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Formation, Isomerization, and Derivatization of Keggin Tungstoaluminates

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Trends in the stability of α- and *β*-Keggin heteropolytungstates of the second-row main-group heteroatoms Al(III), Si(IV), and P(V) are elaborated by data that establish the roles of kinetic and thermodynamic control in the formation and isomerization of Keggin tungstoaluminates. Slow, room-temperature co-condensation of Al(III) and W(VI) (2:11 molar ratio) in water gives a pH 7 solution containing β_1 and β_2 isomers of $[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (β_1- and β_2-**1**). Partial equilibration of this kinetic product mixture by gentle heating (2 h at 100 °C) or, alternatively, co-condensation of Al(III) and W(VI) for 2.5 h at 100 °C both give mixtures of β_2-, β_3-, and α-**1**. Full equilibration, by prolonged heating (25 days at 100 °C), gives an isomerically pure solution of α-**1**, thus demonstrating that isomerization occurs in the direction $\beta_1 \rightarrow \beta_2 \rightarrow \beta_3 \rightarrow \alpha$. Furthermore, kinetically controlled conversions of **1** to $H_5[AlW_{12}O_{40}]$ (**2**)—achieved by heating pH 0−0.2 solutions of **1** for 5 days at 100 °C—occur with retention of isomeric integrity, such that α-**1** is converted to α-**2** (92%; 8% *β*), while mixtures of β_2- and β_3-**1** are converted to *β*-**2** (87%; 13% α). These data, when combined with previously reported observations (equilibria between α- and *β*-**2**, kinetically controlled hydrolyses of α-**2** to α-$[AlW_{11}O_{39}]^{9-}$ (α-**3**) and of *β*-**2** to β_2-**3**, and equilibria between β_3- and α-**3**), provide a comprehensive picture regarding the roles of kinetic and thermodynamic control. Finally, a general method for preparation of the isomerically pure derivatives α-$K_{9-n}[AlM^{n+}W_{11}O_{39}]$ (**4**), M^{n+} = Al(III), $[V^{IV}O]^{2+}$, $[V^{V}O]^{3+}$, Mn(II), Mn(III), Mn(IV), Co(II), and Co(III), is provided. The presence of Mn(IV) is confirmed by cyclic voltammetry, pK_a values of the aquo ligands on **4** are determined by pH titration, and the isomeric structure of these derivatives is established by ^{27}Al, ^{51}V, and ^{183}W NMR and IR spectroscopies and X-ray crystallography.

Introduction

The formation and structural rearrangement of Keggin dodecatungstosilicates, *β*- and α-$[SiW_{12}O_{40}]^{4-}$,[1] and of undecatungstosilicates, β_1-, β_2-, β_3-, and α-$[SiW_{11}O_{39}]^{8-}$,[2] along with the preparation of first-row transition-metal (M^{n+}) substituted derivatives, α-$[SiM^{n+}W_{11}O_{39}]^{(8-n)-}$,[1] are well established. In water, the *β* isomers of $[SiW_{12}O_{40}]^{4-}$ and $[SiW_{11}O_{39}]^{8-}$ spontaneously rearrange completely to α structures.[1,3] In contrast, we recently reported[4] that the analogous Keggin tungstoaluminates, $[AlW_{12}O_{40}]^{5-}$ and $[AlW_{11}O_{39}]^{9-}$, exist in aqueous solution as equilibria between α and *β* isomers. At pH 0 (473 K in H_2O), α-$H_5[AlW_{12}O_{40}]$ is more stable than *β*-$H_5[AlW_{12}O_{40}]$ by 2.1 kcal mol^{-1}; i.e., the change in Gibbs free energy ($\Delta G = -RT \ln K$) associated with isomerization from *β* to α is −2.1 kcal mol^{-1}.[5,6] The difference in energy between α- and *β*-$Na_9[AlW_{11}O_{39}]$ (pD 7 at 333 K in D_2O) is even smaller: the α isomer is more stable by only 0.3 kcal mol^{-1}. This unprecedented behavior clearly distinguishes the tungstoaluminates from their second-row ($[SiW_{12}O_{40}]^{4-}$ and $[PW_{12}O_{40}]^{3-}$) analogues. In particular, differences in energy between α and *β* isomers decrease markedly as the heteroatom, X, is varied from P(V) or Si(IV) to Al(III) (the Δ*G* values above are necessarily much smaller than those of P(V) or Si(IV) analogues). As a result, the relative energies of new tungstoaluminate derivatives cannot be inferred by reference to isostructural silicate or phosphate analogues. At the same time, the number of atoms present in these anions, combined with the subtle differences in energy associated with their α and *β* structures, impose limitations on the predictive value of even rigorous, state-of-the-art theoretical (density-functional theory) calculations.[7−9]

High-yield synthetic routes to an elaborate family of Keggin tungstoaluminates now make it possible to clarify the roles of kinetic and thermodynamic control in the formation and isomerization of these cluster anions. Specifically, we herein report the formation and characterization of β_1, β_2, β_3, and α isomers of the undecatungstodialuminate anion, $[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (**1**). Moreover, we provide data that demonstrate kinetic and thermodynamic control over the formation and subsequent isomerization of **1** and the retention of isomeric integrity in kinetically controlled conversions of **1** (β_1, β_2, β_3, and α isomers) to $H_5[AlW_{12}O_{40}]$ (**2**; *β* and α isomers). These data are combined with information regarding the formation and equilibration of β_2-, β_3-, and α-$[AlW_{11}O_{39}]^{9-}$ (**3**),[4] to provide an integrated

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(1) Tézé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2151−2154.

(2) Tézé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 999−1002.

(3) A chronological list of key reports documenting efforts to rationalize the structure and dynamics of Keggin anions is provided in the Introduction of ref 4.

(4) Weinstock, I. A.; Cowan, J. J.; Barbuzzi, E. M. G.; Zeng, H.; Hill, C. L. *J. Am. Chem. Soc.* **1999**, *121*, 4608−4617.

(5) Kepert, D. L. *Inorg. Chem.* **1969**, *8*, 1556−1558.

(6) Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2008−2010.

(7) Maestre, J. M.; Lopez, X.; Bo, C.; Poblet, J. M.; Casañ-Pastor, N. *J. Am. Chem. Soc.* **2001**, *123*, 3749−3758.

(8) Lopez, X.; Maestre, J. M.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 9571−9576.

(9) Wang, S. H.; Jansen, S. A. *Chem. Mater.* **1994**, *6*, 2130−2137.

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summary of collective findings. These findings further elaborate recently identified trends[4] in the thermodynamic and kinetic stabilities of α- and *β*-Keggin heteropolytungstates of the second-row main-group heteroatoms, Al(III), Si(IV), and P(V). Finally, we report a general method for the preparation of useful, isomerically pure derivatives, α-$K_{9-n}[AlM^{n+}W_{11}O_{39}]$ (**4**), M^{n+} = Al(III), $[V^{IV}O]^{2+}$, $[V^{V}O]^{3+}$, Mn(II), Mn(III), Mn(IV), Co(II), and Co(III).

Experimental Section

Materials and Methods. All materials used were reagent grade. $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (reaction mixture containing three isomers, one of C_1 symmetry and two of C_s symmetry) and α-$K_9[AlW_{11}O_{39}]$ were prepared as described.[4] Infrared and UV−vis spectra were acquired using Nicolet 510M FTIR and Hewlett-Packard 8452A spectrophotometers. pH measurements (synthesis and isomerization reactions) were made using an Orion model 250A pH meter. Electrochemical data were obtained using a BAS CV-50W electrochemical analyzer with a glassy-carbon working electrode and a Ag/AgCl reference electrode. Electrolyte solutions were either 1 mM in polyoxometalate in 1.0 M sulfate (1 M in sulfate, prepared from 1 M solutions of $NaHSO_4$ and Na_2SO_4) or 5 mM in polyoxometalate dissolved in 0.2 M acetate electrolyte (prepared from 0.2 M solutions of acetic acid and potassium acetate). All reduction potentials are reported relative to the normal hydrogen electrode (NHE).

Acquisition of ^{27}Al and ^{183}W NMR Spectra. Reported ^{27}Al spectra were collected on a Varian UNITY 600 MHz spectrometer at 156.2 MHz; ^{183}W spectra were obtained using a Varian UNITY 400 NMR at 16.66 MHz. External references were, for ^{27}Al, 0.10 M $AlCl_3{\cdot}6H_2O$ ($[Al(H_2O)_6]^{3+}$, $\delta = 0$ ppm) and, for ^{183}W, 0.2 M $Na_2WO_4{\cdot}2H_2O$ (WO_4^{2-}(aq), $\delta = 0$ ppm). Precise locations of ^{183}W NMR signals assigned to corresponding W atoms in identical anions vary, probably due to ion pairing,[10−12] with the nature and concentration of the countercation present, with the concentration of the Keggin anions present, and with total ionic strength. Changes in these variables also affect ^{27}Al NMR line widths. The NMR software package NUTS (1-D version, distributed by Acorn NMR Inc., Fremont, CA) was used to process the spectroscopic data.

pH Titrations. NaOH was obtained from Fisher Scientific and standardized using potassium hydrogen phthalate (GFS Chemicals). The H_2SO_4 solution was obtained from Fisher Scientific and standardized (0.499 M) using NaOH solutions prepared for this purpose. Standardized aqueous HCl (0.100 M) was used as received from Fisher Scientific. pH values were determined using Beckman 210 or Orion model 230A pH meters. $Na_7[AlCo^{II}(H_2O)W_{11}O_{39}]{\cdot}14H_2O$ was prepared by ion exchange from $K_7[AlCo^{II}(H_2O)W_{11}O_{39}]{\cdot}14H_2O$.[13] Titrations to low and high pH values were carried out by additions of small aliquots of either acid or base from a 10-mL buret to stirred, aqueous polyoxometalate-salt solutions.

Isomerically Selective Preparation of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Mixture of β_1 and β_2 Isomers). $Na_2WO_4{\cdot}2H_2O$ (10.0 g, 0.030 mol) was dissolved in water (200 mL) in a beaker. HCl (6 M) was added dropwise (ca. 4 mL), allowing any precipitate of tungstic acid to dissolve, until the pH of the solution decreased to 7.7. A solution of $AlCl_3{\cdot}6H_2O$ (1.33 g, 0.005 mol) in water (40 mL) was added dropwise over a 2-week period to the vigorously stirred tungstate solution. After each addition of several drops of aqueous $AlCl_3$, the solution became cloudy due to precipitation of Al(III) and was stirred until the cloudiness dissipated. Near the start of the 2-week addition, dissolution of precipitated Al(III) salts required 30 min−1 h of stirring after addition of each several-drop aliquot of aq $AlCl_3$. As the reaction progressed, dissolution of the precipitated Al(III) salts slowed. As a result, it was necessary to stir the reaction mixture for several hours after the addition of each aliquot of aq $AlCl_3$. After approximately half of the $AlCl_3$ solution had been added, insoluble Al(III) salts persisted and no further $AlCl_3$ was added (i.e., the reaction could only be taken halfway to completion). The mixture was filtered through diatomaceous earth (Celite) to give a clear solution, which was concentrated under vacuum at 30−35 °C to a volume of 50 mL. Acetone (ca. 50 mL) was combined with the concentrated solution in a separatory funnel, the mixture was shaken, and two layers formed. The bottom (dense and viscous) layer contained $Na_6[Al(AlOH_2)W_{11}O_{39}]$, along with tungstate and paratungstates (Na^+ salts), and was collected and evaporated to an oil (ca. 3.5 g) under vacuum at 30−35 °C. A ^{183}W NMR spectrum of 2 g of this oil dissolved in 4.0 mL of D_2O revealed the presence of two isomers of $[Al(AlOH_2)W_{11}O_{39}]$,$^{6-}$ β_1 and β_2 (35% and 65%, respectively). ^{27}Al NMR (D_2O, 0.1 M; δ, ppm ($\Delta\nu_{1/2}$, Hz)): 73.6 (160) and 6.4 (1200). ^{183}W NMR (δ, ppm): β_1 isomer, −34.2, −67.3, −122.8, −171.1, −181.8, −224.1; β_2 isomer, −71.0, −96.5, −107.8, −110.7, −119.8, −132.2, −140.9, −155.4, −167.5, −180.0, −247.7. (See Figure S1 in the Supporting Information.)

Isomerization of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Mixture of β_1 and β_2 Isomers) to a Mixture Containing β_2, β_3, and α Isomers. A 1.5 g sample of the mixture containing β_1- and β_2-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ (prepared as described immediately above) was dissolved in water (30 mL), heated at reflux for 2 h, concentrated to dryness, and redissolved in 4 mL of D_2O. The ^{183}W NMR spectrum revealed the presence of β_2- and β_3-$[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (ca. 45 and 30%, respectively), α-$[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (ca. 25%), and some residual β_1-$[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (ca. 5%) (uncertainties in percentage values are ±10%). ^{27}Al NMR (D_2O, 0.1 M; δ, ppm ($\Delta\nu_{1/2}$, Hz)): 73.6 (160) and 6.4 (1200). ^{183}W NMR (δ, ppm): β_2 isomer, −70.3, −97.0, −110.4, −111.0, −120.6, −133.1, −141.1, −154.5, −167.3, −180.0, −247.1; β_3 isomer, −38.2, −72.7, −119.7, −170.2, −180.6, −223.2; α isomer, −60.9, −108.4, −133.8, −147.3, −158.5, −212.4. (See Figure S2 in the Supporting Information.)

Isomerically Selective Preparation of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Mixture of β_2 and β_3 Isomers) in Water/Acetonitrile. The following preparation yields no α isomer. $Na_2WO_4{\cdot}2H_2O$ (10.0 g, 30.4 mmol) was dissolved in water (100 mL) in a 250-mL round-bottomed flask. HCl (6 M, 3.5 mL) was added dropwise (allowing any precipitate of tungstic acid to dissolve) until the pH of the solution decreased to 7.7. CH_3CN (30 mL) was added and the clear solution heated to reflux. $AlCl_3{\cdot}6H_2O$ (1.33 g, 5.5 mmol) in water (40 mL) was added dropwise over 2.5 h via a pressure-equalized dropping funnel. The addition was carried out slowly so that the solution became only minimally cloudy. If the solution became opaque, however, the addition was temporarily stopped and the solution stirred until it became more clear. After all the $AlCl_3$ was added, the now cloudy reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was then concentrated to dryness by rotary evaporation (the temperature of the water bath did not exceed 35 °C), and the resulting solid was dried under vacuum overnight at room temperature. ^{27}Al NMR (D_2O, 0.1 M; δ, ppm ($\Delta\nu_{1/2}$, Hz)): 73.6 (160) and 6.4 (1200). ^{183}W NMR (δ, ppm): β_2 isomer, ca. 65%, −70.2, −97.0, −108.4, −111.0, −132.7, −133.3, −141.1, −154.4, −166.0, −179.5, −246.4; β_3 isomer, ca. 35%, −38.4, −72.9, −119.8, −169.9, −180.1, −221.2. (See Figure S3 in the Supporting Information.)

High-Yield Preparation of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Mixture of β_2, β_3, and α Isomers). A solution containing three isomers of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ was prepared as previously reported:[4] $Na_2WO_4{\cdot}2H_2O$ (100 g, 0.304 mol; 11 equiv) was dissolved in water, acidified to pH 7.7 by addition of HCl, and heated to reflux, after which an aqueous solution of $AlCl_3{\cdot}6H_2O$ (13.32 g, 0.0552 mol; 2 equiv) was added dropwise over 90 min. The reaction mixture was then kept at reflux for 1 h and filtered. This preparation yields $Na_6[Al(AlOH_2)W_{11}O_{39}]$ as the only product observable by ^{27}Al NMR spectroscopy. Attention is now paid to identification of the three isomers present in the reaction mixture:

Identification of β_2, β_3, and α Isomers. The ^{183}W NMR spectrum of the reaction mixture (Figure 1A in the Results and Discussion) reveals the presence of 23 signals associated with tungsten atoms in three structural isomers, α (C_s symmetry; 6 signals, δ (ppm)): −62.2, −107.4,

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(10) Kirby, J. F.; Baker, L. C. W. *Inorg. Chem.* **1998**, *37*, 5537−5543.
(11) Grigoriev, V. A.; Hill, C. L.; Weinstock, I. A. *J. Am. Chem. Soc.* **2000**, *122*, 3544−3545.
(12) Grigoriev, V. A.; Cheng, D.; Hill, C. L.; Weinstock, I. A. *J. Am. Chem. Soc* **2001**, *123*, 5292−5307.
(13) Geletii, Y. V.; Bailey, A. J.; Cowan, J. J.; Weinstock, I. A.; Hill, C. L. *Can. J. Chem.* **2001**, *123*, 792−794.

−135.9, −147.6, −158.3, −211.0), β_2 (C_1 symmetry, 11 signals), and (most probably) β_3 (C_s symmetry, 6 signals), were observed between −43 and −200 ppm. The presence of the β_2 isomer is established by the observation of a group of 11 signals of effectively equal intensities. Assignment of the 6 signals associated with the α isomer was made by observation of increases in their intensities upon addition of authentic α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ to the isomer mixture. (α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ was prepared as described in the following paragraph and characterized by comparison to samples obtained by addition of $AlCl_3$ to α-$K_9[AlW_{11}O_{39}]$; see preparation of α-$K_6[Al(AlOH_2)W_{11}O_{39}]$, below.) The results of this doping experiment dictate that our earlier, tentative assignment of the 23 signals to the presence of β_1, β_2, and β_3 isomers (β_1, β_3, and α isomers all possess C_s symmetry) be modified (see Experimental Section in ref 4). While two isomers of C_s symmetry are present, one of these is clearly the α isomer. The remaining isomer of C_s symmetry is assigned by recourse to literature precedent: the kinetic product obtained upon preparation of $Na_8[SiW_{11}O_{39}]$ is the β_2 isomer, which, upon heating, is converted sequentially to β_3 and, finally, to α, the most stable of the four isomers of $Na_8[SiW_{11}O_{39}]$.[1,2,14,15] In the present case (Figure 1A), both β_2 and α isomers are present. It follows that the remaining β isomer of C_s symmetry is β_3.

Isomerization of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Mixture of β_2, β_3, and α Isomers) to α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$. The reaction mixture containing α, β_2, and β_3 isomers of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (and NaCl byproduct), described immediately above, was heated at reflux for 25 days. The solution was then cooled to room temperature and concentrated to dryness under vacuum to give a white amorphous solid. The ^{27}Al NMR spectrum (Figure 1B, inset; in the Results and Discussion) is effectively unchanged. The ^{183}W NMR spectrum, however (Figure 1B), now contains only 6 signals, assigned, by comparison to authentic samples, to α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$. Probably due to ion pairing[10−12] and ionic strength effects, the precise locations of the six signals associated with α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ vary with the concentrations of Na^+ and the Keggin anions present. As a result, the 6 signals assigned to the α isomer in Figure 1B possess slightly different chemical shifts than do those of the signals attributed to the same W atoms in Figure 1A.[16,17]

Conversions of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ to $H_5[AlW_{12}O_{40}]$. As previously reported,[4] crude reaction mixtures containing $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (and NaCl byproduct) can be converted in situ to $H_5[AlW_{12}O_{40}]$. To accomplish this, the pH of the $Na_6[Al(AlOH_2)W_{11}O_{39}]$ solution is first decreased to near 0 by addition of concentrated H_2SO_4. The acidified solution is then heated at reflux for 5 days. Attention is now paid to the relative ratios of specific isomers in reactant and product mixtures:

Conversion of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (β_2 and β_3) to β-$H_5[AlW_{12}O_{40}]$. A mixture of solid β_2- and β_3-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ (2.0 g, including NaCl byproduct; prepared in water/acetonitrile as described above) was dissolved in water (10 mL) and acidified with 5 mL of concentrated H_2SO_4 to a final pH of 0.2. The solution was heated at reflux for 5 days. A small amount of fine yellow precipitate present was removed by filtration, and the ^{27}Al NMR spectrum of the filtrate was obtained. The starting material, β_2- and β_3-$[Al(AlOH_2)W_{11}O_{39}]^{6-}$, was absent, having been converted to $[AlW_{12}O_{40}]^{5-}$ (87% β and 13% α).

Conversion of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (80% β_2 and β_3; 20% α) to $H_5[AlW_{12}O_{40}]$ (80% β; 20% α). A reaction mixture containing $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (β_2, β_3, and α isomers; Figure 1A in the Results and Discussion) was prepared in water at 100 °C as described above (see High-Yield Preparation of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Mixture of β_2, β_3, and α Isomers)). Integration of the ^{183}W NMR signals in Figure 1A indicates that the reaction mixture contains 80 ± 10% β_2- and β_3-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ and 20 ± 10% α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ (uncertainties reflect variation in the relative intensities of signals associated with like numbers of W atoms in the ^{183}W NMR spectrum itself). Conversion to $H_5[AlW_{12}O_{40}]$ by heating at reflux at near-zero pH gives a kinetic product distribution containing very similar ratios of β to α isomers (isomer ratios were quantified by ^{27}Al NMR spectroscopy). Observed ratios in repeat experiments are similar to those in the parent reaction mixture: 80−85% β-$H_5[AlW_{12}O_{40}]$ and 15−20% α-$H_5[AlW_{12}O_{40}]$.

Conversion of α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ to α-$H_5[AlW_{12}O_{40}]$. A reaction mixture containing isomerically pure α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ and NaCl was prepared (see above: Isomerization of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Mixture of β_2, β_3, and α Isomers) to α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$). The pH of the α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ solution was then decreased to 0.2 by addition of concentrated H_2SO_4 and heated at reflux for 5 days. The product ($H_5[AlW_{12}O_{40}]$) was isolated by ether extraction (leaving NaCl and $AlCl_3$ in the aqueous phase) and concentrated to dryness under vacuum. Yield: 5.8 g (51%). ^{27}Al NMR (δ, ppm): 72.1 (α, 92% of total $H_5[AlW_{12}O_{40}]$ product), 71.7 (β, 8% of total $H_5[AlW_{12}O_{40}]$ product).

Preparation of the Monosubstituted Anions, α-$K_{9-n}[AlM^{n+}W_{11}O_{39}]$. α-$K_6[Al(AlOH_2)W_{11}O_{39}]\cdot 12H_2O$. α-$K_9[AlW_{11}O_{39}]\cdot 12H_2O$ (5.18 g, 1.58 mmol) was stirred as a slurry in 15 mL of deionized water. A solution of $AlCl_3\cdot 6H_2O$, (0.38 g, 1.5 mmol, in 5 mL of water) was then added dropwise by pipet. After being stirred at room temperature for 15 min, the mixture was heated in a warm (60 °C) water bath with stirring until the solution became clear, approximately 5 min. The solution was cooled to room temperature, filtered to remove a fine precipitate, and cooled at 5 °C for several hours. Colorless crystals were collected and air-dried on a coarse frit. Yield: 3.77 g (75%). ^{27}Al NMR (D_2O; δ, ppm ($\Delta\nu_{1/2}$, Hz)): 74.3 (78.5) and 8.8 (205.5). ^{183}W NMR (δ, ppm (integration)): −60.7 (2), −103.2 (2), −132.0 (1), −142.9 (2), −152.0 (2), −205.1 (2). IR (KBr pellet): 948, 876, 799, 765, 735 (sh), 685, 531, 497, 365 (m) and 325 (w) cm^{-1}. Anal. Calcd (found) for $K_6[Al(AlOH_2)W_{11}O_{39}]\cdot 14H_2O$: H, 0.94 (0.87); W, 63.10 (62.80); Al, 1.68 (1.62); K, 7.32 (7.04).

α-$K_6[AlV^VW_{11}O_{39}]$. This derivative can be prepared and isolated as a yellow crystalline solid by addition of $VOSO_4$ to a slurry of α-$K_9[AlW_{11}O_{39}]$ in water, to give a solution of α-$K_7[AlV^{IV}W_{11}O_{39}]$, followed by addition of 2 equiv of HCl and oxidation by ozone (6% in O_2).[4] More conveniently, solutions of α-$K_7[AlV^{IV}W_{11}O_{39}]$ can be oxidized by Br_2 (in place of HCl and ozone).

α-$K_7[AlMn^{II}(OH_2)W_{11}O_{39}]\cdot 12H_2O$. α-$K_9[AlW_{11}O_{39}]\cdot 12H_2O$, (10.0 g, 3.05 mmol) was suspended in water (100 mL). A solution of $MnSO_4\cdot H_2O$ (0.516 g, 3.05 mmol) in water (10 mL) was added rapidly by pipet. The slurried mixture was stirred in a water bath at 80 °C for 10 min until a clear golden solution was formed. After cooling of the pH 6 solution to room temperature, it was filtered and refrigerated at 5 °C overnight. The product, a golden amorphous powder, was collected and dried on a coarse frit. The product was recrystallized from a minimum of warm (60 °C) water. Yield: 8.5 g (86%). ^{183}W NMR (δ, ppm): −63.6, −108.2, −134.1, −136.3, −142.5, −188.1 (broad; ca. 20−30 Hz each). IR (KBr pellet): 933 (m), 871 (m), 796 (s), 766 (sh), 698 (m), 526 (w), 486 (w), 365 (m) and 320 (w) cm^{-1}. Anal. Calcd (found) for $K_7[AlMn(OH_2)W_{11}O_{39}]\cdot 12H_2O$: H, 0.81 (0.79); W, 62.53 (62.34); Al, 0.83 (0.96); Mn, 1.70 (1.44); K, 8.43 (8.20).

α-$K_6[AlMn^{III}(OH_2)W_{11}O_{39}]\cdot 14H_2O$. α-$K_9[AlW_{11}O_{39}]\cdot 12H_2O$ (20.0 g, 6.1 mmol) was suspended in water (100 mL), and a solution of $MnSO_4\cdot H_2O$ (1.03 g in 10 mL of water, 6.1 mmol) was added dropwise by pipet. The mixture was stirred for 10 min in a water bath at 80 °C until the golden-colored solution became clear. The pH of the solution was reduced to 3 by addition of 1 M HCl, and a solution of NaOCl (4.33 g of 5.25% solution subsequently diluted by a factor of 2; 0.5 equiv) was added. After ca. 75% of the NaOCl had been added, the pH had increased to 5.3 and additional HCl was added to return the pH to 3. The remaining NaOCl solution was then added. During addition of NaOCl, the color of the solution changed from golden yellow to deep pink-purple. The solution was concentrated under vacuum until a precipitate began to form and then cooled to 5 °C overnight. The pink precipitate was collected on a coarse glass frit, dried under vacuum, and recrystallized from a minimum of warm (60 °C) water. The crystals obtained (12.45 g; 63%) were suitable for X-ray crystal-structure

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(14) Canny, J.; Tézé, A.; Thouvenot, R.; Hervé, G. *Inorg. Chem.* **1986**, *25*, 2114−2119.

(15) Tézé, A.; Hervé, G.; Finke, R. G.; Lyon, D. K. *Inorg. Synth.* **1990**, *27*, 85−135.

(16) Hastings, J. J.; Howarth, O. W. *J. Chem. Soc., Dalton Trans.* **1992**, 209−215.

(17) Andersson, I.; Hastings, J. J.; Howarth, O. W.; Pettersson, L. *J. Chem. Soc., Dalton Trans.* **1996**, 2705−2711.

determination. ^{183}W NMR (δ, ppm): −65.3, −109.5, −135.8, −137.6, −144.1, −189.6 (line widths of ≤5 Hz). IR (KBr pellet): 945 (m), 870 (s), 794 (s), 746 (s), 699 (sh), 537 (br, w), 489 (w), 365 (m) and 325 (w) cm^{-1}. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 498 (220) and 524 (210). Anal. Calcd (found) for $K_6[AlMn(OH_2)W_{11}O_{39}]\cdot 14H_2O$: H, 0.94 (0.87); W, 62.59 (63.02); Al, 0.83 (0.79); Mn, 1.70 (1.71); K, 7.23 (7.16).

α-$K_5[AlMn^{IV}(OH_2)W_{11}O_{39}]\cdot 10H_2O$. α-$K_8[AlMn^{II}(OH_2)W_{11}O_{39}]\cdot 13H_2O$ (10.0 g, 3.1 mmol) was dissolved in H_2O (100 mL), and an excess of $K_2S_2O_8$ (5.0 g, 18.5 mmol) was added. The mixture was heated to 90 °C, and the solution began to change color from gold to pink to brown. After 15 min of further heating, the solution was cooled to room temperature and filtered to remove excess $K_2S_2O_8$. The brown filtrate was concentrated to dryness and the resulting solid recrystallized 3 times from pH 4.7 potassium acetate buffer. Yield: 6.5 g (68%). IR (KBr pellet): 953 (m), 880 (s), 833 (m), 827 (m), 798 (s), 695 (s), 668 (sh), 618 (w), 593 (s), 559 (s), 418 (w), 370 (m) and 325 (w) cm^{-1}. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 490 (200). Poorly defined, very broad ^{183}W NMR signals were observed. Anal. Calcd (found) for $K_5[AlMn(OH_2)W_{11}O_{39}]\cdot 10H_2O$: W, 64.81 (64.65); Al, 0.86 (0.81); Mn, 1.76 (1.77); K, 6.24 (6.35).

α-$K_7[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot 14H_2O$.[13] Synthesis and purification was similar to that used for the preparation of α-$K_7[Al(Mn^{II}OH_2)W_{11}O_{39}]$, above, except that $Co(NO_3)_2\cdot 6H_2O$ (0.88 g, 3.05 mmol) was used in place of $MnSO_4\cdot H_2O$. After heating, the dark pink pH 7 solution was cooled to 5 °C and a red powder precipitated from solution. Recrystallization from a minimum of warm water at pH 7 gave red crystals (7.3 g, 74%). IR (KBr pellet): 952 (m), 935 (s), 891 (s), 798 (m), 697 (m), 533 (w), 486 (w), 370 (m) and 330 (w) cm^{-1}. No signals were observed by ^{183}W NMR spectroscopy. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 550 (50). Anal. Calcd (found) for $K_7[AlCo(OH_2)W_{11}O_{39}]\cdot 14H_2O$: Al, 0.82 (0.88); W, 61.76 (62.26); Co, 1.80 (1.73); K, 8.33 (8.16).

α-$K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot 9H_2O$. α-$K_9[AlW_{11}O_{39}]\cdot 12H_2O$ (20 g, 6.1 mmol) was suspended in water (100 mL). The slurry was heated gently (40−45 °C) and a solution of $Co(NO_3)_2\cdot 6H_2O$ (2.15 g, 6.1 mmol, in 10 mL H_2O) was added quickly by pipet. The slurry became pink in color and darkened after it was stirred for 20 min at 40 °C. The remaining solid (unreacted α-$K_9[AlW_{11}O_{39}]$) was then removed by filtration through a medium-frit funnel; the pH of the filtrate was 6.5. The pH of the solution was decreased to 2.9 by addition of 3 M HCl and the volume of the solution reduced by ca. 50% under vacuum. The solution was cooled to 5 °C overnight. The first crop yielded ca. 1.0 g (5%) of cubic red crystals, some of which were submitted for low-temperature X-ray crystal-structure determination, taking care to avoid loss of any waters of hydration. The composition of the refracted crystal was calculated to be $K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot 11H_2O$. The remaining crystals were air-dried (with some loss of water) and submitted for elemental analysis. Anal. Calcd (found) for α-$K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot 9H_2O$: Al, 0.84 (0.84); W, 62.60 (62.70); Co, 2.74 (2.97); K, 7.26 (7.04).

α-$K_6[AlCo^{III}(OH_2)W_{11}O_{39}]\cdot 14H_2O$. α-$K_9[AlW_{11}O_{39}]\cdot 12H_2O$ (20.0 g, 6.1 mmol) was stirred in H_2O (100 mL), and a solution of $Co(NO_3)_2\cdot 6H_2O$ (1.76 g, 6.1 mmol, in 10 mL of H_2O) was added dropwise to the slurry by pipet. The reaction mixture was stirred in a hot water bath (80 °C) until a clear solution was obtained. After cooling of the solution to room temperature, it was filtered and acidified by addition of 3 M HCl (4 mL) to a pH of 2 to neutralize the hydroxide generated upon oxidation of Co(II) to Co(III) by ozone. A gentle stream of ozone (6% in O_2) was then passed through the solution until it became dark green in color. The solution was concentrated under reduced pressure until a precipitate began to form. The mixture was then cooled to 5 °C overnight. The resulting dark green crystals were collected on a coarse frit, dried under vacuum, and recrystallized in a minimum amount of warm water. Yield: 11.33 g (58%). ^{27}Al NMR (D_2O; δ, ppm ($\Delta\nu_{1/2}$, Hz)): 74.0 (240). ^{183}W NMR (δ, ppm (integration)): +148.5 (2), −60.3 (2), −89.7 (2), −120.6 (1), −146.6 (2) and −149.0 (2). IR (KBr pellet): 945 (m), 882 (s), 800 (s), 756 (s), 698 (sh), 533 (w), 494 (w), 375 (m), and 335 (w) cm^{-1}. UV−vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 676 (55). Anal. Calcd (found) for $K_6[AlCo(OH_2)W_{11}O_{39}]\cdot 14H_2O$: H, 0.93 (0.84); W, 62.51 (62.47); Al, 0.83 (0.80); Co, 1.82 (1.77); K, 7.22 (7.18).

pH Titrations of Main-Group- and Transition-Metal-Substituted Anions, α-$[AlM^{n+}W_{11}O_{39}]^{(9-n)-}$. α-$K_7[AlMn^{II}W_{11}O_{39}]$. The following procedure used in the titration of $K_7[AlMn^{II}W_{11}O_{39}]$ was typical: A 25 mM solution of $K_7[AlMn^{II}W_{11}O_{39}]$ (100 mL) was prepared. (The low solubility of this salt precluded use of a more concentrated solution.) The solution was titrated with 0.499 M H_2SO_4, the addition of acid continuing until the pH of the solution decreased to ca. 3. The solution was then titrated with 0.964 M NaOH until base hydrolysis of the polyoxometalate was observed at pH values above ca. 8. A single point of inflection corresponding to the addition or loss of one proton was observed near pH 5. This pK_a value is well below that likely due to reversible deprotonation of the water ligand on Mn(II) (see titration of the more acidic anion, $K_6[AlMn^{III}W_{11}O_{39}]$, immediately below) and is more likely associated with reversible protonation of the 7− anion itself. The solution was cooled to near 0 °C to attempt to observe an inflection point due to deprotonation of the aquo ligand on Mn(II) prior to hydrolytic decomposition at high pH values. Even at 0 °C, however, titration to pH values higher than 8 resulted in hydrolysis of the anion; deprotonation of the aquo ligand on the Mn(II) addendum atom was not observed.

α-$K_6[AlMn^{III}W_{11}O_{39}]$. An inflection point observed at pH 7.3 was attributed to reversible deprotonation of the aquo ligand on the Mn(III) addendum atom.

α-$K_5[AlMn^{IV}W_{11}O_{39}]$. No points of inflection were detected over a range of pH values from 3 to 10. Elemental analysis (5 K^+ ions found after crystallization of $K_5[AlMn^{IV}W_{11}O_{39}]$ from acetate-buffered pH 4.7 solution) indicates that an aquo (H_2O) ligand is bound to the Mn(IV) addendum atom over the range of pH values investigated.

α-$Na_7[AlCo^{II}W_{11}O_{39}]$. A 0.013 M solution of $Na_7[AlCo^{II}W_{11}O_{39}]$ (25 mL) was prepared and cooled in an ice bath to 4 °C. The solution, initially at pH 3.6, was titrated with 0.104 M NaOH until the pH of the solution reached 10.8. The solution was then reverse titrated with 0.100 M HCl until the pH reached 3.1. As was the case for the 7− anion, $K_7[AlMn^{II}W_{11}O_{39}]$, one inflection point was observed at ca. pH 5 and is assigned to reversible protonation of the 7− anion itself.

α-$K_6[AlCo^{III}W_{11}O_{39}]$. A 0.014 M solution of $K_6[AlCo^{III}W_{11}O_{39}]$ (25 mL) was prepared, cooled in an ice bath to 4 °C, adjusted to pH 2.8 by addition of 3 drops of 3M HCl, and titrated with 0.104 M NaOH. Addition of base was continued until indications of base hydrolysis of the anion were observed (at pH values near 11 at 4 °C). One inflection point, observed at ca. pH 10, is associated with reversible deprotonation of the aquo ligand on the Co(III) addendum atom.

α-$K_6[Al(Al)W_{11}O_{39}]$. A single point of inflection at pH 8.8 is associated with reversible deprotonation of the aquo ligand on the Al(III) addendum atom.

X-ray Crystallographic Studies. Single crystals of $K_6[AlMn^{III}(OH_2)W_{11}O_{39}]\cdot 16H_2O$ and $K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot 11H_2O$, suitable for X-ray analysis, were each covered with Paratone oil and suspended within a nylon loop. The samples were each mounted on a Bruker D8 AXS single-crystal X-ray diffractometer equipped with a Bruker APEX SMART CCD area detector. Diffraction intensities were measured at −173 °C using Mo K**α** graphite-monochromated radiation (0.710 73 Å) and a combination of ϕ and ω scans with 10 s frames traversing about ω at 0.3° increments. Data collection and cell refinement were performed using Bruker SMART[18] and SAINT[19] software, while data reduction was performed with Bruker SAINT software. The molecular structure of each complex was determined using direct methods and Fourier techniques and refined by full-matrix least squares (SHELXTL version 5.10).[20] A multiple absorption correction for each data set was applied using the program SADABS.[21] For $K_6[AlMn^{III}(H_2O)W_{11}O_{39}]\cdot 16H_2O$ each addendum-atom site within the Keggin anion was assigned 1/12 Mn character and 11/12 W

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(18) *Bruker SMART version 5.55*; Bruker: Madison, WI, 2000.
(19) *Bruker SAINT version 6.02*; Bruker: Madison, WI, 2000.
(20) *Bruker SHELXTL version 5.10*; Bruker: Madison, WI, 2000.
(21) Sheldrick, G. M. *SADABS version 2.03*: University of Göttingen: Göttingen, Germany, 2001.

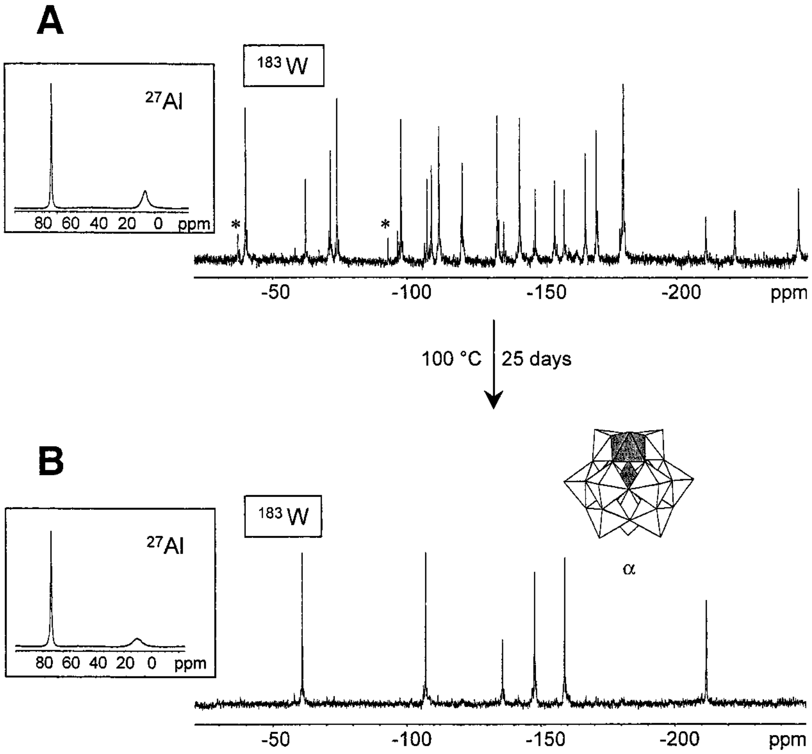

Figure 1. NMR spectra (^{183}W and ^{27}Al) of $[Al(AlOH_2)W_{11}O_{39}]^{6-}$. (A) ^{183}W NMR (44 000 scans; 48 h) and ^{27}Al NMR (inset) spectra of a reaction mixture containing β_2, β_3, and α isomers of $[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (β_2-, β_3-, and α-**1**), obtained by co-condensation of Al(III) and W(VI) for 2.5 h at 100 °C. Two signals, identified by asterisks (*), could not be identified. (B) ^{183}W NMR (11 000 scans; 12 h) and ^{27}Al NMR (inset) spectra of α-$[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (α-**1**) obtained by heating the mixture in (A) for 25 days at 100 °C.

character. W and K atoms were refined using anisotropic thermal parameters. All O atoms within the Keggin anion were refined using isotropic thermal parameters. The thermal parameters U_{ij} for Al(1) and all Mn atoms were fixed at 0.0100. For $K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot 11H_2O$, each addendum-atom site within the Keggin anion was assigned 1/12 Co character and 11/12 W character. All W atoms were refined anisotropically and the Co-atom contribution to the addendum-atom sites within the Keggin anion was given a fixed U_{ij} thermal parameter of 0.030. Al(1), O(1), O(2), O(3), and O(4) were refined with fixed isotropic thermal parameters; all other nonsolvent O atoms and K atoms were refined with anisotropic thermal parameters. O(w1), O(w2), O(w6), O(w8), O(w9), and O(w10) (water molecules) were refined with anisotropic thermal parameters, while all other solvent O atoms were refined with isotropic thermal parameters. Hydrogen atoms were not included in the final refinements of either structure. The largest residual electron density for each structure was located close to the W addendum atoms (11/12 W character) and is most likely due to imperfect absorption corrections often encountered in heavy-metal atom structures. Additional details of data collection and structure refinement are given in Results and Discussion and provided as Supporting Information.

Results and Discussion

Preparation of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ ($Na_6$1, Mixture of β_2, β_3, and α Isomers). Co-condensation of Al(III) and W(VI) (2:11 molar ratio) in water for 2.5 h at 100 °C gives a pH 7 solution of $[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (**1**) in effectively quantitative yield (based on Al(III)).[4] The ^{27}Al NMR spectrum of the reaction mixture (Figure 1A, inset) contains two signals of effectively equal (1:1) integrated intensities. The signal at 73 ppm is assigned to the pseudotetrahedrally coordinated Al(III) atom at the center of the Keggin ion, while the signal at 8 ppm is assigned to a pseudooctahedrally coordinated Al(III) addendum atom. The product, **1**, is analogous to $[Co^{II}(Co^{II}OH_2)W_{11}O_{39}]^{8-}$, obtained by mild acid condensation of Co(II) and W(VI).[22] In both cases, Al(III) or Co(II), the heteroatom is of appropriate size to replace an octahedrally coordinated W(VI) addendum atom.[23] More information is provided by ^{183}W NMR spectroscopy (Figure 1A), which reveals a kinetic product distribution consisting of 3 structural isomers of **1**: β_2, β_3, and α. (Structures of the β_1, β_2, β_3, and α isomers of **1** are provided in Figure 2.) In all, 23 signals are observed (2 of the 23 signals are

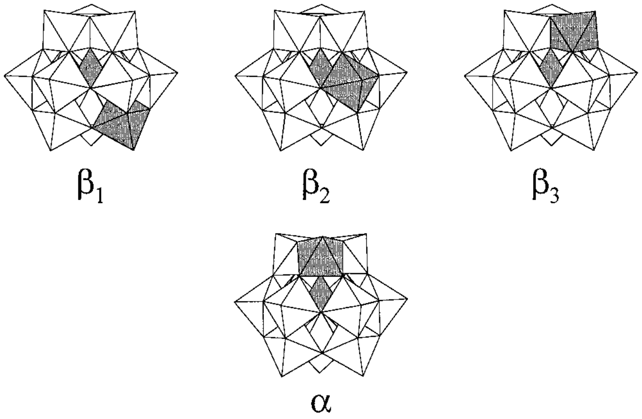

Figure 2. Structures, in polyhedral notation, of the 4 observed isomers of $[Al(AlOH_2)W_{11}O_{39}]^{6-}$. The Al(III) ions are located at the centers of the shaded polyhedra. One Al(III) ion occupies a tetrahedral cavity at the center of the anion, while the second is present in an octahedrally coordinated addendum-atom site. The designations β_1, β_2, and β_3 refer to the position of the Al(III) addendum atom either within (β_3) or in relation to (β_1 and β_2) the 60°-rotated M_3O_{13} triad.

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[22] Baker, L. C. W.; Baker, V. S.; Eriks, K.; Pope, M. T.; Shibata, M.; Rollins, O. W.; Fang, J. H.; Koh, L. L. *J. Am. Chem. Soc.* **1966**, *88*, 2329−2331.

[23] Tabulated radii of octahedrally coordinated Al(III) and Co(II) (high spin) are 0.68 and 0.89 Å, respectively, while octahedral radii of typical addendum atoms V(V), Mo(VI), and W(VI) are 0.68, 0.73, and 0.74 Å, respectively (Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925−946).

coincident). Mixed-addenda β_2-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ (β_2-Na_6**1**, eq 1) is the major product (55%, twice the concentration of each of the other two isomers observed in the reaction mixture). β_2-**1** possesses C_1 symmetry and gives rise to 11 ^{183}W NMR signals (all the W atoms are chemically unique). Analogously, mild acid condensation of SiO_3^{2-} and 11 equiv of WO_4^{2-} initially gives β_2-$[SiW_{11}O_{39}]^{8-}$.[15]

$$2Al^{3+} + 11WO_4^{2-} + 10H^+ \rightarrow \beta_2\text{-}[Al(AlOH_2)W_{11}O_{39}]^{6-}\ (\beta_2\text{-}\mathbf{1}, \text{major product}) + 4H_2O \quad (1)$$

The two less abundant products in Figure 1A are isomers of C_s symmetry (β_3-Na_6**1** and α-Na_6**1**, ca. 25 and 20% respectively), each of which give rise to 6 ^{183}W NMR signals (see Experimental Section for ^{183}W NMR data). Identification of the 6 signals associated with the α isomer was made by observation of increases in their intensities upon addition of authentic α-**1** to the isomer mixture. The remaining set of 6 signals is assigned to the β_3 isomer by recourse to close chemical precedent: the kinetic product obtained upon condensation of Si(IV) and W(VI), β_2-$Na_8[SiW_{11}O_{39}]$, is converted sequentially, upon heating, to β_3 and, finally, to α, the most stable of the four isomers of $Na_8[SiW_{11}O_{39}]$.[15]

Observation of β_1-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ (β_1-$Na_6$1). A fourth isomer (most likely β_1, Figure 2) is consistently observed in ^{183}W NMR spectra of reaction mixtures prepared by very slow condensation of Al(III) with W(VI) (2:11 equiv) in water at room temperature. Generally, however, this and other such attempts to obtain kinetic product distributions containing higher concentrations of the β_1 isomer (reactions at 60, 40, and 22 °C were attempted) were hampered by precipitation of salts of Al(III). At 100 °C (i.e., as in eq 1), the reaction is sufficiently rapid that **1** (β_2, β_3, and α isomers) is obtained in effectively quantitative yield in 2.5 h. At room temperature, however, even with very slow addition of Al(III) over a 2-week period, only ca. 50% of the Al(III) solution can be added before significant precipitation of insoluble Al(III) salts. Despite this, an incomplete room-temperature reaction mixture was concentrated to dryness and ^{27}Al and ^{183}W NMR spectra obtained. The ^{27}Al NMR spectrum is similar to that inset within Figure 1A, while the ^{183}W NMR (Figure S1, Supporting Information) reveals the presence of β_2-**1** (major Al(III)-containing product; ca. 65%) and a set of 6 signals not previously observed (ca. 35%). The 6 new signals, which do not correspond in number or in chemical-shift value to those attributable to paratungstate A or B,[16] are assigned to β_1-**1** (C_s symmetry).

Partial Equilibration of β_1- and β_2-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ (β_1- and β_2-$Na_6$1). Further support for assignment of the new set of 6 signals to β_1-**1** is obtained by partial equilibration of the reaction mixture: mild heating of the β_1, β_2 mixture (2 h at 100 °C) results in a uniform decrease in intensity of the 6 ^{183}W NMR signals assigned to β_1-**1** and corresponding increases in the intensities of the signals, 12 in all, associated with β_3- and α-**1** (Figure S2, Supporting Information). The resulting spectrum (Figure S2) is very similar to that shown in Figure 1A.

Full Equilibration of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ ($Na_6$1, Mixture of β_2, β_3, and α Isomers). Full equilibrium was achieved by heating the reaction mixture in Figure 1A (mixture of β_2, β_3, and α isomers) at reflux for 25 days. While the ^{27}Al NMR spectrum remains relatively unchanged (Figure 1B, inset), the ^{183}W NMR spectrum now contains the 6 signals (2:2:2:2:2:1 intensity ratios) assigned to α-$Na_6[Al(AlOH_2)W_{11}O_{39}]$ (α-Na_6**1**).

The kinetically controlled co-condensations and thermodynamically controlled isomerization reactions described above establish that isomers of **1** (Figure 2) spontaneously interconvert from β_1 to α in the order $\beta_1 \rightarrow \beta_2 \rightarrow \beta_3 \rightarrow \alpha$.

Acidity of the Terminal Aquo Ligand on the Al(III) Addendum Atom. pH titration data indicate that the aquo ligand on the Al(III) addendum atom of **1** possesses a pK_a of 8.8. This value is similar to that reported for α-$[B(AlOH_2)W_{11}O_{39}]^{6-}$ (pK_a of 7−8) and in line with the increases in pK_a values observed upon increases in anion charge for the series α-$[P(AlOH_2)W_{11}O_{39}]^{4-}$ (pK_a of ca. 4), α-$[Ge(AlOH_2)W_{11}O_{39}]^{5-}$ (pK_a of 5−6), and α-$[Si(AlOH_2)W_{11}O_{39}]^{5-}$ (pK_a of 6−7).[24]

Retention of Isomeric Integrity in Conversions of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ ($Na_6$1) to $H_5[AlW_{12}O_{40}]$ ($H_5$2). Addition of concentrated H_2SO_4 (final pH of 0.3) to solutions of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (Na_6**1**), followed by heating at reflux for 5 days, results in the condensation of **1** to $H_5[AlW_{12}O_{40}]$ (H_5**2**) and Al^{3+}.[4] We now report that **2** is formed by a mechanism through which the relative orientations of the four M_3 triads present in **1** are largely retained (eqs 2 and 3). Thus, a mixture of β_2- and β_3-**1** (prepared by condensation of Al(III) and W(VI) in water/acetonitrile;[25] see Experimental and Figure S3 in Supporting Information) gives 87% β-**2** (eq 2), while a mixture of β_2-, β_3-, and α-**1** (80 ± 10% β isomers, 20 ± 10% **α**) gives 80% β-**2** and 20% α-**2**.[26] Analogously, α-**1** gives 92% α-**2** (eq 3). Equations 2 and 3 describe kinetic product distributions, observed after reflux for 5 days.[27]

$$12[Al(AlOH_2)W_{11}O_{39}]^{6-}\ (\beta_2 \text{ and } \beta_3) + 56H^+ \rightarrow 11[AlW_{12}O_{40}]^{5-}\ (87\%\ \beta,\ 13\%\ \alpha) + 13Al^{3+} + 40H_2O \quad (2)$$

$$12[Al(AlOH_2)W_{11}O_{39}]^{6-}\ (\alpha) + 56H^+ \rightarrow 11[AlW_{12}O_{40}]^{5-}\ (8\%\ \beta,\ 92\%\ \alpha) + 13\ Al^{3+} + 40H_2O \quad (3)$$

Hydrolyses of $[AlW_{12}O_{40}]^{5-}$ (2) to $[AlW_{11}O_{39}]^{9-}$ (3). As is true for formation of β_2-$[SiW_{11}O_{39}]^{8-}$ from β-$[SiW_{12}O_{40}]^{4-}$,[14,15] β_2-$[AlW_{11}O_{39}]^{9-}$ (β_2-**3**) is the kinetic product first observed upon hydrolysis of β-$[AlW_{12}O_{40}]^{5-}$ (β-**2**). Similarly, α-**3** is the first product obtained upon hydrolysis of α-**2**. However, while heating solutions of β_2-$[SiW_{11}O_{39}]^{8-}$ results in complete conversion to α-$[SiW_{11}O_{39}]^{8-}$,[1,2] we previously reported[4] that thermal equilibration of aqueous $Na_9[AlW_{11}O_{39}]$ (60 °C at neutral pH) gives a mixture of β_3 (40%) and α (60%) isomers.

Having identified the isomeric structures of **1** resulting from kinetically and thermodynamically controlled co-condensations of 2 Al(III) and 11 W(VI) (as Na_2WO_4) and, similarly, the kinetically and thermodynamically controlled isomer distributions obtained upon conversions of **1** to **2** and of **2** to **3**, we summarize our collective findings in Figure 3 (the Na^+ countercations present in all cases have been omitted for clarity).

Synthesis of Isomerically Pure α-$K_9[AlW_{11}O_{39}]$ (α-$K_9$3). The synthesis and isolation of isomerically pure α-$K_9[AlW_{11}O_{39}]$ (α-K_9**3**) differs from the reactions summarized in Figure 3 in

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(24) Zonnevijlle, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2742−2750.

(25) Himeno, S.; Takamoto, M.; Ueda, T. *J. Electroanal. Chem.* **1999**, *465*, 129−135.

(26) The 10% uncertainties reflect variation in the relative intensities of signals associated with like numbers of W(VI) atoms in specific isomers observed in ^{183}W NMR spectra. In general, integration of the sharp ^{27}Al NMR signals associated with α and β isomers of **2** is more accurate. On the basis of ^{27}Al NMR spectra and several replications of the condensation reaction, conversion of the reaction mixture to **2** gives 80−85% β-**2** and 15−20% α-**2**.

(27) At pH 0 and 200 °C, equilibration of α and β isomers of **2** to an equilibrated mixture (9:1 α-to-β ratio at equilibrium) occurs in 6 days (see ref 4). The position of equilibrium at 100 °C (as in eqs 2 and 3) is not known. However, isomerization at 100 °C is slow.

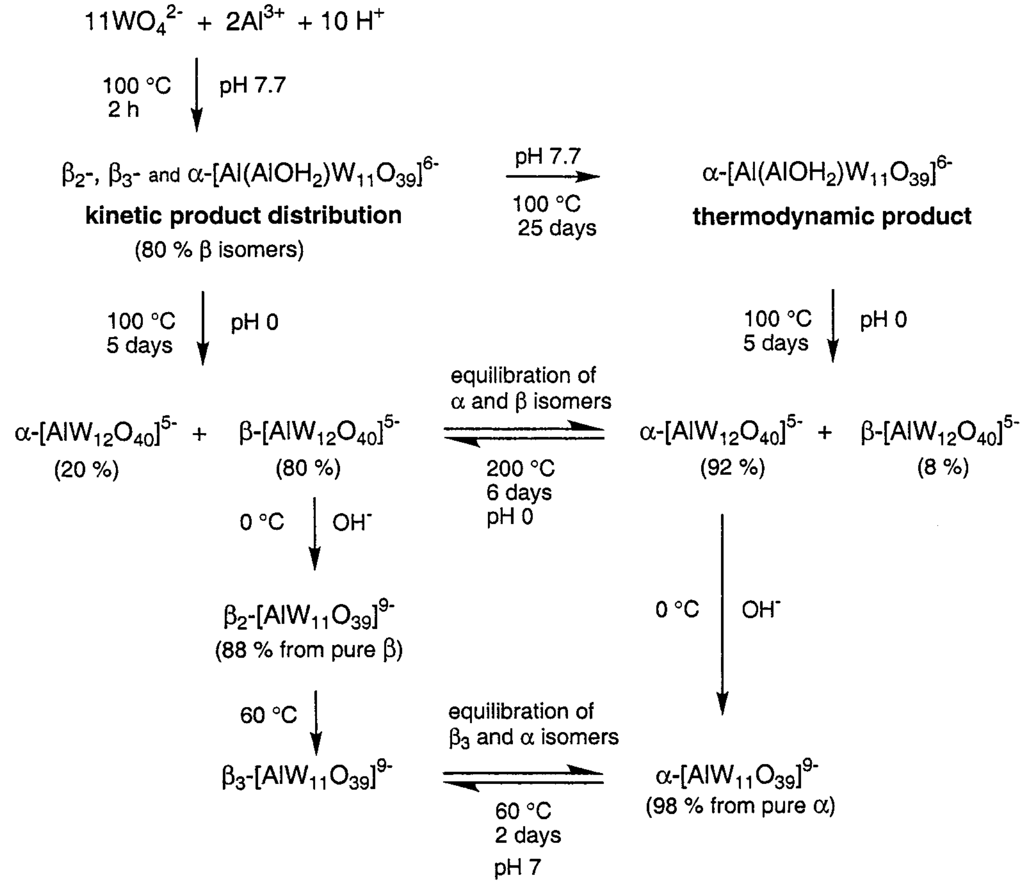

Figure 3. Kinetic and thermodynamic products. Percentage values in parentheses are kinetic product distributions. After heating of β- or α-$[AlW_{12}O_{40}]^{5-}$ at 200 °C for 10 days at pH 0, an equilibrated mixture ($K_{\beta\rightarrow\alpha} = 9.1$) is obtained. After heating of β_2- or α-$[AlW_{11}O_{39}]^{9-}$ at 60 °C for 2 days at pH 7, an equilibrated mixture of β_3- and α-$[AlW_{11}O_{39}]^{9-}$ is obtained ($K_{\beta3\rightarrow\alpha} = 0.67$). β_3-$[AlW_{11}O_{39}]^{9-}$ (no percentage yield indicated) was not isolated as a kinetically stable product but rather was identified by ^{183}W NMR (and by ^{51}V NMR of its V(V) derivative, β_3-$[AlVW_{11}O_{40}]^{6-}$) after equilibration at 60 °C.

that K^+ is now introduced in order to facilitate high-yield precipitation of the α isomer. Neutralization and hydrolysis of α- or β-$H_5[AlW_{12}O_{40}]$ (α- or β-H_5**2**) by K_2CO_3 in water at 60 °C gives effectively 100% α-$K_9[AlW_{11}O_{39}]$ (α-K_9**3**) as a sparingly soluble precipitate (2 g dissolve in 100 mL of water at room temperature) in 92% yield.[28] If β-H_5**2** (or mixtures of α- and β-H_5**2**) is used as a starting material, the isomerization or rearrangement of β-**2** prerequisite to high-yield precipitation of α-K_9**3** occurs within the 60−90 min required to carry out the hydrolysis reaction. This is synthetically advantageous as either α- or β-H_5**2** (or mixtures of these) can be used to obtain isomerically pure α-K_9**3** in high yield.

At pH 0, equilibration (via isomerization) of β-**2** and α-**2** requires 6 days at 200 °C. At pH 6, isomerization of β-**2** to α-**2** (>95% α-**2** at equilibrium) requires 3 days at 100 °C. The rate of isomerization therefore appears to increase dramatically with pH.[29] During hydrolysis of **2**, the pH is maintained between 7.5 and 8.5. Within this range of pH values, isomerization of β-**2** to α-**2** appears to occur within 60−90 min at 60 °C and, notably, before hydrolysis of α-**2** to α-$[AlW_{11}O_{39}]^{9-}$ (α-**3**). The hydrolysis product, α-**3**, possesses only limited kinetic stability. Thus, if a solution of α- or β-H_5**2** is hydrolyzed by treatment with NaOH (rather than with K_2CO_3, as described above) a solution of relatively soluble α-Na_9**3**, rather than a precipitate of sparingly soluble α-K_9**3**, is obtained. Subsequent isomerization of α-Na_9**3** to an equilibrium mixture of β_3- and α-Na_9**3** (Figure 3) is difficult to avoid. However, when K_2CO_3 is used to carry out the combined neutralization, isomerization, and hydrolysis reaction, the low solubility imparted by introduction of the K^+ countercation results in rapid precipitation of the kinetic product, α-K_9**3**.[30] Pure α-K_9**3** can thus be obtained in high yield.

Main-Group- and Transition-Metal-Substituted Derivatives, α-$K_{9-n}[AlM^{n+}W_{11}O_{39}]$. Isomerically pure derivatives, α-$K_{9-n}[AlM^{n+}W_{11}O_{39}]$ (**4**) are prepared by stirring slurries of α-K_9**3** in hot aqueous solutions containing salts of main-group and first-row transition-metal cations, M^{n+}, where M^{n+} = Al(III), $[V^{IV}O]^{2+}$, Mn(II), and Co(II). Additional derivatives are obtained by oxidation of V(IV) to V(V), of Mn(II) to Mn(III) and Mn(IV), and of Co(II) to Co(III). Even after heating at temperatures as high as 80 °C for minutes to hours as required for the heterogeneous metalation or subsequent homogeneous oxidation reactions to reach completion, the substituted derivatives, **4**, isolated in high yield, are exclusively α.

More specifically, when white amorphous α-K_9**3** is stirred as a slurry in aqueous solutions of $VOSO_4$ (at room tempera-

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(28) A preliminary description of this synthesis can be found in the Experimental section of ref 4, wherein we state that "under certain conditions, α-$K_9[AlW_{11}O_{39}]$ can be obtained in high yield." We now provide data that elaborate upon that observation.

(29) Anderson, T. M.; Hill, C. L. Submitted for publication.

(30) Equilibration of dilute aqueous solutions of α-K_9**3** has been observed. A dilute solution of α-K_9**3** (0.5 g in 100 mL of water) was held at room temperature for 90 min. Isomerization to a mixture of α and β isomers was indicated by ^{51}V NMR spectroscopy of the solution after metalation by addition of $VOSO_4$, and oxidation of V(IV) to V(V) by Br_2. A 1:1 mixture of β_3-**3** and α-**3**, each representing ca. 40% of the total concentration of V(V), was observed, along with a relatively small amount (ca. 20%) of β_2-**3**.

Table 1. IR Bands and Assignments

compd	$W{=}O_{term}$[a]	$W{-}O_c{-}W$[a]	$W{-}O_e{-}W$[a]	$Al{-}O_{tet}$[a,b]	$W{-}O_c{-}W$ (bend)
α-$Na_5[AlW_{12}O_{40}]$	956	880	798	757	372 s, 329 m
β-$Na_5[AlW_{12}O_{40}]$	960	892	797	758	368 m, 354 m
α-$K_9[AlW_{11}O_{39}]$	937	868	789	755 w, 704	370 s, 325 m
α-$K_6[Al(AlOH_2)W_{11}O_{39}]$[c]	948	876	799	764, 735 w	365 s, 325 m
α-$K_6[AlV^{V}W_{11}O_{40}]$	950	878	794	756	370 s, 330 m
α-$K_7[AlMn^{II}(OH_2)W_{11}O_{39}]$	933	871	797	766 w, 698	365 s, 320 m
α-$K_6[AlMn^{III}(OH_2)W_{11}O_{39}]$	945	870	794	746, 699 w	365 s, 325 m
α-$K_5[AlMn^{IV}(OH_2)W_{11}O_{39}]$	953	880	798	695, 668 w	370 s, 325 m
α-$K_7[AlCo^{II}(OH_2)W_{11}O_{39}]$	952, 935	891	798	754 w, 697	370 s, 330 m
α-$K_6[AlCo^{III}(OH_2)W_{11}O_{39}]$	945	882	800	756	375 s, 335 m

[a] $W{=}O_{term}$ = terminal W−O stretching mode; $W{-}O_c{-}W$ = corner-shared (intertriad) W−μ_2-O−W stretching mode; $W{-}O_e{-}W$ = edge-shared (intratriad) W−O−W stretching mode; $Al{-}O_{tet}$ = central Al−(μ_4-O)$_4$ stretching mode. [b] Separation between these bands, due to the effect of reduction in symmetry of the anion on the central AlO_4 moiety, ranges from ca. 25 to 50 cm^{-1}. [c] An additional, unassigned band appears at 685 cm^{-1}.

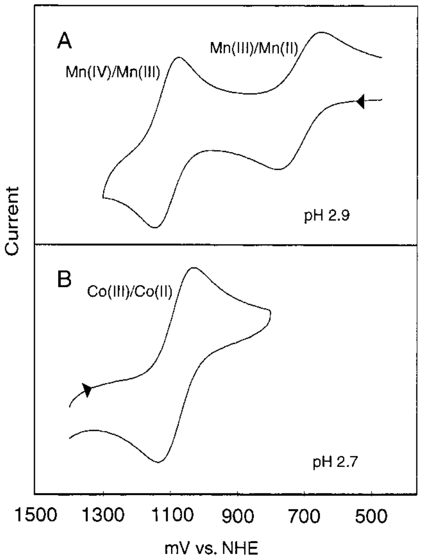

Figure 4. Cyclic voltammograms showing successive 1e$^-$ oxidations of α-$[AlMn^{II}(OH_2)W_{11}O_{39}]^{7-}$ to α-$[AlMn^{III}(OH_2)W_{11}O_{39}]^{6-}$ and α-$[AlMn^{IV}(OH_2)W_{11}O_{39}]^{5-}$ (A) and the 1e$^-$ oxidation of α-$[AlCo^{II}(OH_2)W_{11}O_{39}]^{7-}$ to α-$[AlCo^{III}(OH_2)W_{11}O_{39}]^{6-}$ (B).

ture), $MnSO_4$, or $Co(NO_3)_2$ (both at 80 °C), gradual dissolution of the white solid and change in color of the solution indicate formation of α-$K_7[AlV^{IV}W_{11}O_{40}]$, α-$K_7[AlMn^{II}(OH_2)W_{11}O_{39}]$, or α-$K_7[AlCo^{II}(OH_2)W_{11}O_{39}]$, respectively (eq 4, M^{n+} = $[VO]^{2+}$, Mn(II), or Co(II)).

$$\alpha\text{-}K_9\mathbf{3} + M^{2+} + H_2O \rightarrow \alpha\text{-}K_7[Al(M^{II}OH_2)W_{11}O_{39}] + 2K^+ \tag{4}$$

Subsequent oxidations, of V(IV) by Br_2, of Mn(II) by NaOCl, and of Co(II) by ozone,[31] give respectively α-$K_6[AlV^{V}W_{11}O_{40}]$,[32] α-$K_6[AlMn^{III}(OH_2)W_{11}O_{39}]$, and α-$K_6[AlCo^{III}(OH_2)W_{11}O_{39}]$. In addition, reaction of α-$K_7[AlMn^{II}(OH_2)W_{11}O_{39}]$ with $K_2S_2O_8$ gives α-$K_5[AlMn^{IV}(OH_2)W_{11}O_{39}]$.[33] The latter two of these oxidative transformations were observed by cyclic voltammetry (Figure 4). One quasi-reversible 1e$^-$ couple, Co(II)/Co(III), was observed for solutions of α-$K_7[AlCo^{II}(OH_2)W_{11}O_{39}]$ (Figure 4B), while two quasi-reversible 1e$^-$ couples, Mn(II)/Mn(III) and Mn(III)/Mn(IV), were observed for solutions of α-$K_7[AlMn^{II}(OH_2)W_{11}O_{39}]$ (Figure 4A). At pH 7 in water, the 1e$^-$ reduction of α-$[AlV^{V}W_{11}O_{40}]^{6-}$ to α-$[AlV^{IV}W_{11}O_{40}]^{7-}$ was observed as a quasi-reversible couple at +480 mV (NHE). At more negative potentials, successive reductions of W(VI) to W(V) were observed in aqueous solutions of **4** (M^{n+} = $[VO]^{2+}$, Mn(II), or Co(II)) between −410 and −570 mV (NHE) (see Figure S6 in Supporting Information).[34,35]

Isomeric integrity was confirmed by combined IR and ^{183}W NMR spectroscopies and X-ray crystallography. The IR spectra of the derivatives, **4**, are diagnostically characteristic of α isomers. In general, four characteristic IR bands appear in the spectra of Keggin heteropolyanions. For the Keggin tungstoaluminates reported here, three bands are readily assigned by comparison to literature values:[36] W=O terminal, 930−960 cm^{-1}; W−μ_2-O−W corner-sharing, 860−895 cm^{-1}; W−O−W edge-sharing, 785−805 cm^{-1} (Table 1). The fourth band (Al−O_{tet} in Table 1) is associated with a stretching mode of the central Al−(μ_4-O)$_4$ moiety. This band is split into two new bands as the symmetry of the α-anion is decreased from T_d to C_s, either by introduction of a vacancy, as in α-$[AlW_{11}O_{39}]^{9-}$, or by substitution, as in α-$[AlMn^{II}W_{11}O_{39}]^{7-}$.[37] One of the new bands is strong and possesses a maximum near that of the Al−(μ_4-O)$_4$ band in the parent T_d anion, α-$[AlW_{12}O_{40}]^{5-}$, while the other new band is weaker and its location more variable. Finally, the bands observed at 400−300 cm^{-1} (Table 1) arise from bending modes of the corner-shared (intertriad) W−μ_2-O−W linkages and differ for α and β isomers. The presence of one band between 365 and 375 cm^{-1} (medium and somewhat broad) and one at 320−335 cm^{-1} (weak, sharp) is diagnostic for the α isomer.[38]

The ^{183}W NMR spectrum of α-$K_6[AlV^{V}W_{11}O_{40}]$ was previously established[4] by correlation of ^{183}W and ^{51}V NMR spectra (the β_1, β_2, β_3, and α isomers each possess distinct ^{51}V NMR spectra).[39] The new derivatives for which ^{183}W NMR spectra could be obtained (i.e., Mn(II), Mn(III), and Co(III)) each possess 6 signals (Table 2). In each case, a *single* set of 6 signals, indicative of the presence of a *single* isomer of C_s symmetry, is observed. (Only broad features and no distinct signals were observed in ^{183}W NMR spectra of the V(IV), Mn(IV), and Co-

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(31) Weinstock, I. A.; Atalla, R. H.; Reiner, R. S.; Moen, M. A.; Hammel, K. E.; Houtman, C. J.; Hill, C. L.; Harrup, M. K. *J. Mol. Catal., A* **1997**, *116*, 59−84.

(32) An alternate method for the synthesis of α-$K_6[AlV^{V}W_{11}O_{40}]$ is reported in ref 4.

(33) Zhang, X. Y.; Pope, M. T.; Chance, M. R.; Jameson, G. B. *Polyhedron* **1995**, *14*, 1381−1392.

(34) Toth, J. E.; Anson, F. C. *J. Am. Chem. Soc.* **1989**, *111*, 2444−2451.

(35) Couto, F. A. R. S.; Cavaleiro, A. M. V.; de Jesus, J. D. P.; Simao, J. E. J. *Inorg. Chim. Acta* **1998**, *281*, 225−228.

(36) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207−216.

(37) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Chem. Res., Synop.* **1977**, 46−47.

(38) Thouvenot, R.; Fournier, M.; Franck, R.; Rocchiccioli-Deltcheff, C. *Inorg. Chem.* **1984**, *23*, 598−605.

(39) Leparulo-Loftus, M. A.; Pope, M. T. *Inorg. Chem.* **1987**, *26*, 2112−2120.

Table 2. Chemical-Shift Values (ppm; Integration in Parentheses) of Signals in ^{183}W NMR Spectra of Main-Group- and Transition-Metal-Substituted Anions

$K_6[AlV^VW_{11}O_{40}]$	$K_6[AlCo^{III}(OH_2)W_{11}O_{39}]$	$K_7[AlMn^{II}(OH_2)W_{11}O_{39}]^a$	$K_6[AlMn^{III}(OH_2)W_{11}O_{39}]$	$K_6[Al(AlOH_2)W_{11}O_{39}]$
−83.1 (2)	+148.5 (2)	−63.6 (2)	−65.3 (2)	−60.7 (2)
−99.1 (2)	−60.3 (2)	−108.2 (2)	−109.5 (2)	−103.2 (2)
−119.5 (2)	−89.7 (2)	−134.1 (2)	−135.8 (2)	−132.0 (1)
−123.0 (1)	−120.6 (1)	−136.3 (1)	−137.6 (1)	−142.9 (2)
−124.0 (2)	−146.6 (2)	−142.5 (2)	−144.1 (2)	−152.0 (2)
−144.4 (2)	−149.0 (2)	−188.1 (2)	−189.6 (2)	−205.1 (2)

[a] Slightly broad ^{183}W NMR signals were observed. No signals were observed in spectra of $K_5[AlMn^{IV}(OH_2)W_{11}O_{39}]$ or $K_7[AlCo^{II}(OH_2)W_{11}O_{39}]$.

(II) derivatives.) Finally, X-ray crystallographic analyses of $K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]{\cdot}11H_2O$ and $K_6[AlMn^{III}(OH_2)W_{11}O_{39}]{\cdot}16H_2O$ establish that both are α isomers (Figure 5 and Tables 3 and 4). While disorder, typical of crystals of these anion, precludes location of the addendum-atom positions substituted by Co(II) or Mn(III) (see Figure 5 caption, Experimental Section, and Supporting Information), the crystallographic data unequivocably confirm assignment of the 6-line ^{183}W NMR spectra to α isomers of **4**.

At the pH values at which these derivatives were isolated (pH 3−5) aquo ligands are present on the Mn(II), Mn(III), Mn(IV),[40] Co(II), and Co(III) addendum atoms (see Experimental Section for pH titration data).

Data reported above (Figures 1 and 2) demonstrate that α-$Na_6[Al(AlOH_2)W_{11}O_{40}]$ is substantially lower in energy than its *β*-isomer analogues. In addition, data acquired during the preparation of the derivatives, **4**, suggest that K^+ salts of **4** possess substantial kinetic (if not thermodynamic) stabilities in water. In additional work, aqueous solutions of the V(IV) and V(V) derivatives, α-$K_7[AlV^{IV}W_{11}O_{40}]$ and α-$K_6[AlV^VW_{11}O_{40}]$ (10 mM solutions of each in water at pH 5.5), were heated at 100 °C for 12 h. No evidence for the formation of *β* isomers was seen by ^{51}V NMR spectroscopy (Br_2 was added to the D_2O solution of α-$K_7[AlV^{IV}W_{11}O_{40}]$ prior to spectral acquisition). Also, no isomerization was detected by ^{183}W NMR after heating a 0.1 M solution of α-$Na_6[AlMn^{III}(OH_2)W_{11}O_{39}]$[41] at 200 °C for 24 h at pH 5 in water. These preliminary observations suggest that, while the relative energies of the α and *β* isomers of most of the derivatives, **4**, reported here are unknown, the α isomers may prove to be substantially lower in energy than their *β* analogues.[42] Minimally, however, available data indicate that reactions[13] of K^+ salts of the derivatives, **4**, reported here, can be carried out in water at 0−80 °C and at pH values of from ca. 3 to 8 without isomerization to *β* isomers.

Trends in the Kinetic and Thermodynamic Stabilities of α- and *β*-Keggin Heteropolytungstates. The data in Figure 3 further elaborate recently established trends[4] in thermodynamic and kinetic stabilities of α- and *β*-Keggin heteropolytungstates of the second-row main-group heteroatoms, Al(III), Si(IV), and P(V). Experimental and theoretical data[8] indicate that the differences in energy (Δ*G*) between *β* (higher energy, less stable) and lower-energy α-Keggin structures increase as the heteroatom, X, is varied from Al(III) to Si(IV) to P(V). As a result, relative thermodynamic stabilities of *β* isomers increase accordingly as X is varied from P(V) to Si(IV) to Al(III). Experimental data demonstrate that the kinetic stabilities of *β*

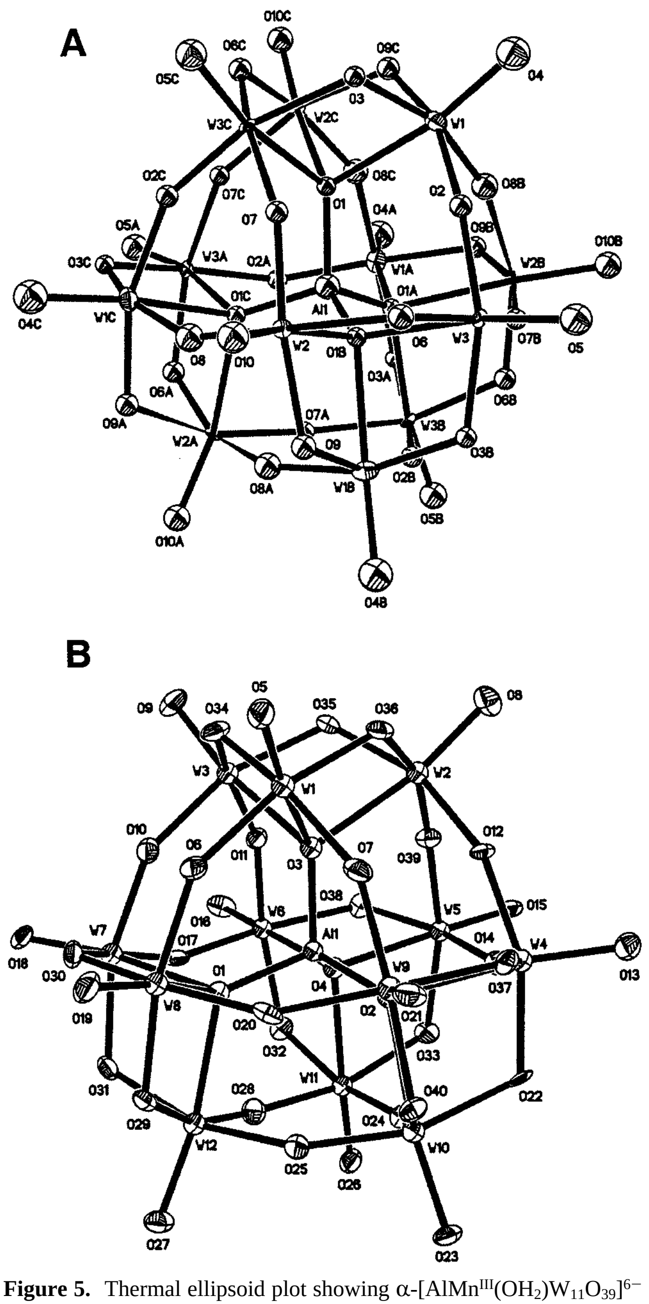

Figure 5. Thermal ellipsoid plot showing α-$[AlMn^{III}(OH_2)W_{11}O_{39}]^{6-}$ (A) and α-$[AlCo^{II}(OH_2)W_{11}O_{39}]^{7-}$ (B). Thermal ellipsoids are drawn at 80% probability in (A) and 30% probability in (B). In the solution of the structure of α-$[AlMn^{III}(OH_2)W_{11}O_{39}]^{6-}$, each addendum-atom site was assigned 1/12 Mn character and 11/12 W character, and in the solution of the structure of α-$[AlCo^{II}(OH_2)W_{11}O_{39}]^{7-}$, each addendum-atom site was assigned 1/12 Co character and 11/12 W character (see Experimental Section). For clarity, all W/Mn sites in (A) and all W/Co sites in (B) are labeled as W only.

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[40] On the basis of EXAFS and other data (Zhang, X. Y,; Pope, M. T.; Chance, M. R.; Jameson, G. G. *Polyhedron* **1995**, *14*, 1381−1392), the Mn(IV)-substituted Keggin tungstozincate anion, $K_7[(ZnO_4)W_{11}MnO_{36}H]{\cdot}19H_2O$, is reported to possess an hydroxo ligand on Mn(IV).

[41] The one-step hydrothermal synthesis of aqueous solutions of α-$Na_6[AlMn^{III}(OH_2)W_{11}O_{39}]$ will be reported elsewhere.

[42] The kinetic stabilities and relative energies of Na^+ and K^+ salts of **4** and of salts of **4** possessing various useful countercations (e.g., Li^+ or quaternary ammonium) and in useful solvents other than water remain to be fully evaluated.

Table 3. X-ray Crystallographic Data

	$K_6[AlMn^{III}(OH_2)W_{11}O_{39}]\cdot16H_2O$	$(K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot11H_2O)_2$
empirical formula	$H_{34}O_{56}AlK_6MnW_{11}$	$H_{60}O_{108}Al_2Co_3K_{12}W_{22}$
a (Å)	12.5335(4)	15.6315(16)
b (Å)	12.5335(4)	15.6328(16)
c (Å)	17.6353(9)	15.6522(16)
α (deg)	90	90.024(2)
β (deg)	90	60.011(2)
γ (deg)	90	60.039(2)
V (Å^3)	2770.30(19)	2706.0(5)
Z	2	1
fw	3269.14	6532.83
space group	$P\bar{4}2_1c$ (No. 114)	$P\bar{1}$ (No. 2)
T (°C)	−173	−173
λ (Å)	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	3.919	4.005
μ (mm^{-1})	23.535	24.310
max/min e Å^{-3}	3.197, −5.197	4.448, −4.573
R1 ($I > 2.0\sigma(I)$)[a]	0.0430	0.0616
wR2 ($I > 2.0\sigma(I)$)[b]	0.1163	0.1317

[a] $R1 = \sum||F_o| - |F_c||/\sum(|F_o|)$. [b] $wR2 = \sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 4. Selected Bond Lengths (Å) and Angles (deg)

	bond	bond length (Å)	angle (deg)	bond angle (deg)
$K_6[AlMn^{III}(OH_2)W_{11}O_{39}]\cdot16H_2O$	Al(1)−O(1)	1.747(6)	Al(1)−O(1)−W(1)	121.9(3)
	W(1)−O(1)	2.248(6)	W(1)−O(1)−W(2C)	94.5(2)
	W(1)−O(2)	1.926(6)	W(1)−O(3)−W(3C)	116.5(3)
	W(1)−O(3)	1.933(6)	W(1)−O(2)−W(3)	151.5(3)
	W(1)−O(4)	1.728(7)		
$K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot11H_2O$	Al(1)−O(3)	1.764(7)	Al(1)−O(3)−W(3)	122.2(3)
	W(3)−O(3)	2.244(7)	W(3)−O(3)−W(2)	95.0(3)
	W(3)−O(10)	1.931(7)	W(3)−O(35)−W(2)	117.7(4)
	W(3)−O(35)	1.941(7)	W(1)−O(6)−W(8)	151.3(4)
	W(3)−O(9)	1.760(8)		

isomers likewise increase as X is varied from P(V) to Si(IV) to Al(III). These parallel trends explain why β-Keggin tungstosilicates constitute a more elaborate family of readily isolable structures than do β-Keggin tungstophosphates. In water, however, all X = Si(IV) or P(V) anions spontaneously rearrange to substantially more stable α isomers. Further to the left along this continuum, β and α tungstoaluminate structures are generally closer to one another in energy, and severe conditions are sometimes needed to bring isomerization reactions to completion. With regard to thermodynamic stability, a mixed picture emerges: In some cases (**2** and **3**), α−β equilibria are observed; in other cases (**1** and perhaps certain salts of **4**), complete isomerization to α isomers is observed.

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Supporting Information Available: ^{183}W NMR spectra for a mixture of β_1 and β_2 isomers of $Na_6[Al(AlOH_2)W_{11}O_{39}]$ (β_1- and β_2-**1**) (Figure S1), the partial equilibration of β_1- and β_2-**1** to a mixture of β_2-, β_3-, and α-**1** (Figure S2), and a mixture of β_2- and β_3-**1** prepared in H_2O/CH_3CN (Figure S3), thermal ellipsoid plots that include the countercations K^+ and $Co(H_2O)_6$ (represented by isotropic boundaries) in $K_6[AlMn^{III}(OH_2)W_{11}O_{39}]\cdot16H_2O$ (Figure S4) and $K_6(Co^{II}(H_2O)_6)_{0.5}$-$[AlCo^{II}(OH_2)W_{11}O_{39}]\cdot11H_2O$ (Figure S5), cyclic voltammograms showing successive reductions of W(VI) to W(V) in **4** ($M^{n+} = [VO]^{2+}$, Mn(II), or Co(II), Figure S6), selected bond distances (Å) and angles (deg) for $K_6[AlMn^{III}(OH_2)W_{11}O_{39}]\cdot16H_2O$ and $K_6(Co^{II}(H_2O)_6)_{0.5}[AlCo^{II}$-$(OH_2)W_{11}O_{39}]\cdot11H_2O$ (Tables S1−S3), and X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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