

Equilibria between α and β Isomers of Keggin HeteropolytungstatesIra A. Weinstock,^{*,†} Jennifer J. Cowan, Elena M. G. Barbuzzi, Huadong Zeng, and Craig L. Hill

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Abstract: Conventional wisdom maintains that β isomers of fully oxidized Keggin heteropolytungstates, $[X^{n+}W^{VI}_{12}O_{40}]^{(8-n)-}$ (X = main-group or transition-metal cation), are unstable with respect to α structures such that isomeric rearrangements all occur in the direction $\beta \rightarrow \alpha$. Contrary to this view, equilibria between α and β forms of the Keggin anion $[Al^{III}W_{12}O_{40}]^{5-}$ (α - and β -**1**) have now been observed. Moreover, a trend in kinetic and thermodynamic stabilities of β isomers in the order $X = Al(III) > Si(IV) > P(V)$ has been established, and the difference in energy between α and β isomers (α - and β -**1**) has been quantified for the first time. Mild acid condensation of WO_4^{2-} , followed by addition of $Al(III)$, gave $[Al(AlOH_2)W_{11}O_{39}]^{6-}$ (**2**)—three β -isomer derivatives, β_1 (C_s symmetry), β_2 (C_1), and β_3 (C_s), with the α derivative (C_s) a minor product—in nearly quantitative yield by ^{27}Al NMR spectroscopy. Acidification of the reaction mixture to pH 0 and refluxing cleanly converted **2** to $H_5[Al^{III}W_{12}O_{40}]$ (**1**)—mostly β -**1** (yellow, C_{3v}), with α -**1** (white, T_d) a minor product. Samples of each isomer were isolated by fractional crystallization and characterized by ^{27}Al and ^{183}W NMR, IR, and UV–vis spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction. The Al–O bond length in the T_d AlO_4 group at the center of α -**1** (hydrated potassium salt of α -**1**; final $R_1 = 3.42\%$) establishes a trend in X–O bond lengths in the $[X^{n+}O_4]^{(8-n)-}$ groups of α -Keggin anions of 1.74(1), 1.64(2), and 1.53(1) Å, respectively, for $X = Al(III)$, $Si(IV)$, and $P(V)$. Equilibria between isomers of **1** were observed by heating separate 0.1 M aqueous solutions of either pure α or β anions under identical conditions. The progress of the reaction was measured, and the relative concentrations of the α and β isomers present at equilibrium were determined by ^{27}Al NMR spectroscopy. First-order rate constants for approach to equilibrium of α - and β -**1** at 473 K were $k_{1(\alpha \rightarrow \beta)} = 7.68 \times 10^{-7} s^{-1}$ and $k_{-1(\beta \rightarrow \alpha)} = 6.97 \times 10^{-6} s^{-1}$. The equilibrium ratio of β -**1** to α -**1** (k_1/k_{-1}) was $K_{eq(473 K, 0.1 M 1)} = 0.11 \pm 0.01$. From $\Delta G = -RT \ln K_{eq}$, α -**1** is more stable than β -**1** by $2.1 \pm 0.5 kcal mol^{-1}$. Controlled hydrolysis of α -**1** gave the monolacunary derivative α - $Na_9[AlW_{11}O_{39}]$ (α -**3**; C_s); hydrolysis of β -**1** gave β -**3** (C_1) as the major product. Thermal equilibration of the lacunary Keggin heteropolytungstates could also be achieved: Independently heated solutions of either α -**3** or β -**3** (0.13 M of either isomer in D_2O at 333 K; natural pH values of ca. 7) both gave solutions containing α -**3** (60%) and a single β -**3** isomer of C_s symmetry (40%). Using $K_{eq} = 1.5$, the two isomers differ in energy by 0.3 kcal mol⁻¹.

Introduction

Efforts to rationalize the structure and dynamics of Keggin anions, $[X^{n+}W^{VI}_{12}O_{40}]^{(8-n)-}$ (X = main-group or transition-metal cation), have occupied chemists for over a century.¹ Nonetheless, a lack of agreement between theory and experiment regarding relative energies of the α and β isomers of these cluster anions has remained unresolved.

In 1826 Berzelius^{1a} reported the preparation of $(NH_4)_3[PMo_{12}O_{40}]$, and in 1864 Marignac^{1b} observed two isomers—now designated α and β ^{1h}—of “tungstosilicic acid” (H_4 -

$[SiW_{12}O_{40}]$). After the structure of α - $H_3[PW_{12}O_{40}]$ was solved by Keggin in 1933^{1g} (Figure 1, α), detailed physical descriptions of α - and β -Keggin and related anions were carried out by Souchay, Massart, Contant, Fruchart, Tézé, Hervé, and colleagues.¹⁰ In 1969 Kepert¹ⁱ noted that, relative to corner sharing between any two MO_6 octahedra, edge sharing introduces unfavorable Coulombic repulsions between the two metal cations. The repulsion becomes particularly important when a third MO_6 group is added to a pair of edge-shared octahedra because the central cation is thus subjected to opposing electrostatic repulsions. However, depending on which edges are shared by the central octahedron, the M–M–M angle might be 60°, 90°, 120°, or 180°, the 60° interaction being the most favorable. Kepert thus concluded that the α -Keggin structure, with four groups of M_3O_{13} triads (60° M–M–M angles), each connected to one another by corner-shared linkages, possessed the geometry most favorable for minimizing Coulombic repulsions. Baker and Figgis then proposed^{1j} (1970) that the β structure (Figure 1, β), confirmed by X-ray crystallography in 1973^{2a}) might be derived from 60° rotation of one M_3O_{13} triad

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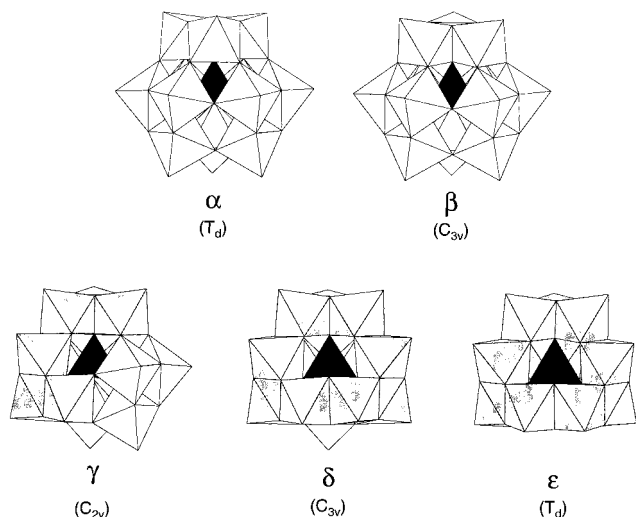


Figure 1. Baker-Figgis isomers of the Keggin anion. The central, tetrahedrally coordinated heteroatom (black) is surrounded by four W_3O_{13} triads, each consisting of three edge-shared MO_6 octahedra. The five isomers are related to one another by successive 60° rotations of each of the four triads (rotated triads are shaded). In the α and β isomers, the four triads are connected to one another exclusively by corner-shared linkages. In the γ , δ , and ϵ isomers, corner-shared linkages between triads are replaced, respectively, by one, three, and six edge-shared linkages.

about a 3-fold axis of the α anion. Additional isomers— γ , δ , and ϵ —were postulated to result from 60° rotations of the remaining triads (Figure 1, γ to ϵ).

In Keggin heteropolytungstates, the four W_3O_{13} triads in the α (T_d) and β (C_{3v}) isomers (Figure 1, α and β) are linked to one another exclusively by corner-shared octahedra ($W\cdots W$ separations of ca. 3.70 Å).^{1k} As a result, rotation of the W_3O_{13} triad introduces little change in Coulombic repulsion between W (d^0 , +6) ions in the overall structure. In the γ , δ , and ϵ isomers (Figure 1), however, corner-shared linkages are successively replaced by one to six edge-shared octahedra ($W\cdots W$ separations of ca. 3.42 Å).^{1k} On the basis of Kepert's arguments,¹ⁱ Pope^{1k} (1976) suggested that while γ , δ , and ϵ isomers should be increasingly unstable, the α and β structures should be similar in energy. Experimental observations, however, have suggested otherwise.^{1k,3} Indeed, because rearrangements of fully oxidized Keggin heteropolytungstates all occur in the direction $\beta \rightarrow \alpha$, the latter isomer has long been regarded as more stable.^{1n,3,4} As articulated by Tézé and Hervé in 1977,³ "In the α and β isomers, in accordance with Pope, electrical interactions would be of similar energy; this conclusion is not in agreement with the isomerization of heteropolyanions which always occurs in the direction $\beta \rightarrow \alpha$." This conclusion has been further supported by recent calculations.¹ⁿ

Moreover, because $\beta \rightarrow \alpha$ rearrangements all proceed to "completion", equilibrium concentrations of β isomers have

never been determined. As a result, K_{eq} values—and hence the relative energies of the two isomers—have not been measured. Keggin anions possessing the α structure are known for a range of heteroatoms, X (e.g., X = $2H^+$, Co(II/III), Zn(II), B(III), Ga(III), Si(IV), Ge(IV), P(V), As(V)). β -Keggin anions are less common: their stabilities vary with both the nature of the heteroatom and the overall charge of the cluster. While β anions of the group V elements, β - $[XW_{12}O_{40}]^{3-}$, X = P(V), As(V), are unknown,^{4b,5} β isomers of the group IV elements, β - $[XW_{12}O_{40}]^{4-}$, X = Si(IV), Ge(IV), possess substantial kinetic stabilities (in the order Si > Ge)^{2b,6} as does β -metatungstate (β - $[H_2W_{12}O_{40}]^{6-}$),^{4i,7} a Keggin anion with X = $2H^+$. Notably however, β -dodecatungstate anions of the group III elements, β - $[XW_{12}O_{40}]^{5-}$, X = B(III),⁸ Ga(III),⁹ have not been reported. Nevertheless, the dramatic increase in stability of the β isomer obtained by replacing P(V) with Si(IV) suggested that this trend might extend to $[Al^{III}W_{12}O_{40}]^{5-}$ (**1**). We now report equilibria between α and β isomers of **1**, the first observation of equilibria between fully oxidized Keggin heteropolytungstates, and the measurement of their relative energies. To accomplish this, it was necessary to synthesize and characterize individual α and β isomers of **1**, an anion about which surprisingly little is known.

Reports concerning the use of Keggin anions and their derivatives in a wide variety of applications constitute a large and rapidly growing literature.¹⁰ All the more noteworthy therefore is the relatively small number of reports published concerning $[Al^{III}W_{12}O_{40}]^{5-}$ (**1**). (For example, a quick Chemical Abstracts search provided 1161 "hits" for $[PW_{12}O_{40}]^{3-}$ and 811 hits for $[SiW_{12}O_{40}]^{4-}$; we are aware of only 11 articles that mention $[AlW_{12}O_{40}]^{5-}$.) One noteworthy exception deserves mention. In 1981, soon after Pope's suggestion that α - and β -Keggin anions might be similar in energy, Akitt and Farthing¹¹ published the ²⁷Al NMR spectrum of an isomeric mixture of **1**. In that report, however, the most detailed published to date, Akitt and Farthing (and subsequent authors as well¹²), failed to recognize that α and β isomers were present.

(5) Xin, F.; Pope, M. T. *Organometallics* **1994**, *13*, 4881–4886. Although unstable in water with respect to rearrangement to the α isomer, the polymolybdate anion β - $[PMo_{12}O_{40}]^{3-}$ can be isolated by oxidation of the $4e^-$ -reduced anion β - $[PMo_{12}O_{40}]^{7-}$ in organic solvents. Similarly, Contant obtained evidence for formation of the $1e^-$ -reduced anion β - $[PW_{12}O_{40}]^{4-}$ during polarographic study of α - $[PW_{12}O_{40}]^{3-}$ in water (Contant, R. *Can. J. Chem.* **1987**, *65*, 568–573). Upon oxidation of β - $[PW_{12}O_{40}]^{4-}$, however, isomerization to the α isomer was instantaneous. Degrees of kinetic stability have been observed for the trimetalated derivatives A - β - $[PM_3W_9O_{40}]^{n-}$, M = V(V), $n = 6$, or Mo(VI), $n = 3$ (ref 4l). This suggests that under suitable conditions kinetic stability might also be observed for M = W(VI) (M. T. Pope, personal communication).

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The relative scarcity of information available concerning **1** is likely due to synthetic difficulties. These difficulties stem from the ability of Al(III) to compete with W(VI) for addendum atom sites in $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ during condensation polymerization. (Competition between Al(III) and W(VI) might be attributable in part to their similarity in size.¹³) This is a problem not typically encountered in the synthesis of Keggin anions, which is usually quite simple. For example, addition of excess H^+ and X (1 equiv; X = B, Si, Ge, P, As, etc.) to aqueous solutions containing 12 equiv of WO_4^{2-} gives the 1:12 anions $[\text{X}^{n+}\text{W}_{12}\text{O}_{40}]^{(8-n)-}$. However, the same procedure using Al(III)^{11,12a,c,d,14a,b} gives a product mixture that includes substantial amounts of $[\text{Al}(\text{AlO}_2)\text{W}_{11}\text{O}_{39}]^{6-}$ (**2**),¹⁵ a mixed-addendum anion sometimes mistaken for **1**,¹⁶ along with metatungstate, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$.¹⁷ After acidification, concentration to dryness, and baking at 130 °C—a procedure that converts **2** and polytungstates to insoluble oxides—extraction with water gives $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$.^{14a,b} Using this method, Akitt and Farthing prepared $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$ (free of Al-containing byproducts by ²⁷Al NMR) in 10% yield.¹¹ To fully investigate the chemistry of **1** and its derivatives, a better synthetic procedure was sought. In the course of these efforts we discovered that **2** could be prepared in nearly quantitative yield. Taking advantage of the tendency of Al(III) to compete with W(VI) to give **2** (now a key intermediate), it was possible to develop a high-yield one-pot method for the preparation of **1**.

We now report high-yield preparations of $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$ (**1**, mixture of α and β isomers), of the monolacunary derivative $\alpha\text{-K}_9[\text{AlW}_{11}\text{O}_{39}]$,¹⁸ and of the mixed-addendum anion, $\alpha\text{-K}_6[\text{AlV}^{\text{V}}\text{W}_{11}\text{O}_{40}]$. The α and β isomers of **1** are fully characterized by a combination of ²⁷Al and ¹⁸³W NMR, IR, and UV-vis spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction. Thus, uncertainty regarding the interpretation of ²⁷Al NMR spectra of these compounds, first acquired using high-field NMR instruments almost two decades ago,¹¹ can now be satisfactorily dispelled. Finally, equilibria between α - and β -**1** and between α - and β - $\text{Na}_9[\text{AlW}_{11}\text{O}_{39}]$ (α - and β -**3**) in aqueous solution are documented using ²⁷Al and ¹⁸³W NMR spectroscopy. As a result of these efforts, Pope's hypothesis^{1k} is

(13) The ionic radius of octahedrally coordinated Al(III) is 0.68 Å, while those of V(V), Mo(VI), and W(VI)—typical Keggin anion addendum atoms—are 0.68, 0.73, and 0.74 Å, respectively (Shannon and Prewitt effective ionic radii; Huheey, J. E. *Inorganic Chemistry: Principles of structure and reactivity*, 2nd ed.; Harper & Row: New York, 1978; pp 71–74). By contrast, analogous ionic radii of heteroatoms not found in addendum atom sites are much smaller: 0.52, 0.54, and 0.41 Å, respectively, for octahedrally coordinated P(V), Si(IV), and B(III). (When these heteroatoms are tetrahedrally coordinated at the center of α -Keggin anions, their ionic radii are 0.1–0.2 Å shorter; see Figure 6). Other cations found both at the center of Keggin ions and in addendum atoms sites also possess larger ionic radii (e.g., 0.89 and 0.76 Å, respectively, for octahedrally coordinated Co(II) and Ga(III)).

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(15) The ²⁷Al NMR spectra of reaction mixtures containing **2** are published in refs 11 and 12c. In ref 12c the possibility that **2** might be present is suggested; none of the compounds present in the reaction mixture were isolated. See also: Carrier, X.; d'Espinose de la Caillerie, J.-B.; Lambert, J.-L.; Che, M. *J. Am. Chem. Soc.* **1999**, 121, 3377–3381. Carrier, X.; Lambert, J.-F.; Che, M. *Stud. Surf. Sci. Catal.* **1998**, 118, 469–476.

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(17) The metatungstate is formed by condensation of the stoichiometric excess of WO_4^{2-} (1 equiv of excess W(VI) for every 1 equiv of **2** formed).

(18) $\alpha\text{-K}_9[\text{AlW}_{11}\text{O}_{39}]$ is a versatile precursor to mixed-addenda derivatives, $\alpha\text{-}[\text{AlM}^{n+}\text{W}_{11}\text{O}_{39}]^{(9-n)-}$ (M = main-group or transition-metal cation), to be reported elsewhere.

confirmed, a trend in kinetic and thermodynamic stabilities of β isomers in the order X = Al(III) > Si(IV) > P(V) is established, and the difference in energy between α and β isomers is quantified for the first time.

Experimental Section

Instrumentation and Procedures. All materials used were reagent grade, with the exception of sodium tungstate dihydrate, which was Folin reagent grade. Infrared and UV-vis spectra were acquired using Nicolet 510 FTIR and Hewlett-Packard 8452A spectrophotometers. pH measurements 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 Ag/AgCl reference electrode. Electrolyte solutions were prepared from acetate buffer (sodium salt form) or from H_2SO_4 (details below). All reduction potentials are reported relative to the normal hydrogen electrode (NHE).

Acquisition of ²⁷Al, ⁵¹V, and ¹⁸³W NMR Spectra. Reported ²⁷Al and ⁵¹V NMR spectra were collected on a General Electric GN 500 spectrometer at 130.3 and 131.1 MHz, respectively. ¹⁸³W NMR spectra were obtained using a Varian UNITY 400 NMR at 16.66 MHz. External references were, for ²⁷Al, 0.10 M $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ($[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, $\delta = 0$ ppm), for ⁵¹V, 10 mM $\text{H}_4[\text{PVMo}_{11}\text{O}_{40}]^{19}$ in 0.60 M NaCl ($\delta = -533.6$ ppm relative to neat VOCl_3 ; chemical shifts are reported relative to VOCl_3 at $\delta = 0$ ppm), and, for ¹⁸³W, 0.2 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (WO_4^{2-} (aq), $\delta = 0$ ppm). The 0.10 M solution of AlCl_3 was also used as an external integration reference during kinetic experiments to assess whether decomposition of the tungstoaluminate complexes occurred. Spectral parameters for ²⁷Al were the following: pulse width, 18 μs ; sweep width, 13500 Hz (wide window) or 2350 Hz, 5 s delay (narrow window, used for accurate integration). The NMR software package NUTS (1-D version, distributed by Acorn NMR Inc., Fremont, CA) was used to process and correct for “rolling” in the baselines of ¹⁸³W NMR spectra.

Additional Comments Regarding the Acquisition of ²⁷Al NMR Spectra. A broad resonance (from ca. 105–35 ppm) was consistently observed in ²⁷Al NMR spectra of dilute samples. The quality and composition of the glass NMR tube (e.g., ratios of Si(IV), B(III), and Al(III) and trace metals) had only a modest effect on the intensity of this broad resonance, which was also observed in spectra acquired with no sample tube in the NMR probe. Therefore, the broad signal appeared to arise from aluminum in glass components, both in the sample tube and in the NMR probe (we used a GE reverse polarization transfer probe, tunable to nuclei in the range between ¹⁵N and ³¹P).

Several techniques were studied in efforts to minimize the influence of this signal: “left-shifting” of the data (this removes data points from the FID; it was typically necessary to remove the first five data points to eliminate the broad signal), subtraction of background spectra, or simply increasing the concentration of Al(III) in the sample solution. Left-shifting is an effective cosmetic technique that works because the Al nuclei in the glassy components relax much more rapidly than do those in the solution sample. Hence, most of the information concerning the broad signal is contained in the first few data points of the FID. However, this is not a preferred method because integrations of left-shifted spectra are unreliable. In addition, subtraction of background spectra did not prove reliable. In practice concentrated samples were used, thus avoiding artificial baseline corrections. This method is particularly effective if the signals of interest are sharp and close to one another, as are those observed for α - and β - $[\text{AlW}_{12}\text{O}_{40}]^{5-}$. To minimize variations in intensities of ²⁷Al signals arising from Al(III) ions in the glass sample tubes, all spectra were acquired using NMR tubes of the same quality and composition obtained from a single manufacturer: Wilmad grade 528-PP (Wilmad Glass, Buena, NJ).

Synthesis and Characterization. $\text{Na}_6[\text{Al}(\text{AlO}_2)\text{W}_{11}\text{O}_{39}]$ (2**).** Solutions of **2** (three β isomers and a small amount of the α isomer) were prepared and the reaction mixtures filtered and used in the preparation of **1** without further workup. (Due to the high solubility of **2** and the similarity of its solubility with that of NaCl present in high concentra-

(19) Pettersson, L.; Andersson, I.; Selling, A.; Grate, J. H. *Inorg. Chem.* **1994**, 33, 982–993.

tion, isolation of **2** by crystallization or precipitation from the reaction mixture proved difficult. Analytically pure samples of the less soluble potassium salt of α -**2** (to be reported elsewhere) were prepared, however, by addition of Al(III) to α -K₉[AlW₁₁O₃₉], **4**, below.) A solution of Na₂WO₄·2H₂O (100 g, 0.304 mol, in 400 mL of water) was acidified to pH 7.7 (monitored by pH meter) with 23 mL of 12 M HCl. The acid was added in small (1–2 mL) increments, allowing time between additions for the local precipitate of metatungstate to dissolve. The acidified solution was heated to reflux, and a solution of AlCl₃·6H₂O (13.32 g, 0.0552 mol, in 80 mL of water) was added slowly via addition funnel over about 90 min. The addition was performed slowly enough that the reaction mixture did not become opaque, but some cloudiness was permitted. The mixture was heated at reflux for 1 h, cooled, and filtered through diatomaceous earth (Celite). The filtrate contained [Al(OH)₂W₁₁O₃₉]⁶⁻ in nearly quantitative yield by ²⁷Al NMR: resonances at 73 ppm (central, tetrahedrally coordinated Al atom; $\Delta\nu_{1/2}$ = 97.5 Hz) and 8 ppm (octahedrally coordinated Al atom; $\Delta\nu_{1/2}$ = 236.5 Hz) were observed. ¹⁸³W NMR (near-neutral pH): 23 signals ranging from –43 to –200 ppm; tentatively associated with two isomers of C₃ symmetry (6 signals each) and one of C₁ symmetry (11 signals). These signals are tentatively assigned to β_1 (C₃), β_2 (C₁), and β_3 (C₃) isomers of **2** on the basis of the following evidence: (1) The six signals observed in the ¹⁸³W NMR spectrum of α -**2** (to be reported elsewhere) were absent. (2) Reaction of the mixture of β -**2** isomers with H⁺ gave mostly β -**1**, while reaction of α -**2** with H⁺ gave mostly α -**1**. (Details of the latter reactions, which pertain to the mechanism of formation of **1** from **2**, will be reported elsewhere.) The pK_a of the aquo ligand on the sixth coordination site of the octahedrally coordinated Al(III) addendum atom in pure α -**2** (determined by base titration of the K⁺ salt) is 8.5. By analogy, the empirical formula given for **2** (isomer mixture at near-neutral pH) is written with an aquo ligand on the Al(III) addendum atom.

H₅[AlW₁₂O₄₀] (1, Mixture of α and β Isomers). Concentrated H₂SO₄ (ca. 20 mL) was added to the ca. 500 mL solution of **2** to bring the pH to 0. An additional 3 mL of concentrated H₂SO₄ was then added. The solution was heated at reflux until ²⁷Al NMR spectra indicated that conversion to **1** was complete (Figure 2, bottom), about 5–7 days. The free acid of **1** (α and β mixture) was isolated by extraction with diethyl ether.²⁰ Concentrated H₂SO₄ (147 mL) was added to the reaction mixture containing H₅[AlW₁₂O₄₀], [Al(H₂O)₆]Cl₃, NaCl, and H₂SO₄. After cooling, 500 mL of diethyl ether was added, and the mixture was shaken carefully. Upon standing, three layers separated, and the bottom (heteropolyanion etherate) layer was collected. The shaking, venting, and collecting procedure was repeated until three layers no longer formed; as the extraction neared completeness the aqueous middle layer appeared less cloudy. The combined etherate layers were dried over a hot water bath. The highly water-soluble product (69.5 g, 95% crude yield; no byproducts observed by ²⁷Al NMR) was reprecipitated from a minimum of hot (80 °C) water to give 50.46 g of analytically pure **1** (64%; mixture of α and β). IR (KBr pellet): 972, 899, 795 (broad), 747 (broad), 538, and 477 cm⁻¹. Anal. Calcd (Found) for H₅[AlW₁₂O₄₀]·15H₂O: H, 1.12 (1.15); W, 70.07 (70.23); Al, 0.86 (0.89).

α -Na₅[AlW₁₂O₄₀] (Sodium Salt of α -1). A 101.34 g sample of H₅[AlW₁₂O₄₀] (mixture of α and β isomers) was dissolved in 125 mL of water and filtered. The pH of the solution was adjusted to ca. 6 using 150 mL of 0.2 M NaOH, and was then heated at reflux for 3 days. At this point, the solution contained about 95% α -[AlW₁₂O₄₀]⁵⁻ and 5% β -[AlW₁₂O₄₀]⁵⁻ (²⁷Al NMR). After cooling to room temperature, the solution was concentrated by rotary evaporation until a precipitate formed, and was then cooled overnight at 5 °C. White crystalline α -Na₅[AlW₁₂O₄₀] (100% α isomer by ²⁷Al NMR) was collected on a coarse glass frit and air-dried. Yield (two crops): 86.51 g (82.3%). ¹⁸³W NMR, δ : –112.8 ppm. ²⁷Al NMR, δ : 72.1 ppm ($\Delta\nu_{1/2}$ = 1.1 Hz). IR (KBr pellet, cm⁻¹): 955 (m), 883 (s), 799 (s), 758 (s), 534 (w), 498 (w), 468 (m), 471 (m). IR (CsI pellet, cm⁻¹): 372 (broad, strong), 329 (sharp, m), and 242 (sharp, m). UV: λ_{\max} = 262 nm, ϵ = 3.5 × 10⁴ cm⁻¹ M⁻¹ (four measurements between 0.9 and 6.0 × 10⁻⁵ M α -**1**, R² = 0.995). Anal. Calcd (Found) for Na₅[AlW₁₂O₄₀]·13H₂O: H, 0.81 (0.78); W, 68.47 (68.22); Al, 0.84 (0.88); Na, 3.57 (3.39).

α -H₅[AlW₁₂O₄₀] (α -1). The sodium salt of α -**1**, α -Na₅[AlW₁₂O₄₀] (15 g, 4.66 mmol), was dissolved in 20 mL of water. Concentrated sulfuric acid (7 mL) was added and the solution cooled in an ice bath. The acidified solution was transferred to a separatory funnel, and 25 mL of diethyl ether was added. The mixture was carefully shaken and vented; three layers formed on standing. The bottom layer (the etherate of the heteropolyacid) was collected and dried over a hot water bath. Amorphous α -H₅[AlW₁₂O₄₀] was collected as a white precipitate, redissolved in a minimum of water, and cooled overnight at 5 °C to give 10.54 g (72.7%) of reprecipitated pure product. ¹⁸³W NMR, δ : –110.1 ppm. ²⁷Al NMR, δ : 72.1 ppm ($\Delta\nu_{1/2}$ = 1.5 Hz). Anal. Calcd (Found) for H₅[AlW₁₂O₄₀]·12H₂O: H, 0.94 (0.90); W, 71.30 (70.85); Al 0.87 (0.91). ²⁷Al and ¹⁸³W NMR spectra are shown in Figure 2.

α -K₅[AlW₁₂O₄₀]. A 5.0 g sample of H₅[AlW₁₂O₄₀] (mixture of α and β isomers) was dissolved in 5 mL of water, and 10 mL of saturated aqueous KCl solution was added. The solution was placed in a vial, capped, and stored at room temperature in the dark for several weeks. Colorless crystals of the K⁺ salt of the α (less soluble) isomer formed slowly. One of the crystals was used to obtain X-ray crystallographic data (below). ²⁷Al NMR, δ : 72.2 ppm ($\Delta\nu_{1/2}$ = 0.84 Hz). Anal. Calcd (Found) for K₅[AlW₁₂O₄₀]·17H₂O: H, 1.02 (1.07); W, 65.37 (64.76); Al, 0.80 (0.78); K, 5.79 (5.68).

Crystal Structure Data for α -K₅[AlW₁₂O₄₀]·17H₂O. A well-formed colorless crystal (0.31 × 0.24 × 0.21 mm) was mounted on a glass fiber and centered on a standard Siemens SMART CCD area detector system equipped with a normal-focus molybdenum-target X-ray tube. A total of 1271 frames of data were collected at –100 °C using a narrow frame method with scan widths of 0.3° in ω and an exposure time of 30 s/frame ($2\theta_{\max}$ = 57.42°). Frames were integrated with the Siemens Saint program to yield a total of 25389 reflections, of which 3274 were independent (R_{int} = 10.22%, R_{sig} = 11.98%) and 3274 were above 4 σ (F). The data were corrected for absorption using Sheldrick's SADABS program. The corrected data were used for subsequent solution and refinement. The structure was solved by direct methods and refined by full-matrix least-squares-on- F^2 techniques (reflections with $F^2 > 2\sigma(F_o^2)$), using anisotropic temperature factors for all the atoms in the Keggin anions except that isotropic temperature factors were used for Al, O1, O2, and O3, which had negative defined temperature factors when refined anisotropically. The crystalline water oxygen atoms were also refined isotropically. Disorder in some of the potassium cations and water molecules was observed: Partial occupancies were used for two water molecules with higher temperature factors during the final stage of refinement, and partial occupancies and common anisotropic parameters were employed for K3 and K4 during final refinements. At final convergence, R_1 = 3.42%, R_2 = 7.45%, and GOF = 1.02 for 143 parameters. Bond lengths (Å) and angles are reported in Table 2.

β -Na₅[AlW₁₂O₄₀] (Sodium Salt of β -1). Pale yellow, amorphous H₅[AlW₁₂O₄₀], **1**, (73.9 g, 0.0237 mol; 18.8% α and 81.2% β) was dissolved in 150 mL of water and filtered through a medium frit. To neutralize the acid, a solution of 0.75 M Na₂CO₃ (141 mL, 0.106 mol) was added dropwise via pipet to a final pH of 2.4. The solution was concentrated by rotary evaporation until precipitate began forming; it was then cooled to 5 °C. The product, a pale yellow crystalline solid, was collected on a medium glass frit and dried under vacuum. The first crop (3.0 g) was 71.1% β (28.9% α), the second crop (17.6 g) contained 92.6% β (7.4% α), and the third crop (27.42 g) contained 89.7% β (10.3% α). The third crop was carefully recrystallized again from warm water to give a precipitate (13.17 g) which contained 97.5% β (2.5% α). The precipitate was collected on a coarse frit and dried under vacuum overnight. ²⁷Al NMR, δ : 71.7 ppm ($\Delta\nu_{1/2}$ = 6.2 Hz). IR (KBr pellet, cm⁻¹): 966 (m), 893 (m), 799 (s), 757 (s), 545 (w), 481 (w); IR (CsI pellet, cm⁻¹): 368 (broad, m), 354 (broad, m), 246 (broad, w). UV: λ_{\max} = 266 nm, ϵ = 2.7 × 10⁴ cm⁻¹ M⁻¹ (five UV measurements between 0.9 and 6.0 × 10⁻⁵ M β -**1**, R² = 0.995). Anal. Calcd (Found) for Na₅[AlW₁₂O₄₀]·13H₂O: H, 0.81 (0.80); W, 68.47 (68.12); Al, 0.84 (0.91); Na, 3.57 (3.77).

β -H₅[AlW₁₂O₄₀] (β -1). A 7.5 g sample of β -Na₅[AlW₁₂O₄₀] (97.5% β and 2.5% α) was dissolved in 20 mL of water. Concentrated sulfuric acid (18.0 M, 5.0 mL) was added, and the resulting solution was cooled to 15 °C in an ice bath. The solution was transferred to a 60 mL

(20) Tsigdinos, G. A.; Hallada, J. C. *Inorg. Chem.* **1968**, *7*, 437.

separatory funnel, and 15 mL of diethyl ether was added. The mixture was carefully shaken and vented in the manner described in the preparation of $H_5[AlW_{12}O_{40}]$ and allowed to stand until three layers separated. The bottom etherate layer was collected, dried, redissolved in a minimum of hot water, and cooled at 5 °C. The precipitate, an amorphous yellow material, was collected on a medium frit and dried in vacuo at room temperature. Yield: 5.35 g, 73.9% (97.5% α and 2.5% β). Alternatively, isomerically pure β -**1** can be obtained by careful fractional crystallization from mixtures of the free acids of α - and β -**1**. ^{27}Al and ^{183}W NMR spectra of β -**1** are shown in Figure 2. ^{183}W NMR, δ (relative intensities, $^2J_{W-O-W}$ coupling constants): -110.8 (1, 9.5 Hz), -118.7 (2, 9.8 and 3.1 Hz), -136.8 (1, 3.1 Hz) ppm. ^{27}Al NMR, δ : 71.6 ppm ($\Delta\nu_{1/2}$ = 5.1 Hz). Anal. Calcd (Found) for $H_5[AlW_{12}O_{40}] \cdot 13H_2O$: H, 1.00 (0.88); W, 70.88 (71.02); Al, 0.87 (0.83).

α -Na₉[AlW₁₁O₃₉] (α -3). α -Na₉[AlW₁₂O₄₀] (2.95 g, 0.92 mmol) was dissolved in 2.0 mL of D₂O and the solution cooled to 4 °C. (Hydrolysis in D₂O gave a higher ratio of α to β than was obtained when the reaction was carried out in water.) NaOH (0.22 g, 6 equiv, dissolved in 2.0 mL of D₂O and cooled to 4 °C) was added slowly with stirring, keeping the pH below 9.5. After about one-third of the NaOH was added, the product began to precipitate and the mixture became thick and gel-like. Two additional mL of D₂O was added, and the addition of base was continued. The reaction mixture was allowed to stand for 15 min, and the precipitate was collected and dried overnight under vacuum at 25 °C. Yield 1.76 g (62%); 82% α -**3** and 18% β -**3** based on the ratio of α -**1** to β -**1** measured by ^{27}Al NMR after metalation with W(VI) by addition of paratungstate and HCl: A 0.050 g sample of the product was dissolved in 0.125 mL of D₂O, and 1.5 equiv of W(VI) (0.12 mL of aqueous paratungstate solution, prepared by adjusting a solution of Na₂WO₄ to pH 7 with 3 M HCl; final [W(VI)] = 0.20 M) was added, followed by addition of 0.23 mL of 0.5 M HCl (1.5 molar excess). ^{183}W NMR, δ (relative intensities): -97.6 (2), -99.1 (2), -114.1 (1), -138.5 (2), -147.9 (2), -199.2 (2) ppm. ^{27}Al NMR, δ : 66.9 ppm ($\Delta\nu_{1/2}$ = 783 Hz). IR (KBr pellet): 935 (m), 870 (s), 843 (sh), 795 (s), 756 (sh), 697 (m) cm⁻¹. Anal. Calcd (Found) for Na₉[AlW₁₁O₃₉] · 15H₂O: H, 0.96 (0.93); W, 64.19 (63.82); Al, 0.86 (0.76); Na, 6.57 (6.30).

β -Na₉[AlW₁₁O₃₉] (β -3). NaOH (1.11 g, 0.029 mol) was dissolved in 6 mL of cold water and added slowly to a cold (4 °C) vigorously stirred aqueous solution of β -Na₅[AlW₁₂O₄₀] (15.0 g, 0.0047 mol; 90% β and 10% α , dissolved in 9.0 mL of water and cooled). As in the preparation of α -**3**, the solution soon became thick and gelatinous. During subsequent addition of the NaOH solution (all was added eventually), the pH was not allowed to increase beyond 9.5. The solid present after addition of the NaOH was immediately collected on a medium glass frit and dried overnight under vacuum at room temperature. Yield: 8.93 g (61%); 92% β -**3** and 8% α -**3** based on the ratio of α -**1** to β -**1** (^{27}Al NMR) after addition of paratungstate and HCl. ^{183}W NMR of the major β -**3** product (δ): 11 signals; -71.9, -89.0, -97.3, -106.4, -108.8, -139.9, -139.9 (two coincident signals), -144.8, -178.7, -200.6, -214.0 ppm. IR (KBr pellet): 939 (m), 861 (sh), 836 (sh), 800 (s), 746 (sh), 699 (m) cm⁻¹. ^{27}Al NMR, δ : 66.7 ppm ($\Delta\nu_{1/2}$ = 702 Hz). Anal. Calcd (Found) for Na₉[AlW₁₁O₃₉] · 12H₂O: H, 0.78 (0.73); W, 65.31 (65.05); Al, 0.87 (0.84); Na, 6.68 (6.76).

Addition of 1 equiv of vanadyl sulfate (VOSO₄) to a D₂O solution of the lacunary product, followed by oxidation with Br₂, gave a yellow solution whose ^{51}V NMR spectrum was dominated by a broad ($\Delta\nu_{1/2}$ = ca. 200 Hz) signal at -532 ppm. On the basis of the 11-signal ^{183}W NMR spectrum of the lacunary precursor, this signal was assigned to the β_2 isomer of the V(V) derivative of **3**. Three smaller but similarly broad ^{51}V NMR signals were assigned to the α isomer (-536 ppm; see preparation of α -K₉[AlW₁₁O₃₉], **5**, below) and to the two remaining β isomers (-539 and -544 ppm). In support of these assignments, Pope observed ^{51}V NMR signals for the three isomers of β -Cs₅[SiVW₁₁O₄₀] in H₂O at -549.5 (β_2), -550.3 (β_3), and -556.4 (β_1) ppm (Leparulo-Loftus, M. S., Pope, M. T. *Inorg. Chem.* **1987**, *26*, 2112-2120).

α -K₉[AlW₁₁O₃₉] (4**; Potassium Salt of α -3).** The potassium salts of the V(V)- and W(VI)-substituted derivatives of α -**3** were prepared for use as kinetically stable ^{27}Al , ^{51}V , and ^{183}W NMR standards. The preparation and use of these compounds were made possible by the

observations that (1) under certain conditions, α -K₉[AlW₁₁O₃₉] can be obtained in high yield and (2) the potassium salts of V(V)- and W(VI)-substituted derivatives of α - and β -**3** (i.e., α - and β -K₉[AlW₁₁O₄₀] and α - and β -K₅[AlW₁₂O₄₀]) are kinetically stable at room temperature. A 43.76 g sample of $H_5[AlW_{12}O_{40}]$ (14.1 mmol; mixture of α and β isomers) was dissolved in 100 mL of water and heated to 60 °C in a beaker fitted with a variable-temperature pH meter. With constant stirring, 6.97 g of solid K₂CO₃ · 1.5H₂O (42.3 mmol, 3 equiv) was added slowly. Foaming (formation of CO₂) was observed, and the addition was carried out slowly to prevent the reaction mixture from overflowing the beaker. A solution of 11.62 g of K₂CO₃ · 1.5H₂O (70.5 mmol, 5 equiv) in 20 mL of water was then added dropwise with care taken to keep the pH below 8 until at least 75% of the carbonate solution had been added. The product, a white powder, began precipitating during the course of the addition. During addition of the final 25% of the carbonate solution, the pH was allowed to increase to 8.5; final pH values typically ranged from 8 to 8.25. The mixture was then cooled to 5 °C for several hours. The precipitate, α -K₉[AlW₁₁O₃₉] (white powder), was collected on a medium-porosity glass frit, washed with three 20 mL portions of water, and air-dried. Because the product is only sparingly soluble in water (2 g in 100 mL at 22 °C), reprecipitation is impractical. Yield: 41.8 g (92%); 100% α isomer based on ^{27}Al , ^{51}V , and ^{183}W NMR spectra (as applicable) of α -K₅[AlW₁₂O₄₀] (see above) and α -K₆[AlW₁₁O₄₀] (below) derivatives. Metalated derivatives (to be reported elsewhere) are obtained by reaction of α -K₉[AlW₁₁O₃₉] (as a slurry in water) with aqueous solutions of metal-cation salts. The W(VI) derivative, α -K₅[AlW₁₂O₄₀], was prepared by reaction of α -K₉[AlW₁₁O₃₉] with paratungstate followed by addition of HCl as described in the preparation of **1** from **3** (above). ^{27}Al NMR of α -K₉[AlW₁₁O₃₉], δ : 63.3 ppm ($\Delta\nu_{1/2}$ = 1735 Hz). IR (KBr pellet): 937, 868, 789, 756 (shoulder), 704, 524, 493 cm⁻¹. Anal. Calcd (Found) for K₉[AlW₁₁O₃₉] · 13H₂O: H, 0.80 (0.77); W, 62.05 (61.87); Al, 0.83 (0.78); K, 10.80 (10.92).

α -K₆[AlV^WW₁₁O₄₀] (5**).** VOSO₄ · 3H₂O (12.20 mL of a 0.5 M solution, 6.1 mmol) was added dropwise to a slurry of K₉[AlW₁₁O₃₉] (20 g, 6.1 mmol) in 50 mL of water to give a purple solution of K₇[AlV^WW₁₁O₄₀] (ca. 0.1 M). Two equiv of HCl (4 mL of a 3 M solution) was added to the solution in order to consume the hydroxide generated upon subsequent oxidation of V(IV) to V(V) by reaction with ozone. A stream of ozone was then bubbled through the solution until its color changed to bright yellow. Oxygen was bubbled through the solution for several minutes to remove unreacted ozone; the solution was concentrated by rotary evaporation to half its initial volume. After cooling overnight at 5 °C, yellow crystalline α -K₆[AlV^WW₁₁O₄₀] was collected on a medium frit, air-dried, and recrystallized from a minimum of hot (80 °C) water. Yield: 12.95 g (66%). ^{183}W NMR, δ (relative intensities): -83.1 (2), -99.1 (2), -119.5 (2), -123.0 (1), -124.0 (2), -144.4 (2) ppm. ^{27}Al NMR, δ : 72.5 ppm ($\Delta\nu_{1/2}$ = 175 Hz). ^{51}V NMR, δ : -535.5 ppm ($\Delta\nu_{1/2}$ = 220 Hz). IR (KBr pellet): 950 (m), 878 (s), 794 (s), 756 (s), 542 (w), 487 (w) cm⁻¹. Anal. Calcd (Found) for K₆[AlV^WW₁₁O₄₀] · 13H₂O: H, 0.82 (0.78); W, 63.02 (62.97); Al, 0.84 (0.88); V, 1.59 (1.88); K, 7.31 (7.29).

Equilibration Reactions. Equilibration of α -H₅[AlW₁₂O₄₀] (α -1) and β -H₅[AlW₁₂O₄₀] (β -1). Teflon-lined bombs (25 mL volume) each containing 20 mL solutions of either α -**1** (0.10 M; 100% α) or β -**1** (0.10 M; 96% β , 4% α) were heated in a 200 °C oven. Aliquots were removed from each bomb periodically, and isomer ratios of **1** in each reaction were calculated from integrated ^{27}Al NMR signals. For each sample, ^{27}Al NMR spectra were acquired using both wide (13500 Hz) and narrow (2350 Hz) sweep widths. The larger sweep width was used to look for any Al-containing byproducts (none were observed), while the narrow window allowed for more accurate integrations of the two closely spaced ^{27}Al resonances from α - and β -[AlW₁₂O₄₀]⁵⁻. Quantitative ^{27}Al NMR spectra were acquired using the narrow (2350 Hz) sweep width, 18 μ s pulse width, and 5 s delay. Integration relative to 0.10 M [Al(H₂O)₆]Cl₃ (used as an external reference by placement in the inner compartment of a coaxial NMR tube) was used to ensure that no decomposition of **1** had occurred. All Keggin anions remained fully oxidized throughout the isomerization experiment.

Equilibration of α -Na₉[AlW₁₁O₃₉] (α -3) and β -Na₉[AlW₁₁O₃₉] (β -3). Samples (0.13 M each) of α -**3** (82% α ; 18% β) and β -**3** (87% β ;

13% α) in D₂O (1.0 g in 2.5 mL D₂O) were each heated separately in sealed, septa-covered glass vials to 60 °C. Because ²⁷Al is a quadrupolar nucleus ($I = 5/2$), NMR signals arising from ²⁷Al nuclei in highly symmetrical environments (cf. Al(III) in α - and β -1; Figure 2, bottom) are narrow, while signals arising from Al(III) in significantly distorted environments (as in **3**) are broad.²¹ Thus, to quantify ratios of α - and β -3, it was necessary to convert these monolacunary ions to derivatives that possessed sharp, readily quantifiable ²⁷Al NMR signals. The W(VI) derivatives, α - and β -1, were an obvious choice. Thus, aliquots from the equilibrating solutions of α - and β -3 were quenched by rapid conversion to kinetically stable mixtures of α - and β -1 (free-acid forms): 0.12 mL aliquots were placed in an ice-water bath, and 1.5 equiv of W(VI) (0.12 mL of paratungstate solution, prepared by adjusting a solution of Na₂WO₄ to pH 7 with 3 M HCl; final [W(VI)] = 0.20 M) was added, followed by addition of 0.23 mL of 0.5 M HCl (1.5 molar excess). Metalation of β ₁-, β ₂-, and β ₃-3 gives β -1; metalation of α -3 gives α -1. Quantitative ²⁷Al NMR spectra were acquired using a narrow (2350 Hz) sweep width, 18 μ s pulse width, 5 s delay, and 0.10 M [Al(H₂O)₆]³⁺ as external reference. No decomposition was observed over the course of the isomerization experiment, and all Keggin anions remained fully oxidized.

Observation of a Single β -3 Isomer of C_s Symmetry. Observation of the conversion of β ₂-3 to an equilibrium mixture containing a single β -3 isomer of C_s symmetry and α -3 (i.e., after heating for over 100 h at 60 °C, Figure 5) was accomplished using a combination of ⁵¹V and ¹⁸³W NMR as follows: Addition of 1 equiv of VOSO₄ to the equilibrated reaction mixture, followed by oxidation with Br₂, gave a yellow solution. At equilibrium, the signal associated with the V(V) derivative of the β ₂ lacunary isomer (−532 ppm; see the preparation of β -3, above) had nearly completely disappeared. Instead, two broad (ca. 220 Hz) signals (−536 and −539 ppm) of roughly equal intensities now dominated the ⁵¹V NMR spectrum. By comparison with the ⁵¹V NMR spectrum of α -K₆[AlVW₁₁O₄₀], **5** (−535.5 ppm; see above), the signal at −536 ppm was assigned to α -Na₆[AlVW₁₁O₄₀] (the V(V) derivative of α -3) and the second (−539 ppm) was assigned to the V(V) derivative of the new β -3 isomer. Analogous changes were observed by ¹⁸³W NMR of the equilibrated solution of lacunary ions. In the ¹⁸³W NMR spectrum of the equilibrated reaction mixture of lacunary anions, 12 signals (two sets of six signals) were observed (the 11 signals originally present—assigned to β ₂-3, C₁ symmetry—were now absent). One set of six signals (intensity ratios of 2:2:2:2:2:1) matched those observed in the ¹⁸³W NMR spectrum of α -3 (see the preparation of α -3, above). The remaining set of six signals (intensity ratios of 2:2:2:2:2:1) were assigned to a β -3 isomer of C_s symmetry (β ₁-3 or β ₂-3). δ (relative intensities): −32.9 (1), −122.3 (2), −147.7 (2), −151.8 (2), −152.7 (2), −174.1 (2) ppm. The six signals associated with α -3 ranged from −97 to −199 ppm. Thus, the outlying signal (−32.9 ppm; relative intensity of 1) was unequivocally assigned to the β -3 isomer (see also ref 29).

Calculations. The sum $k_1 + k_{-1}$ was calculated by fitting experimental time vs concentration data to the equation $([\alpha-1] - [\alpha-1]_{\infty}) / ([\alpha-1]_0 - [\alpha-1]_{\infty}) = e^{-(k_1+k_{-1})t}$. The constants $[\alpha-1]_0$ and $[\alpha-1]_{\infty}$ are the concentrations of α -1 at $t = 0$ h and at equilibrium, respectively, while $[\alpha-1]$ is the concentration of α -1 at time t . The equilibrium constant, $K_{eq} = [\beta-1]_{\infty} / [\alpha-1]_{\infty}$, is implicit in the model equation. Concentration $([\alpha-1])$ vs time data were fitted to the model equation by nonlinear least-squares regression using the Solver function from Microsoft Excel with the term $k_1 + k_{-1}$ an adjustable parameter. The rate constants k_1 and k_{-1} were then determined from the definition of K_{eq} ($K_{eq} = k_1/k_{-1}$) using the calculated value for the sum $k_1 + k_{-1}$. The difference in energy between isomers was calculated using $\Delta G = -RT \ln K_{eq}$, where $T = 473$ K.

Electrochemical Data. Cyclic Voltammetry. Cyclic voltammograms²² were obtained at room temperature using 1.1 mM solutions of α - and β -Na₅[AlW₁₂O₄₀] dissolved in 2 M sodium acetate buffer at pH 4.8 and in 0.49 M H₂SO₄ (determined by titration with standardized NaOH(aq) solution). The 2 M sodium acetate solution was chosen to match the conditions used by Rocchiccioli-Deltcheff^{22d,e} in polaro-

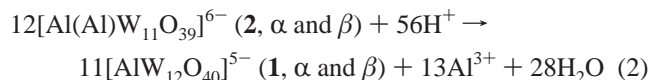
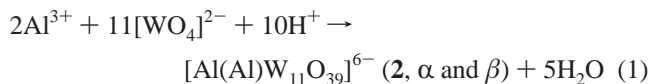
graphic analysis of α and β isomers of [SiW₁₂O₄₀]⁴⁻ and [GeW₁₂O₄₀]⁴⁻. The low-pH experiments were carried out to measure the reduction potentials of the α and β isomers at an [H⁺] close to that present during the equilibration of α - and β -1 (0.10 M H₅[AlW₁₂O₄₀], i.e., 0.50 M H⁺). α -K₄[SiW₁₂O₄₀] (1.1 mM) was used as a coulometric standard to determine the number of electrons involved in the first reduction waves of each POM anion in each electrolyte solution.^{22a,f} (The first reduction of α -[SiW₁₂O₄₀]⁴⁻ involves 1e⁻ even at HClO₄ concentrations as high as 3 M.^{22f}) Cyclic voltammograms were recorded for each anion in both electrolyte media using four scan rates, 15, 25, 50, and 100 mV s⁻¹. In all cases, values of $E_{pa} - E_{pc}$ were in the range expected for electrochemical quasi-reversibility (34–66 mV) and did not change significantly with scan rate (the largest change was from $E_{pa} - E_{pc} = 50$ mV at 100 mV s⁻¹ to 58 mV at 50 mV s⁻¹ for the reduction of α -Na₅[AlW₁₂O₄₀] in 0.49 M H₂SO₄).

(a) α -Na₅[AlW₁₂O₄₀]. At pH 4.8, the first reduction of α -Na₅[AlW₁₂O₄₀] (1e⁻; $i_{pc}(\alpha-1)/i_{pc}([\text{SiW}_{12}\text{O}_{40}]^{4-}) = 1.06 \pm 0.05$) occurred at a potential of $E_{av} = (E_{pa} + E_{pc})/2 = -601 \pm 2$ mV ($E_{pa} - E_{pc} = 61 \pm 5$ mV over the four scan rates). In 0.49 M H₂SO₄, a 2e⁻ reduction ($i_{pc}(\alpha-1)/i_{pc}([\text{SiW}_{12}\text{O}_{40}]^{4-}) = 1.95 \pm 0.02$) was observed at $E_{av} = -621 \pm 1$ mV ($E_{pa} - E_{pc} = 54 \pm 4$ mV).

(b) β -Na₅[AlW₁₂O₄₀]. At pH 4.8, the first reduction of β -Na₅[AlW₁₂O₄₀] (1e⁻; $i_{pc}(\beta-1)/i_{pc}([\text{SiW}_{12}\text{O}_{40}]^{4-}) = 1.03 \pm 0.04$) occurred at a potential of $E_{av} = (E_{pa} + E_{pc})/2 = -495 \pm 1$ mV ($E_{pa} - E_{pc} = 61 \pm 3$ mV). In 0.49 M H₂SO₄, a 2e⁻ reduction ($i_{pc}(\beta-1)/i_{pc}([\text{SiW}_{12}\text{O}_{40}]^{4-}) = 2.29 \pm 0.03$) was observed at $E_{av} = -454 \pm 1$ mV ($E_{pa} - E_{pc} = 37 \pm 4$ mV). (Further electrochemical data concerning these and related Keggin tungstaluminate derivatives will be reported elsewhere).

Results and Discussion

Preparation and Characterization of [AlW₁₂O₄₀]⁵⁻. Addition of Al³⁺ (2 equiv) to a hot aqueous solution of WO₄²⁻ (11 equiv, previously polymerized to paratungstate by addition of HCl) gives [Al(AlOH₂W₁₁O₃₉)⁶⁻ (**2**, α and β mixture) in nearly quantitative yield (²⁷Al NMR) (eq 1). By acidifying the reaction mixture to pH 0 and refluxing, **2** is cleanly converted to H₅[Al^{III}W₁₂O₄₀] (mixture of α - and β -1, eq 2).



This method is analogous to that used to prepare [Co^{II}W₁₂O₄₀]⁶⁻ by reaction of [Co^{II}Co^{III}W₁₁O₃₉]⁸⁻ with H⁺.²³ The ²⁷Al NMR of a typical reaction mixture containing **1** and Al³⁺ (eq 2) is shown at the bottom of Figure 2. Also shown are ²⁷Al and ¹⁸³W NMR spectra of isomerically pure samples of α - and β -1 (free acids).

An ²⁷Al NMR spectrum similar to that shown in Figure 2 (bottom) was reported by Akitt and Farthing in 1981.¹¹ They observed narrow resonances at 71.7 and 71.2 ppm (relative to [Al(H₂O)₆]³⁺), each associated with a tetrahedrally coordinated Al(III) ion. Although the two compounds were isolated and preliminary X-ray diffraction data obtained (unit-cell dimensions only), the presence of α and β isomers went unrecognized. The authors concluded that “the preparation appears to produce two

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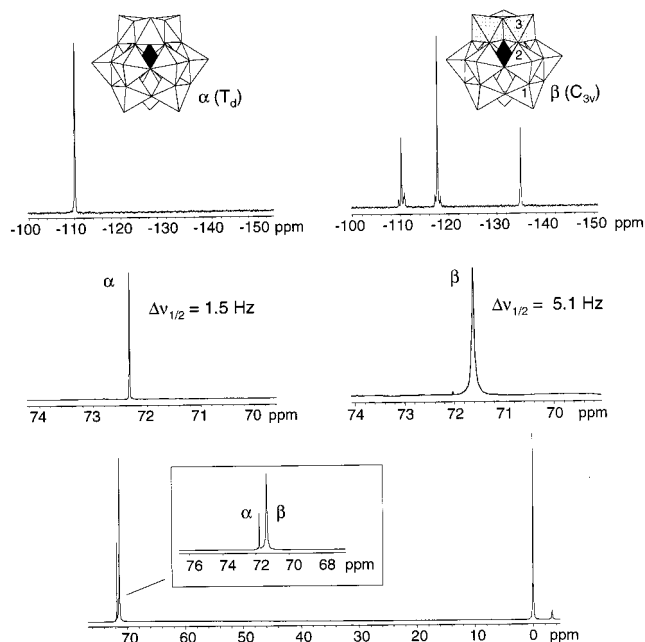


Figure 2. Bottom: ^{27}Al NMR spectrum of a reaction mixture containing α - and β - $\text{H}_5[\text{Al}^{\text{III}}\text{W}_{12}\text{O}_{40}]$ (α - and β -**1**; see the inset) and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Middle and top: ^{27}Al and ^{183}W NMR spectra and structures (in polyhedral notation) of α -**1** (left) and β -**1** (right). The ^{27}Al atom (100% abundance; $I = 5/2$) occupies a tetrahedral site (α -**1**, $\Delta\nu_{1/2} = 1.5$ Hz) or pseudotetrahedral site (β -**1**, $\Delta\nu_{1/2} = 5.1$ Hz) located at the center of the $\text{W}^{\text{VI}}_{12}\text{O}_{40}^{8-}$ shell of WO_6 octahedra.

1:12 anions which differ slightly in some way ... it could be a structural difference, although this might lead to distortion of the symmetry around the AlO_4 unit and thus to a broadened line. Alternatively, it could indicate protonation of the anion to give a $[\text{H}_3\text{AlW}_{12}\text{O}_{40}]^{2-}$ ion which would presumably retain its symmetry by proton exchange." Notably, due to the quadrupolar broadening discussed by Akitt and Farthing, the line width of the ^{27}Al NMR signal associated with the Al atom in β -**1** ($\Delta\nu_{1/2} = 5.1$ Hz; Figure 2, right) is somewhat larger than that of the signal arising from the Al atom at the center of the more highly symmetrical α -**1** isomer ($\Delta\nu_{1/2} = 1.5$ Hz; Figure 2, left).

The presence of two 1:12 compounds in the preparation of $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ has been discussed in few other reports. Nomiya and Miwa in 1983^{12a} did not isolate or explicitly observe the two 1:12 compounds, but rather performed solution and solid-state IR studies using the product mixture. The authors concluded that, of the explanations suggested by Akitt and Farthing, i.e., protonation or a difference in structure, the latter seemed more likely. The possible presence of α and β isomers was not mentioned. In a 1986 review article, Chauveau^{12b} reprinted Akitt and Farthing's ^{27}Al NMR spectrum¹¹ but made no mention of α or β isomers. An ^{27}Al NMR spectrum of a reaction mixture containing **1** was published by Fedotov and Kazanskii in 1987,^{12c} but was of insufficient resolution to observe two distinct signals. Finally, in 1989, Lunk^{12d} attributed Akitt and Farthing's observation of two ^{27}Al NMR signals to the presence of both protonated and unprotonated forms of the Keggin anion. It is now clear that Akitt and Farthing actually prepared a mixture of α - and β - $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$.

In the T_d anion, α -**1**, all 12 W atoms are chemically equivalent, and a single signal at -110.1 ppm is observed in its ^{183}W NMR spectrum (Figure 2, top left). Characteristic of β Keggin anions,^{41,24} which due to rotation of one W_3O_{13} triad by 60° about a C_3 axis of the anion possess C_{3v} symmetry and therefore three sets of chemically distinct W atoms, three signals

Table 1. Assignment of Signals Observed in the ^{183}W NMR Spectrum of β - $\text{H}_5[\text{AlW}_{12}\text{O}_{40}]$

δ (ppm)	$^2J_{\text{W-O-W}}$ (Hz), corner (av)	$^2J_{\text{W-O-W}}$ (Hz), edge (av) ^a	assignment
-110.8	9.5	none	site 3
-118.7	9.8	3.1	site 2
-136.8	none	3.1	site 1

^a Because the tungsten satellites were not fully resolved, the coupling constants reported here were estimated from the broadening at the base of the signal.

with relative intensities of 1:2:1 are observed in the ^{183}W NMR spectrum of β -**1** (Figure 2, top right). (By contrast, in ^{183}W NMR spectra of γ -Keggin anions, four signals with relative intensities of 1:1:2:2 are observed.^{24o}) The larger intensity signal in the ^{183}W NMR spectrum of β -**1** (-118.7 ppm) is assigned to the six equivalent "belt" W atoms (Figure 2, top right; site 2). On the basis of the magnitudes of the observed coupling constants, the remaining signals are readily assigned (Table 1). Corner sharing via $\mu_2\text{-O}$ atoms between adjacent WO_6 octahedra in polyoxoanion structures typically gives rise to coupling constants ($^2J_{\text{W-O-W}}$) of ca. 7.5–15 Hz, while edge sharing gives rise to $^2J_{\text{W-O-W}}$ values of about 2.5–6 Hz.^{24c,f,g,25} Thus, the signal at -110.8 ppm ($^2J_{\text{W-O-W}} = 9.5$ Hz) is assigned to the W atoms in the 60° -rotated triad (site 3 in Figure 2), which are linked by corner sharing to the six belt W atoms. The signal at -136.8 ppm ($^2J_{\text{W-O-W}} = 3.1$ Hz) is assigned to the three W atoms located opposite to the rotated triad (site 1), which are linked by edge sharing to the six belt W atoms.

Additional spectroscopic data obtained (IR and UV-vis) are also characteristic of α - and β -Keggin anions. In the α isomer (Na^+ salt form), two bands, one broad and strong and the other sharp (medium), are observed between 400 and 300 cm^{-1} ; in the IR spectrum of the β isomer (Na^+ salt), the two bands are replaced by a set of several overlapping broad bands. Similar differences observed in IR spectra of α - and β - $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ were related to small changes in the $\text{W}-\mu_2\text{-O}-\text{W}$ angles associated with corner-shared intertriad linkages.^{22e,24o} In addition to the slight difference in color between the two isomers (α -**1** is colorless, while the β isomer is a characteristic pale

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(25) These coupling constants are half the values normally reported in the polyoxometalate literature for analogous spin-spin splittings. In 1981 (early in the application of ^{183}W NMR spectroscopy to the study of polyoxometalates), Doppelt (ref 24c) reported the $^2J_{\text{W-O-W}}$ coupling constants observed in ^{183}W NMR spectra of a series of α - and β -Keggin heteropolytungstates as the total distance in hertz from tungsten satellite to tungsten satellite rather than as the "splitting" of the signal, normally defined as the distance in hertz from one tungsten satellite to the central resonance. This error has been carried forward and repeated in the polyoxometalate literature since that time. The values reported here follow accepted convention (Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, 1977; p 212).

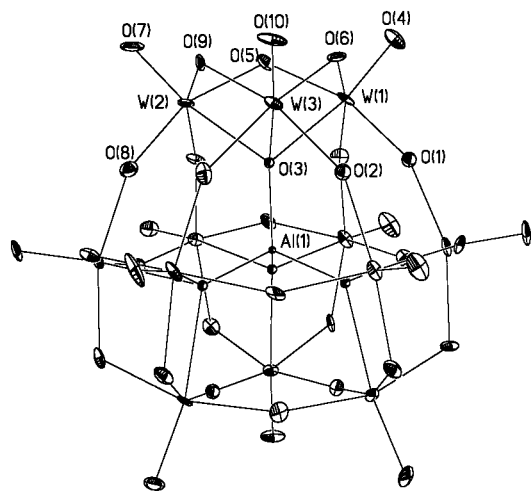


Figure 3. ORTEP drawing of α -K₅[Al^{III}W₁₂O₄₀] \cdot 17H₂O (α -1) with thermal ellipsoid plot (30% probability).

yellow^{2b}), the extinction coefficient at λ_{\max} ($\epsilon = 3.5 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ at 262 nm) in the UV spectrum of the α isomer (Na⁺ salt form) in water is substantially larger than that of the β isomer ($\epsilon = 2.7 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ at 266 nm). Analogous differences have been observed in the UV-vis spectra of α - and β -[SiW₁₂O₄₀]⁴⁻,^{2b,4a,24c}

Also consistent with these structural assignments, the first 1e⁻-reduction potential of the β isomer is 106 mV more positive than that of the α isomer. Reduction potentials in 2 M sodium acetate buffer at pH 4.8 are $(E_{\text{pc}} + E_{\text{pa}})/2 = -601$ and -495 mV (vs NHE), respectively, for α -1 and β -1. This result is consistent with polarographic data obtained by Rocchiccioli-Deltcheff^{22d} for isomers of [SiW₁₂O₄₀]⁴⁻ (-260 mV for α and -140 mV for β) and [GeW₁₂O₄₀]⁴⁻ (-200 mV for α and -110 mV for β) at pH 5 in 2.0 M sodium acetate buffer.²⁶

The structure of α -1 (K⁺ salt) was definitively established by X-ray crystallography²⁷ (Figure 3; see the Experimental Section). The AlO₄ group at the center of α -1 defines a regular tetrahedron (O-Al-O angles of from 108.9(6) $^\circ$ to 110.5(5) $^\circ$) with an Al-O bond length of 1.742(8) Å (Table 2). The three W atoms associated with the edge-shared octahedra in the W₃O₁₃ triads are separated from one another by W \cdots W distances of 3.32 Å, while separations between W atoms in corner-shared octahedra (intertriad linkages) are 3.71 Å. These distances are similar to published values of 3.4 and 3.7 Å.^{1k}

Controlled Hydrolysis of α -[AlW₁₂O₄₀]⁵⁻ (α -1). Careful reaction of NaOH with α -1 (Na⁺ salt) gives the monolacunary derivative α -Na₉[AlW₁₁O₃₉] (α -3; Scheme 1) as the major product (82%) and β -3 as a minor product (18%; mixture of β -lacunary structures described in greater detail below). Relative yields of the α -3 and β -3 derivatives were calculated from the ratio of α -1 to β -1 quantified by ²⁷Al NMR after metalation of the crude product mixture with W(VI). The metalation was accomplished by addition of paratungstate and HCl (Scheme 1).

Retention of isomeric integrity upon hydrolysis of α -1 to the monolacunary derivative, i.e., no isomerization upon removal

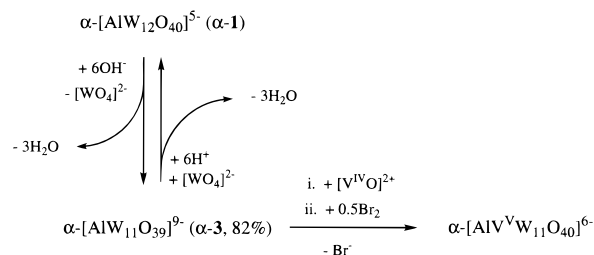
(26) Similar (ca. 100 mV) differences between reduction potentials were also observed by Rocchiccioli-Deltcheff (ref 22d) for α and β isomers of [SiMo₁₂O₄₀]⁴⁻, [GeMo₁₂O₄₀]⁴⁻, [PMo₁₂O₄₀]³⁻, and [AsMo₁₂O₄₀]³⁻ in 1:1 water/dioxane with 0.5 M HClO₄.

(27) Crystal data for α -K₅[AlW₁₂O₄₀] \cdot 17H₂O: colorless crystal, dimensions of 0.31 \times 0.24 \times 0.21 mm, hexagonal P6₃22, with $a = 19.0720(1)$ Å, $c = 12.5658$ Å, $V = 3958.34(7)$ Å³, $d_c = 4.223$ g cm⁻³, and $Z = 3$. At final convergence, $R_1 = 3.42\%$, $R_2 = 7.45\%$, and GOF = 1.02 for 143 parameters.

Table 2. Selected Bond Distances (Å) and Angles (deg) of α -1

Distances			
Al(1)-O(3)	1.742(8)	W(1)-O(6)	1.976(8)
W(1)-O(3)	2.265(8)	W(2)-O(5)	1.961(8)
W(2)-O(3)	2.253(8)	W(2)-O(9)	1.901(9)
W(3)-O(3)	2.276(8)	W(3)-O(6)	1.911(9)
W(1)-O(4)	1.704(8)	W(3)-O(9)	1.964(8)
W(2)-O(7)	1.710(9)	W(1)-O(1)	1.910(8)
W(3)-O(10)	1.704(8)	W(2)-O(8)	1.896(9)
W(1)-O(5)	1.894(8)	W(3)-O(2)	1.899(8)
Angles			
O(3)-Al(1)-O(3a)	108.9(6)	W(1)-O(5)-W(2)	118.3(4)
O(3)-Al(1)-O(3b)	110.5(5)	W(1)-O(6)-W(3)	117.0(4)
O(3)-Al(1)-O(3c)	109.0(5)	W(2)-O(9)-W(3)	118.9(4)
Al(1)-O(3)-W(1)	121.9(4)	W(1)-O(1)-W(3b)	152.9(5)
Al(1)-O(3)-W(2)	123.1(4)	W(2)-O(8)-W(3c)	151.8(5)
Al(1)-O(3)-W(3)	121.7(4)	W(3)-O(2)-W(2b)	150.3(5)

Scheme 1



of any one of the 12 [W^{VI}=O]⁴⁺ moieties from the structure shown in Figure 2 (top left) or in Figure 3, would give an anion possessing C_s symmetry. Consistent with this requirement, a set of six signals present in integrated-area ratios of 2:2:2:2:2:1 was observed in the room temperature ¹⁸³W NMR spectrum of α -3. (Signals associated with β -3, a minor product of the hydrolysis reaction, were also present.) The structure of α -3 was further confirmed by comparison of the ²⁷Al and ⁵¹V NMR spectra of its V(V) derivative—prepared by in-situ addition of vanadyl sulfate followed by oxidation with Br₂ (Scheme 1)—with the ²⁷Al and ⁵¹V NMR spectra of the kinetically stable potassium-salt analogue, α -K₆[AlV^VW₁₁O₄₀] (5). (See the Experimental Section for preparation and characterization of α -K₉[AlW₁₁O₄₀], 4, and 5.)

Controlled Hydrolysis of β -[AlW₁₂O₄₀]⁵⁻ (β -1). In principle, controlled hydrolysis of β -1 might give three β lacunary anions, derived by removal of the [W=O]⁴⁺ ions associated with the octahedra labeled 3, 2, and 1 in Figure 2 (top right). Analogous monolacunary derivatives of β -[SiW₁₂O₄₀]⁴⁻ have been studied in detail by Tézé and Hervé.^{3,4h,28} Using their nomenclature, the β_3 derivative (C_s symmetry) is obtained by removal of a [W=O]⁴⁺ ion from the 60 $^\circ$ -rotated W₃O₁₃ cap (i.e., removal of the [W=O]⁴⁺ ion from octahedron 3 in the structure shown at the top right in Figure 2). Removal of a [W=O]⁴⁺ ion from a belt position (octahedron 2 or its equivalent) gives a monolacunary anion possessing C₁ symmetry (designated β_2), in which all 11 W atoms are chemically inequivalent (Figure 4). The β_1 derivative (C_s symmetry) is obtained by removal of a [W=O]⁴⁺ ion from the W₃O₁₃ triad at the bottom of the structure (octahedron 1 or its equivalent).

Hervé^{4h} reported that mild hydrolysis of β -[SiW₁₂O₄₀]⁴⁻ gave the β_2 monolacunary derivative, β_2 -[SiW₁₁O₃₉]⁸⁻. Analogously, hydrolysis of β -1 gives the β_2 derivative (i.e., β_2 -Na₉[AlW₁₁O₃₉], β_2 -3; Figure 4) as the major product (C₁; 11 signals of equal

(28) (a) Tézé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 999–1002. (b) Robert, F.; Tézé, A.; Hervé, G.; Jeannin, Y. *Acta Crystallogr.* **1980**, *B36*, 11–15.

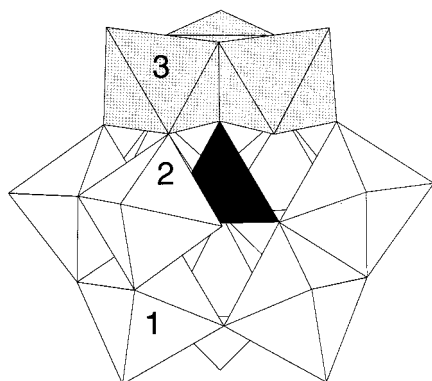


Figure 4. Structure (in polyhedral notation) of the monolacunary anion, $\beta_2\text{-Na}_9[\text{AlW}_{11}\text{O}_{39}]$ ($\beta_2\text{-3}$), obtained by controlled hydrolysis of $\beta\text{-Na}_5[\text{Al}^{\text{III}}\text{W}_{12}\text{O}_{40}]$ ($\beta\text{-1}$).

intensity by ^{183}W NMR). Two minor products, a $\beta\text{-3}$ isomer of C_s symmetry (six signals; either $\beta_1\text{-3}$ or $\beta_3\text{-3}$) and $\alpha\text{-3}$ (six signals) are also observed.

Equilibria between α - and β Isomers. The occurrence of Keggin anions in two isomeric forms was noted over 125 years ago. It was then many years before controversy regarding their structures was finally laid to rest. The structure of the α isomer was solved by Keggin in 1933; that of the β isomer was confirmed 40 years later. Since then, attempts to rationalize the relative stabilities of the two isomers on the basis of seemingly reasonable electrostatic arguments have proven elusive. Coulombic arguments suggest that the two structures should be similar in energy; experimentally, however, only $\beta \rightarrow \alpha$ rearrangements have been observed. Data concerning $\alpha\text{-}\beta$ rearrangements have been obtained largely through study of tungstosilicates ($[\text{SiW}_{12}\text{O}_{40}]^{4-}$) and their derivatives. Unlike ^{29}Si , however, which has a natural abundance of 4.7% and an NMR sensitivity at constant field strength of 0.079 relative to ^1H (1.00), ^{27}Al has a natural abundance of 100% and a much larger sensitivity (0.207). Having isolated and characterized individual α and β isomers of $[\text{AlW}_{12}\text{O}_{40}]^{5-}$ (α - and $\beta\text{-1}$) and their monolacunary derivatives, $\alpha\text{-3}$ and $\beta_2\text{-3}$, we are now in a position to use high-field ^{27}Al NMR to address the issue of their relative energies.

Equilibria between α - and $\beta\text{-1}$ (free acids, 0.10 M in water at 200 °C; natural $[\text{H}^+] = 0.50$ M) and between α - and $\beta\text{-3}$ (0.13 M in D_2O at 60 °C; natural pH ca. 7) were readily observed by ^{27}Al NMR (Figure 5). For the isomerization reaction $\alpha\text{-1} \rightarrow \beta\text{-1}$, the equilibrium ratio of $\beta\text{-1}$ to $\alpha\text{-1}$ gives $K_{\text{eq}(473\text{ K}, 0.1\text{ M } 1)} = 0.11 \pm 0.01$ (Figure 5). First-order rate constants⁴¹ for approach to equilibrium at 473 K ($k_1/k_{-1} = 0.11$; nonlinear least-squares regression using the Solver function in Microsoft Excel) are $k_{1(\alpha\text{-}\beta)} = 7.68 \times 10^{-7} \text{ s}^{-1}$ and $k_{-1(\beta\text{-}\alpha)} = 6.97 \times 10^{-6} \text{ s}^{-1}$. From $\Delta G = -RT \ln K_{\text{eq}}$, $\alpha\text{-1}$ is more stable than $\beta\text{-1}$ by $2.1 \pm 0.5 \text{ kcal mol}^{-1}$.³⁰

As the mixture of lacunary anions, **3**, approaches equilibrium, the 11 ^{183}W NMR signals assigned to $\beta_2\text{-3}$ disappear, while the 12 signals assigned to a mixture of one $\beta\text{-3}$ isomer of C_s symmetry (6 signals; either $\beta_1\text{-3}$ or $\beta_3\text{-3}$) and to $\alpha\text{-3}$ (C_s symmetry) increase in intensity.²⁹ Tézé and Hervé reported that

(29) In the ^{183}W NMR spectrum of $\alpha\text{-Na}_9[\text{GaW}_{11}\text{O}_{39}]$, an unanticipated set of six signals, which included one unusually far downfield resonance at -16.2 ppm, was attributed to $\alpha\text{-}[\text{GaNaW}_{11}\text{O}_{39}]^{8-}$ (the Na^+ -substituted lacunary anion; ref 24e). Although ion pairing between Na^+ and $[\text{GaW}_{11}\text{O}_{39}]^{9-}$ ions is likely, this specific structural assignment (i.e., coordination of a Na^+ ion by the lacunary site of the defect anion) may be incorrect. We attribute a similarly far downfield signal (-32.9 ppm) observed in spectra of Na^+ salts of equilibrated **3** to a unique β isomer of C_s symmetry (probably $\beta_3\text{-3}$).

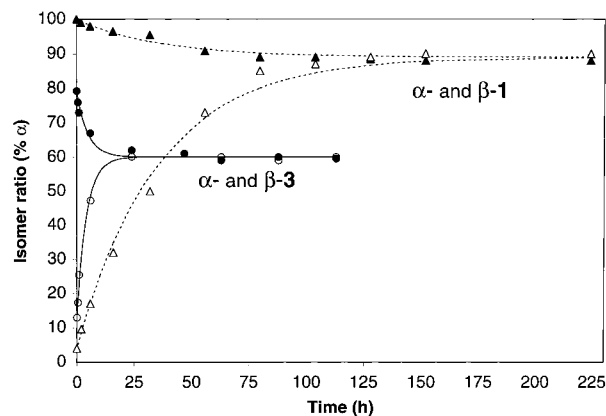


Figure 5. Isomerization of $\alpha\text{-1}$ (\blacktriangle) and $\beta\text{-1}$ (\triangle) and of $\alpha\text{-Na}_9[\text{AlW}_{11}\text{O}_{39}]$ ($\alpha\text{-3}$; \bullet) and $\beta_2\text{-Na}_9[\text{AlW}_{11}\text{O}_{39}]$ ($\beta_2\text{-3}$; \circ). Approach to equilibrium between $\alpha\text{-1}$ and $\beta\text{-1}$ in water is shown by dashed curves; approach to equilibrium between solutions initially containing mostly $\alpha\text{-3}$ (82%; 18% β) and mostly $\beta_2\text{-3}$ (87%; 13% α) in D_2O is shown by solid curves.

isomerizations of $\beta\text{-}[\text{SiW}_{11}\text{O}_{39}]^{8-}$ anions occur in the direction $\beta_1 \rightarrow \beta_2 \rightarrow \beta_3 \rightarrow \alpha$.^{3,4h} By analogy with the direction of isomerization of $\beta\text{-}[\text{SiW}_{11}\text{O}_{39}]^{8-}$ anions, the major $\beta\text{-3}$ isomer present at equilibrium with $\alpha\text{-3}$ is likely $\beta_3\text{-3}$. Figure 5 shows that the dominant $\beta\text{-3}$ isomer and $\alpha\text{-3}$ are close in energy. From the equilibrium ratio of the concentrations of the β -lacunary isomer (40% of the total concentration of **3**) and $\alpha\text{-3}$ (60% of the total), the equilibrium constant for the isomerization reaction $\beta\text{-3} \rightarrow \alpha\text{-3}$ is ca. $K_{\text{eq}(333\text{ K}, 0.13\text{ M } 3)} = 1.5$. From $\Delta G = -RT \ln K_{\text{eq}}$, $\alpha\text{-3}$ is more stable than the $\beta\text{-3}$ isomer by $0.3 \text{ kcal mol}^{-1}$.

These data show that α and β isomers of Keggin tungstoaluminates are similar to one another in energy and refute the conventional wisdom that rearrangements of fully oxidized Keggin anions occur exclusively in the direction $\beta \rightarrow \alpha$. These results also support the argument, based solely on electrostatic repulsion between W(VI) cations within the tungsten oxide framework of the cluster anions, that α and β isomers should be similar in energy.^{1k} At the same time, a trend in the kinetic and thermodynamic stabilities of isostructural β -Keggin heteropolytungstates is now apparent.

Trends in the Structure and Stability of α - and β -Keggin Anions. The $\text{Al}-\mu_4\text{-O}$ bond length in the $T_d \text{AlO}_4$ group at the center of $\alpha\text{-1}$ (Table 2) establishes a trend in $\text{X}-\mu_4\text{-O}$ bond lengths of 1.53(1),³¹ 1.64(2),^{2c} and 1.74(1) Å, respectively for $\text{X} = \text{P(V)}$, Si(IV) , and Al(III) in α Keggin $[\text{X}^n+\text{W}^{\text{VI}}_{12}\text{O}_{40}]^{(8-n)-}$ (Figure 6). Notably, however, the size of the cavity occupied by the $[\text{X}^n+\text{O}_4]^{(8-n)-}$ groups within the neutral $\text{W}_{12}\text{O}_{36}$ shell remains fairly constant: In $\alpha\text{-1}$, the sum of $\text{Al}-\mu_4\text{-O}$ (1.74 Å) and $\mu_4\text{-O}-\text{W}$ (2.26 ± 0.02 Å) bond lengths is 4.00 Å. Analogous bond-distance sums in $\alpha\text{-}[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{3-}$ are 3.97 and 3.96 Å, respectively (Figure 6). This similarity supports the suggestion (proposed by Day and Klemperer^{1j}) that Keggin anions might be viewed as anionic $[\text{X}^n+\text{O}_4]^{(8-n)-}$ subunits encapsulated by neutral $\text{W}_{12}\text{O}_{36}$ cages. In keeping with this view, the size of the XO_4 tetrahedron varies with the size, charge, and electronegativity of the heteroatom, X. The ionic radii of the heteroatoms increase from right to left

(30) Values of k and K_{eq} (and thus calculated values for ΔG) vary with temperature, solvent, ionic strength, and the nature of the counterion. Pairing between Na^+ ions (1.17 M) and **3** (a 9- anion) is almost certainly present; ion pairing between H^+ (0.50 M) and **1** (the conjugate base of a strong Brønsted acid) is strongly suspected (Weinstock, I. A. *Chem. Rev.* **1998**, *98*, 113–170).

(31) Brown, G. M.; Noe-Spirlet, M. R.; Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1977**, *B33*, 1038.

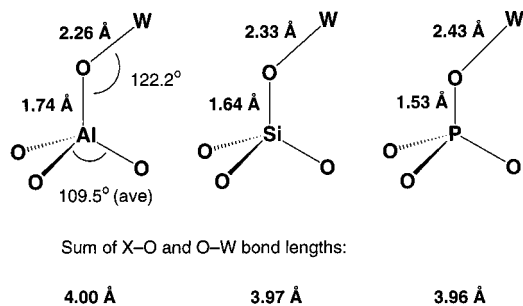


Figure 6. Variation in X–O bond lengths (Å) of $[X^{n+}O_4]^{(8-n)-}$ tetrahedra located within neutral $W_{12}O_{36}$ shells of α -Keggin heteropolytungstates containing second-row main-group heteroatoms, X = Al(III), Si(IV), and P(V). As X–O bond lengths increase from right to left, distances from the $[X^{n+}O_4]^{(8-n)-}$ structures to the $W_{12}O_{36}$ shell (O–W) decrease commensurately.

(i.e., from P(V) to Al(III)), while their valencies and electronegativities decrease. Thus, within the cavity defined by the $W_{12}O_{36}$ cage, the XO_4 tetrahedra expand in size from $[PO_4]^{3-}$ to $[AlO_4]^{5-}$ (Figure 6).

Shannon and Prewitt effective ionic radii (Å) and Allred-Rochow electronegativities of the tetrahedral heteroatoms, X, are, for P(V), 0.31 Å and 2.06, for Si(IV), 0.40 Å and 1.74, and, for Al(III), 0.53 Å and 1.47.³² In addition, the shortest X– μ_4 -O bond distance is found in $[PO_4]^{3-}$, while the longest is found in $[AlO_4]^{5-}$. Because the size of the $W_{12}O_{36}$ cage remains constant, the longest μ_4 -O–W bond distance is found in $[PW_{12}O_{40}]^{3-}$, while that in $[AlW_{12}O_{40}]^{5-}$ is the shortest (Figure 6). Thus, by all five indices—heteroatom size, charge, and electronegativity, X– μ_4 -O bond distance, and μ_4 -O–W bond distance—it follows that the ability of each μ_4 -O atom to donate negative charge density to the three W atoms to which it is coordinated (Figure 3) should increase from right to left with X = P(V) < Si(IV) < Al(III). Notably, this trend parallels the relative stabilities of β -Keggin isomers. While β - $[PW_{12}O_{40}]^{3-}$ is unknown,^{4b,5} β - $[SiW_{12}O_{40}]^{4-}$ possesses substantial kinetic

(32) J. E. Huheey *Inorganic Chemistry: Principles of structure and reactivity*, 2nd ed.; Harper & Row: New York, 1978.

stability^{2b,6} and β - $[AlW_{12}O_{40}]^{5-}$, the only member of the series for which K_{eq} of α – β isomerization is available, possesses the greatest kinetic and thermodynamic stability. Finally, it bears noting that the correlation between donation of negative charge density to W by μ_4 -O atoms and β -isomer stability runs parallel to the observation that β isomers are stabilized upon electron reduction of fully oxidized α -Keggin anions.^{4e,33}

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for α - $K_5[AlW_{12}O_{40}] \cdot 17H_2O$ (PDF). An X-ray crystallographic file, in CIF format, is available through the Internet only. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(33) In 2 M sodium acetate buffer, the first $1e^-$ -reduction potential of the sodium salt of β -1 is 106 mV more positive than that of the sodium salt of α -1. This difference between the $1e^-$ -reduction potentials of the α and β isomers is consistent with results obtained by Roccicchioli-Deltcheff for a series of α - and β -Keggin anions (refs 22d and 26). Reduction potentials of the β isomers were generally 90–120 mV more positive than those of the α isomers. In 0.49 M H^+ solution (a medium more pertinent to the equilibration experiments reported here) the difference in reduction potential between α - and β -1 is even greater (–621 vs –454 mV, a difference of 167 mV). In addition, unlike at high $[Na^+]$ (1 M Na^+ from 2 M sodium acetate buffer at pH 4.8), where $1e^-$ reductions were observed, in 0.49 M H^+ solution the first cathodic waves of both α - and β -1 appear to involve $2e^-$ each (see ref 22f for a detailed discussion of the effects of H^+ concentration on the cyclic voltammetric behavior of α - $[SiW_{12}O_{40}]^{4-}$ and α - $[PW_{12}O_{40}]^{3-}$). Thus, assignment of a correlation between reduction potentials and relative stabilities of fully oxidized α and β structures would appear to require data necessary for construction of a full thermodynamic cycle, i.e., the relative energies of the $1e^-$ - and $2e^-$ -reduced ions (in addition to the relative energies of the two fully oxidized ions, reported here).