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Synthesis and Characterization of Water-Soluble, All-Inorganic Composition, Dawson-Type Trisubstituted Heteropolytungstates. Effect of Alkali Metal Countercations (Li, Na, K, and Cs) on the $P_2W_{15}Nb_3O_{62}^{9-}$ Polyoxoanion

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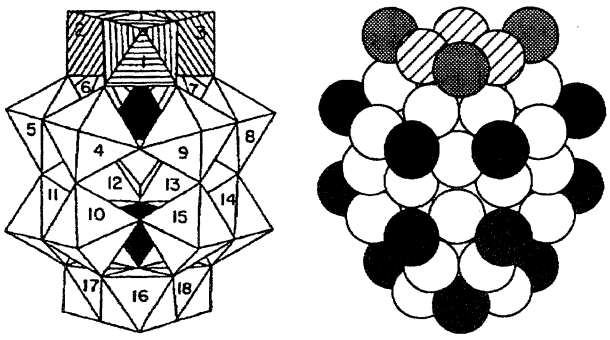
The water-soluble form of the Dawson-type trisubstituted tungstoheteropolyanion, B-α-$P_2W_{15}Nb_3O_{62}^{9-}$, was synthesized as its nona alkali-metal salts of Li, K, and Cs. Analytically pure compounds, obtained as homogeneous colorless solids, had nonahydrate for the nonalithium (Li_9) salt, tetrahydrate for the nonasodium (Na_9) salt, trihydrate for the nonapotassium (K_9) salt and trihydrate for the nonacaesium (Cs_9) salt, respectively, after each was dried overnight at room temperature under 10^{-3}—10^{-4} Torr. TG/DTA analyses show that they can be made with 25 water for the Li_9 salt, 23 water for the Na_9 salt, 9 water for the K_9 salt, and 8 water for the Cs_9 salt under atmospheric conditions. A compositional characterization was accomplished by complete elemental analyses and TG/DTA, and structural characterization was achieved by a combination of FT-IR and variable-temperature solid-state ^{31}P NMR and by both ^{31}P and ^{183}W NMR measurements at room temperature in D_2O and DMSO-d_6 solutions. The amount of hydrated waters, solubility in solvents and ease of crystallization were significantly influenced by the alkali-metal countercations. These cation-dependent properties are useful for selecting polyoxoanion precursor favorable to the crystallization of $P_2W_{15}Nb_3O_{62}^{9-}$-supported organometallic complexes. The effects of the cations (Li, K, Na, and Cs) on the $P_2W_{15}Nb_3O_{62}^{9-}$ were observed as different hydrated structures of the polyoxoanion and its cation-dependent thermal stability in the solid state by a combination of TG/DTA and FT-IR measurements, and also as a spectral change of the downfiled ^{31}P signal due to interactions of the polyoxoanion with the countercations and/or with hydrated waters by variable-temperature (VT) solid-state GHD/MAS ^{31}P NMR spectroscopy.

Polyoxoanions are molecular metal-oxide clusters which resemble discrete fragments of solid metal oxides. Recently, we reported on the synthesis of the nonasodium salt of Dawson-type triniobium-substituted polyoxoanion B-α-$P_2W_{15}Nb_3O_{62}^{9-}$.[1a] That work was aimed at providing a water-soluble form of the important $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion (Fig. 1); prior to that work, the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion had been available only as its organic solvent-soluble, but water-insoluble, nonakis (TBA) salt (TBA = $[(n\text{-}C_4H_9)_4N]$).[1b] Hence, the nonasodium salt of $P_2W_{15}Nb_3O_{62}^{9-}$ extended the well-documented organometallic chemistry of $P_2W_{15}Nb_3O_{62}^{9-}$ into aqueous media.[1a]

In a separate account, full details concerning the synthesis and isolation of a polyoxoanion-supported organometallic complex $[\{(\eta^5\text{-}C_5Me_5)Rh\}(P_2W_{15}Nb_3O_{62})]^{7-}$ as its heptakis (TBA) salt were reported.[1b,1d] In this compound, the organometallic moiety, $[(\eta^5\text{-}C_5Me_5)Rh]^{2+}$, is bonded to three bridging Nb_2O oxygens that cap the $P_2W_{15}Nb_3O_{62}^{9-}$ Dawson-type polyoxoanions, as shown by a single-crystal X-ray diffraction analysis for its mixed $(TBA)_6Na$ salt.[1d] Nevertheless, there exists a crystallization problem in the $P_2W_{15}Nb_3O_{62}^{9-}$-supported organometallic complexes, e.g., the $(TBA)_7$ salt; even the mixed $(TBA)_{7-x}Na_x$ salts of the supported $(C_5Me_5)Rh^{2+}$ complex, soluble in organic solvents (e.g., CH_3CN, DMSO, and acetone) and insoluble in water, are hard to crystallize.

Very recently, it was realized that by using the nonasodium salt of $P_2W_{15}Nb_3O_{62}^{9-}$ the concept of water solubility and all-inorganic composition could be extended to $[\{(\eta^5\text{-}C_5Me_5)Rh\}(P_2W_{15}Nb_3O_{62})]^{7-}$.[1e] The nonasodium salt of $P_2W_{15}Nb_3O_{62}^{9-}$ and the heptasodium salt of $[\{(\eta^5\text{-}C_5Me_5)Rh\}(P_2W_{15}Nb_3O_{62})]^{7-}$ have never been derived by direct cation-metathesis from their TBA salts, but have been obtained by their own synthetic routes.[1a,1e] Also, as previously shown in heterogeneous catalysts using classical Keggin-type heteropolyanions, the amount of solvated water, and therefore the porosity, thermal stability and surface area, can be controlled by the use of different countercations.[2]

A clarification of the cation-dependent properties of the



(a) (b)

Fig. 1. (a) Polyhedral and (b) space-filling representation of the Dawson-type heteropolyanion α-1,2,3-$P_2W_{15}Nb_3O_{62}^{9-}$. In (a) the three niobiums are represented by hatched octahedra in the 1—3 positions. The WO_6 octahedra occupy the 4—18 positions and two PO_4 groups are shown as the internal, black tetrahedron. In (b) the open circles represent bridging tungsten oxygens (W_2O), while the black circles represent terminal tungsten oxygens (WO). Niobium bridging oxygens (Nb_2O) are depicted by hatched circles, whereas niobium terminal oxygens (NbO) are shown as gray circles. From the space-filling representation it becomes clear that heteropolyoxoanions are composed of a close-packed array of oxygens, and this representation, in turn, reveals their potential as a soluble metal oxide analog.

polyoxoanion helps to overcome the crystallization problem of the $P_2W_{15}Nb_3O_{62}^{9-}$-supported organometallic complexes, and also to design novel types of solid-base heterogeneous catalysts.[2,3] Furthermore, *the synthetic procedure described herein provides a general route to cation metathesis of polyoxoanion-supported complexes.*[1e,4]

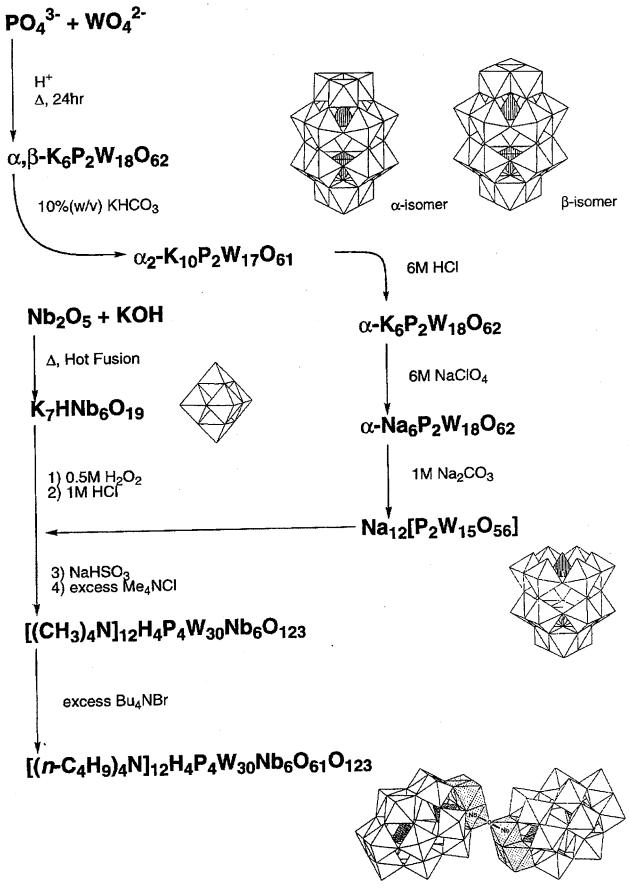
Herein we provide full details concerning the synthesis and isolation of the alkali metal salts of $P_2W_{15}Nb_3O_{62}^{9-}$ as its Li salt with 25 water (**2**), as its K salt with 9 water (**1**) and as its Cs salt with 8 water (**3**) under atmospheric conditions. We also give the characteristics of the polyoxoanion with these alkali metal salts, including the previously prepared Na salt (**4**). Also reported are the compositional characterization by full elemental analyses, thermogravimetric and differential thermal analyses (TG/DTA), and structural characterization by FT-IR and variable-temperature solid-state ^{31}P NMR as well as by solution ^{31}P and ^{183}W NMR spectroscopies at room temperature. The effects of alkali-metal countercations on the thermal stability of $P_2W_{15}Nb_3O_{62}^{9-}$ were observed in the solid state by a combination of TG/DTA and FT-IR measurements; also observed was a change in the ^{31}P signal in the PO_4 moiety closer to the Nb_3O_6 site in the Dawson structure by using variable-temperature (VT) solid-state ^{31}P NMR spectroscopy.

Experimental

General Conditions. The following were used as received: $LiClO_4$, KBF_4, 0.5 M LiOH (aq), 0.5 M KOH (aq), CsOH, EtOAc, CH_3CN, $(CH_3)_2CO$, $(CH_3)_2SO$ (all from Wako) (1 M=1 mol dm^{-3}); $LiBF_4$, DMSO-d_6 (Aldrich), and D_2O (Merck). Solid $CsBF_4$ was prepared in analogy with the synthesis of KBF_4 reported in the literature.[5,6] $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ was prepared as previously described,[1c,1d] via the 7 steps shown in Scheme 1.

Instrumentation and Analytical Procedures. Elemental analyses on samples dried overnight at room temperature under 10^{-3}—10^{-4} Torr (1 Torr = 133.322 Pa) were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out using a Seiko SSC 5000 TG/DTA 300 system and a Rigaku TG 8101D and TAS 300 data-processing system. TG/DTA measurements were run under air with a temperature ramp of 5 °C min^{-1} between 20 and 550 °C.[7]

Solution ^{31}P NMR (161.70 MHz) spectra were recorded at 22 °C in 5 mm o.d. tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data-processing system, and were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts were reported as negative for resonances upfield of H_3PO_4 ($\delta = 0$). Solution ^{183}W NMR (16.50 MHz) spectra were recorded at 22 °C in 10 mm o.d. 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. These spectra were referenced to an external standard of saturated Na_2WO_4–D_2O solution by the substitution method. Chemical shifts were reported on the δ scale with resonances upfield of Na_2WO_4 ($\delta = 0$) as negative.



Scheme 1. Preparation of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$.

Solid-state ^{31}P NMR spectra were measured over a wide range of temperatures by high-resolution solid state NMR. Variable-temperature (VT) ^{31}P high-power proton decoupling (GHD)/magic angle spinning (MAS) NMR spectra were recorded over the temperature range 24 to 140 °C using a JEOL EX 270 spectrometer equipped with a VT GHD/MAS accessory operating at 109.25 MHz. The single 90° pulse (4.0 μs) in combination with GHD without cross-polarization was used to generate the spectra. A silicon nitride ceramic cylindrical-type rotor was used. Line narrowing was achieved by high-order decoupling and magic angle spinning. The spinning rate was set to about 6 kHz. A variable-temperature (VT) controller was used for all of the probe temperatures at which measurements were taken. The spectral width and data points were 54.3 kHz and 8 k, respectively. The spectra were usually accumulated 600—2000 times at a repetition time of 5 s to achieve a reasonable signal-to-noise ratio. The ^{31}P NMR chemical shifts were calibrated indirectly through external $(NH_4)_2HPO_4$ [1.6 ppm relative to H_3PO_4 ($\delta = 0$)]. The experimental errors of the isotropic ^{31}P chemical shift values are estimated to be about 0.5 ppm. Spinning side bands did not appear due to a sufficient spinning rate.

Synthesis of $K_9P_2W_{15}Nb_3O_{62}\cdot 9H_2O$ (1). The present preparation is based on a major modification of the previously reported synthesis of $Na_9P_2W_{15}Nb_3O_{62}\cdot 23H_2O$ **4**[1a] by using KBF_4 and a 0.5 M aqueous KOH solution instead of $NaBF_4$ and a 0.5 M aqueous NaOH solution. The target compound was formed by a stoichiometric reaction in an aqueous/CH_3CN system, and isolated by crystallization from a solution of unbuffered pH 8 water.

In a 300 mL beaker were placed 5.00 g (0.451 mmol) of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ and 50 mL of CH_3CN. Warming the mixture to 50—60 °C and stirring resulted in a clear, pale-yellow solution. While the solution temperature was maintained at 50—60 °C, solid KBF_4 (0.681 g, 5.412 mmol, 12 equiv) was added, followed by stirring for 30 min, during which time all of the KBF_4 remained undissolved. To this warm suspension, the dropwise addition of 5.41 mL (2.71 mmol, 6 equiv) of a 0.5 M aqueous KOH solution resulted in the formation of a cloudy suspension containing white precipitates. After the addition of the base was completed, stirring was continued for an additional 20 min. (Separation of $K_9P_2W_{15}Nb_3O_{62}$ and $[(n\text{-}C_4H_9)_4N]BF_4$ from their mixture was accomplished by reprecipitation with CH_3CN. $[(n\text{-}C_4H_9)_4N]BF_4$ is soluble in CH_3CN, whereas the nonapotassium salt of heteropolyanion is not.) By the addition of 50 mL of CH_3CN to the reaction mixture, followed by stirring for 20 min in an ice-cooled bath, white precipitates were produced, which were collected on a medium glass frit, washed with CH_3CN (20 ml×3), then with 500 mL of ethyl acetate (unreacted KBF_4 is dissolved in a large excess of ethyl acetate), finally with ether (40 mL×2), and dried overnight in a 55 °C oven. Next, this crude precipitate was added to ca. 50 mL of unbuffered pH 8 water (the pH was adjusted with a diluted KOH aqueous solution) and redissolved by warming to 60 °C. The warm, cloudy solution was filtered through folded filter paper (Whatman No. 5), and the clear filtrate was rotary evaporated at 60 °C until it became slightly cloudy. This concentrated solution was cooled to room temperature and then placed in a refrigerator at 5 °C overnight. Colorless crystals resulted, which were dried in a 55 °C oven. At this stage, the ^{31}P NMR spectra of this crystalline compound measured in DMSO-d_6 at room temperature showed a signal at −8.6 ppm, probably due to the protonated species of the heteropolyoxoanion. Recrystallizations from unbuffered pH 8 water were repeated until no signal at −8.6 ppm in the ^{31}P NMR in DMSO-d_6 was detected. Analytically pure colorless crystals were obtained in 2.6 g yield (63%). The compound is soluble in water and DMSO, but insoluble in CH_3CN and ethyl acetate.

Microanalysis. Analytical results for the sample dried overnight at room temperature under 10^{-3}—10^{-4} Torr: Found: H, 0.30; K, 7.52; P, 1.46; W, 60.9; Nb, 6.05; O, 22.8%; Total 99.0%. Calcd for $H_6K_9P_2W_{15}Nb_3O_{65}$, or $K_9P_2W_{15}Nb_3O_{62}\cdot 3H_2O$: H, 0.13; K, 7.83; P, 1.38; W, 61.3; Nb, 6.20; O, 23.1%. TG/DTA done under atmospheric conditions: weight loss of 3.63% found with a temperature ramp of 5 °C min^{-1} below 500 °C with an endothermic point at 101 °C; calcd 3.52% for $x = 9$ in $K_9P_2W_{15}Nb_3O_{62}\cdot xH_2O$. IR (KBr) (Fig. 2(c)) 1617m, 1086s, 1058w, 1015w, 945s, 913s, 765s, br, 527w cm^{-1}. ^{31}P NMR (D_2O, 23 °C) (Fig. 3(a)) $\delta = -7.7$ (1.0 P, $\Delta\nu_{1/2} = 2.3$ Hz), −14.3 (1.0 P, $\Delta\nu_{1/2} = 3.0$ Hz). ^{31}P NMR (DMSO-d_6, 23 °C) (Fig. 3(b)) $\delta = -7.8$ (1.0 P, $\Delta\nu_{1/2} = 3.3$ Hz); −14.3 (1.0 P, $\Delta\nu_{1/2} = 2.9$ Hz). ^{183}W NMR (D_2O, 45 °C) $\delta = -147.6$ (3W, $\Delta\nu_{1/2} = 2.7$ Hz), −173.2 (6W, $\Delta\nu_{1/2} = 5.6$ Hz), −216.1 (6W, $\Delta\nu_{1/2} = 3.4$ Hz). ^{183}W NMR (D_2O, 25 °C) measured for the solution obtained by cation-exchanging the potassium salt in D_2O with excess of $LiClO_4$, followed by filtering off the $KClO_4$: $\delta = -152.2$ (3W, $\Delta\nu_{1/2} = 2.9$ Hz); −177.9 (6W, $\Delta\nu_{1/2} = 4.8$ Hz), −220.0 (6W,

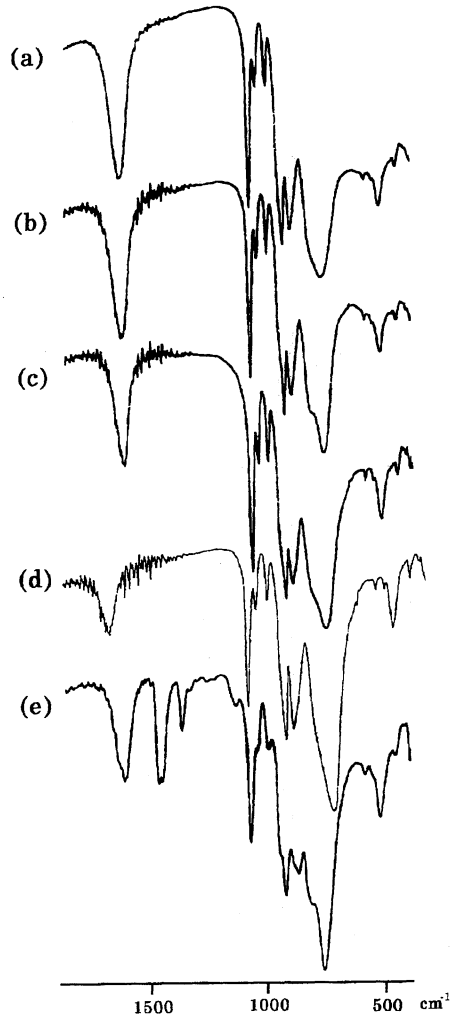


Fig. 2. The FT-IR spectra, measured as KBr disks of (a) $Li_9P_2W_{15}Nb_3O_{62}$ **2**, of (b) $Na_9P_2W_{15}Nb_3O_{62}$ **4**, of (c) $K_9P_2W_{15}Nb_3O_{62}$ **1**, of (d) $Cs_9P_2W_{15}Nb_3O_{62}$ **3**, and of (e) $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ **5** demonstrating that the polyoxoanion regions of the IR of these salts are completely coincident.

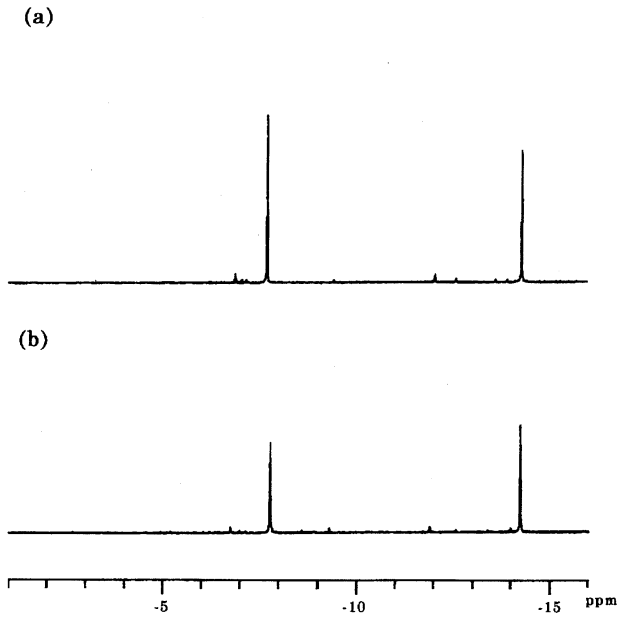


Fig. 3. Solution ^{31}P NMR spectra of $K_9P_2W_{15}Nb_3O_{62}$ **1** measured at 23 °C in (a) D_2O and (b) DMSO-d_6.

$\Delta\nu_{1/2}$ = 3.8 Hz). ^{183}W NMR (DMSO-d_6, 23 °C) δ = −135.6 (3W, $\Delta\nu_{1/2}$ = 14.0 Hz), −161.2 (6W, $\Delta\nu_{1/2}$ = 9.8 Hz), −201.8 (6W, $\Delta\nu_{1/2}$ = 16.1 Hz). Solid-state ^{31}P NMR (Fig. 6) (26.4 °C) δ = −6.8, −7.5, −14.1 ($\Delta\nu_{1/2}$ = 46 Hz). Solid-state ^{31}P NMR (60.0 °C) δ = −6.7, −7.5, −13.8 ($\Delta\nu_{1/2}$ = 92 Hz). Solid-state ^{31}P NMR (80.0 °C) δ = −6.7, −7.5, −13.7 ($\Delta\nu_{1/2}$ = 108 Hz). Solid-state ^{31}P NMR (120.0 °C) δ = −6.7, −7.5, −13.7 ($\Delta\nu_{1/2}$ = 139 Hz). Solid-state ^{31}P NMR (140.0 °C) δ = −6.7, −13.6 ($\Delta\nu_{1/2}$ = 146 Hz). Solid-state ^{31}P NMR (the sample measured at 140.0 °C was cooled and remeasured at 25.6 °C) δ = −6.8, −7.6, −14.2 ($\Delta\nu_{1/2}$ = 131 Hz).

Synthesis of $Li_9P_2W_{15}Nb_3O_{62}\cdot 25H_2O$ (2). Handling of the very hygroscopic $LiBF_4$ was performed in a glove box. The target compound was formed in an aqueous/CH_3CN system and isolated by reprecipitation with excess acetone from a solution of unbuffered pH 8 water.

In a glove box, 0.305 g (3.25 mmol, 12 equiv) of solid $LiBF_4$ were added to 3.00 g (0.271 mmol) of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ dissolved in 20 mL of CH_3CN in a 200 mL beaker. To the clear solution taken out from the glove box, 3.25 mL (1.63 mmol, 6 equiv) of a 0.5 M aqueous LiOH solution was added dropwise. After the stirring aqueous solution became cloudy, an oil precipitate formed. Stirring was continued for an additional 20 min. The supernatant was discarded by decantation. The colorless oil precipitate was changed to a dry powder by washing three times with ca. 10 mL CH_3CN. It was dried overnight in a 55 °C oven. The crude materials were redissolved in ca. 10 mL of unbuffered pH 8 water. The cloudy solution was filtered through filter paper (Whatman No. 5). To the clear colorless filtrate about 100—150 mL of acetone were added dropwise with stirring. The white precipitates were reprecipitated. The mother liquor was removed by decantation, and the precipitates were dried overnight in a 55 °C oven. The yield was 1.9 g (76%). The compound is very soluble in water, soluble in MeOH, EtOH, and DMSO and slightly soluble in CH_3CN, but insoluble in acetone and ethyl acetate.

Microanalysis. Analytical results for the sample dried overnight at room temperature under 10^{-3}—10^{-4} Torr: Found: H, 0.28; Li, 1.55; P, 1.83; W, 63.6; Nb, 6.57; O, 26.0%; total 99.8%. Calcd for $H_{18}Li_9P_2W_{15}Nb_3O_{71}$, or $Li_9P_2W_{15}Nb_3O_{62}\cdot 9H_2O$: H, 0.42; Li, 1.45; P, 1.44; W, 63.9; Nb, 6.46; O, 26.3%. TG/DTA done under atmospheric conditions: weight loss of 9.87% found with a temperature ramp of 5 °C min^{-1} below 400 °C with an endothermic point at 82 °C; calcd 9.78% for x=25 in $Li_9P_2W_{15}Nb_3O_{62}\cdot xH_2O$. IR (KBr) (Fig. 2(a)) 1631m, 1087s, 1059w, 1015w, 949s, 916s, 791s, br, 599w, 533s, 463w cm^{-1}. ^{31}P NMR (D_2O, 25 °C) (Fig. 4(a)) δ = −7.8 (1.0 P, $\Delta\nu_{1/2}$ = 2.7 Hz), −14.3 (1.0 P, $\Delta\nu_{1/2}$ = 3.0 Hz). ^{31}P NMR (MeOH-d_4, 25 °C) (Fig. 4(c)) δ = −7.2 (1.0 P, $\Delta\nu_{1/2}$ = 2.2 Hz), −13.6 (1.0 P, $\Delta\nu_{1/2}$ = 2.7 Hz). ^{31}P NMR (DMSO-d_6, 25 °C) (Fig. 4(b)) δ = −7.1 (1.0 P, $\Delta\nu_{1/2}$ = 3.1 Hz), −14.0 (1.0 P, $\Delta\nu_{1/2}$ = 2.3 Hz); δ [minor peak] = −4.0 ($\Delta\nu_{1/2}$ = 4.4 Hz), −10.0 ($\Delta\nu_{1/2}$ = 4.4 Hz). ^{183}W NMR (Fig. 5) (D_2O, 25 °C) δ = −152.4 (3W, $\Delta\nu_{1/2}$ = 3.6 Hz), −178.1 (6W, $\Delta\nu_{1/2}$ = 4.9 Hz), −220.3 (6W, $\Delta\nu_{1/2}$ = 3.8 Hz). ^{183}W NMR (MeOH-d_4, 25 °C) δ = −159.1 (3W, $\Delta\nu_{1/2}$ = 4.9 Hz), −188.5 (6W, $\Delta\nu_{1/2}$ = 5.6 Hz), −232.0 (6W, $\Delta\nu_{1/2}$ = 4.7 Hz). ^{183}W NMR (DMSO-d_6, 25 °C) δ = −137.1 (3W, $\Delta\nu_{1/2}$ = 17.8 Hz), −161.7 (6W, $\Delta\nu_{1/2}$ = 10.8 Hz), −214.4 (6W, $\Delta\nu_{1/2}$ = 12.7 Hz); δ [minor peak] = −199.8 ($\Delta\nu_{1/2}$ = 8.5 Hz). Solid-state ^{31}P NMR (Fig. 6) (27.3 °C) δ = −6.8, −8.0, −14.3 ($\Delta\nu_{1/2}$ = 185 Hz). Solid-state ^{31}P NMR (60.0 °C) δ = −6.7, −7.9, −14.2 ($\Delta\nu_{1/2}$ = 185 Hz). Solid-state ^{31}P NMR (80.0 °C) δ = −6.7, −7.9, −14.1 ($\Delta\nu_{1/2}$ = 177 Hz). Solid-state ^{31}P NMR (100.0 °C) δ = −6.7, −7.9, −13.9 ($\Delta\nu_{1/2}$ = 180 Hz). Solid-state ^{31}P NMR (120.0 °C) δ = −6.7, −7.9,

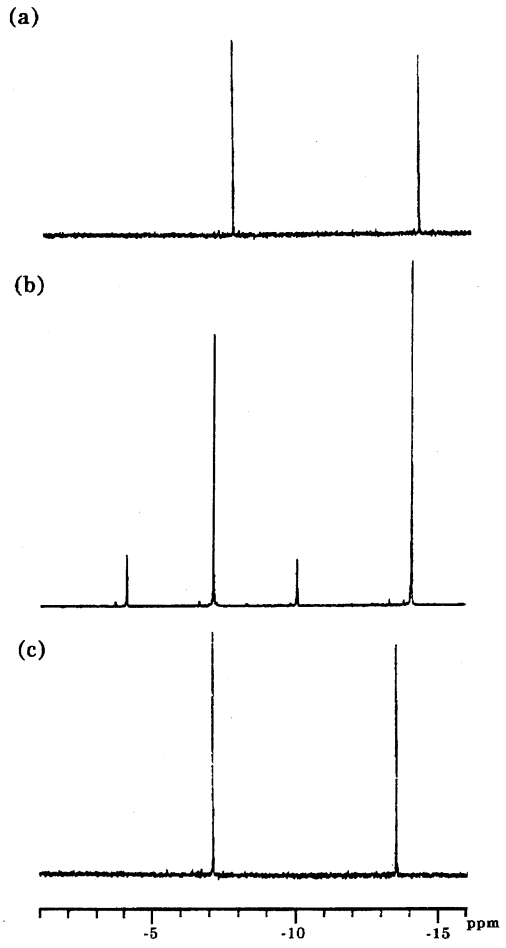


Fig. 4. Solution ^{31}P NMR spectra of $Li_9P_2W_{15}Nb_3O_{62}$ **2** measured at 25 °C in (a) D_2O, (b) DMSO-d_6, and (c) MeOH-d_4.

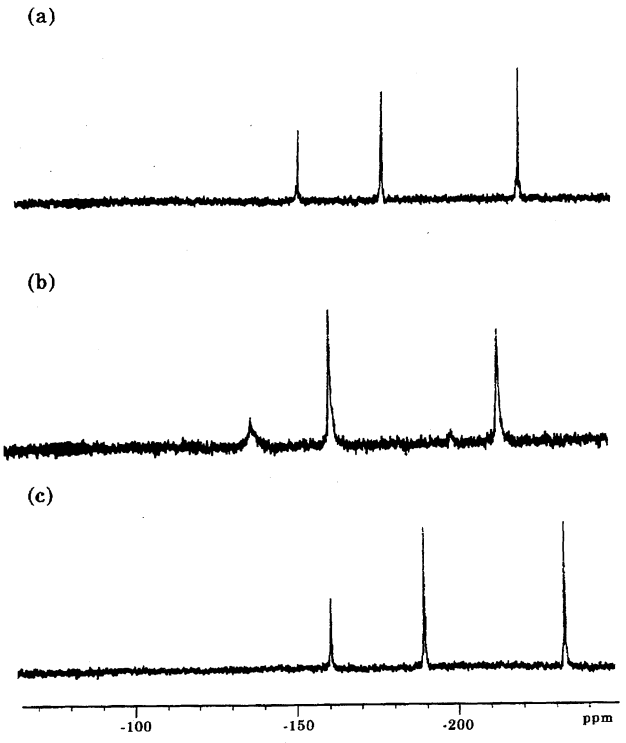


Fig. 5. Solution ^{183}W NMR of $Li_9P_2W_{15}Nb_3O_{62}$ **2** measured at 25 °C in (a) D_2O, (b) DMSO-d_6, and (c) MeOH-d_4.

−13.7 ($\Delta\nu_{1/2}$ = 185 Hz). Solid-state ^{31}P NMR (the sample measured at 120 °C was cooled and remeasured at 27.0 °C) δ = −6.8, −8.0, −14.3 ($\Delta\nu_{1/2}$ = 170 Hz).

In a separate, unsuccessful attempt, the isolation of the solid Li_9 salt by cation-exchange from the K_9 salt using an excess of $LiClO_4$ failed. The precipitate obtained by reprecipitation with excess acetone was insoluble in MeOH and EtOH, and the ^{31}P NMR in DMSO-d_6 showed a two-line spectrum, δ = −7.7 and −14.1 ppm. The compound obtained in this way was probably a mixed-countercation (K, Li)$_9$ species.

Synthesis of $Cs_9P_2W_{15}Nb_3O_{62}\cdot 8H_2O$ (3). The target compound was formed in an aqueous/DMSO system and isolated by reprecipitation from unbuffered pH 8 water at 90 °C.

In a 200 mL beaker were placed 5.00 g (0.451 mmol) of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ and 80 mL of DMSO. Stirring resulted in a clear pale-yellow solution. Solid $CsBF_4$ (1.19 g, 5.41 mmol, 12 equiv) was added, followed by stirring for 60 min, during which time all of the $CsBF_4$ completely dissolved. To this clear pale-yellow solution, the dropwise addition of 5.41 mL (2.71 mmol, 6 equiv) of a 0.5 M aqueous CsOH solution resulted in the formation of a cloudy suspension containing white precipitates. After the addition of the base was completed, stirring was continued for an additional 1 h, during which the cloudy suspension became white. With centrifuging, the white precipitates settled at the bottom of the centrifuge tube. The slightly cloudy supernatant solution was discarded by decantation, the white precipitates were washed with ca. 20 mL DMSO, and the suspension was centrifugated again. (The filtration of the white precipitates with fine glass frit or fine filter paper is difficult, because of the excessively fine powder, and resulted in lower yields.) This work-up was repeated once more, during

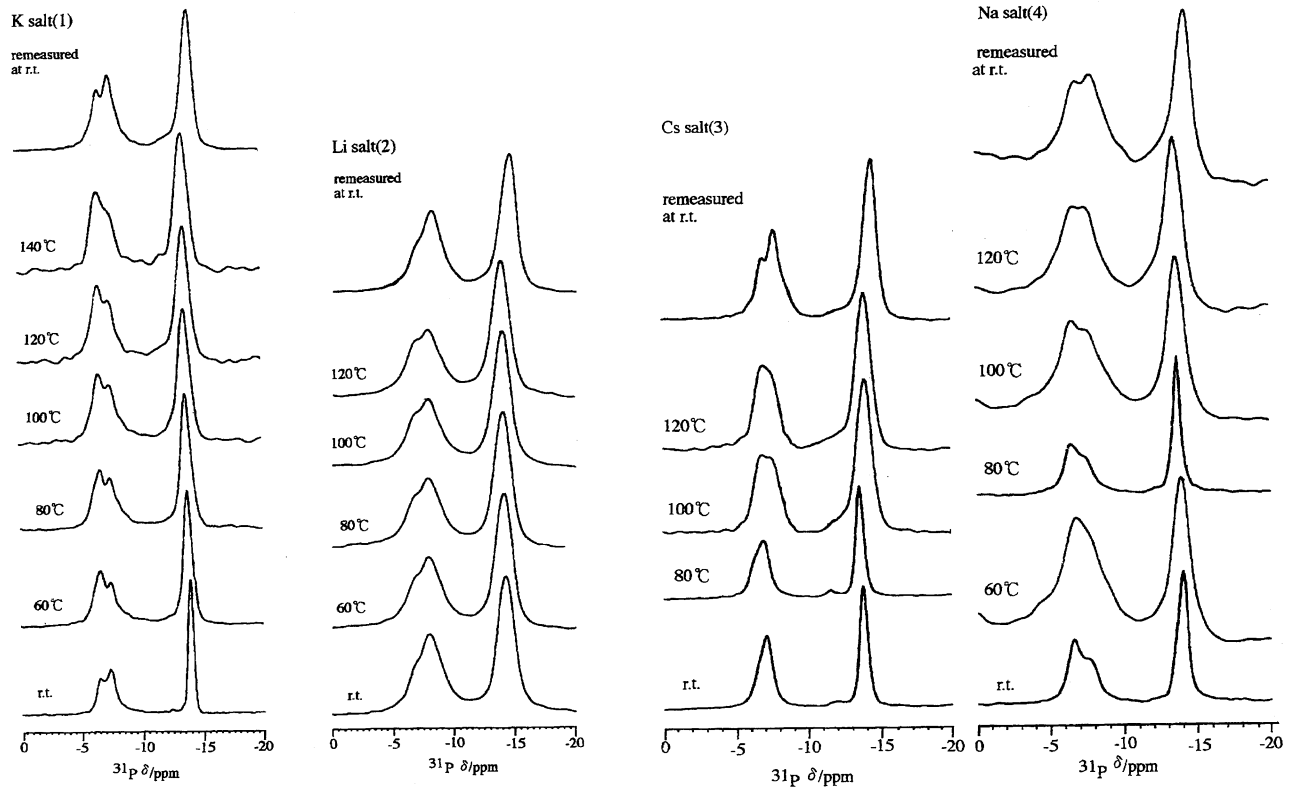


Fig. 6. Variable-temperature solid-state GHD/MAS ^{31}P NMR spectra of $K_9P_2W_{15}Nb_3O_{62}$ **1**, $Li_9P_2W_{15}Nb_3O_{62}$ **2**, $Cs_9P_2W_{15}Nb_3O_{62}$ **3**, and $Na_9P_2W_{15}Nb_3O_{62}$ **4**. In these spectra, after the sample was cooled from the highest temperature, the top spectrum was remeasured at room temperature.

which time unreacted $CsBF_4$ was completely removed. Next, the white precipitates were washed with ca. 30 mL CH_3CN, and then centrifuged. This work-up was carried out for a total of five times. The final precipitates were dried overnight in a 55 °C oven. The white powder was dissolved in 150 mL of unbuffered pH 8 water at 90 °C. The cloudy solution was passed through filter paper (Whatman No. 5). The clear colorless filtrate was placed in a refrigerator at 5 °C overnight. The compound, a colorless powder, was collected on a medium glass frit, thoroughly dried by suction, and dried overnight in a 55 °C oven. An analytically pure, colorless powder was obtained in 2.3 g yield (47%). The compound was soluble in hot water and a large amount of hot DMSO, but insoluble in MeOH, EtOH, CH_3CN, DMF, and ethyl acetate.

Microanalysis. Analytical results for the sample dried overnight at room temperature under 10^{-3}—10^{-4} Torr: Found: H, 0.03; Cs, 21.6; P, 1.12; W, 51.8; Nb, 5.14; O, 19.7%; total 99.4%. Calcd for $H_6Cs_9P_2W_{15}Nb_3O_{65}$, or $Cs_9P_2W_{15}Nb_3O_{62}\cdot 3H_2O$: H, 0.11; Cs, 22.4; P, 1.16; W, 51.6; Nb, 5.22; O, 19.5%. TG/DTA done under atmospheric conditions: weight loss of 2.76% found with a temperature ramp of 5 °C min^{-1} below 378 °C with an endothermic point at 154 °C; calcd 2.65% for $x=8$ in $Cs_9P_2W_{15}Nb_3O_{62}\cdot x H_2O$. IR (KBr) (Fig. 2(d)) 1618m, 1086s, 1059w, 1014w, 944s, 913s, 768s, br, 598w, 564w, 530m, 462w cm^{-1}. ^{31}P NMR (D_2O, 70 °C) $\delta=-7.4$ (1.0 P, $\Delta\nu_{1/2}=2.2$ Hz), -13.9 (1.0 P, $\Delta\nu_{1/2}=2.7$ Hz). ^{31}P NMR (DMSO-d_6, 23 °C) $\delta=-7.7$ (1.0 P, $\Delta\nu_{1/2}=5.8$ Hz), -14.4 (1.0 P, $\Delta\nu_{1/2}=4.6$ Hz). Solid-state ^{31}P NMR (Fig. 6) (25.4 °C) $\delta=-7.4$ ($\Delta\nu_{1/2}=138$ Hz), -14.1 ($\Delta\nu_{1/2}=108$ Hz). Solid-state ^{31}P NMR (80.0 °C) $\delta=-6.8$, -7.5, -13.9 ($\Delta\nu_{1/2}=139$ Hz). Solid-state ^{31}P NMR (100.0 °C) $\delta=-6.8$ ($\Delta\nu_{1/2}=108$ Hz), -13.9 ($\Delta\nu_{1/2}=139$ Hz). Solid-state ^{31}P NMR (120.0 °C) $\delta=-6.9$ ($\Delta\nu_{1/2}=216$ Hz), -13.9 ($\Delta\nu_{1/2}=139$ Hz). Solid-state ^{31}P NMR (the sample measured at 120.0 °C was cooled and remeasured at 25.5 °C) $\delta=-6.9$, -7.6, -14.4 ($\Delta\nu_{1/2}=123$ Hz).

A separate, unsuccessful attempt to isolate the solid Cs_9 salt by a cation-exchange from the K_9 salt using excess of $CsClO_4$ failed. A preparation based on a stoichiometric reaction in an aqueous/CH_3CN system and precipitation from a solution of unbuffered pH 8 water at 90 °C gave a compound which showed the ^{31}P NMR in D_2O at 70 °C major peaks at -7.4 and -14.0 ppm and minor peaks at -9.1 and -13.6 ppm, probably due to contamination of the starting dimeric compound, $P_4W_{30}Nb_6O_{123}^{16-}$.

Synthesis of $Na_9P_2W_{15}Nb_3O_{62}\cdot 23H_2O$ (4). This compound was previously prepared and fully characterized in the form with 23 water;[1a] the crystal structure of the form containing 2 CH_3CN solvated and 23 water has already been determined by single-crystal X-ray diffraction.[1f] Here, the compound prepared according to the previously reported method[1a] was recharacterized in order to compare the properties of compounds **1**—**3** under the same conditions. The amount of water of hydration under atmospheric conditions, found previously,[1a] was reproducible.

Microanalysis. Analytical results for the sample dried overnight at room temperature under 10^{-3}—10^{-4} Torr: Found: H, 0.09; Na, 4.73; P, 1.37; W, 62.9; Nb, 6.34; O, 24.0%; total 99.4%. Calcd for $H_8Na_9P_2W_{15}Nb_3O_{66}$, or $Na_9P_2W_{15}Nb_3O_{62}\cdot 4H_2O$: H, 0.18; Na, 4.74; P, 1.42; W, 63.1; Nb, 6.38; O, 24.2%. TG/DTA done under atmospheric conditions:[7] weight loss of 9.20% found below 500 °C with endothermic points at 84, 130 and 137 °C; calcd 8.79% for $x=23$ in $Na_9P_2W_{15}Nb_3O_{62}\cdot x H_2O$. Solid-state ^{31}P NMR (Fig. 6) (26.6 °C) $\delta=-7.0$ ($\Delta\nu_{1/2}=173$ Hz), -14.3 ($\Delta\nu_{1/2}=96$ Hz). Solid-state ^{31}P NMR (60.0 °C) $\delta=-6.7$ ($\Delta\nu_{1/2}=177$ Hz), -13.9 ($\Delta\nu_{1/2}=154$ Hz). Solid-state ^{31}P NMR (80.0 °C) $\delta=-6.5$, -7.7, -13.9 ($\Delta\nu_{1/2}=154$ Hz). Solid-state ^{31}P NMR (100.0 °C) $\delta=-6.5$, -7.6, -13.8 ($\Delta\nu_{1/2}=162$ Hz). Solid-state ^{31}P NMR (120.0 °C) $\delta=-6.7$, -7.7, -13.7 ($\Delta\nu_{1/2}=170$ Hz). Solid-state ^{31}P NMR (the sample measured at 120.0 °C was cooled and remeasured at 26.9 °C) $\delta=-6.7$, -7.9, -14.2 ($\Delta\nu_{1/2}=154$ Hz).

Separately, this compound was successfully obtained by a reaction in CH_3CN of the monomeric precursor $[(n\text{-}C_4H_9)_4N]_5H_4P_2W_{15}Nb_3O_{62}$, which was prepared using a recently found, improved method without any synthetic work-ups of the dimer $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$,[1i] with 5 equiv of $NaBF_4$ and subsequent with 4 equiv of NaOH, followed by repeated reprecipitations from unbuffered pH 8 water with excess CH_3CN.[1j]

Results and Discussion

Synthetic Reactions, General Properties, and Compositions. The alkali-metal salts of the Dawson-type heteropolyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$ have been formed by a stoichiometric reaction of the organic solvent-soluble, dimeric precursor $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ with MBF_4 and MOH (M = Li, K, and Cs), as follows:

$$[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123} + 6\,MOH + 12\,MBF_4 \longrightarrow 2M_9P_2W_{15}Nb_3O_{62} + 12\,[(n\text{-}C_4H_9)_4N]BF_4 + 5H_2O \quad (1)$$

The key points in the syntheses of $M_9P_2W_{15}Nb_3O_{62}$ (M=Li, K, Cs) are as follows: (a) the use of stoichiometric amounts (12 equiv) of MBF_4 (M=Li, K, Cs) to allow for an exchange of the 12 $[(n\text{-}C_4H_9)_4N]^+$ countercations of the dimeric, organic solvent-soluble precursor, $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$; (b) the use of DMSO as a solvent in, especially, the synthesis of Cs^+ salt, otherwise, $CsBF_4$ was not exchanged to $[(n\text{-}C_4H_9)_4N]^+$ countercations; (c) the use of a total of 6 equiv of MOH (M=Li, K, Cs) to react with the four protons in the dimer (requiring 4 equiv of OH^-) and to hydrolytically cleave the bridging Nb–O–Nb bond (requiring an additional 2 equiv of OH^- and forming two H_2O); and (d) the removal of $[(n\text{-}C_4H_9)_4N]BF_4$ as a byproduct from the reaction mixture and purification to give analytically pure white solids by reprecipitation with excess amounts of acetone or recrystallization from a hot aqueous system of unbuffered pH 8 water.

The molecular formula of K_9 (**1**), Li_9 (**2**), Cs_9 (**3**), and Na_9 (**4**) salts, with 3 water, 9 water, 3 water, and 4 water, respectively, are based on complete elemental analyses performed for samples dried overnight at room temperature under 10^{-3}—10^{-4} Torr (all elements, including oxygen, 99.0, 99.8, 99.4, and 99.4% totals are observed; see the Experimental section). On the other hand, TG/DTA measurements performed under atmospheric conditions show the presence of 9 water for **1**, 25 water for **2**, 8 water for **3**, and 23 water for **4**, respectively. The TG data estimates the apparent amount of water both intrinsic hydrated water and adsorbed water, via the weight loss observed between 20 and 500 °C. The DTA curves clearly show the presence of intrinsic hydrated water as endothermic peaks at 101 °C for **1**, 82 °C for **2**, 154 °C for **3**, and 84, 130, and 137 °C for **4**. Thus, each of the following can be significantly affected by countercations: the amounts of hydrated water and adsorbed water, solubilities in water and in organic solvents, and ease of crystallization.

Infrared Spectra and Thermal Analysis. Infrared spectra (Fig. 2(a)—Fig. 2(e)) of the compounds **1**—**4** and of the previously obtained $[(n\text{-}C_4H_9)_4N]_9$ salt **5**[1a] show the presence of the characteristic Dawson-type polyoxoanion IR bands between 1100 and 700 cm^{-1}. In the spectrum shown in Fig. 2(e), the very intense C–H vibrations of the $[(n\text{-}C_4H_9)_4N]^+$ countercations are observed at 1486—1381 cm^{-1}. These observations demonstrate that the Dawson-type, "$P_2W_{18}O_{62}^{n-}$" heteropolytungstate framework remains intact under the synthesis conditions.[8]

The effect of alkali-metal cations on the $P_2W_{15}Nb_3O_{62}^{9-}$ thermal-stability was observed in the solid state. Exothermic peaks without an accompanying weight loss were observed at different temperatures at around 500 °C with alkali metal ions: 473 °C for the Li salt **2**, 492 °C for the Na salt **4**, 529 °C for the K salt **1**, and 534 °C for the Cs salt **3**. FT-IR measurements after the samples were heated above such exothermic temperatures (up to ca. 550 °C) showed that *the Dawson structure of the polyoxoanion was not maintained.* Thus, the polyoxoanions degradate or decompose above these exothermic temperatures; such temperatures indicate the following order of relative thermal stability of the polyoxoanions with different cations: Cs salt **3** > K salt **1** ≫ Na salt **4** > Li salt **2**.

Solution ^{31}P and ^{183}W NMR Spectra. Further solution characterization relied on multinuclear ^{31}P and ^{183}W NMR (Table 1 and Table 2). A ^{31}P NMR spectrum measured at 23 °C of $K_9P_2W_{15}Nb_3O_{62}$ **1** in D_2O (Fig. 3) shows primarily two resonances at $\delta=-7.7$ and -14.3 ppm with integrated intensities of 1 : 1, as expected for the two types of phosphorus present, and as previously observed in $Na_9P_2W_{15}Nb_3O_{62}$ **4** in D_2O at 22 °C ($\delta=-7.8$ and -14.3).[1a] The downfield resonance ($\delta=-7.7$) is assigned to the phosphorus closest to the Nb_3O_6 site, whereas the upfield resonance at $\delta=-14.3$ is known to be due to the phosphorus closer to the W_3O_6 cap (Fig. 1). The two-line ^{31}P NMR spectrum (Fig. 3) requires the presence of a single species in solution, and, therefore, precludes the existence of even minor impurities. The clean, two-line ^{31}P NMR spectrum of **1** was also observed in a DMSO-d_6 solution at 23 °C, although their chemical shifts were very slightly altered ($\delta=-7.8$ and -14.3). A ^{31}P NMR spectrum of $Cs_9P_2W_{15}Nb_3O_{62}$ **3** with low solubility in water was measured at 70 °C in D_2O to show a clean two-line spectrum at $\delta=-7.4$ and -13.9 ppm due to a single species present. On the other hand, the ^{31}P NMR spectra (Fig. 4) of $Li_9P_2W_{15}Nb_3O_{62}$ **2**, at 25 °C in D_2O and in MeOH-d_4 showed the two-line spectra at ($\delta=-7.8$ and -14.3) and at ($\delta=-7.2$ and -13.6), respectively, whereas that measured at 25 °C in DMSO-d_6 (Fig. 4(b)) showed two sets of major peaks at $\delta=-7.1$ and -14.0 with 1 : 1 intensities and minor peaks at $\delta=-4.0$ and -10.0 ppm with equal intensities. With the addition of MeOH-d_4, only the minor peaks disappeared as the amount of MeOH-d_4 increased. The ^{31}P NMR spectral pattern, two sets of two-line spectra in the DMSO-d_6 solution of **2**, is quite different from that previously observed in DMSO-d_6 solutions of mixed salts, such as $[(n\text{-}C_4H_9)_4N]_5Na_3[\{(cod)Ir\}(P_2W_{15}Nb_3O_{62})]$.[1g,1h] In the latter spectrum, only the ^{31}P resonance of the PO_4 moiety closer to the Nb_3O_6 site in the Dawson structure has been observed as a line-broadened signal, flanked by two smaller peaks, which were caused by ion-pairing interactions between Na^+ and $P_2W_{15}Nb_3O_{62}^{9-}$. In contrast to other cation salts, the results from **2** suggest that a molecular species or adduct

Table 1. Comparison of the Chemical Shifts in Solution and Solid-State ^{31}P NMR Spectra Reported for $M_9P_2W_{15}Nb_3O_{62}$ (M=Li, Na, K, Cs)

	δ (D_2O)	δ (DMSO-d_6)	δ (MeOH-d_4)	δ (Solid-state)[c]
$Li_9P_2W_{15}Nb_3O_{62}$ **2**[b]	−7.8, −14.3	−7.1, −14.0 (−4.00, −10.0)*	−7.2, −13.6	−6.8, −8.0, −14.3
$Na_9P_2W_{15}Nb_3O_{62}$ **4**[a]	−7.8, −14.3	−7.6, −14.1	—	−7.0, −14.3
$K_9P_2W_{15}Nb_3O_{62}$ **1**[b]	−7.7, −14.3	−7.8, −14.3	—	−6.8, −7.5, −14.1
$Cs_9P_2W_{15}Nb_3O_{62}$ **3**[b]	−7.4, −13.9	−7.7, −14.4	—	−7.4, −14.1

a) Ref. 1a. b) This work. The solution NMR data of Li, Na, and K salts were obtained at 23 °C and those of the less soluble Cs salt at 70 °C. c) This work. Measurements were performed at room temperature. *) Minor peaks.

Table 2. Comparison of the Chemical Shifts in Solution ^{183}W NMR Spectra Reported for $M_9P_2W_{15}Nb_3O_{62}$ (M=Li, Na, K, Cs)

	δ (D_2O)	δ (DMSO-d_6)	δ (MeOH-d_4)
$Li_9P_2W_{15}Nb_3O_{62}$ **2**[b]	−152.4, −178.1, −220.3	−137.1, −161.7, (−199.8)*, −214.4	−159.1, −188.5, −232.0
$Na_9P_2W_{15}Nb_3O_{62}$ **4**[a]	−151.6, −177.2, −219.8	−137.4, −163.5, −206.9	—
$K_9P_2W_{15}Nb_3O_{62}$ **1**[b]	−147.6, −173.2, −216.1	−135.6, −161.2, −201.8	—
$Cs_9P_2W_{15}Nb_3O_{62}$ **3**[b]	—	—	—

a) Ref. 1a. b) This work. The data for the Li salt were obtained from measurements at 23 °C and those for the K salt at 45 °C. *) Minor peak.

formed between **2** and DMSO molecules is present in neat DMSO solvent.

The ^{183}W NMR spectrum measured at 45 °C for the K_9 salt **1** in D_2O shows three peaks at $\delta=-147.6$, -173.2, and -216.1 ppm with integrated intensities of 1 : 2 : 2. This spectral pattern is in accord with the presence of two tungsten belts consisting of six WO_6 octahedra each and a tungsten cap of three WO_6 octahedra, as is expected for a Wells–Dawson heteropolyanion (Fig. 1). The three-line ^{183}W NMR spectrum also requires that the heteropolyanion as a single species has an overall C_{3v} symmetry. The three-line ^{183}W NMR was also observed in a DMSO-d_6 solution. The ^{183}W NMR of the Cs_9 salt **3** was not measured in D_2O or in DMSO-d_6, because of its low solubility, even at elevated temperature. The 25 °C ^{183}W NMR spectra (Fig. 5, Table 2) of the Li_9 salt **2**, both in D_2O and in MeOH-d_4, also showed typical three-line spectra with integrated intensities of 1 : 2 : 2 (at $\delta=-152.4$, -178.1, -220.3, and at $\delta=-159.1$, -188.5, -232.0, respectively). On the other hand, the ^{183}W NMR (Fig. 5(b)) of **2** in DMSO-d_6 at 25 °C showed a minor broad peak at $\delta=-199.8$ in addition to the three-line spectrum consisting of major peaks at $\delta=-137.1$, -161.7, and -214.4. The $\delta=-137.1$ peak among the major peaks is specially broadened, and all of the major peaks are much more shifted to the downfield. In correlation to the minor two-line ^{31}P NMR spectrum observed in DMSO-d_6, the minor peak observed at $\delta=-137.1$ may be a part of the "three-line spectrum" of the new species or adduct formed between **2** and DMSO molecules in neat DMSO solvent, because the other two minor peaks are possibly obscured by the major peaks. Thus, only the Li_9 salt shows the cation effect in DMSO solution as an adduct formation between **2** and DMSO molecules.

Solid-State GHD/MAS ^{31}P NMR Spectra. Variable-temperature solid-state GHD/MAS ^{31}P NMR spectra of the polyoxoanions with different cations **1**—**4** are shown in Fig. 6, and their chemical shifts at room temperature listed in Table 1. Solid-state MAS ^{31}P NMR spectra, consisting of the much broader, or split, downfield signal and the upfield signal as a single peak, are significantly different from the spectral pattern observed in the solution ^{31}P NMR spectra, although both the solid-state and solution ^{31}P NMR spectra correspond. Therefore, the downfield signal can then be assigned to the phosphorus closer to the Nb_3O_6 site and the upfield signal to the phosphorus closer to the W_3O_6 Site.

The solid-state ^{31}P NMR of the K salt **1** at room temperature has three distinct resonances consisting of two split broad downfield peaks ($\delta=-6.8$ and -7.5; their separation is $\Delta\delta=0.7$) and one major upfield peak ($\delta=-14.1$). As the temperature was elevated (from room temperature to 140 °C), the intensity of the -6.8 ppm signal gradually increased, compared to that of the -7.5 ppm signal, with only a slight shift of their chemical shifts downfield, and both signals coalesced around 140 °C. The upfield signal at -14.1 ppm as a single peak was also shifted downfield and broadened as the temperature increased. The sample measured at 140 °C was cooled, and then remeasured at room temperature. The resulting spectrum was almost the original spectral pattern, i.e., the chemical shift of the upfield signal returned to the original position and the splitting of the downfield signal appeared again, although the relative intensity of the -6.8 and -7.5 ppm signals were slightly different from that of the starting spectrum.

It was previously found in solid-state ^{31}P NMR measurements of the $H_3PW_{12}O_{40}\cdot nH_2O$ that the solid-state ^{31}P resonances reflect the number of hydrated water interacting with the polyoxoanion.[9a] Some of water molecules were removed from the hydrated structures of the present polyoxoanion by elevating the temperature; the dehydrating behavior was dependent on the countercation, as observed in the TG/DTA measurements (see the Experimental section for details). Thus, the solid ^{31}P NMR spectra of the K salt **1** indicate there exist at least two types of hydrated structures of the polyoxoanion, even at room temperature: one is the much more dehydrated species assignable to the $\delta=-6.8$ ppm signal; the other is the more hydrated species assignable to the $\delta=-7.5$ ppm signal, although such species can not be definitely distinguished in the upfield signal. The spectrum remeasured at room temperature, after the sample was heated up to 140 °C, indicates that the partial rehydration of the dehydrated species formed during heating takes place with the moisture in air.

In the solid-state ^{31}P NMR spectra of other salts at elevated temperature, the temperature-depending behavior of both the downfield and upfield signals appears to be similar to that of the K salt, although the splitting of the downfield signal is not clear compared with that of the K salt. Also, in other salts, the effect of the countercation is most clearly observed in the change of the downfield signal with elevated temperature.

In the solid-state MAS ^{31}P NMR spectrum of the α-$P_2W_{18}O_{62}^{6-}$ polyoxoanion with D_{3h} symmetry, the isotropic chemical shift has been observed at -13 ± 0.2 ppm as a single peak.[9d] Thus, the observation of the VT solid-state ^{31}P NMR as a function of different countercations should consider intercations of the α-$P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion with the countercations and/or with hydrated water.

As for the fact that the downfield signal, rather than the upfield signal, is markedly effected by the countercation, we can discuss at least two effects, which apparently cause the inhomogenities of the polyoxoanion in the crystals[9] and have never been seen in an aqueous solution. One is a solid-state ion-pairing effect formed between the alkali metal cation and the Nb_3O_6 cap site of the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion; the other is a dependence of the cation on the removal of the hydrated water from the crystal lattice at elevated temperature. The former effect is supported by single-crystal X-ray crystallography of the Na salt **4**,[1f] (described below); the latter effect is supported by the cation-dependent weight losses accompanying the different endothermic peaks, observed in the TG/DTA measurements.

The structure of α-$P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion has been determined by X-ray analysis for the single crystal of $Na_9P_2W_{15}Nb_3O_{62}\cdot 2CH_3CN\cdot 23H_2O$;[1f] two molecules are present in the unit cell. The crystals contain Na^+ and $P_2W_{15}Nb_3O_{62}^{9-}$ ions and CH_3CN and H_2O solvated

molecules. In the crystals, the cations are distributed fairly uniformly around the polyoxoanion, although the two cap ends of the Dawson-type polyoxoanion are not equivalent. All cations, except for Na (2), which is bonded only to one CH_3CN and five water molecules, are bonded to at least one oxygen atom of the polyoxoanion in addition to water, while Na (1) bridges two adjacent polyoxoanions and Na (6) and Na (7) each bridge three polyoxoanions. The packing diagram for $Na_9P_2W_{15}Nb_3O_{62}$ shows a Na^+ "cloud" that surrounds each polyoxoanion with $Na^+\cdots O$–M (M=Nb, W) distances of 2.3—2.5 Å. *The multiple-bridging Na^+ ions contribute to the solid-state ion-paring interactions, which are formed between the Na^+ ion and primarily the more basic Nb_3O_6 cap of the $P_2W_{15}Nb_3O_{62}{}^{9-}$polyoxoanion.* The solid-state ion-pairing interactions also persist even in nonaqueous solutions, which have caused the line-broadening and the additional smaller peaks of ^{31}P resonance of the PO_4 moiety closer to the Nb_3O_6 site, as observed in the ^{31}P NMR measured in DMSO-d_6 solution of $[(n\text{-}C_4H_9)_4N]_5Na_3[\{(cod)Ir\}(P_2W_{15}Nb_3O_{62})]$. This ion-paring effect can be readily removed by adding three equivalents of the cryptand Kryptofix 2.2.2.[1g,1h)]

The solid-state ^{31}P NMR spectra observed here show that such solid-state ion-pairing interactions between the cation and the Nb_3O_6 site of the polyoxoanion commonly exist in other cation salts as well.

Conclusion

In conclusion, the water-soluble alkali metal salts of the Dawson-type heteropolyoxoanion, $M_9P_2W_{15}Nb_3O_{62}$ (M=Li, K, Cs), have been isolated, in 76, 63, and 47% yields and on a 1.9, 2.6, and 2.3-g scale, and have been unequivocally characterized, both in solution and in the solid state. The effects of the alkali-metal countercations on the $P_2W_{15}Nb_3O_{62}{}^{9-}$ were observed in the solid state (as a cation-dependent thermal-stability), and also in the spectral changes of the ^{31}P signal of the PO_4 unit closer to the Nb_3O_6 site in the Dawson structure. The order of the relative thermal-stability in the solid state was found to be: Cs salt **3**>K salt **1**≫Na salt **4**>Li salt **2**. In the solid-state ^{31}P NMR spectra, the effect of the countercation was clearly observed particularly in the downfield signal. The solid-state ^{31}P NMR spectral changes at elevated temperature were dependent upon both the degree of hydration at room temperature and the dehydration processes during heating. The fact that the downfield signal was markedly effected by the countercation was primarily interpreted in terms of solid-state ion-pairing intercations between the cation and the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion. The title complexes are also of interest as possible new type of solid -base catalysts; studies of such catalyses are planned.[3e)]

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7) In more precise TG/DTA measurements, done with a temperature ramp of 1 °C min^{-1} for Keggin-type heteropolytungstates containing only solvated waters, weight loss of 9.40% (calcd for 16 hydrated water, 9.45%) has been observed below 300 °C with an endothermic point at 91 °C for analytically pure $Na_7SiW_9Nb_3O_{40}\cdot 16H_2O$.[4)]

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