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Synthesis and Characterization of the Water-Soluble, All-Inorganic Composition, Keggin- Type Triniobium(V)-Substituted $SiW_9Nb_3O_{40}{}^{7-}$ Heteropolyoxoanions with Alkali Metal Countercations (Li^+, Na^+, K^+, and Cs^+)[#]

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The Keggin-type triniobium(V)-substituted tungstoheteropolyanion, A-β-$SiW_9Nb_3O_{40}{}^{7-}$, was synthesized as its hepta alkali-metal salts of Li^+, Na^+, K^+, and Cs^+ countercations. These alkali-metal salts were useful for allowing the crystallization of $SiW_9Nb_3O_{40}{}^{7-}$, itself, and/or the $SiW_9Nb_3O_{40}{}^{7-}$-supported organometallic complexes, as well as controlling the water solubility of these complexes. The analytically pure compounds, obtained as homogeneous colorless solids via a stoichiometric reaction of the $(Bu_4N)_6H_2Si_2W_{18}Nb_6O_{77}$, (Nb–O–Nb)$_3$-bridged anhydride with the corresponding alkali tetrafluoroborates, and then with the alkali hydroxides, were compositionally characterized by complete elemental analyses, TG/DTA and FABMS spectra. They were structurally characterized by FT-IR and solution ^{183}W NMR measurements, as well as solid-state CP/MAS and GHD/MAS ^{29}Si NMR and solution ^{29}Si NMR measurements. The cation-dependent properties of these heteropolytungstates in the solid state were observed in the thermal stabilities, the amounts of hydrated water and adsorbed water, the solubilities in water and in organic solvents, and in the ease of crystallization.

Polyoxoanions are molecular metal-oxide clusters which resemble discrete fragments of solid metal oxides. The chemistry of triniobium(V)-substituted Dawson- and Keggin-type heteropolytungstates, which has been exploited by Finke's group, has been extended not only to the synthesis and characterization of novel polyoxoanion-supported organometallic complexes as their organic-solvent soluble forms in all-Bu_4N salts and mixed Bu_4N/Na salts,[1)] but also to novel catalyst precursors for the hydrogenation of cyclohexene,[2a)] the oxidation of cyclohexene with dioxygen,[2b)] and allylic epoxidation with H_2O_2;[2d)] more recently, these complexes have led to iridium nanocluster chemistry.[2c,2f)]

In our own work, we recently reported on the isolation of a nonasodium salt of the Dawson-type triniobium-substituted polyoxoanion $P_2W_{15}Nb_3O_{62}{}^{9-}$,[1a)] and also on the heptasodium salt of polyoxoanion-supported organometallic complex $[\{\eta^5\text{-}C_5Me_5)Rh\}P_2W_{15}Nb_3O_{62}]^{7-}$.[1e)] These studies, the syntheses of the water-soluble, all-inorganic composition compounds, were initially aimed at solving a crystallization problem, that is, the finding that organic-solvent soluble and water-insoluble forms, such as all-Bu_4N salts or mixed Bu_4N/Na salts, were hard to crystallize. In fact, crystal-structure determinations for this class of polyoxoanions have been limited to $Na_9P_2W_{15}Nb_3O_{62}\cdot 23H_2O\cdot 2MeCN$[1f)] and $Na(Bu_4N)_6[\{(\eta^5\text{-}C_5Me_5)Rh\}P_2W_{15}Nb_3O_{62}]\cdot 10MeCN\cdot 10Me_2CO$.[1d)] Very recently, through the synthesis of the alkali-metal salts (Li^+, Na^+, K^+, and Cs^+), we also clarified the cation-dependent properties of the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion, including its thermal stability, solubility, ease of crystallization, hydration structure around the polyoxoanion, and solid-state ion-pairing interaction between the countercation and the polyoxoanion.[1j)] In a separate account, it has been well-documented that the amount of solvated water [and, therefore, the porosity, thermal stability and surface area in the heterogeneous catalysts by classical Keggin heteropolyanions $PM_{12}O_{40}{}^{3-}$ (M = Mo and W)] can be controlled by salt-formation with different counterions.[3)]

In the Keggin-type polyoxoanion $SiW_9Nb_3O_{40}{}^{7-}$, three niobium atoms are substituted in the A-site of the β-Keggin structure (Fig. 1A). In its polyoxoanion-supported complex, the organometallic group $[(\eta^5\text{-}C_5Me_5)Rh]^{2+}$ is bonded to two bridging W–O–Nb oxygens and a bridging W–O–W oxygen that occupy the B-site of the Keggin-type polyoxoanion $SiW_9Nb_3O_{40}{}^{7-}$.[4)] In the present work we extended the concept of *water solubility* and *an all-inorganic composition* in the Dawson type heteropolytungstates to the Keggin-type heteropolytungstates, specifically to the syntheses of the heptasodium salt of Keggin-type trisubstituted polyoxo-

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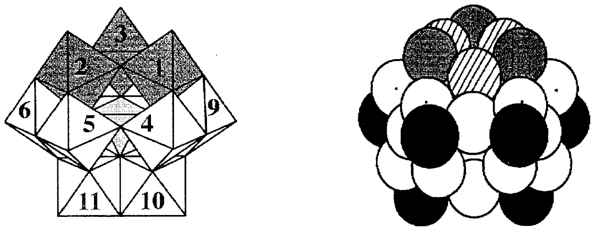
[#] This work follows our previous work in the Refs. 1a, 1e, 1j, and 4d.



(A) (B)

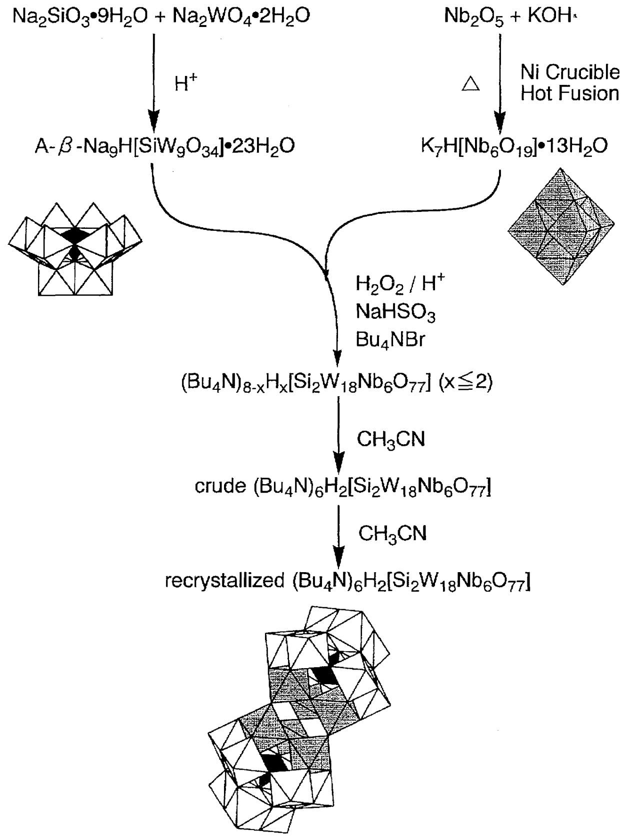
Fig. 1. (A) polyhedral and (B) space-filling representation of the Keggin-type heteropolyanion β-1,2,3-$SiW_9Nb_3O_{40}{}^{7-}$. In (A) the three niobiums are represented by gray octahedra in the 1—3 positions. The WO_6 octahedra occupy the 4—12 positions and one SiO_4 group is shown as the internal, 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–O–Nb and Nb–O–W) are depicted by hatched and dotted circles, respectively, 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 soluble metal-oxide analogs.

anion $SiW_9Nb_3O_{40}{}^{7-}$ and the pentasodium salt of polyoxoanion-supported organometallic complex $[\{(\eta^5\text{-}C_5Me_5)Rh\}SiW_9Nb_3O_{40}]^{5-}$.[4d] Isolation of the all-sodium salts has required their own preparation and purification schemes, including the proper choice of an appropriate solvent system: The all-sodium salt of the polyoxoanion-supported complex was derived from the all-sodium salt of the polyoxoanion in mixed DMSO/CH_3CN media with rather specific volume ratios.[1a,1e,1j,4d]

Herein we report on the full details concerning the synthesis and isolation of the all-inorganic composition salts of $SiW_9Nb_3O_{40}{}^{7-}$ as its K^+ salt and with 5—6 hydrated water (**1**), as its Li^+ salt with 11—12 water (**2**), and as its Cs^+ salt with 7—8 water (**3**) under atmospheric conditions. Reported also are the compositional characterizations of **1**—**3** by full elemental analyses, as well as thermogravimetric and differential thermal analyses (TG/DTA), and of **1** by fast atom bombardment mass spectroscopy (FABMS); their structural characterization has been substantiated by FT-IR, by variable-temperature solid-state ^{29}Si NMR and by room-temperature solution ^{183}W and ^{29}Si NMR spectroscopies. The thermal stabilities of **1**—**3** were determined by a combination of TG/DTA and FT-IR measurements.

Experimental

General Conditions. The following were used as received: Nb_2O_5, LiOH, KOH (85%), $Na_2SiO_3\cdot9H_2O$, $Na_2WO_4\cdot2H_2O$, $NaHSO_3$, $NaBF_4$, KBF_4, HBF_4, $(n\text{-}C_4H_9)_4NBr$, 12 M, 6 M, and 0.5 M HCl (aq), 30% H_2O_2 (aq), 0.5 M NaOH (aq), 0.5 M KOH (aq), ethanol, diethyl ether, acetone, acetonitrile (all from Wako) (1 M = 1 mol dm^{-3}); CsOH (Kanto); $LiBF_4$ (Aldrich) and D_2O, DMSO-d_6 (99.9 atom % D, containing 0.05% TMS (v/v)), TMS (Merck). Solid $CsBF_4$ was prepared in analogy with the synthesis of KBF_4 reported in the literature.[5,6] $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$ was prepared as previously described[4b] via the five steps shown in Scheme 1.



Scheme 1. Preparation of $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$.

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 Mikroanalytishes Labor Pascher (Remagen, Germany). Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer in KBr disks at room temperature. TG/DTA were carried out using 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 500 °C.

FAB mass spectral measurements were carried out at the Environmental Health Sciences Center, Oregon State University (Corvallis, Oregon, USA) using a Kratos MS-50TC mass spectrometer (Manchester, England) and Kratos DS-90 data-processing system. Approximately a 50 μg sample was dissolved in 2 μL of 0.1 M oxalic acid in 2 : 1 thioglycerol/glycerol directly on the target. The positive-ion spectra were acquired with an acceleration voltage of 8 kV, using an Ion Tech FAB gun (Teddington, UK), at 7—8 kV with xenon gas. The scan speed was 30 seconds/decade, and the mass resolving power was either 1000 or 2500.

Solution ^{183}W NMR (16.50 MHz) spectra were recorded at 25 °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. ^{183}W NMR spectra were measured in D_2O[7] and 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 (δ = 0) as negative.

Solution ^{29}Si NMR (79.30 MHz) spectra were recorded at 25

°C in 5 mm o.d. quartz glass tubes for ^{29}Si NMR measurements on a JEOL JNM-EX 400 FT-NMR spectrometer. These spectra were measured in a D_2O solution with reference to an external standard of DSS in a D_2O solution, and in a DMSO-d_6 solution with reference to an external standard of TMS, both by the substitution method. Chemical shifts were reported on the δ scale with resonances upfield of DSS or TMS (δ = 0) as negative.

Solid-state ^{29}Si NMR spectra (53.54 MHz) were recorded on a JEOL EX 270 spectrometer. A variable-temperature (VT) controller was used for the probe temperature control and measurements. Two different pulse sequences were used: the usual spin-lock cross-polarization (CP) sequence and a single 90° pulse in combination with high-power proton decoupling (GHD) without cross-polarization. For the two complexes ($M = Li^+$ and K^+) the ^{29}Si NMR spectra were measured by the CP/MAS (magic angle spinning) method, but for the complexes ($M = Na^+$ and Cs^+) the spectra were measured by the GHD method because of the low signal-to-noise (S/N) ratio with the CP/MAS method. Specimens (ca. 100 mg) were contained in a silicon nitride ceramic cylindrical-type rotor. Line narrowing was achieved by high-order decoupling and magic-angle spinning. The spinning rate was set to about 6 kHz. The spectral width and data points were 10.0 kHz and 8 k, respectively. The spectra were accumulated 5000—10000 times at a repetition time of 5 s to achieve a reasonable S/N. The chemical shifts were calibrated indirectly through external polydimethylsilane (PDMS; −34.11 ppm relative to TMS with δ = 0). The experimental errors of the isotropic ^{29}Si chemical-shift values were estimated to be about 0.5 ppm. Spinning side bands did not appear due to the use of a sufficient spinning rate.

Synthesis of $K_7SiW_9Nb_3O_{40}\cdot xH_2O$ [x = 5—6] (1). In a 200-mL beaker were placed 5.00 g (0.756 mmol) of $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$ and 50 mL of CH_3CN. Warming the mixture to 50—60 °C and stirring resulted in a clear pale-yellow solution. To the solution solid KBF_4 (0.571 g, 4.536 mmol, 6 equiv) was added, followed by stirring for 1 h, during which time all of the KBF_4 did not dissolve. To this suspension, 12.1 mL (6.05 mmol, 8 equiv) of a 0.50 M KOH aqueous solution was added. At the bottom of the beaker, an oily material formed. Stirring was continued for 30 min. The solution was cooled to room temperature and then stored in a refrigerator at 5 °C for two days. A white precipitate formed. After removing the mother liquor by decantation, the residue was washed with CH_3CN (30 mL × 3). The residue in the beaker was placed in an oven at 55 °C overnight.

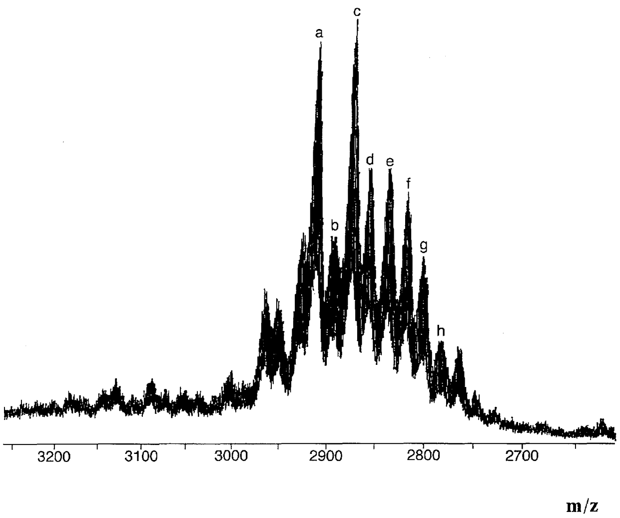
Purification was accomplished by repeated reprecipitations with excess CH_3CN from a solution of unbuffered pH 8 water ($[(n\text{-}C_4H_9)_4N]BF_4$ is soluble in CH_3CN, whereas the heptapotassium salt of the heteropolytungstate is not). This crude precipitate was redissolved in 30 mL of unbuffered pH 8 water, followed by filtration through a folded filter paper (Whatman No. 2). To the clear, colorless filtrate with stirring, 300 mL of CH_3CN was slowly added from a dropping funnel at a rate of one drop per second. A white powder which formed at the bottom of the beaker was stored in a refrigerator overnight. This white precipitate was collected on a fine glass frit, washed with CH_3CN (50 mL × 3) and then dried in an oven at 55 °C overnight. The reprecipitation, from a solution of unbuffered pH 8 water using excess of CH_3CN, was repeated twice. The yield of white powder was 1.1 g (24.5%, for the x = 5 hydrated species).

It was confirmed by the disappearance of the FT-IR 1084 cm^{-1} band that the contaminated BF_4^- was completely removed by the present work-up. The final compound was hygroscopic, very soluble in water and soluble in DMSO, but insoluble in CH_3CN, methanol, ethanol, THF, 1,4-dioxane, acetone, ether, dichloromethane, and ethyl acetate.

This compound was readily crystallized as colorless needles within a week with vapor diffusion from 25 mL acetone into an aqueous solution of 0.2 g of the sample dissolved in 3.0 mL of pH 8 unbuffered solution. The crystals, collected on a medium glass frit and washed 4—5 times with a small amount of acetone, were obtained in 0.17 g (85%) yield.

Microanalysis. Found: H, 0.12; K, 9.43; Si, 1.06; W, 57.4; Nb, 9.65; O, 23.3; total 100.96%. Calcd for $H_2K_7SiW_9Nb_3O_{41}$, or $K_7SiW_9Nb_3O_{40}\cdot H_2O$: H, 0.07; K, 9.43; Si, 0.97; W, 57.2; Nb, 9.63; O, 22.7%. A weight loss of 3.54% (weakly solvated or adsorbed water) was observed during overnight drying at room temperature under reduced pressure (10^{-3}—10^{-4} Torr) before the analysis. TG/DTA was performed under atmospheric conditions: a weight loss of 3.38% was found with a temperature ramp of 5 °C min^{-1} below 500 °C, with a clear endothermic point at 90.5 °C; calcd 3.03% for x = 5 and 3.62% for x = 6 in $K_7SiW_9Nb_3O_{40}\cdot xH_2O$. A positive-ion FABMS (Fig. 2): a molecular ion peak, $[M+H]^+ = m/z$ 2875.8 was observed for $M = K_7SiW_9Nb_3O_{40}$. IR (KBr) (Fig. 3(b)): 993m, 954s, 883s, 794s, 539m, 474w cm^{-1}. ^{183}W NMR (D_2O, 25 °C) δ = −118.0 (6W, $\Delta\nu_{1/2}$ = 1.7 Hz), −124.9 (3W, $\Delta\nu_{1/2}$ = 1.8 Hz). ^{183}W NMR (DMSO-d_6, 25 °C) δ = −95.1 (6W, $\Delta\nu_{1/2}$ = 4.5 Hz), −113.1 (3W, $\Delta\nu_{1/2}$ = 2.8 Hz). ^{29}Si NMR (D_2O, 25 °C) (Fig. 5(b)) δ = −82.8; Solid-state ^{29}Si NMR (CP/MAS 80 Hz, 25 °C) (Fig. 5(a)) δ = −81.5; Solid-state ^{29}Si NMR (GHD/MAS 40 Hz, 25 °C) δ = −81.8; Solid-state ^{29}Si NMR (GHD/MAS 40 Hz, 70 °C) δ = −79; Solid-state ^{29}Si NMR (GHD/MAS 40 Hz, 100 °C) δ = −81.

The synthetic procedure has been successfully scaled-up by a



	Found	Calcd	Formula
a	2913.7	2914	$[M+K]^+$
b	2895.8	2898	$[M+K-O]^+$
c	2875.8	2876	$[M+H]^+$
d	2858.8	2860	$[M+H-O]^+$
e	2839.8	2838	$[M-K+2H]^+$
f	2819.9	2822	$[M-K+2H-O]^+$
g	2803.9	2800	$[M-2K+3H]^+$
h	2783.9	2784	$[M-2K+3H-O]^+$

Fig. 2. Positive-ion FAB mass spectrum of $K_7SiW_9Nb_3O_{40}$, **1**. Only peaks corresponding to cation exchange and loss of O, as well as the molecular ion peak $[M+H]^+$, are observed, where $M = K_7SiW_9Nb_3O_{40}$.

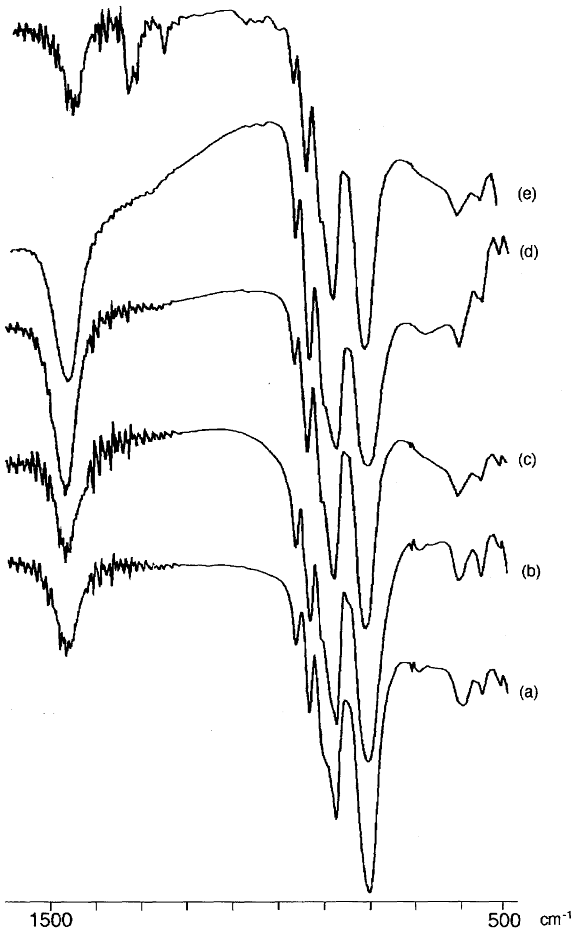


Fig. 3. The FT-IR spectra, measured as KBr disks of (a) $Cs_7SiW_9Nb_3O_{40}$, **3** of (b) $K_7SiW_9Nb_3O_{40}$, **1** of (c) $Na_7SiW_9Nb_3O_{40}$, **4** of (d) $Li_7SiW_9Nb_3O_{40}$, **2** and of (e) $[(n\text{-}C_4H_9)_4N]_7SiW_9Nb_3O_{40}$ demonstrating that the polyoxoanion region (1100—700 cm^{-1}) of the IR bands of these salts are completely coincident, except for the vibrational bands characteristic of $[(n\text{-}C_4H_9)_4N]^+$ (1380—1485 cm^{-1}).

factor of 4, resulting in an 8.2 g (50%) yield, and was independently and successfully repeated by one of us.

Microanalysis. Found: H, 0.40; K, 9.03; Si, 1.6; W, 56.8; Nb, 9.47; O, 22.9; total 100.2%. Calcd for $H_6K_7SiW_9Nb_3O_{43}$, or $K_7SiW_9Nb_3O_{40}\cdot 3H_2O$: H, 0.21; K, 9.34; Si, 1.0; W, 56.5; Nb, 9.52; O, 23.5%. The weight loss observed during drying overnight at room temperature under reduced pressure before the analysis: 2.88%. TG/DTA done under atmospheric conditions: weight loss of 5.28% found below 500 °C; calcd 5.28% for $x = 11$ in $K_7SiW_9Nb_3O_{40}\cdot xH_2O$. IR (KBr) 1633s ($H_2O$), 994m, 955s, 885s, 795s, 538m, 475m cm^{-1}. ^{183}W NMR (D_2O, 25 °C) $\delta = -118$ (6W), -125 (3W).

Synthesis of $Li_7SiW_9Nb_3O_{40}\cdot xH_2O$ [$x = 11$—12] (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, 0.426 g (4.536 mmol, 6 equiv) of solid $LiBF_4$ was added to 5.00 g (0.756 mmol) of $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$ dissolved completely in 50 mL of CH_3CN in a 200-mL beaker. During 20-min stirring, a clear colorless solution was obtained. After an additional 1 h stirring, a clear solution was taken out of the glove box. To the solution 12.1 mL (6.05 mmol, 8 equiv) of a 0.5 M LiOH aqueous solution was added dropwise using a pipet. The stirred solution became cloudy, and then a colorless oil formed at the bottom of the beaker. Stirring was continued for an additional 30 min, and then the solution was placed in a refrigerator at 5 °C overnight. The clear supernatant mother liquor was discarded by decantation and the colorless, oily precipitate was washed three times with 30 mL CH_3CN. The resulting oil was dried in an oven at 55 °C.

The crude material was redissolved in 50 mL of unbuffered pH 8 water, which had been prepared using a 0.5 M LiOH aqueous solution. The solution was filtered once through filter paper (Whatman No. 2). To the stirred, clear and colorless filtrate, 300 mL of CH_3CN was added dropwise from a dropping funnel. The solution changed to a cloudy suspension, and a white, oily precipitate reprecipitated at the bottom of the beaker. After standing in a refrigerator at 5 °C overnight, the mother liquor was removed by decantation, and the white precipitate was washed three times with 30 mL CH_3CN, then dried overnight in an oven at 55 °C. This reprecipitation procedure was repeated twice more. A white powder was obtained in 2.3 g yield (53.4%, for the $x = 11$ hydrated species). Compound **2** was very hygroscopic, extremely soluble in water and moderately soluble in MeOH, EtOH, DMF, and DMSO, but insoluble in CH_3CN, acetone, ether, benzene, hexane, and ethyl acetate.

Microanalysis. Found: H, 0.41; Li, 1.67; Si, 1.09; W, 59.8; Nb, 10.2; O, 25.8; total 99.0%. Calcd for $H_{10}Li_7SiW_9Nb_3O_{45}$, or $Li_7SiW_9Nb_3O_{40}\cdot 5H_2O$: H, 0.37; Li, 1.77; Si, 1.02; W, 60.4; Nb, 10.2; O, 26.3%. The weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}—10^{-4} Torr) before the analysis: 4.45%. TG/DTA done under atmospheric conditions: weight loss of 7.23% found with a temperature ramp of 5 °C min^{-1} below 440 °C, with a clear endothermic point at 104.7 °C; calcd 6.95% for $x = 11$ and 7.53% for $x = 12$ in $Li_7SiW_9Nb_3O_{40}\cdot xH_2O$. IR (KBr) (Fig. 3(d)): 996m, 884s, 795s, 539m, 473m cm^{-1}. ^{183}W NMR (D_2O, 25 °C) (Fig. 4(a)) $\delta = -122.2$ (6W, $\Delta\nu_{1/2} = 3.7$ Hz), -128.2 (3W, $\Delta\nu_{1/2} = 3.8$ Hz). ^{183}W NMR (DMSO-d_6, 25 °C) (Fig. 4(b)) $\delta = -95.0$ (6W,

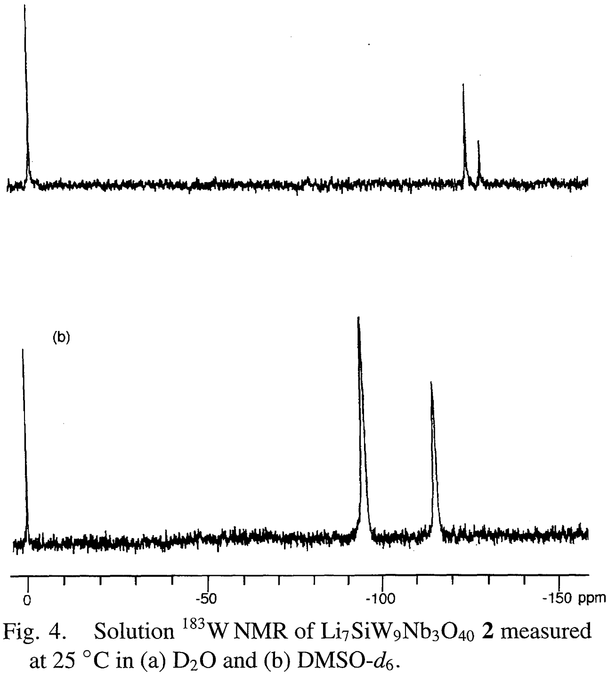


Fig. 4. Solution ^{183}W NMR of $Li_7SiW_9Nb_3O_{40}$ **2** measured at 25 °C in (a) D_2O and (b) DMSO-d_6.

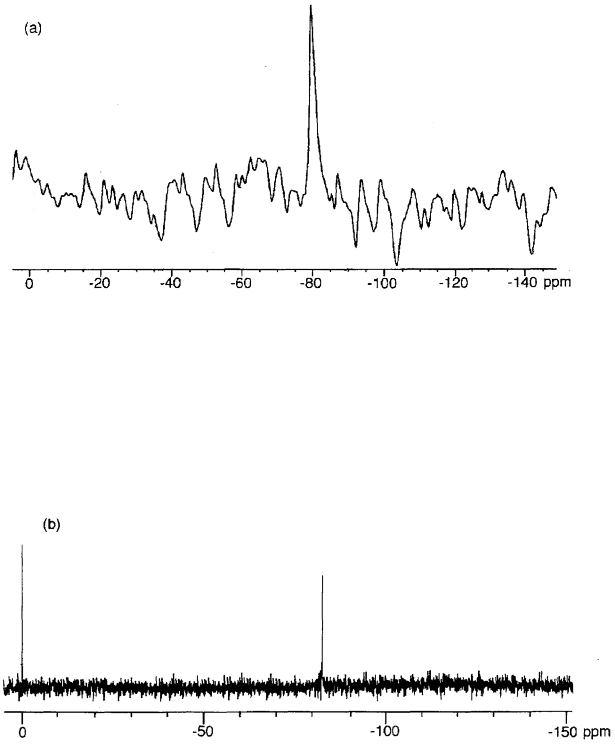


Fig. 5. Solid-state CP/MAS ^{29}Si NMR (a) and solution ^{29}Si NMR in D_2O (b), measured at 25 °C, of $K_7SiW_9Nb_3O_{40}$ **1**.

$\Delta\nu_{1/2}$ = 19.2 Hz), -115.2 (3W, $\Delta\nu_{1/2}$ = 15.3 Hz). ^{29}Si NMR (D_2O, 25 °C) δ = -82.9; Solid-state ^{29}Si NMR (CP/MAS 40 Hz, 26 °C) δ = -81.7; Solid-state ^{29}Si NMR (GHD/MAS 40 Hz, 25 °C) δ = -81.9; Solid-state ^{29}Si NMR (GHD/MAS 10 Hz, 25 °C) δ = -81.7.

Synthesis of $Cs_7SiW_9Nb_3O_{40}\cdot xH_2O$ [x = 7—8] (3). In a 200-mL beaker 5.00 g (0.756 mmol) of $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$ was dissolved in 50 mL of CH_3CN that had been previously well-dried by molecular sieves 3A. To a clear solution, 1.007 g (4.551 mmol, 6 equiv) of $CsBF_4$ was added. Within one hour of stirring the solution became clear [Note: sometimes the solution became cloudy, when the CH_3CN used was not thoroughly dried]. To the clear solution, 12.1 mL (6.05 mmol, 8 equiv) of a 0.5 M CsOH aqueous solution was added using a pipet; the 0.5 M CsOH solution was previously prepared by dissolving solid CsOH in water and the concentration was determined by titration with 0.5 M hydrochloric acid. The resulting suspension was stirred at room temperature overnight. A white precipitate, collected on a fine glass frit, was washed three times with 50 mL CH_3CN and then dried in an oven at 55 °C overnight. At this stage the yield of white powder was 3.6 g.

The 3.6 g of crude material was redissolved in 50 mL of warm, unbuffered pH 8 solution, (prepared using a 0.5 M CsOH aqueous solution), followed by heating at 50 °C. The clear colorless filtrate was passed once through a folded filter paper (Whatman No. 2). Next, 300 mL CH_3CN was added dropwise using a dropping funnel. The solution containing the white precipitate was placed in a refrigerator at 5 °C overnight. The resulting colorless powder was collected on a fine glass frit, washed three times with 50 mL CH_3CN, and then dried in an oven at 55 °C overnight. The resultant white powder was finally obtained in 1.5 g yield (27.1%, for the x = 7 hydrated species). It was sparingly cold water-soluble, but hot water-soluble, and organic solvent-insoluble as expected.

Microanalysis. Found: H, 0.08; Cs, 26.0; Si, 0.88; W, 46.4; Nb, 7.88; O, 19.1; total 100.3%. Calcd for $H_6Cs_7SiW_9Nb_3O_{43}$, or $Cs_7SiW_9Nb_3O_{40}\cdot 3H_2O$: H, 0.17; Cs, 25.9; Si, 0.78; W, 46.2; Nb, 7.77; O, 19.2%. The weight loss observed during drying at room temperature under 10^{-3}—10^{-4} Torr overnight before the analysis: 3.89%. TG/DTA done under atmospheric conditions: weight loss of 3.56% found with a temperature ramp of 5 °C min^{-1} below 500 °C with an endothermic point at 99.8 °C; calcd 3.44% for x = 7 and 3.91% for x = 8 in $Cs_7SiW_9Nb_3O_{40}\cdot xH_2O$. IR (KBr) (Fig. 3(a)) 956m, 884s, 788s, 529m cm^{-1}. ^{183}W NMR (D_2O, 70 °C) δ = -110.6 (6W, $\Delta\nu_{1/2}$ = 5.72±0.31 Hz), -118.3 (3W, $\Delta\nu_{1/2}$ = 4.31±0.31 Hz). Solid-state ^{29}Si NMR (GHD/MAS, at 25 °C) δ = -81.

Synthesis of $Na_7SiW_9Nb_3O_{40}\cdot xH_2O$ [x = 16—17] (4). This compound was previously prepared on an 11.3 g scale and fully characterized in the form with x = 16 water.[4d] Here, the compound was reprepared in a yield of 2.6 g (56%), recharacterized and compared with the properties of compounds **1**—**3** under the same conditions. The amount of water of hydration under atmospheric conditions found previously (x = 16)[4d] was observed herein to be reproducible.

Microanalysis. Found: H, 0.30; Na, 5.73; Si, 1.04; W, 58.2; Nb, 9.90; O, 24.4; total 99.6%. Calcd for $H_8Na_7SiW_9Nb_3O_{44}$, or $Na_7SiW_9Nb_3O_{40}\cdot 4H_2O$: H, 0.28; Na, 5.68; Si, 0.99; W, 58.4; Nb, 9.83; O, 24.8%. The weight loss observed during drying overnight at room temperature under reduced pressure (10^{-3}—10^{-4} Torr) before the analysis: 4.17%. TG/DTA done under atmospheric conditions: weight loss of 9.88% found with a temperature ramp 5 °C min^{-1} below 500 °C with clear endothermic points at 45.9 and 90.1 °C; calcd 9.44% for x = 16 and 9.97% for x = 17 in $Na_7SiW_9Nb_3O_{40}\cdot xH_2O$. IR (KBr) (Fig. 3(c)): 958s, 885s, 796s, 538m, 474w cm^{-1}. ^{183}W NMR (D_2O, 25 °C) δ = -121.6 (6W, $\Delta\nu_{1/2}$ = 2.59 Hz), -127.7 (3W, $\Delta\nu_{1/2}$ = 2.80 Hz). ^{183}W NMR (DMSO-d_6, 25 °C) δ = -93.9 (6W, $\Delta\nu_{1/2}$ = 14.12±0.31 Hz), -114.2 (3W, $\Delta\nu_{1/2}$ = 10.22±0.31 Hz). ^{29}Si NMR (D_2O, 25 °C) δ = -82.8. ^{29}Si NMR (DMSO-d_6, 25 °C) δ = -82.5. Solid-state ^{29}Si NMR (GHD/MAS 40 Hz, 25 °C) δ = -81.6; Solid-state ^{29}Si NMR (GHD/MAS 10 Hz, 25 °C) δ = -81.6.

Results and Discussion

Synthetic Reactions, Composition Proof and General Properties. The alkali-metal salts of the Keggin-type heteropolyoxoanion, $SiW_9Nb_3O_{40}{}^{7-}$, have been derived from a stoichiometric reaction of the organic solvent-soluble, (Nb–O–Nb)$_3$ anhydride precursor $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$,[4b] with MBF_4 and subsequently with the required amount of MOH (M = Li, Na, K, and Cs) as follows (Eq. 1):

$$[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77} + 6MBF_4 + 8MOH \longrightarrow 2M_7SiW_9Nb_3O_{40} + 6[(n\text{-}C_4H_9)_4N]BF_4 + 5H_2O \quad (1)$$

The key points in the synthesis of $M_7SiW_9Nb_3O_{40}$ (M = Li, Na, K, and Cs) are as follows: (a) the use of stoichiometric amounts (6 equiv) of MBF_4 to allow for an exchange of the 6 $[(n\text{-}C_4H_9)_4N]^+$ countercations of the organic solvent-soluble, (Nb–O–Nb)$_3$ anhydride precursor, $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$; (b) the use of a total of 8 equiv of MOH to react with the two protons in the (Nb–O–Nb)$_3$

anhydride (requiring 2 equiv of OH^-) and to hydrolytically cleave the three bridging Nb–O–Nb bonds (requiring an additional 6 equiv of OH^-) and forming a total of $5H_2O$; and (c) 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 CH_3CN from an aqueous solution of unbuffered, pH 8 water.

The molecular formula of K_7 (**1**), Li_7 (**2**), Cs_7 (**3**), and Na_7 (**4**) salts, with 1 water, 5 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, 100.96, 99.0, 100.3, and 99.6%, totals, respectively, are observed; see the Experimental Section). The molecular formula of **1** was also established by the FABMS spectrum in the positive-ion mode (Fig. 2), which showed the parent or molecular ion peak at $[M+H]^+ = m/z$ 2875.8 ($M = K_7SiW_9Nb_3O_{40}$) and the characteristic cation-exchange and fragmentation processes. The cation-exchange process in **1** is clearly observed by K^+ exchange with H^+, and the fragmentation pattern is dominated by a loss of O (m/z 16), both processes of which are consistent with other FABMS spectral data previously reported for $H_4SiW_{12}O_{40}\cdot 26H_2O$,[8a)] $K_4H_3SiW_9V_3O_{40}\cdot 3H_2O$,[8a)] $(Bu_4N)_4[(CpTi)SiW_9V_3O_{40}]$,[8a,8c)] and $(Bu_4N)_6[H_2Si_2W_{18}Nb_6O_{77}]$.[8b)] On the other hand, TG/DTA measurements performed under atmospheric conditions show the presence of 5—6 water for **1**, 11—12 water for **2**, 7—8 water for **3**, and 16—17 water for **4**, respectively. We have handled these samples, as the indicated hydrated compounds, under atmospheric conditions. The TG data estimate the total amount of water, both intrinsic water of hydration and the adsorbed water from the atmosphere, 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 90.5 °C for **1**, 104.7 °C for **2**, 99.8 °C for **3**, and 45.9 and 90.1 °C for **4**.

The water-solubility of salts **1**—**4**, judged qualitatively by a preparation of the solution for NMR measurements, is strongly affected by the countercations; the order at room temperature was found to be $\mathbf{2} \gg \mathbf{4} > \mathbf{1} \gg \mathbf{3}$. The Li_7 salt **2** is also soluble in several organic solvents, such as MeOH, EtOH, DMF, and DMSO. Of particular note is the ease of crystallization found for the K_7 salt, **1**. Thus, each of the following can be significantly affected by countercations: the amounts of intrinsic hydrated water and adsorbed water, solubilities in water and in organic solvents, and the ease of crystallization.

Infrared Spectra and Thermal Analysis. The solid FT-IR spectra (Fig. 3(a)—Fig. 3(d)), measured as KBr disks, of $M_7SiW_9Nb_3O_{40}$ ($M = Li^+$, Na^+, K^+, and Cs^+) obtained here and of $[(n\text{-}C_4H_9)_4N]_7SiW_9Nb_3O_{40}$ (Fig. 3(e)) separately prepared according to Ref. 4b, are completely coincident (except, of course, the absence of typical vibrational bands due to $[(n\text{-}C_4H_9)_4N]^+$ countercations observed in the 1485—1380 cm^{-1} region in the all alkali-metal salts). In these spectra, the characteristic and intense 690 cm^{-1} band, due to the vibration of three bridging Nb–O–Nb linkages present in the $(Nb\text{–}O\text{–}Nb)_3$ anhydride precursor $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$,[4b)] disappears. Infrared measurements confirm that the Keggin-type "$SiW_{12}O_{40}{}^{n-}$" heteropolytungstate framework remains intact under the conditions of the synthesis.[9)]

The effect of alkali-metal cations on the thermal-stability of $SiW_9Nb_3O_{40}{}^{7-}$ was observed in the solid state. Exothermic peaks without an accompanying weight loss were observed at around 500 °C with alkali metal ions: 431 °C for the Li salt **2**, 517 °C for the Na salt **4**, 605 °C for the K salt **1**, and 402 °C for the Cs salt **3**. FT-IR measurements, after the samples were heated above such exothermic temperatures (up to ca. 998 °C), showed that *the Keggin structure of the polyoxoanion is 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: K^+ salt $\mathbf{1} \gg Na^+$ salt $\mathbf{4} \gg Li^+$ salt $\mathbf{2} > Cs^+$ salt **3**. This sequence is in surprising contrast to the cation-dependent thermal stability observed in the Dawson-type $P_2W_{15}Nb_3O_{62}{}^{9-}$: Cs^+ salt > K^+ salt ≫ Na^+ salt > Li^+ salt.[1j)]

Solution ^{183}W NMR Spectra. The ^{183}W NMR spectrum of $Li_7SiW_9Nb_3O_{40}$ **2** in D_2O (Fig. 4(a)) shows primarily two peaks at −122.2 (6W) and −128.2 (3W) ppm with integrated intensities 2 : 1. The integrated intensities are in accord with the presence of a tungsten belt consisting of six WO_6 octahedra and a tungsten cap of three WO_6 octahedra, as expected for a Keggin heteropolyanion (Fig. 1A). Such a two-line ^{183}W NMR spectrum in D_2O was also observed in $K_7SiW_9Nb_3O_{40}$ **1** at ($\delta = -118.0$ and -124.9) and in $Na_7SiW_9Nb_3O_{40}$ **4** at ($\delta = -121.6$ and -127.7). On the other hand, the two-line ^{183}W NMR of the Cs_7 salt **3** was measured in D_2O at 70 °C ($\delta = -110.6$ and -118.3) because of its low solubility at room temperature. The two-line ^{183}W NMR spectrum requires that the heteropolyanion as a single species has an overall C_{3v} symmetry. The clean, two-line ^{183}W NMR spectra of **1**, **2**, and **4** were also observed in a DMSO-d_6 solution, although their chemical shifts were significantly altered ($\delta = -95.1$ and -113.1 for **1**, $\delta = -95.0$ and -115.2 for **2** (Fig. 4(b)), $\delta = -93.9$ and -114.2 for **4**) and their line widths were considerably broadened (see the $\Delta_{1/2}$ values in the Experimental Section) due to a solvent effect and/or the rapid equilibrium of the ion-pairing[1g)] present in the solution.

The solution ^{183}W NMR spectra of the related, Keggin-type, tri-substituted and thus overall average C_{3v} symmetry heteropolytungstates have been recently measured, specifically the 2 : 1 sharp signals for the A-β-$(Me_4N)_3PW_9Mo_3O_{40}$ in CD_3CN at −91.4 and −101.5 ppm,[10a)] for the A-β-$(Bu_4N)_4H_2PW_9V_3O_{40}$ in CD_3CN in the presence of 100 equivalents of H_2O at −99.4 and −107.6 ppm,[10b)] and for A-β-$Cs_6PW_9V_3O_{40}$ in D_2O, which shows peaks at −106.7 and −117.9 ppm.[10b)] Finke's group has found that, in the ^{183}W NMR of A-β-$(Bu_4N)_4H_3SiW_9V_3O_{40}$ in initially dry CD_3CN at 21 °C, the broad, low S/N ^{183}W resonance was gradually transformed to the expected two lines of 2 : 1 intensity at −108.4 (6W) and −110.1 (3W) ppm with ca.

10 equivalents of H_2O.[11a)] They have also observed the two-line ^{183}W NMR spectra for the $(Bu_4N)_5H_2SiW_9V_3O_{40}$ in dry CD_3CN by the addition of 100 equivalents of water, at −105.0 ppm (6W) and −109.5 (3W), but for the $(Bu_4N)_7SiW_9V_3O_{40}$ in dry CD_3CN at −81.1 (6W) and −101.4 ppm (3W).[11a)] These papers and observations are of historical significance as the first proven examples of prototypic tautomerism in polyoxometalates.[11a)]

Solution ^{29}Si NMR and Solid-State CP/MAS and GHD/MAS ^{29}Si NMR Spectra. Solution ^{29}Si NMR spectrum of **1** in D_2O (Fig. 5(b)) shows only one resonance at $\delta = -82.8$ ppm; in **2** the signal appears at $\delta = -82.9$ ppm. The singlet-line spectrum in **4** was observed at $\delta = -82.8$ ppm in D_2O and $\delta = -82.5$ ppm in DMSO-d_6. These chemical shifts are in a reasonable region, as expected for the SiO_4 group occupying the central tetrahedral site in the Keggin structure.[11c,11d)] However, the countercation does not significantly influence the chemical shifts of the solution ^{29}Si NMR.

On the other hand, solid-state CP/MAS ^{29}Si NMR at 25 °C was measured at −81.5 ppm for **1** (Fig. 5(a)) and at −81.7 ppm for **2**, and solid-state GHD/MAS ^{29}Si NMR at 25 °C at −81.8 ppm for **1**, at −81.9 ppm for **2**, at −81 ppm for **3**, and at −81.6 ppm for **4** were measured. The variable-temperature (VT) GHD/MAS ^{29}Si NMR spectra for **1** were also measured at −79 ppm at 70 °C and at −81 ppm at 100 °C. From the VT solid-state GHD/MAS ^{31}P NMR recently measured for the Dawson-type $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion with different (Li^+, Na^+, K^+, and Cs^+) countercations, it has been found that the hydration structure around this polyoxoanion is significantly influenced by the countercations.[1j)] The present solid-state ^{29}Si NMR measurements were almost insensitive to the cation-dependent hydration environment around the $SiW_9Nb_3O_{40}{}^{7-}$ polyoxoanion; this is despite the fact that TG/DTA measurements indicate that the hydration structure is likely to be significantly changed by the different countercations.

Compared with the NMR of constitutional elements, such as ^{31}P, ^{183}W, ^{51}V, and ^{29}Si of the heteropolyanions, it is not surprising that the ^{29}Si NMR is not highly sensitive to the environment, solvents, or to the ^{29}Si NMR measurement in either solution or the solid-state. In fact, for the unsubstituted heteropolytungstate, $H_4SiW_{12}O_{40}\cdot 26H_2O$, the ^{29}Si NMR in D_2O at −84.7 ppm and the solid-state ^{29}Si NMR at −85.0 ppm have been reported and are virtually identical.[11b)] Furthermore, in the solution the ^{29}Si NMR spectra of the related Keggin-type tri-substituted heteropolytungstates the following are observed: one narrow line at −83.0 ppm for $(Bu_4N)_4H_3SiW_9V_3O_{40}$ in CD_3CN with ca. 10 equivalents of H_2O, one line at −84.19 ppm for $(Bu_4N)_6HSiW_9V_3O_{40}$ in CD_3CN, a singlet at −83.85 ppm for $(Bu_4N)_5H_2SiW_9V_3O_{40}$ in CD_3CN following the addition of 100 equivalents of water, one line at −83.38 ppm for $(Bu_4N)_7SiW_9V_3O_{40}$ in CD_3CN, and one line at −83.5 ppm for $K_6HSiW_9V_3O_{40}\cdot 3H_2O$ in D_2O.[11a)]

Conclusion

In conclusion, analytically pure forms of the water-soluble, alkali metal salts of the Keggin-type heteropolyoxoanion, $M_7SiW_9Nb_3O_{40}$ ($M = Li^+$, Na^+, K^+, and Cs^+) have been isolated, in 53, 56, 25, and 27% yields and on a 2.3, 2.6, 1.1, and 1.5-g scale, respectively. These new salts have been unequivocally characterized, both in solution and in the solid-state, and the full details of the synthesis and isolation were presented. The molecular formula of $M = K^+$ compound **1** was established by a positive ion FABMS spectrum. The clean two-line ^{183}W NMR spectra, with a 2 : 1 intensity ratio in D_2O, demonstrate an overall C_{3v} symmetry of the $SiW_9Nb_3O_{40}{}^{7-}$ polyoxoanion. The effects of the alkali-metal countercations on the $SiW_9Nb_3O_{40}{}^{7-}$ were observed in the solid-state as a cation-dependent thermal-stability of the Keggin structure. The order of the relative thermal-stability was found to be: K^+ salt **1** $\gg$ Na^+ salt **4** $\gg$ Li^+ salt **2** > Cs^+ salt **3**. In the solid-state ^{29}Si NMR spectra, no significant effect of the countercation is observed. This is in contrast to the Dawson-type heteropolytungstates, in which the hydration structure around the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion is significantly influenced by the countercations, with resulting solid-state ^{31}P NMR spectral changes through solid-state ion-pairing interactions between the cation and the $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion. The cation-dependent properties of the present $SiW_9Nb_3O_{40}{}^{7-}$ heteropolytungstates manifest themselves, instead, in: the amounts of intrinsic hydrated water and adsorbed water, solubilities in water and insolubility in organic solvents, and in the ease of crystallization—especially of the K^+ salt. The title complexes are also of interest as a possible new type of solid-base catalysts; studies of such catalyses are planned.

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7) For 30—60 mM H_2O solutions of the K_7 (**1**) and Na_7 (**4**) salts, which were in the same range of the concentration used for the ^{183}W NMR measurements in D_2O, the measured pH level was between 7.4 and 7.6. The pD value was calculated by pD = pH +0.4: a) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960); b) R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini, and M. Fournier, *Inorg. Chem.*, **16**, 2916 (1977).

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