggin-type heteropolyacids, i.e., $H_3[PW_{12}O_{40}]\cdot nH_2O$ ($n = 6$,[5a,b] 21,[5c] and 29[5d]) and $H_3[PMo_{12}O_{40}]\cdot nH_2O$ (n = 13–14,[5e] 29–31,[5f,g] ca. 30[5h]). Thus, we have been interested in studying the (1) synthesis, isolation, and crystallization of novel POM-based protonic acids; (2) single-crystal X-ray structure; and (3) acidity in organic solvent.

In this work, a novel free-acid form of POM, $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot31H_2O$ (**1**) ($H_8[\mathbf{1a}]\cdot31H_2O$), was synthesized using three different methods (Methods 1–3), and the molecular structure of **1a** was successfully determined. In Method 1, a cation-exchange resin column was used to separate precursor $K_{14}H_2[\mathbf{2a}]\cdot26H_2O$ (**2**) (**2a** = $[Ti_2(P_2W_{15}O_{56})_2]^{16-}$), whereas in Methods 2 and 3, a traditional

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ether-extraction method was applied to the isolated or in situ generated compound of the tetrameric Ti–O–Ti anhydride species of trititanium(IV)-substituted Dawson POM, $K_{25}[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl]\cdot 55H_2O$ (**3**).[6a] In Methods 2 and 3, the molecular structure of the final product was quite different from those of the precursors. Based on the molecular design of the novel solid-state Brønsted acids and the yield, Method 1 was found to be superior to the other methods. The molecular structure of **1a** is comprised of two tri-lacunary Dawson POMs $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ with an $\alpha\alpha$-type junction linked through two octahedral titanium(IV) centers, i.e., it is a di-lacunary species of a saturated sandwich complex, $[M_4(H_2O)_2(\alpha\text{-}P_2W_{15}O_{56})_2]^{n-}$ (M = transition-metal ions).[7] The degree of protonation of the oxygen atoms in the lacunary sites in the sandwich complex anion was found to be pH-dependent in accordance with ^{31}P NMR observations. Thus, with regard to the oxygen atoms in the lacunary sites, the non-protonated species **2**, partially protonated species Na_5H_9[**4a**]$\cdot 38H_2O$ (**4**) (**4a** = $[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]^{14-}$), and completely protonated species **1** were isolated in this work.

Herein, we report full details of the synthesis and unequivocal characterization of **1** with complete elemental analysis, TG/DTA, FT-IR, (^{31}P, ^{183}W) NMR, and potentiometric titration with *n*-butylamine. The molecular structure of **1a** is discussed. Measurement of the acidity of **1** using a Hammett indicator in acetonitrile solution is also discussed.

Experimental

Instrumentation/Analytical Procedures. Complete elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). The samples were dried at room temperature and under 10^{-3}–10^{-4} Torr overnight before analysis. The infrared spectra were recorded on a Jasco 4100 FT-IR spectrometer in KBr disks at room temperature. The TG/DTA data were acquired using a Rigaku Thermo Plus 2 series TG/DTA TG 8120 instrument. The TG/DTA measurements were carried out under atmospheric conditions with a temperature ramp of 4 °C per min between 20 and 500 °C.

^{31}P NMR (161.70 MHz) spectra in D_2O solution were recorded in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and a JEOL EX-400 NMR data processing system. The ^{31}P NMR spectra were referenced with an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. The ^{31}P NMR signals were shifted to −0.101 ppm by using 85% H_3PO_4 as a reference instead of 25% H_3PO_4. ^{183}W NMR (16.50 MHz) spectra were recorded in 10 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer equipped with a JEOL NM-40T10L low-frequency tunable probe and a JEOL EX-400 NMR data processing system. The ^{183}W NMR spectra measured in D_2O were referenced with an external standard of saturated Na_2WO_4–D_2O solution. The ^{183}W NMR signals were shifted to −0.787 ppm by using a 2 M Na_2WO_4 solution as a reference instead of saturated Na_2WO_4 solution.

Potentiometoric titration with *n*-butylamine and the measurement of the potential (E/mV) in acetonitrile[8] were carried out with an MP120 pH meter (METTLER TOLEDO). A typical procedure followed for the titration is as follows: 10 µmol of the heteropolyacid was dissolved in 50 mL of CH_3CN, and the solution was stirred for 3 h. The titration of the CH_3CN solution using 5 µmol of *n*-butylamine was monitored.

Measurement of the acidity in the CH_3CN solution using the Hammett indicator, 1,9-diphenyl-1,3,6,8-nonatetraen-5-one (dicinnamalacetone: $pK_a = -3.0$ for the protonated indicator), was performed according to the literature using a Jasco V-560 UV/VIS/NIR spectrometer,[3e] and the Hammett acidity constant H_0 was evaluated, in which $H_0 = pK_a - \log[AH^+]/[A]$ at equilibrium; AH^+ (protonated indicator: red (λ_{max} 540 nm)) $\rightleftarrows$ A (free indicator: yellow (λ_{max} 360 nm)) + H^+. An acetonitrile solution containing $[H^+]_{initial} = 4.0 \times 10^{-4}$ M and $[A]_{initial} = 4.0 \times 10^{-5}$ M was prepared and used for the UV–vis absorption measurements.

Materials. The following materials were used as received: Amberlite IR120B NA, the Hammett indicator, 1,9-diphenyl-1,3,6,8-nonatetraen-5-one (dicinnamalacetone: $pK_a = -3.0$ for the protonated indicator) (all from Wako); D_2O (Isotec). The precursors $K_{25}[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl]\cdot 55H_2O$ (**3**)[6a] and $Na_{12}[P_2W_{15}O_{56}]\cdot nH_2O$ (n = 19–21)[9] were prepared according to the literature and identified.

Preparations of the Precursor $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot 26H_2O$ (2). To a suspension of 0.717 g (2.30 mmol) of $Ti(SO_4)_2\cdot 4H_2O$ in water (40 mL), 6 M aqueous HCl solution (2.0 mL) was added. To the colorless clear solution, water (160 mL) was added, followed by 20 mL of 6 M aqueous HCl solution (pH of the resulting solution was 0.48). Then, $Na_{12}[P_2W_{15}O_{56}]\cdot 19H_2O$ (10.0 g, 2.31 mmol) was immediately added to this solution, followed by stirring for 15 min. The pale yellow clear solution obtained was refluxed for 1 h, during which time the solution gradually changed to a yellow homogeneous solution. To the hot solution, KCl (20.0 g, 0.27 mol) was immediately added, and the colorless clear solution obtained was cooled to room temperature. The white precipitate was collected on a membrane filter (JG 0.2 µm). The powder was redissolved in 30 mL aqueous HCl solution (pH 2.0) on a water bath at 80 °C. The solution was cooled to room temperature and allowed to stand overnight in a refrigerator at 4 °C. The white precipitate formed was collected on a membrane filter (JG 0.2 µm), washed with ethanol (twice with 30 mL) and Et_2O (twice with 30 mL), and dried in vacuo for 2 h. The white powder obtained in 40.3% yield (3.97 g) was not hygroscopic. It was soluble in water and DMSO but was less soluble in MeOH, EtOH, and acetone, sparingly soluble in CH_3CN and insoluble in CH_2Cl_2, $CHCl_3$, EtOAc, and Et_2O.

Microanalysis: Calcd for $K_{14}H_2[Ti(P_2W_{15}O_{56})_2]\cdot 3H_2O$ or $H_8K_{14}P_4W_{30}Ti_2O_{115}$: H, 0.10; P, 1.52; W, 67.84; Ti, 1.18; O, 22.63; K, 6.73%. Found: H, 0.10; P, 1.42; W, 67.90; Ti, 1.20; O, 22.4; K, 6.35; total 99.37%. A weight loss of 4.80% was observed during the course of drying at room temperature at 10^{-3}–10^{-4} Torr overnight before elemental analysis, suggesting the presence of 22–23 weakly solvated or adsorbed water molecules. TG/DTA under atmospheric conditions: a weight loss of 5.39% was observed at below 500 °C with endothermic points at 54.0, 89.6, and 126.4 °C; calcd 5.48% for $x = 26$ in $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot xH_2O$. IR (KBr) (polyoxometalates region): 1087s, 1062w, 1019w, 948vs, 892w, 847w, 765vs, 598w, 528w cm^{-1}. ^{31}P NMR (23.0 °C, D_2O): δ −5.84, −13.4. ^{183}W NMR (the sodium salt was in situ-generated by the cation-exchange reaction of the potassium salt **2** in D_2O with an excess amount of $NaClO_4$. After filtering off the produced $KClO_4$, ^{183}W NMR of the filtrate was measured (22.1 °C, D_2O)): δ −144.2 (1W + 2W), −183.7 (2W), −194.2 (2W), −196.7 (2W), −201.1 (2W), −202.1 (2W), −209.4 (2W).

Compound **2** was not hygroscopic in nature. The number of water molecules (26) in the formula of **2** was determined as the sum of the water molecules (3) found in the elemental analyses and the water molecules (22–23) estimated from the weight losses observed during the course of drying before the analyses. This number of water molecules in **2** was in agreement with that (26) observed by the TG/DTA measurements under atmospheric conditions.

Preparation of $Na_5H_9[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]\cdot 38H_2O$ (4). To a suspension of $Ti(SO_4)_2\cdot 4H_2O$ (0.717 g, 2.30 mmol) in water (40 mL), 6 M aqueous HCl solution (2.0 mL) was added. To the colorless clear solution, water (160 mL) and 6 M aqueous HCl solution (20 mL) (pH of the resulting solution was 0.48) were added. Then, $Na_{12}[P_2W_{15}O_{56}]\cdot 19H_2O$ (10.0 g, 2.31 mmol) was immediately added to the solution, followed by stirring for 15 min. The pale yellow clear solution was refluxed for 1 h, during which time the solution gradually changed to a yellow clear solution. The solution was evaporated to ca. 20 mL on a rotary evaporator at 40 °C. A whitish-yellow powder precipitated and was deposited and was removed by a filter paper (Whatman #2). The colorless clear filtrate was allowed to stand overnight in a refrigerator at 4 °C. The white powder formed was collected on a membrane filter (JG 0.2 µm) and dried in vacuo for 2 h. The hygroscopic white powder, obtained in 20.3% yield (1.95 g), was soluble in water, MeOH, EtOH, and DMSO, sparingly soluble in CH_3CN, and insoluble in CH_2Cl_2, $CHCl_3$, and Et_2O.

Microanalysis: Calcd for $Na_5H_9[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]\cdot 7H_2O$ or $H_{25}Na_5P_4W_{30}Ti_2O_{119}$: H, 0.32; P, 1.59; W, 70.90; Ti, 1.23; O, 24.47; Na, 1.48%. Found: H, 0.27; P, 1.50; W, 70.50; Ti, 1.28; O, 24.0; Na, 1.50; total 99.05%. A weight loss of 6.70% was observed during the course of drying at room temperature under 10^{-3}–10^{-4} Torr overnight before the elemental analysis, suggesting the presence of 31–32 weakly solvated or adsorbed water molecules. TG/DTA under atmospheric conditions: a weight loss of 5.05% was observed at below 500 °C with endothermic points at 89.0, 112.3, 135.7, and 303.6 °C; calcd 5.04% for $x = 23$ in $Na_5H_9[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]\cdot xH_2O$. IR (KBr) (polyoxometalates region): 1224 (SO_4^{2-}), 1090s, 958vs, 920m, 847w, 773s, 690m, 528m cm^{-1}. ^{31}P NMR (22.9 °C, D_2O): δ −6.06, −12.8.

The final product was contaminated with SO_4^{2-} ions as shown in the IR spectrum. The number of water molecules (38) in the formula of **4** was determined as the sum of the water molecules (7) found in the elemental analyses and the water molecules (31–32) estimated from the weight losses observed during the course of drying before the analyses. However, the number of water molecules in **4** was not in agreement with that (23) observed by the TG/DTA measurements under atmospheric conditions; this can be attributed to the hygroscopic nature of **4**.

Preparations of $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$ (1). Method 1: Derivation from the precursor $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot 26H_2O$ (**2**) using the cation-exchange resin column [Amberlite IR120B NA].

The precursor **2** (3.0 g, 0.369 mmol) was dissolved in water (100 mL) in a water bath at above 90 °C. After being cooled to room temperature, the colorless clear solution was passed through a cation-exchange resin column (Amberlite IR120B NA, 100 mL) at a rate of 1.8 drops per second. Then, water (400 mL) was passed through the column. It was confirmed that the pH of the eluent became the same as that of water. The aqueous solution was evaporated to dryness on a rotary evaporator at 80 °C and dried in vacuo for 2 h. The yellow powder obtained in 82.7% yield (2.48 g) was highly soluble in water, soluble in acetone, MeOH, EtOH, and DMSO, sparingly soluble in CH_3CN and EtOAc, and insoluble in CH_2Cl_2, $CHCl_3$, and Et_2O. Compound **1**, which was very hygroscopic, was very sensitive to metalware, i.e., its color changed to blue when it was in contact with metalware.

Microanalysis; Calcd for $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 8H_2O$ or $H_{32}P_4W_{30}Ti_2O_{120}$: H, 0.39; P, 1.61; W, 71.93; Ti, 1.25; O, 24.81%. Found: H, 0.46; P, 1.59; W, 71.8; Ti, 1.35; O, 24.8; K, <0.1; total 100.00%. A weight loss of 5.1% was observed during the course of drying at room temperature under 10^{-3}–10^{-4} Torr overnight before the elemental analysis, suggesting the presence of 22–23 weakly solvated or adsorbed water molecules. TG/DTA under atmospheric conditions: a weight loss of 4.74% was observed at below 500 °C with endothermic points at 66.1, 91.9, 146.6, 204.5, and 288.7 °C; calcd 4.70% for $x = 21$ in $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot xH_2O$. IR (KBr) (polyoxometalates region): 1091s, 961vs, 919m, 773s br, 687m, 530m, 487w cm^{-1}. ^{31}P NMR (22.4 °C, D_2O): δ −6.41, −12.8. ^{183}W NMR (22.6 °C, D_2O): δ −113.0 (1W), −149.1 (2W), −176.3 (2W), −180.8 (2W), −186.5 (2W), −195.5 (2W), −196.3 (2W), −225.4 (2W). A scale-up synthesis was possible.

Pale yellow crystals were obtained by slow evaporation in a refrigerator overnight after concentrating the aqueous solution passed through the cation-exchange resin (100 mL) using 10 g of the precursor **2** in total 600 mL of water (initial 200 mL and then 400 mL) to ≈2 mL. The crystals were used for X-ray crystallography.

Method 2: Derivation by applying the ether-extraction method for the separately isolated, tetrameric precursor $K_{25}[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl]\cdot 55H_2O$ (**3**).

Precursor **3** (6.00 g, 0.338 mmol) was dissolved in aqueous solution (70 mL) with pH 2.0, which was adjusted with a 1 M aqueous HCl solution. To the colorless clear solution in an ice bath, concentrated sulfuric acid (20 mL, commercially available 95% sulfuric acid) was added. [Note: At this stage, when 12 M aqueous HCl was used instead of sulfuric acid, formation of an ether-adduct was not observed.] The pale yellow solution obtained was transferred to a separatory funnel, into which 200 mL of Et_2O was added. After vigorous shaking, the funnel was left to stand for 30 min to form three layers. The lowest layer of the pale yellow ether-adduct was taken out, and 20 mL of water was added to it. The pale yellow clear solution was concentrated to ca. 2 mL with a rotary evaporator at 50 °C. The solution was placed in a refrigerator at 4 °C overnight, during which time pale yellow crystals were formed. These crystals were, collected on a membrane filter (JG 0.2 µm) and dried in vacuo for 2 h. Highly water-soluble and hygroscopic pale yellow crystals were obtained with a 27.4% yield (1.48 g).

Microanalysis; Calcd for $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 8H_2O$ or $H_{32}P_4W_{30}Ti_2O_{120}$: H, 0.42; P, 1.61; W, 71.75; Ti, 1.25; O, 24.98%. Found: H, 0.37; P, 1.62; W, 71.6; Ti, 1.34; O, 25.0; K, 0.04; S, <0.2; Cl, <0.1; total 99.97%. A weight loss of 4.1% was observed during the course of drying at room temperature under 10^{-3}–10^{-4} Torr overnight before elemental analysis, suggesting the presence of 18–19 weakly solvated or adsorbed water molecules. In TG/DTA under atmospheric conditions, a weight loss of 5.62% was observed at below 500 °C with endothermic points at 61.5, 123.8, 134.8, 192.2, and 285.4 °C; calcd 5.64% for $x = 25$ in $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot xH_2O$. IR (KBr) (polyoxometalates region): 1091s, 963vs, 919s, 844s, 772s br, 685s, 531m, 426w cm^{-1}. ^{31}P NMR (26.0 °C, D_2O): δ −6.43, −12.8. ^{183}W NMR (24.2 °C, D_2O): δ −113.7 (1W), −148.1 (2W), −176.0 (2W), −181.4 (2W), −186.1 (2W), −195.6 (2W + 2W), −223.1 (2W).

Method 3: Derivation by applying an ether-extraction method for the in situ generated tetrameric precursor from $Na_{12}[P_2W_{15}O_{56}]\cdot 21H_2O$ and $Ti(SO_4)_2\cdot 4H_2O$.

A solution of $Ti(SO_4)_2 \cdot 4H_2O$ (2.2 g, 7.05 mmol) dissolved in water (20 mL) was diluted with more water (60 mL); then, 2.8 mL of 6 M aqueous HCl solution was added. $Na_{12}[P_2W_{15}O_{56}] \cdot 21H_2O$ (10.0 g, 2.29 mmol) was added to the solution over more than a 10 min period. The pale yellow clear solution obtained was stirred for 30 min, followed by the addition of 12 M aqueous HCl (80 mL). The solution was transferred to a separatory funnel, and Et_2O (300 mL) was added to it. After vigorous shaking, it was left to stand for 30 min. Three layers were formed. The pale yellow oil or ether-adduct in the lowest layer was collected and was dissolved in water (23 mL). The solution was concentrated to ca. 5 mL with a rotary evaporator at 50 °C. The concentrated solution was placed in a refrigerator at 4 °C for two days, during which pale yellow rod crystals were formed. These crystals were collected on a membrane filter (JG 0.2 µm) and dried in vacuo for 2 h. Highly water-soluble and hygroscopic pale yellow crystals were obtained with a 20.0% yield (1.85 g).

Microanalysis; Calcd for $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2] \cdot 2H_2O$ or $H_{20}P_4W_{30}Ti_2O_{114}$: H, 0.27; P, 1.63; W, 72.77; Ti, 1.26; O, 24.06%. Found: H, 0.36; P, 1.60; W, 69.2; Ti, 1.39; O, 24.6; Na, <0.05; total 97.2%. The observed value of the W analysis contained a larger range of error; however, this could be attributed to the experiments. In fact, the difference in the observed and calculated values for W is close to the difference (ca. 2.8%) in the sum of the observed values from the total 100%. A weight loss of 5.22% was observed during the course of drying at room temperature under 10^{-3}–10^{-4} Torr overnight before elemental analysis, suggesting the presence of 23–24 weakly solvated or adsorbed water molecules. TG/DTA under atmospheric conditions: a weight loss of 5.67% was observed at below 500 °C with endothermic points at 60.6, 67.8, 101.0, 112.4, 134.2, 193.3, and 284.0 °C; calcd 5.59% for $x = 25$ in $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2] \cdot xH_2O$. IR (KBr) (polyoxometalates region): 1091s, 960vs, 918s, 845s, 775s br, 684s, 532m, 421w cm^{-1}. ^{31}P NMR (25.1 °C, D_2O): δ −6.44, −12.8. ^{183}W NMR (22.6 °C, D_2O): δ −113.9 (1W), −148.3 (2W), −176.1 (2W), −181.6 (2W), −186.2 (2W), −195.6 (2W), −195.7 (2W), −223.3 (2W).

The ^{183}W NMR of the two compounds obtained by Methods 2 and 3 were consistent each other and were also consistent with the ^{183}W NMR of the compound obtained by Method 1. The pale yellow crystals obtained by Method 3 were also used for X-ray diffraction measurements. Structure analysis showed that the molecular structures of the compounds obtained by Methods 1 and 3 were essentially the same.

X-ray Crystallography. A pale yellow crystal of **1** obtained by Method 1 ($0.12 \times 0.06 \times 0.09\,mm^3$) was immersed in liquid paraffin (Paratone-N) to prevent its degradation. Data collection was performed on a Bruker SMART APEX CCD diffractometer at 90 K in the range of $2.28 < \theta < 28.28°$. The intensity data were automatically corrected for Lorentz and polarization effects during integration. The structure was solved by direct methods (program SHELXS-97),[10a] followed by subsequent difference Fourier calculation and refinement by the full-matrix, least-square procedure on F^2 (program SHELXL-97).[10b] Absorption correction was performed using SADABS (empirical absorption correction).[10c] The site occupancy factor of the oxygen atoms as cystallization waters was fixed to 0.5 for O15–O17 and 1 for the other oxygen atoms.

Crystal data for $H_{78}O_{143}P_4Ti_2W_{30}$; $M_r = 8101.80$, triclinic, space group $P\bar{1}$, $a = 12.0234(7)$, $b = 14.8118(8)$, $c = 16.9639(10)$ Å, $\alpha = 92.6520(10)$, $\beta = 103.3060(10)$, $\gamma = 95.6820(10)°$, $V = 2918.1(3)$ Å^3, $Z = 1$, $D_{calcd} = 4.610\,Mg\,m^{-3}$, $\mu(Mo\,K\alpha) = 29.748\,mm^{-1}$. $R1 = 0.0618$, $wR2 = 0.1482$ (for all data). $R_{int} = 0.1221$, $R1 = 0.0506$, $wR2 = 0.1341$, GOF = 1.017 (38248 total reflections, 14445 unique reflections where $I > 2\sigma(I)$). The maximum and minimum residual density (6.260 and −4.882 eÅ^{-3}) were located at 0.81 Å from W14 and 0.80 Å from W12, respectively.

The final cycle of refinement, including the atomic coordinates and anisotropic thermal parameters (all atoms) converged at $R = 0.0618$ and $R_w = 0.1482$. No hydrogen atoms were included in the refinement. Fifteen tungsten atoms, one titanium atom, and two P atoms were clearly identified. Thus, the main features of the molecular structure of the polyoxoanion were clarified. However, it is frequently impossible in POM chemistry due to the disorder to locate and assign all the water molecules of crystallization unequivocally by single crystal XRD. These features are all too commonly in polyoxoanion crystallography.

Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666); e-mail crysdata@fiz-karlsruhe.de), on quoting the depository numbers. CSD-417649 (formula/code: hmu111) for **1**.

Results and Discussion

Synthesis and Compositional Characterization. The novel POM-based solid protonic acid $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2] \cdot 31H_2O$ (**1**) was synthesized by three different methods (Fig. 1): (1) a cation-exchange column method using the separately prepared precursor $K_{14}H_2[Ti_2\{P_2W_{15}O_{56}\}_2] \cdot 26H_2O$ (**2**), which was unequivocally characterized by using a complete elemental analysis, TG/DTA, FT-IR, and ^{31}P and ^{183}W NMR spectroscopy (see Experimental Section); (2) a traditional ether-extraction method using the separately prepared precursor, i.e., the tetrameric Dawson POM $K_{25}[\{P_2W_{15}Ti_3O_{57.5}(OH)_3\}_4Cl] \cdot 55H_2O$ (**3**); (3) an ether-extraction method applied for the in situ generated tetrameric Dawson POM derived from $Na_{12}[P_2W_{15}O_{56}] \cdot 21H_2O$ and $Ti(SO_4)_2 \cdot 4H_2O$. Complete elemental analysis, TG/DTA, FT-IR, and ^{31}P and ^{183}W NMR showed that essentially the same compound was obtained from all the methods. Method 1 was superior to Methods 2 and 3 with regard to the synthetic yields and molecular design. Compound **1** was obtained by Method 1 in 82.7% yield (2.48 g), whereas the yields obtained by Methods 2 and 3 were 27.4% (1.48 g) and 20.0% (1.85 g), respectively. The molecular structure of the final product obtained by Method 1 corresponded to that of the precursor, whereas from Methods 2 and 3, the two structures were different.

The composition and molecular formula of the crystalline sample of **1** obtained by Method 1 were consistent with the complete elemental analysis, TG/DTA, FT-IR, (^{31}P, ^{183}W) NMR spectroscopy, X-ray crystallography, and potentiometric titration. In the complete elemental analysis performed on a sample that was dried at room temperature under 10^{-3}–10^{-4} Torr overnight before analysis, all elements including oxygen, (total 100.0% for **1**) were observed, the data of which were consistent with the composition of $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2] \cdot 8H_2O$. It was also confirmed that there was no contamination by potassium from precursor **2**. The weight loss observed during the course of drying before the analysis was 5.1%, which corresponded to 22–23 weakly solvated or adsorbed water molecules. On the other hand, the TG/DTA measurements under atmospheric conditions showed a weight

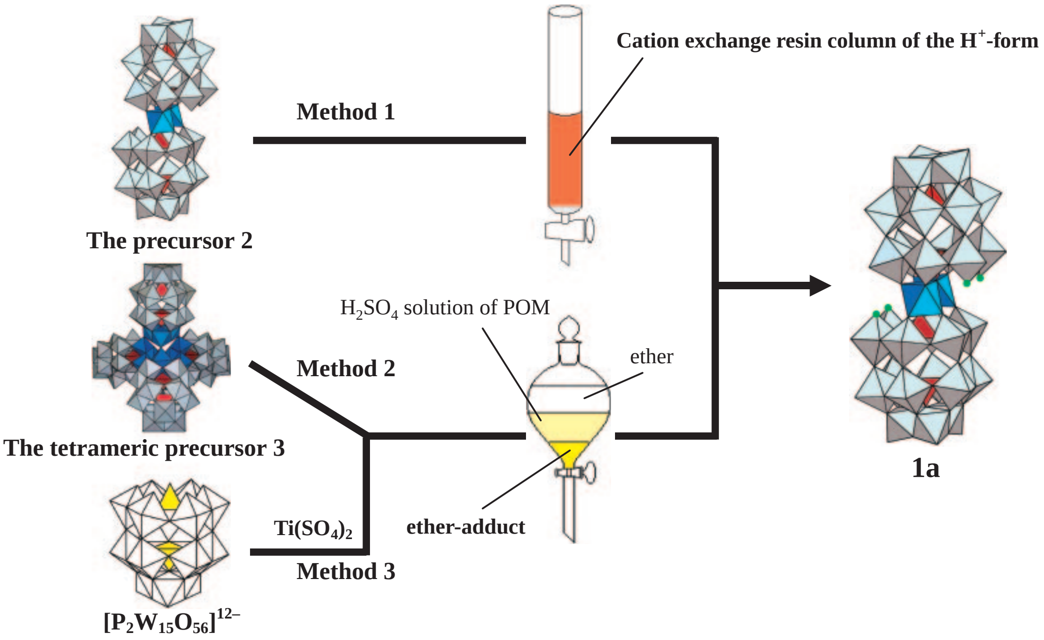


Fig. 1. Scheme of the three methods for synthesis of **1a**.

loss of 4.74% at 427.1 °C with endothermic peaks at 66.8, 91.3, 146.6, 203.9, and 288.1 °C due to the dehydration of 20–21 water molecules. The number of water molecules (31) in the formula of **1** was determined as the sum of the water molecules (8) found in the complete elemental analysis and the water molecules (22–23) estimated from the weight losses observed during the course of drying before the analysis. However, the number of water molecules in **1** was not in agreement with that (20–21) obtained from the TG/DTA measurements under atmospheric conditions; this is attributed to the highly hygroscopic nature of **1**. Thus, the presence of 31 hydrated water molecules in the formula of **1** is based on the elemental analysis.

The solid FT-IR spectrum (Fig. S1) of **1**, measured in a KBr disk, showed the bands at 1090, 1020, 956, 925, 848, 768, 530, and 486 cm^{-1} due to the characteristic vibrational bands of the sandwich complex of the Dawson POM framework.[7] These spectra can be compared to those of **2** and **4**.

Potentiometric titration with *n*-butylamine in CH_3CN[8] was carried out for compounds **1**, **2**, and **4** having different numbers of free protons in order to determine experimentally the effective number of the free protons. From titration curves compound **1** had eight effective free protons, compound **2** had two free protons, and compound **4** had nine free protons (Fig. 2). These results are consistent with the overall formulas of these compounds inclusive of counter ions based on the complete elemental analysis, i.e., H_8[**1a**]·$31H_2O$ (**1**), $K_{14}H_2$[**2a**]·$26H_2O$ (**2**), and Na_5H_9[**4a**]·$38H_2O$ (**4**). Therefore, the molecular formulas such as $[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]^{8-}$ (**1a**), $[Ti_2(P_2W_{15}O_{56})_2]^{16-}$ (**2a**), and $[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]^{14-}$ (**4a**) are rationalized. The partially protonated species **4a** obtained as a sodium salt in this study may be similar to $(NH_4)_{14}[TiP_2W_{15}O_{55}OH]_2$, as recently reported by the Kortz's group, although the reported ^{31}P NMR values in both studies are not be in agreement (see "^{31}P and ^{183}W NMR and Solution Structure" in Results and Discussion).[6b] The titration curve of **1** also showed a constant value until three protons were consumed, indicating that there were at least two types free protons. The three protons would be readily dissociated, i.e., such protons would actually act as a stronger acid, but the remaining five protons would act as weaker acids. The results of potentiometric titration and full elemental analysis are consistent with the results of bond valence sum (BVS) calculation (see the Molecular Structure), showing that four terminal oxygen atoms at the two lacunary sites of the sandwich structure are completely protonated, i.e., all of the terminal oxygen atoms in the lacunary site of **1a** are doubly protonated in solution and in the solid state.

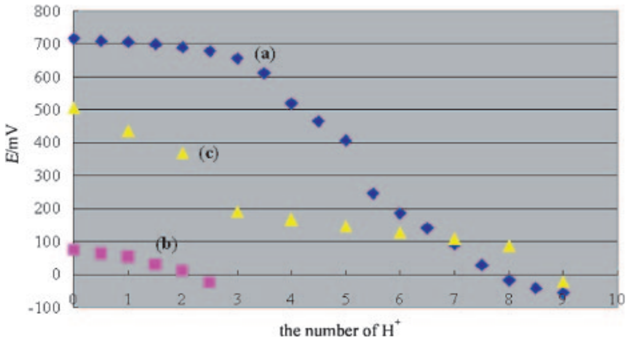
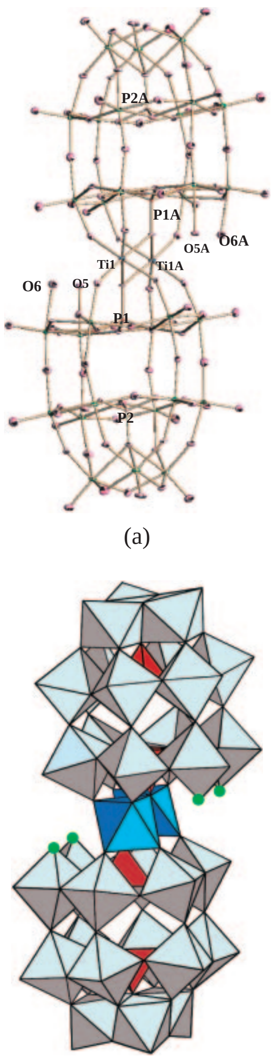


Fig. 2. Potentiometric titration with *n*-butylamine carried out in CH_3CN for (a) $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot31H_2O$ (**1**) (blue), (b) $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot26H_2O$ (**2**) (pink), and (c) $Na_5H_9[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]\cdot38H_2O$ (**4**) (yellow).

Molecular Structure. The crystal system (triclinic), the space group ($P\bar{1}$), and a disorder-free POM unit provided a straightforward solution of the structure as well as a refinement of the solution. The crystal of **1** contained discrete polyoxoanion and lattice water molecules, all located at general positions in this space group. The present polyoxoanion is located on the inversion center.



(a)

(b)

Fig. 3. (a) Molecular structure of **1a** with 50% probability ellipsoids and (b) its polyhedral representation consisting of the two central TiO_6 octahedra (blue), thirty WO_6 octahedra (pale blue), and four internal PO_4 tetrahedra (red). Potential sites of protonation in the lacunary sites are shown with small green circles.

Table 1. Comparison of M–O Bond Distances (Å) in the Lacunary Sites and BVS (Bond Valence Sum) Values of the Relating Oxygen Atoms, between the Free-Acid Form **1** and the NH_4 Salt Reported by Kortz's Group[a)]

$H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$ (**1**)		$(NH_4)_{14}[P_2W_{15}O_{55}Ti(OH)]_2\cdot nH_2O$[b)]	
The terminal oxygen			
W(5)–O(5)	2.238(9)	W(14)–O(14A)	1.770(14)
W(6)–O(6)	2.185(9)	W(15)–O(15A)	2.151(14)
The oxygen bounded to Ti atom			
W(1)–O(1)	1.910(9)	W(10)–O(10A)	1.850(13)
W(2)–O(2)	1.850(8)	W(11)–O(11A)	1.823(12)
W(3)–O(3)	1.832(9)	W(12)–O(12A)	1.825(12)
W(4)–O(4)	1.874(9)	W(13)–O(13A)	1.936(13)
The oxygen bounded to W atom			
Ti(1)–O(1)	1.811(9)	Ti(1)–O(10A)	1.867(13)
Ti(1)–O(2)	1.915(9)	Ti(1)–O(11A)	1.927(12)
Ti(1)–O(3A)	1.939(9)	Ti(1)–O(12A)	1.937(12)
Ti(1)–O(4A)	1.822(9)	Ti(1)–O(13A)	1.788(13)
The oxygen bounded to P atom			
Ti(1)–O(7)	2.148(9)	Ti(1)–O(4P2)	2.192(12)
Ti(1)–O(7A)	2.173(9)	Ti(1)–O(4P2)	2.116(12)

BVS (bond valence sum) values

$H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$ (**1**)		$(NH_4)_{14}[P_2W_{15}O_{55}Ti(OH)]_2\cdot nH_2O$[b)]	
O5	0.420	O14A	1.488
O6	0.485	O15A	0.531
O1	2.030	O10A	2.068
O2	1.962	O11A	2.028
O3	1.973	O12A	2.001
O4	2.104	O13A	2.026
O7	1.919	O4P2	1.897

a) Although the numbering of atoms is different between the two compounds, the bond distances are arranged in order to correspond to each other, as well as the oxygen atoms. b) Ref. 6b.

The molecular structure of **1a** is shown in Fig. 3a, and its polyhedral representation is depicted in Fig. 3b, where the potential protonation sites are shown. Selected bond distances (Å) and angles (°) around the titanium(IV) centers for the Dawson POM unit in **1a** (Table S1) and average bond distances (Å) and angles (°) [range] for the Dawson POM unit (Table S2) are given in the Supporting Information.

The structure analysis showed that **1a** was composed of two trivacant Dawson POMs $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$ (abbreviated $\{P_2W_{15}\}$) linked through two octahedral titanium(IV) centers. Compound **1a** is a di-lacunary species of the saturated sandwich complex of POMs, $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{n-}$ (M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, etc.), in which a sheet of four edge-shared octahedral M units is sandwiched between two $\{P_2W_{15}\}$ subunits.[7] The sandwich complexes are characterized by three types of junctions ($\alpha\alpha$-, $\beta\beta$-, and $\alpha\beta$-) between the two trivacant Dawson units through the metallic center sheet.[7] The junction in **1a** is of the $\alpha\alpha$-type in contrast to the $\beta\beta$-type observed in most saturated sandwich complexes[7a] and the $\alpha\beta$-type observed in rare examples.[7b] The molecular structure of **1a**, including the $\alpha\alpha$-type junction, is essentially the same as that of the polyoxoanion $[P_2W_{15}O_{55}Ti(OH)]_2{}^{14-}$ obtained as the $(NH_4)_{14}$ salt, recently reported by Kortz et al.[6b] The junction is also similar to that of the diiron species $[Na_2(H_2O)_2Fe_2(P_2W_{15}O_{56})_2]^{16-}$ reported by Hill et al.[7c,d] However, the difference between **1a** and the $(NH_4)_{14}$ salt was found in the effect of protonation (Table 1).

From Table 1, only the W–O(terminal) distances between these two POMs are significantly different, whereas other metal–oxygen distances are not. The W–O(terminal) distances in **1** (W(5)–O(5), W(6)–O(6)) are longer than those (W(14)–O(14A), W(15)–O(15A) of the NH_4 salt; the differences are attributed to the effect of the protonation on the terminal oxygen atoms in the lacunary sites. The BVS (bond valence sum) values[11] of such oxygen atoms, which were calculated based on the observed bond distances for **1a**, support that **1** is completely protonated in the solid state, i.e., both the O(5) (0.420) and O(6) (0.485) atoms in **1** are doubly protonated, but not singly protonated (≈1 is expected for the OH group).[12]

On the other hand, in the NH_4 salt,[6b] the corresponding oxygen atoms (O(14A) and O(15A)) have been questionably assigned: O(14A) (1.488) is thought to be unprotonated and O(15A) (0.531) is thought to be singly protonated atom. Thus, not only the actual bond distances between the two POMs but also the interpretation of BVS values are different.

Although the exact group of the polyoxoanion is C_i, because of the space group $P\bar{1}$, it has approximate C_{2h} symmetry resulting from the complete protonation of the terminal oxygen atoms. On the other hand, the NH_4 salt would be C_i symmetry, because of incomplete protonation, i.e., the protonation of only one oxygen atom.

The BVS values of other elements in **1a** reasonably corresponded to the formal valences of Ti^{4+}, W^{6+}, and P^{5+} (Table S3).

The eight protons, which are the counter ions in **1** in the solid state and can not be detected by X-ray crystallography, should be located on the crystallization waters, just as known in traditional heteropolyacids, such as H_3PW_{12} and $H_6P_2W_{18}$.[5]

pH-Varied ^{31}P NMR of $K_{14}H_2[Ti_2\{P_2W_{15}O_{56}\}_2]\cdot 26H_2O$ (2). Compound **2** (0.5 g) was dissolved in 20 mL of H_2O in a water bath at more than 90 °C. After the colorless clear solution was cooled to room temperature, the pH and ^{31}P NMR of the solution were measured. In the ^{31}P NMR spectrum, peaks were observed at δ −5.87, −13.4. Furthermore, solutions with different pH values were prepared by adding drops of 1 M aqueous HCl solution; their ^{31}P NMR data are listed in Table 2.

The pH-varied ^{31}P NMR of **2** in water shows that the degree of protonation of the oxygen atoms at the lacunary sites significantly affects the ^{31}P NMR chemical shift. These data can be compared with the data of ^{31}P NMR in D_2O obtained for the isolated samples considered as the non-protonated species **2**, the partially protonated species **4**, and the completely protonated species **1**.

^{31}P and ^{183}W NMR and Solution Structure. The ^{31}P NMR spectra in D_2O of **1**, **2**, and **4** showed clean two-line spectra based on the Dawson unit (Fig. 4 and Table 3), in which the downfield resonance was assigned to the phosphorus closest to the Ti site and the upfield resonance was assigned to the phosphorus closer W_3 cap. These spectra demonstrate the purity and single product nature of these compounds. It should be noted that the chemical shifts in the downfield signals are remarkably different and dependent upon the compounds.

Table 2. pH-Varied ^{31}P NMR of **2** in H_2O

pH	^{31}P chemical shift/ppm	
3.84	−5.87	−13.40
2.00	−6.08	−13.10
0.77	−6.39	−13.00
0.50	−6.45	−12.90

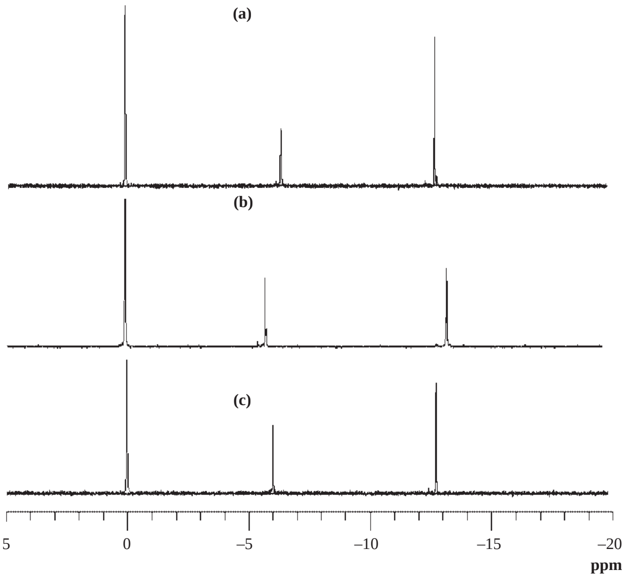


Fig. 4. ^{31}P NMR spectra in D_2O of (a) $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot 31H_2O$ (**1**), (b) $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot 26H_2O$ (**2**), and (c) $Na_5H_9[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]\cdot 38H_2O$ (**4**).

Table 3. ^{31}P NMR in D_2O of **1**, **2**, and **4**

Polyoxometalates	Chemical shift/ppm
$H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)\}_2]\cdot 31H_2O$ (**1**)	−6.41, −12.8
$K_{14}H_2[Ti_2\{P_2W_{15}O_{56}\}_2]\cdot 26H_2O$ (**2**)	−5.84, −13.4
$Na_5H_9[Ti_2\{P_2W_{15}O_{55}(OH)\}_2]\cdot 38H_2O$ (**4**)	−6.06, −12.8

These results are attributed to the different degree of protonation at the lacunary sites of the sandwich complexes. In fact, compound **2** showed the pH-dependent ^{31}P NMR chemical shift (Table 2): the downfield signals shifted to a higher field as the pH was lowered. The ^{31}P NMR of **2** at pH 2.00 was very similar to those of **4**, and the ^{31}P NMR of **2** at pH 0.50 was very similar to that of **1**. Thus, the ^{31}P NMR signals of **2** at pH 3.84, 2.00, and 0.50 can be assigned to those of the non-protonated POM **2a** (C_{2h} symmetry), the partially protonated POM **4a** (C_i symmetry), and those of the fully protonated POM **1a** (C_{2h} symmetry), respectively.

Here, it should be noted that the ^{31}P NMR data (δ −10.5, −13.3)[6b] of the di-lacunary Dawson sandwich complex, $(NH_4)_{14}[P_2W_{15}O_{55}Ti(OH)]_2\cdot nH_2O$, reported by Kortz's group are different from the ^{31}P NMR of **4** and the pH-varied ^{31}P NMR of **2**. In particular, the downfield resonance is significantly different. The reported chemical shifts (δ −10.5, −13.3) are attributed not to $[P_2W_{15}O_{55}Ti(OH)]_2^{14-}$ (see Table 2), but to the monomeric mono-Ti^{IV}-subsutituted Dawson POM, $[P_2W_{17}O_{61}Ti(OH)]^{7-}$ or its Ti–O–Ti bonding dimeric species.[13] It is likely that the sample used for the X-ray structure determination of $[P_2W_{15}O_{55}Ti(OH)]_2^{14-}$ is not representative of the bulk sample used for the ^{31}P NMR measurements.

An ^{183}W NMR spectrum (Fig. 5) of **1** measured in D_2O showed an eight-line spectrum at −113.0 (1W), −149.1 (2W), −176.3 (2W), −180.8 (2W), −186.5 (2W), −195.5 (2W), −196.3 (2W), and −225.4 (2W) ppm. This NMR spectrum, consistent with the C_{2h} symmetry compound, indicates that

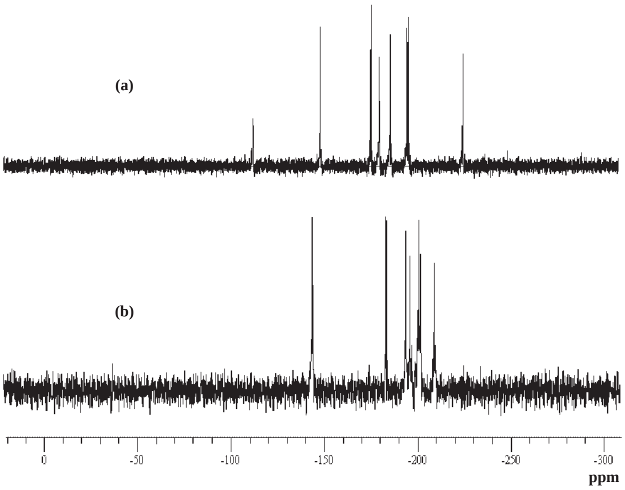


Fig. 5. ^{183}W NMR spectra in D_2O of (a) $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]\cdot31H_2O$ (**1**) and (b) $K_{14}H_2[Ti_2(P_2W_{15}O_{56})_2]\cdot26H_2O$ (**2**).

the solid-state structure of **1** is maintained in solution. The ^{183}W NMR of precursor **2** in D_2O also showed an actual eight-line spectrum at -144.2 (1W + 2W), -183.7 (2W), -194.2 (2W), -196.7 (2W), -201.1 (2W), -202.1 (2W), and -209.4 (2W) ppm. The different chemical shifts from **1** may be attributed to the lacunary sites in **2**, being unprotonated.

Acidity Measurements. In CH_3CN solution, the Hammett indicator, 1,9-diphenyl-1,3,6,8-nonatetraen-5-one (dicinnamalacetone: $pK_a = -3.0$ for the protonated indicator), showed a color change from yellow to red in the presence of **1**, suggesting that the pK_a of **1** is less than -3.0. The Hammett acidity constant H_0 in CH_3CN of **1** (-2.72) was almost the same as that (-2.77) evaluated for homo-Dawson heteropolyacid $H_6[P_2W_{18}O_{62}]\cdot17H_2O$ in CH_3CN.

The stronger acidity of the free-acid form of POM is based on the encapsulated structure of the oxoanions of heteroatom X, in which the protons, considered as counter cations, are separated from the central $XO_4{}^{n-}$ moiety through the $W_{12}O_{36}$ and $W_{18}O_{54}$ shells with zero electric charge, as expressed with $[PW_{12}O_{40}]^{3-} = [(PO_4{}^{3-})(W_{12}O_{36}{}^0)]^{3-}$, $[SiW_{12}O_{40}]^{4-} = [(SiO_4{}^{4-})(W_{12}O_{36}{}^0)]^{4-}$, and $[P_2W_{18}O_{62}]^{6-} = [(PO_4{}^{3-})_2(W_{18}O_{54}{}^0)]^{6-}$.[1c] Therefore, the protons are less influenced by the electronegativity of hetroatoms, such as P and Si, and they are substantially different from those of oxoacids, such as H_2SO_4, HNO_3, H_3PO_4, and so on. Thus, the present results suggest that the surface basicity of **1a** is almost the same as that of $[P_2W_{18}O_{62}]^{6-}$.

Conclusion

The free-acid form of the di-lacunary species of the Dawson POM-based sandwich complex, i.e., a novel solid-state protonic (8H^+) acid, $H_8[\mathbf{1a}]\cdot31H_2O$ **1**, in which **1a** = $[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]^{8-}$, was synthesized by using three different methods, and the molecular structure of **1a** was determined. The molecular structure was essentially the same as that of the ammonium salt recently reported by Kortz's group.[6b] However, the protonation of the terminal oxygen atoms in the lacunary sites was significantly different. The degree of protonation at the lacunary sites in the sandwich complex anion was determined by performing pH-varied ^{31}P NMR measurements using $[Ti_2(P_2W_{15}O_{56})_2]^{16-}$ **2a**. As a matter of fact, the non-protonated species **2**, the partially protonated species **4**, and the fully protonated species **1** were also isolated as solid compounds in this work. Hammett indicator experiments showed that the acidity of **1** in CH_3CN was almost the same as that of the free acid of homo-Dawson POM $[P_2W_{18}O_{62}]^{6-}$. Among the titanium(IV)-substituted Dawson POMs, the present di-lacunary species of the Dawson-type sandwich complexes and the tetrameric Ti–O–Ti anhydride species of tri-titanium(IV)-substituted POMs[6] were observed to have remarkably stable forms. In future, acid catalysis by **1** will be reported.

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Supporting Information

Files on X-ray crystallograpy in CIF format, selected bond distances (Å) and angles (°) around the titanium(IV) centers for the Dawson POM unit in **1a** (Table S1), average bond distances (Å) and angles (°) [range] for the Dawson POM unit (Table S2), bond valence sum (BVS) calculations (Table S3), and FT-IR spectra of **1**, **2**, and **4** (Fig. S1). This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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