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 β1 and β2 isomers of [Al2O2H5]W11O39(β1- and β2-). Partial equilibration of this kinetic product mixture by gentle heating (2 h at 100 °C) or, alternatively, condensation of Al(III) and W(VI) for 2.5 h at 100 °C both give mixtures of β2- and β1- 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 β1 → β2 → β3 → α. Furthermore, kinetically controlled conversions of α to H5[Al2W10O40] (2)-achieved by heating pH 0–0.2 solutions of α for 5 days at 100 °C—occurs with retention of isomeric integrity, such that α-1 is converted to β2- (92%; 8% β), while mixtures of β2- and β1- are converted to β-2 (87%; 13% α). These data, when combined with previously reported observations (equilibria between α- and β-2, 2-kinetically controlled hydrolyses of α-2 to α-[AlW11O39]- (2) and of β-2 to β1-3, and equilibria between β3- and α), provide a comprehensive picture regarding the roles of kinetic and thermodynamic control. Finally, a general method for preparation of the isomerically pure derivatives α-K9-[Al4W10O39] (4), M8+ = Al(III), [V2O4]2-, [V2O4]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 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-[SiW10O36]-, and of undeca-
tungstosilicates, β1- and β2-, and α-[SiW11O39]-, along with the preparation of first-row transition-metal (M+) substituted derivatives, α-[SiM8+W10O36]-, are well established. In water, the β isomers of [SiW10O36]- and [SiW11O39]- spontaneously rearrange completely to α structures.1,3 In contrast, we recently reported4 that the analogous Keggin tungstoaluminates, [AlW10O36]- and [AlW11O39]-, exist in aqueous solution as equilibria between β and α isomers. At pH 0 (473 K in H2O), α-H5[Al2W10O40] is more stable than β-H5-
[Al2W10O40] by 2.1 kcal mol−1; i.e., the change in Gibbs free energy (ΔG = −RT ln K) associated with isomerization from β to α is −2.1 kcal mol−1.5,6 The difference in energy between β- and α-Na2[Al2W10O39] (pD 7 at 333 K in D2O) 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 ([SiW12O40]-) 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 ΔG 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 isostuctural silicate or phosphate analogues. At the same time, 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 β1, β2-, β3, and α-1 of the undeca-
tungstoaluminan, [Al2O2H5]W11O39(β1-) (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 (β1-, β1-3, and α-1) to H5[Al2W10O40] (2)-, β and α isomers). These data are combined with information regarding the formation and equilibration of β2- and β3- and α-[AlW11O39]- (3),4 to provide an integrated

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5 (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.
summary of collective findings. These findings further elaborate recently identified trends 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, isomERICLY pure derivatives, α-K₆[AI₅W₁₁O₃₉] (4), M⁺ = Al(III), [V⁶O₇]²⁻, [V⁷O]⁴⁺, Mn(II), Mn(III), Mn(IV), Co(II), and Co(III).

Experimental Section

Materials and Methods. All materials used were reagent grade.

Na₆[Al(AlOH₂)₆W₁₁O₃₉] (reaction mixture containing three isomers, one of C₁ symmetry and two of C₂ symmetry) and α-K₆[AlW₁₇O₄₉] were prepared as described. 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 an Ag/AgCl reference electrode. Electrolyte solutions were either 1 M in polyoxometalate in 1.0 M sulfate or 5 mM in polyoxometalate dissolved in 0.2 M acetic 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 ⁷¹Al and ⁸³W NMR Spectra. Reported ⁷¹Al spectra were collected on a Varian UNITY 600 MHz spectrometer at 156.2 MHz; ⁸³W spectra were obtained using a Varian UNITY 400 NMR at 16.66 MHz. External references were set for ⁷¹Al, 0.10 M AlCl₃·6H₂O ([Al(H₂O)]¹⁴⁺, δ = 0 ppm) and for ⁸³W, 0.2 M Na₂WO₂·2H₂O (WO₄²⁻ (aq), δ = 0 ppm). Precise locations of ⁸³W NMR signals assigned to corresponding W atoms in identical anions vary, probably due to ion pairing. The nature and concentration of the resulting solution had been added, insoluble Al(III) salts persisted and no further precipitated Al(III) salts required 30 min of stirring after addition of each several-drop aliquot of aq AlCl₃. As the reaction progressed, the solution became opaque, however, the addition was temporarily stopped and the solution stirred until it became more clear.

If the solution became opaque, however, the addition was temporarily stopped and the solution stirred until it became more clear. After all the AlCl₃ was added, the 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.

High-Yield Preparation of Na₆[Al(AlOH₂)₂W₁₁O₄₉] (Mixture of β₆, β₅, and α Isomers). A solution containing three isomers of Na₆[Al(AlOH₂)₂W₁₁O₄₉] was prepared as previously reported: Na₂WO₄·2H₂O (100 g, 0.034 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 AlCl₃·6H₂O (13.3 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 Na₆[Al(AlOH₂)₂W₁₁O₄₉] as the only product observable by ⁷¹Al NMR spectroscopy.

Attention is now paid to identification of the three isomers present in the reaction mixture.

Identification of β₆, β₅, and α Isomers. The ⁸³W NMR spectrum of the reaction mixture (Figure 1A in the Results and Discussion) reveals the presence of 35 signals associated with tungsten atoms in three structural isomers, α (C₂ symmetry; 6 signals, δ (ppm)): −62.2−107.4.

−135.9, −147.6, −158.3, −211.0), βδ (C symmetry, 11 signals), and (most probably) βε (C symmetry, 6 signals), were observed between −43 and −200 ppm. The presence of the βδ 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-[Na₆[Al(OH₂)₂W₁₁O₃₉]] to the isomer mixture. (α-[Na₆[Al(OH₂)₂W₁₁O₃₉]] was prepared as described in the following paragraph and characterized by comparison to samples obtained by addition of AlCl₃ to α-K₆[AlW₁₂O₄₀]; see preparation of α-K₆[Al(OH₂)₂W₁₁O₃₉] below.) The results of this doping experiment dictate that our earlier, tentative assignment of the 23 signals to the presence of α, βδ, and βα isomers all possess C₃ symmetry is modified (see Experimental Section 4). While two isomers of C₃ symmetry are present, one of these is clearly the α isomer. The remaining isomer of C₃ symmetry is assigned by recourse to literature precedent: the kinetic product obtained upon preparation of Na₆[SiW₁₁O₃₉] is the βδ isomer, which, upon heating, is converted sequentially to βα and, finally, to α, the most stable of the four isomers of Na₆[SiW₁₁O₃₉].12,14,15 In the present case (Figure 1A), both βδ and α isomers are present. It follows that the remaining βδ isomer of C₃ symmetry is βα.

Isomerization of Na₆[Al(OH₂)₂W₁₁O₃₉] (Mixture of βδ, βα, and α Isomers) to α-[Na₆[Al(OH₂)₂W₁₁O₃₉]] The reaction mixture containing α, βδ, and βα isomers of Na₆[Al(OH₂)₂W₁₁O₃₉] (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 [27Al NMR spectrum (Figure 1B, inset; in the Results and Discussion) was prepared in water at 100 °C (see High-Yield Preparation of Na₆[Al(OH₂)₂W₁₁O₃₉]) (Mixture of βδ, βα, and α Isomers). The pH of the α-[Na₆[Al(OH₂)₂W₁₁O₃₉]] solution was then decreased to 0.2 by addition of concentrated H₂SO₄ and heated at reflux for 5 days. The product (H₃[AlW₁₂O₄₀]) was isolated by ether extraction (leaving NaCl and AlCl₃ in the aqueous phase) and concentrated to dryness under vacuum. Yield: 5.8 g (51%), [27Al NMR (δ ppm): 72.1 (α, 92% of total H₃[AlW₁₂O₄₀] product), 71.7 (β, 8% of total H₃[AlW₁₂O₄₀] product).

Preparation of the Monosubstituted Anions, α-K₆[Al⁺(Al⁺)W₁₁O₃₉]. α-K₆[Al(OH₂)₂W₁₁O₃₉]12H₂O (α-K₆[Al₆O₇W₁₁O₃₉]: H₂O) (5.18 g, 1.58 mmol) was stirred as a slurry in 15 mL of deionized water. A solution of AlCl₃·6H₂O (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 cold aspirator. Yield: 3.77 g (75%). [27Al NMR (δ ppm (νD, ν), Hz): 74.3 (78.5) and 8.8 (205.5). [19W NMR (δ ppm (integrated)): −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 for K₆[Al(OH₂)₂W₁₁O₃₉]·14H₂O: H, 0.94 (0.87); W, 63.10 (62.80); Al, 1.68 (1.62); K: 7.32 (7.04).

α-K₆[AlW₁₁O₃₇]. This derivative can be prepared and isolated as a yellow crystalline solid by addition of VOSO₄ to a slurry of VO(OC₂H₅)₃ in water, to give a solution of α κ-K₆[AlW₁₁O₃₇], followed by addition of 2 equiv of HCl and oxidation by ozone (6% in O₃). More conveniently, solutions of α-K₆[AlW₁₁O₃₇] can be oxidized by Br₂ (in place of HCl and ozone).

α-K₆[AlMn(II)₄(OH)₂W₁₁O₃₇]H₂O. α-K₆[Al₆O₇W₁₁O₃₉]·2H₂O (10.0 g, 3.05 mmol) was suspended in water (100 mL). A solution of MnSO₄·H₂O (0.516 g, 3.05 mmol) in water (10 mL) was added rapidly by pipet. The slurred 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%). [19W 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 (s), 766 (sh), 698 (m), 526 (w), 486 (w), 365 (m) and 320 (w) cm⁻¹. Anal. Calcd (found) for K₆[Al₆O₇W₁₁O₃₉]·2H₂O: H, 0.91 (0.87); W, 62.63 (62.34); Al, 0.83 (0.96); Mn, 1.71 (1.44). K: 7.93 (8.20).
determination. $^{19}$F 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), 753 (br, w), 489 (w), 365 (m) and 325 (w cm$^{-1}$). UV–vis ($\lambda_{max}$, nm: $\epsilon$, mol L$^{-1}$ cm$^{-1}$): 498 (220) and 524 (210). Anal. Calcd (found) for $\text{K}_5\text{[AlMn(OH)$_2$W$_{11}$O$_{39}$]}$: H, 0.94 (0.87); W, 62.59 (63.02); Al, 0.83 (0.79); Mn, 1.70 (1.71); $\text{K}$, 7.23 (7.16).

- **K$_5$[AlMn(OH)$_2$W$_{11}$O$_{39}$]**

The solution was heated to near 0°C. 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, 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.

- **K$_6$[AlCo(OH)$_2$W$_{11}$O$_{39}$]**

A single point of inflection observed at pH 7.3 was attributed to reversible deprotonation of the aquo ligand on the Mn(III) addendum atom.

- **K$_6$[AlCoW$_{11}$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 $\text{K}_5\text{[AlMn(OH)$_2$W$_{11}$O$_{39}$]}$ from acetate-buffered pH 4.7 solution) indicates that an aquo (H$_2$O) ligand is bound to the Mn(IV) addendum atom over the range of pH values investigated.

- **K$_6$[AlCoW$_{11}$O$_{39}$]**

A 0.014 M solution of $\text{Na}_2\text{[AlCoW$_{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, $\text{K}_5\text{[AlMnW$_{11}$O$_{39}$]}$, one inflection point was observed at ca. pH 5 and is assigned to reversible protonation of the 7–anion itself.

- **K$_6$[AlCoW$_{11}$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 $\text{K}_6\text{[AlMn}(\text{OH})_2\text{W$_{11}$O$_{39}$}]$ and $\text{K}_6\text{[AlCo}(\text{H}_2\text{O})_2\text{W$_{11}$O$_{39}$}]$ 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 Kα graphite-monochromated radiation (0.710 73 Å) and a combination of $\phi$ and $\omega$ scans with 10 s frames traversing about $\phi$ 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 $\text{K}_6\text{[AlMn}(\text{H}_2\text{O})_2\text{W$_{11}$O$_{39}$}]$ each addendum-atom site within the Keggin anion was assigned 1/12 Mn character and 11/12 W

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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 $\text{K}_6(\text{Co}^{\text{II}}(\text{H}_2\text{O})_6)^{0.5-}[\text{AlCo}^{\text{II}}(\text{OH}_2)-\text{W}_{11}\text{O}_{39}]\rightarrow\text{11H}_2\text{O}$, 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 $\text{Na}_6[\text{Al(AlOH}_2)\text{W}_{11}\text{O}_{39}]^{6-}$ ($\text{Na}_6\alpha$, Mixture of $\beta_\alpha\beta_\beta$, and $\alpha$ 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 $[\text{Al(AlOH}_2)\text{W}_{11}\text{O}_{39}]^{6-}$ (I) in effectively quantitative yield (based on Al(III)). The $^{27}\text{Al}$ 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, I, is analogous to $[\text{Co}^{\text{III}}(\text{Co}^{\text{III}}\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{6-}$, obtained by mild acid condensation of Co(II) and W(VI). In both cases, Al(III) or Co(II), the heteroatom is of appropriate size to replace an octahedrally coordinated W(VI) addendum atom. More information is provided by $^{183}\text{W}$ NMR spectroscopy (Figure 1A), which reveals a kinetic product distribution consisting of 3 structural isomers of I: $\beta_2$, $\beta_3$, and $\alpha$. (Structures of the $\beta_2$, $\beta_3$, and $\alpha$ isomers of I are provided in Figure 2.) In all, 23 signals are observed (2 of the 23 signals are

(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 $\beta_2$-Na$_4$[Al(OH)$_2$]W$_{11}$O$_{39}$] ($\beta_2$-Na$_4$I, eq 1) is the major product (55%, twice the concentration of each of the other two isomers observed in the reaction mixture), $\beta_2$-I 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$_2$ and 11 equiv of WO$_4^{2-}$ initially gives $\beta_2$-[SiW$_1$O$_{39}$]$^{2-}$.\textsuperscript{15}

$$2\text{Al}^{3+} + 11\text{WO}_4^{2-} + 10\text{H}^+ \rightarrow \beta_2[\text{Al(OH)}_2\text{W}_{11}\text{O}_{39}]^{6-} (\beta_2$-I, major product) + 4\text{H}_2\text{O} \quad (1)$$

The two less abundant products in Figure 1A are isomers of $C_2$ symmetry ($\beta_3$-Na$_4$I and $\alpha$-Na$_4$I, 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 $\alpha$ isomer was made by observation of increases in their intensities upon addition of authentic $\alpha$-Na$_4$I to the isomeric mixture. The remaining set of 6 signals is assigned to the $\beta_3$ isomer by recourse to close chemical precedent: the kinetic product obtained upon condensation of Si(IV) and W(VI), $\beta_3$-Na$_2$SiW$_1$O$_{39}$, is converted sequentially, upon heating, to $\beta_3$I and, finally, to $\alpha$, the most stable of the four isomers of Na$_4$[SiW$_1$O$_{39}$].\textsuperscript{15}

**Observation of $\beta_1$-Na$_4$[Al(OH)$_2$]W$_{11}$O$_{39}$] ($\beta_1$-Na$_4$I).** A fourth isomer (most likely $\beta_1$, 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 $\beta_3$ 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 $1 (\beta_2$, $\beta_3$, and $\alpha$ 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 complete room-temperature reaction mixture was concentrated to 100% conversion of the reaction mixture to the condensation product (as in eqs 2 and 3). The $\beta_2$- and $\beta_3$-I (prepared by condensation of Al(III) and W(VI) in water/acetonitrile;\textsuperscript{22} see Experimental and Figure S3 in Supporting Information) gives 87% $\beta_2$- (eq 2), while a mixture of $\beta_2$, $\beta_3$, and $\alpha$ (80 ± 10 β isomers, 20 ± 10 γ isomers) gives 80% $\beta_2$ and 20% $\alpha$.\textsuperscript{26} Analogously, $\gamma$-I gives 92% $\alpha$- (eq 3). Equations 2 and 3 describe kinetic product distributions, observed after reflux for 5 days.\textsuperscript{27}

$$12[\text{Al(OH)}_2\text{W}_{11}\text{O}_{39}]^{6-} (\beta_2$ and $\beta_3) + 56\text{H}^+ \rightarrow 11[\text{AlW}_{12}\text{O}_{40}]^{5-} (87% \beta, 13% \gamma) + 13\text{Al}^{3+} + 40\text{H}_2\text{O} \quad (2)$$

$$12[\text{Al(OH)}_2\text{W}_{11}\text{O}_{39}]^{6-} (\alpha) + 56\text{H}^+ \rightarrow 11[\text{AlW}_{12}\text{O}_{40}]^{5-} (8% \beta, 92% \alpha) + 13\text{Al}^{3+} + 40\text{H}_2\text{O} \quad (3)$$

**Hydrolyses of $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ (2) to $[\text{AlW}_{11}\text{O}_{39}]^{6-}$ (3).** As is true for formation of $\beta_2$-[SiW$_1$O$_{39}$]$^{8-}$ from $\beta$-[SiW$_1$O$_{40}$]$^{9-}$,\textsuperscript{14,15} $\beta_2$-[AlW$_{11}$O$_{39}$]$^{9-}$ ($\beta_2$-I) is the kinetic product first observed upon hydrolysis of $\beta$-[AlW$_{11}$O$_{39}$]$^{8-}$ ($\gamma$-2). Similarly, $\alpha$-3 is the first product obtained upon hydrolysis of $\alpha$-2. While heating solutions of $\beta_2$-[SiW$_1$O$_{39}$]$^{8-}$ results in complete conversion to $\gamma$-[SiW$_1$O$_{39}$]$^{8-}$,\textsuperscript{1,2} we previously reported\textsuperscript{4} that thermal equilibration of aqueous Na$_4$[AlW$_1$O$_{39}$] (60 °C at neutral pH) gives a mixture of $\beta_3$ (40%) and $\alpha$ (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$_2$WO$_4$ 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 $\alpha$-K$_5$[AlW$_{11}$O$_{39}$] (K-K$_3$).** The synthesis and isolation of isomerically pure $\alpha$-K$_5$[AlW$_{11}$O$_{39}$] (K-K$_3$) differs from the reactions summarized in Figure 3 in

\begin{align*}
(24) & \text{Zonnevijl}, \text{F.}; \text{Tourné, C. M.}; \text{Tourné, G. F. Inorg. Chem. 1982, 21, 2742–2750.} \\
(26) & \text{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 $\alpha$ and $\beta$ 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% $\beta_2$ and 15–20% $\alpha$.} \\
(27) & \text{At pH 0 and 200 °C, equilibration of $\alpha$ and $\beta$ isomers of 2 to an equilibrated mixture (9:1 $\alpha$-$\beta$ ratio at equilibrium) occurs in 6 days (see ref 4). The position of equilibration at 100 °C (as in eqs 2 and 3) is not known. However, isomerization at 100 °C is slow.}
that K$^+$ is now introduced in order to facilitate high-yield precipitation of the $\alpha$ isomer. Neutralization and hydrolysis of $\alpha$- or $\beta$-H$_3$[AlW$_{12}$O$_{39}$] ($\alpha$- or $\beta$-H$_2$) by K$_2$CO$_3$ in water at 60 °C gives effectively 100% $\alpha$-K$_9$[AlW$_{11}$O$_{39}$] ($\alpha$-K$_9$3) as a sparingly soluble precipitate (2 g dissolve in 100 mL of water at room temperature) in 92% yield. If $\beta$-H$_2$2 (or mixtures of $\alpha$- and $\beta$-H$_2$2) is used as a starting material, the isomerization or rearrangement of $\beta$-2 prerequisite to high-yield precipitation of $\alpha$-K$_9$3 occurs within the 60–90 min required to carry out the hydrolysis reaction. This is synthetically advantageous as either $\alpha$- or $\beta$-H$_2$2 (or mixtures of these) can be used to obtain isomerically pure $\alpha$-K$_9$3 in high yield.

At pH 0, equilibration (via isomerization) of $\beta$-2 and $\alpha$-2 requires 6 days at 200 °C. At pH 6, isomerization of $\beta$-2 to $\alpha$-2 (>95% $\alpha$-2 at equilibrium) requires 3 days at 100 °C. The rate of isomerization therefore appears to increase dramatically with pH. During hydrolysis of $\alpha$-2, the pH is maintained between 7.5 and 8.5. Within this range of pH values, isomerization of $\beta$-2 to $\alpha$-2 appears to occur within 60–90 min at 60 °C and, notably, before hydrolysis of $\alpha$-2 to $\alpha$-[AlW$_{11}$O$_{39}$]$^{3-}$ ($\alpha$-3). The hydrolysis product, $\alpha$-3, possesses only limited kinetic stability. Thus, if a solution of $\alpha$- or $\beta$-H$_2$2 is hydrolyzed by treatment with NaOH (rather than with K$_2$CO$_3$, as described above) a solution of relatively soluble $\alpha$-Na$_9$3, rather than a precipitate of sparingly soluble $\alpha$-K$_9$3, is obtained. Subsequent isomerization of $\alpha$-Na$_9$3 to an equilibrium mixture of $\beta$-3 and $\alpha$-Na$_9$3 (Figure 3) is difficult to avoid. However, when K$_2$CO$_3$ is used to carry out the combined neutralization, isomerization, and hydrolysis reaction, the low solubility imparted by introduction of the K$^+$ counterion results in rapid precipitation of the kinetic product, $\alpha$-K$_9$3. Pure $\alpha$-K$_9$3 can thus be obtained in high yield.

Main-Group- and Transition-Metal-Substituted Derivatives, $\alpha$-[K$_n$$_4$Al$_{1-n}$M$^{x+}$W$_{11}$O$_{39}$] (4) are prepared by stirring slurries of $\alpha$-K$_9$3 in hot aqueous solutions containing salts of main-group and first-row transition-metal cations, M$^{x+}$, where M$^{x+}$ = Al(III), [V$^{IV}$O]$_2$$^{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 $\alpha$.

More specifically, when white amorphous $\alpha$-K$_9$3 is stirred as a slurry in aqueous solutions of VOSO$_4$ (at room temperature)

(28) A preliminary description of this synthesis can be found in the Experimental section of ref 4, wherein we state that “under certain conditions, $\alpha$-[AlW$_{11}$O$_{39}$] can be obtained in high yield.” We now provide data that elaborate upon that observation.

Table 1. IR Bands and Assignments

<table>
<thead>
<tr>
<th>compd</th>
<th>W=O_{cm}</th>
<th>W−O−W</th>
<th>W−O−O−W</th>
<th>Al−O_{cm}</th>
<th>W−O−W (bend)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Na[AlW_{12}O_{40}]</td>
<td>956</td>
<td>880</td>
<td>798</td>
<td>757</td>
<td>372 s, 329 m</td>
</tr>
<tr>
<td>β-Na[AlW_{12}O_{40}]</td>
<td>960</td>
<td>892</td>
<td>797</td>
<td>758</td>
<td>368 m, 354 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>937</td>
<td>868</td>
<td>789</td>
<td>755 w, 704</td>
<td>370 s, 325 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>948</td>
<td>876</td>
<td>799</td>
<td>764, 735 w</td>
<td>365 s, 325 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>950</td>
<td>878</td>
<td>794</td>
<td>756</td>
<td>370 s, 330 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>933</td>
<td>871</td>
<td>797</td>
<td>766 w, 698</td>
<td>365 s, 320 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>945</td>
<td>870</td>
<td>794</td>
<td>746, 699 w</td>
<td>365 s, 325 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>953</td>
<td>880</td>
<td>798</td>
<td>695, 668 w</td>
<td>370 s, 330 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>952, 935</td>
<td>891</td>
<td>798</td>
<td>574 w, 697</td>
<td>370 s, 330 m</td>
</tr>
<tr>
<td>α-K[AlW_{12}O_{40}]</td>
<td>945</td>
<td>882</td>
<td>800</td>
<td>756</td>
<td>375 s, 335 m</td>
</tr>
</tbody>
</table>

W=O_{cm} = terminal W−O stretching mode; W−O−W = corner-shared (intertriad) W−O−W stretching mode; W−O−O−W = edge-shared (intratriad) W−O−W stretching mode; Al−O_{cm} = central Al−(μ-O)_{4} stretching mode.® 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. *An additional, unassigned band appears at 685 cm⁻¹.

Figure 4. Cyclic voltammograms showing successive 1e⁻ oxidations of α-[AlMn(III)(OH₂)W₁₁O₃₉]⁻ to α-[AlMn(III)(OH₂)W₁₁O₃₉]^{+} and the 1e⁻ oxidation of α-[AlCo(II)(OH₂)W₁₁O₃₉]⁻ to α-[AlCo(II)(OH₂)W₁₁O₃₉]^{+} (A). Figure 4B, while two quasi-reversible 1e⁻ couples, Mn(II)/Mn(III) and one at 320–335 cm⁻¹ (weak, sharp) is diagnostic for the α-isomer. Formations of Keggin Tungstoaluminates (47). One of the new bands is strong and possesses a maximum near that of the Al−(μ-O)₂ band in the parent T₄ anion, α-[AlW₁₁O₃₉]^{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−μ₂−O−W linkages and differ for α and β isomers. The presence of one band at 375 cm⁻¹ (medium and somewhat broad) and one at 320−335 cm⁻¹ (weak, sharp) is diagnostic for the α-isomer.

The ¹⁸³W NMR spectrum of α-K_4[AlV₄W₁₁O₃₉] was previously published by correlation of ¹⁸³W and ⁵¹V NMR spectra (38). The new derivatives for which ¹⁸³W NMR spectra could be obtained (i.e., Mn(II), Mn(III), and Co(III)) each possess distinct ⁵¹V NMR spectra (39). The ¹⁸³W NMR spectra of the V(IV), Mn(IV), and Co(III) compounds were observed in aqueous solutions of 4 (M^{n+} = [VO]^{2+}, Mn(II), or Co(II)) between 510 and 670 mV (NHE) (see Figure S6 in Supporting Information). 34,35

Isomeric integrity was confirmed by combined IR and ¹⁸³W NMR spectroscopies and X-ray crystallography. The ¹⁸³W NMR spectra of the derivatives, 4, are diagnostically characteristic of α- and β-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 stretching mode; W (bend) corner-sharing, 860−895 cm⁻¹; W−μ₂−O−W corner-sharing, 860−895 cm⁻¹; W−O−W edge-sharing, 785−805 cm⁻¹ (Table 1). The fourth band (Al−O_{cm} in Table 1) is associated with a stretching mode of the central Al−(μ-O)₂ moiety. This band is split into two new bands as the symmetry of the α-anion is decreased from T₄ to C₄ᵥ, either by introduction of a vacancy, as in α-[AlW₁₁O₃₉]^{5−}, or by substitution, as in α-[AlMn(III)(OH₂)W₁₁O₃₉]^{−}. 37 One of the new bands is strong and possesses a maximum near that of the Al−(μ-O)₂ band in the parent T₄ anion, α-[AlW₁₁O₃₉]^{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−μ₂−O−W linkages and differ for α and β isomers. The presence of one band at 375 cm⁻¹ (medium and somewhat broad) and one at 320−335 cm⁻¹ (weak, sharp) is diagnostic for the α-isomer.

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(32) An alternate method for the synthesis of α-K_4[AlV₄W₁₁O₃₉] is reported in ref. 4.
**Table 2.** Chemical-Shift Values (ppm; Integration in Parentheses) of Signals in $^{183}$W NMR Spectra of Main-Group- and Transition-Metal-Substituted Anions

<table>
<thead>
<tr>
<th>$K_4(\text{AlV}^{IV}W_1\text{O}_{40})$</th>
<th>$K_4(\text{AlCo}^{III}(\text{OH}<em>2)W_1\text{O}</em>{39})$</th>
<th>$K_4(\text{AlMn}^{III}(\text{OH}<em>2)W_1\text{O}</em>{39})$</th>
<th>$K_4(\text{AlMn}^{III}(\text{OH}<em>2)W_1\text{O}</em>{39})$</th>
<th>$K_4(\text{Al}(\text{AlOH}<em>2)W_1\text{O}</em>{39})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-83.1$ (2)</td>
<td>$+148.5$ (2)</td>
<td>$-63.6$ (2)</td>
<td>$-65.3$ (2)</td>
<td>$-60.7$ (2)</td>
</tr>
<tr>
<td>$-119.5$ (2)</td>
<td>$-89.7$ (2)</td>
<td>$-108.2$ (2)</td>
<td>$-109.5$ (2)</td>
<td>$-103.2$ (2)</td>
</tr>
<tr>
<td>$-123.0$ (1)</td>
<td>$-120.6$ (1)</td>
<td>$-134.1$ (2)</td>
<td>$-135.8$ (2)</td>
<td>$-132.0$ (1)</td>
</tr>
<tr>
<td>$-124.0$ (2)</td>
<td>$-146.6$ (2)</td>
<td>$-142.5$ (2)</td>
<td>$-144.1$ (2)</td>
<td>$-142.9$ (2)</td>
</tr>
<tr>
<td>$-144.4$ (2)</td>
<td>$-149.0$ (2)</td>
<td>$-188.1$ (2)</td>
<td>$-189.6$ (2)</td>
<td>$-205.1$ (2)</td>
</tr>
</tbody>
</table>

* Slightly broad $^{183}$W NMR signals were observed. No signals were observed in spectra of $K_4(\text{AlMn}^{III}(\text{OH}_2)W_1\text{O}_{39})$ or $K_4(\text{AlCo}^{III}(\text{OH}_2)W_1\text{O}_{39})$.

---

(II derivatives.) Finally, X-ray crystallographic analyses of $K_6(\text{Co}^{III}(\text{OH}_2)\text{W}_1\text{O}_{39})$, $K_4(\text{AlCo}^{III}(\text{OH}_2)W_1\text{O}_{39})$, $\text{H}_2\text{O}$, and $K_6(\text{AlMn}^{III}(\text{OH}_2)W_1\text{O}_{39})$ establish that both are $\alpha$ 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 unequivocally confirm assignment of the 6-line $^{183}$W NMR spectra to $\alpha$ 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), $^{183}$W, Co(II), and Co(III) addendum atoms (see Experimental Section for pH titration data).

Data reported above (Figures 1 and 2) demonstrate that $\alpha$-Na$_6$-[Al(AlOH)$_2$W$_1$O$_{40}$] is substantially lower in energy than its $\beta$-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, $\alpha$-K$_2(\text{AlV}^{IV}W_1\text{O}_{40})$ and $\alpha$-K$_2(\text{AlV}^{V}W_1\text{O}_{40})$ (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 $\beta$ isomers was seen by $^{51}$V NMR spectroscopy (Br$_2$ was added to the D$_2$O solution of $\alpha$-K$_2(\text{AlV}^{IV}W_1\text{O}_{40}$) prior to spectral acquisition). Also, no isomerization was detected by $^{183}$W NMR after heating a 0.1 M solution of $\alpha$-Na$_6$[AlMn$^{III}$(OH)$_2$W$_1$O$_{39}$] at 200 °C for 24 h at pH 5 in water. These preliminary observations suggest that, while the relative energies of the $\alpha$ and $\beta$ isomers of most of the derivatives, 4, reported here are unknown, the $\alpha$ isomers may prove to be substantially lower in energy than their $\beta$ analogues. Minimally, however, available data indicate that reactions 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 $\beta$ isomers.

**Trends in the Kinetic and Thermodynamic Stabilities of $\alpha$- and $\beta$-Keggin Heteropolytungstates.** The data in Figure 3 further elaborate recently established trends in thermodynamic and kinetic stabilities of $\alpha$- and $\beta$-Keggin heteropolytungstates of the second-row main-group heteroatoms, Al(III), Si(IV), and P(V). Experimental and theoretical data indicate that the differences in energy ($\Delta G$) between $\beta$ (higher energy, less stable) and lower-energy $\alpha$-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 $\beta$ isomers increase accordingly as X is varied from P(V) to Si(IV) to Al(III). Experimental data demonstrate that the kinetic stabilities of $\beta$
isomers likewise increase as X is varied from P(V) to Si(IV) to Al(III). These parallel trends explain why \( \beta \)-Keggin tungstophosphates in water, however, all X = Si(IV) or P(V) anions spontaneously rearrange to substantially more stable \( \alpha \) isomers. Further to the left along this continuum, \( \beta \) and \( \alpha \) tungstoluate 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), \( \alpha \)-\( \beta \) equilibria are observed; in other cases (1 and perhaps certain salts of 4), complete isomerization to \( \alpha \) isomers is observed.

**Acknowledgment.** We thank the DOE (Grant DE-FC36-95GO10090) (I.A.W. and C.L.H.) and the NSF (Grant CHE-9975453) (C.L.H.) for support.

**Supporting Information Available:** \(^{18} \text{W} \) NMR spectra for a mixture of \( \beta_1 \) and \( \beta_2 \) isomers of Na\(_6\)[Al(AlOH\(_2\))W\(_{11}\)O\(_{39}\)] (\( \beta_1 \)- and \( \beta_2 \)-1) (Figure S1), the partial equilibration of \( \beta_1 \)- and \( \beta_2 \)-1 to a mixture of \( \beta_2 \)-, \( \beta_2 \)-, and \( \alpha \)-1 (Figure S2), and a mixture of \( \beta_2 \)- and \( \beta_2 \)-1 prepared in \( \text{H}_2\text{O/CH}_3\text{CN} \) (Figure S3), thermal ellipsoid plots that include the counterions \( \text{K}^+ \) and Co(H\(_2\text{O}\))\(_6\) (represented by isotropic boundaries) in K\(_6\)[AlMn\(^{III}\)(OH\(_2\))W\(_{11}\)O\(_{39}\)]\(16\)H\(_2\)O (Figure S4) and K\(_6\)[Co\(^{III}\)(H\(_2\text{O}\))\(_{6}\)\(_{3-}\)](AlCo\(^{III}\)(OH\(_2\))W\(_{11}\)O\(_{39}\)]\(11\)H\(_2\)O (Figure S5), cyclic voltammograms showing successive reductions of \( \text{W(VI)} \) to \( \text{W(V)} \) in 4 (\( \text{M}^{n-} \) = \{VO\}\(^{2+}\), Mn(II), or Co(II), Figure S6), selected bond distances (\( \text{Å} \)) and angles (deg) for K\(_6\)[AlMn\(^{III}\)(OH\(_2\))W\(_{11}\)O\(_{39}\)]\(16\)H\(_2\)O and K\(_6\)[Co\(^{III}\)(H\(_2\text{O}\))\(_{6}\)\(_{3-}\)](AlCo\(^{III}\)(OH\(_2\))W\(_{11}\)O\(_{39}\)]\(11\)H\(_2\)O (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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