

Stability and Structure in α - and β -Keggin Heteropolytungstates,
[Xⁿ⁺W₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻, X = p-Block Cation

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β -[SiW₁₂O₄₀]⁴⁻ (*C*_{3v} symmetry) is sufficiently higher in energy than its α -isomer analogue that effectively complete conversion to α -[SiW₁₂O₄₀]⁴⁻ (*T*_d) is observed. By contrast, β - and α -[AlW₁₂O₄₀]⁵⁻ (β - and α -1; *C*_{3v} and *T*_d, respectively) are sufficiently close in energy that both isomers are readily seen in ²⁷Al NMR spectra of equilibrated (α - β) mixtures. Recently published DFT calculations ascribe the stability of β -1 to an electronic effect of the large, electron-donating [AlO₄]⁵⁻ (*T*_d) moiety encapsulated within the polarizable, fixed-diameter β -W₁₂O₃₆ (*C*_{3v}) shell. Hence, no unique structural distortion of β -1 is needed or invoked to explain its unprecedented stability. The results of these DFT calculations are confirmed by detailed comparison of the X-ray crystal structure of β -1 (β -Cs_{4.5}K_{0.5}[Al^{III}W₁₂O₄₀]·7.5H₂O; orthorhombic, space group *Pmc*2₁, *a* = 16.0441(10) Å, *b* = 13.2270(8) Å, *c* = 20.5919(13) Å, *Z* = 4 (*T* = 100(2) K)) with previously reported structures of α -1, α - and β -[SiW₁₂O₄₀]⁴⁻, and β -1-[SiMoW₁₁O₄₀]⁴⁻.

Until recently, the relative instability of β isomers of Keggin anions was accepted as a general rule.¹ In 1999, however, as part of an ongoing effort to develop Keggin tungstoaluminates as catalysts for O₂ oxidations in water,² we observed equilibria between β - and α -[Al^{III}W₁₂O₄₀]⁵⁻ (β - and α -1).³ The basis for the small difference in energy between these isomers was recently investigated by Poblet and co-workers.⁴ Based on density-functional-theory (DFT) calculations,⁵ the unprecedented stability of β -1 was attributed entirely to electronic effects ultimately arising from

the presence of the Al(III) heteroatom. This conclusion, however, was predicated on the assumption that β -1 (X = Al) is structurally analogous to unstable β -Keggin heteropolyanions (e.g., X = P or Si). To verify this assumption and to assess the ability of DFT calculations to reliably predict energy changes associated with modifications of polyoxometalate (POM) structure, we obtained a high-quality X-ray crystal structure of β -1. We herein report and discuss crystallographic data for β -Cs_{4.5}K_{0.5}[Al^{III}W₁₂O₄₀]·7.5H₂O, which, for the first time, provide accurate and precise atomic coordinates for a β -Keggin [Xⁿ⁺W₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻ heteropolyanion (X = main-group or transition-metal cation).

In water (pH 0, 200 °C), β -1 is only 2.1 kcal mol⁻¹ higher in energy than is α -1.^{3a} Concerning this unique property of 1, five lines of evidence^{3a} indicated a clear trend: As X is varied from P(V) to Al(III), X- μ_4 -O bond distances in [Xⁿ⁺O₄]⁽ⁿ⁻⁸⁾⁻ tetrahedra increase, and increasing polarization of the X-O bonds shifts electron density toward the fixed-diameter α -W₁₂O₃₆ shell. The retention of tetrahedral (*T*_d) symmetry in [XO₄]^{m-} and the absence of variation in the diameter of the W₁₂O₃₆ shell supported^{3a} the clathrate structural model⁶ of the Keggin ion: [XO₄]^{m-}@W₁₂O₃₆. Still missing, however, was a *causative* relationship between the indicated trend in electronic properties and differences in energy between β and α isomers.^{1,6,7}

In 2001, however, Poblet and co-workers,⁴ one of several groups⁸ involved in the still incipient use of DFT to model the physical properties of POMs, evaluated the relative energies of α - and β -[Xⁿ⁺W₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻ (X = P, Si, Al, etc.). In Poblet's model, isomerization from α to β was described by 60° rotation of a single W₃O₁₃ triad,^{7b} and by attendant reduction in symmetry of the anion from *T*_d to *C*_{3v} (Figure 1).

The fragment interaction method^{9,10} used by Poblet⁴ was predicated on the clathrate structural model⁶ described above. Accordingly, even when encapsulated within lower symmetry

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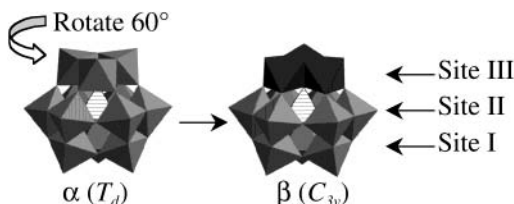


Figure 1. Isomerization of α - to β - $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (in polyhedral notation). The 60° -rotated W_3O_{13} triad is shown in dark gray.

(C_{3v}) β - $W_{12}O_{36}$ shells, coordination about X in $[XO_4]^{m-}$ was presumed to remain tetrahedral (T_d). On the basis of this structural model, Poblet determined that β isomers are stabilized by an orbital interaction (OI) term, which includes both charge transfer ($[XO_4]^{m-} \rightarrow W_{12}O_{36}$) and the polarization of both fragments. Notably, contributions of OI to β -isomer stability increase markedly as X is varied from P to Si to Al, such that the relative stabilities of respective β isomers increase in the same order. Poblet's work thus established a causative relationship between the trend in electronic properties we noted in 1999^{3a} and the unique stability of β -1.

At the same time, Poblet's attribution of β -isomer stability entirely to electronic properties is predicated on the assumption that, apart from larger Al- μ_4 -O and μ_4 -O-W bond distances, β -1 (X = Al) is structurally identical to other less stable β isomers (e.g., X = P or Si). To assess the validity of this assumption, we obtained a reliable and highly precise X-ray crystal structure of β -Cs_{4.5}K_{0.5}[Al^{III}W₁₂O₄₀]·7.5H₂O (β -1) (Figure 2)^{11,12} so that α -^{3a} and β -1 could be compared with other α - and β - $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ pairs.

While numerous α -Keggin anions have been structurally characterized, until now, crystallographic data for only one β - $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ anion, β -[SiW₁₂O₄₀]⁴⁻ (β -2), have been reported¹³ or stored in either the Cambridge Structural Database (CSD)¹⁴ or the Inorganic Crystal Structure Database (ICSD)¹⁵ (Table S1 in the Supporting Information (SI) is a

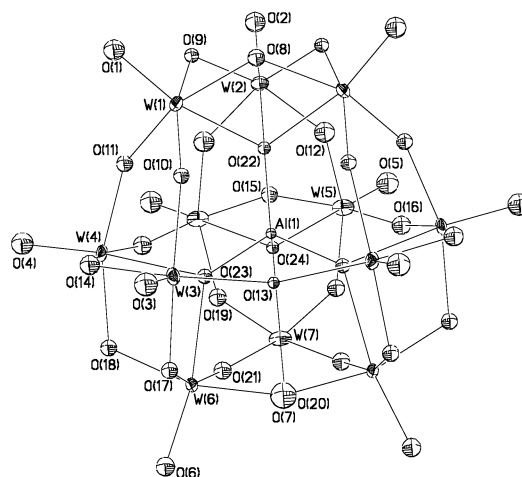


Figure 2. Thermal ellipsoid plot of β -1 (ellipsoids shown at 50% probability).

comprehensive annotated catalog of 142 Keggin heteropolytungstates—main-group or transition-metal heteroatom—structurally characterized by X-ray crystallography). Unfortunately, the crystallographic data in all three published attempts to structurally characterize β -2 are of limited use (unreliable atomic coordinates and large uncertainties; see summary in SI).

Given these uncertainties, the α - and β -1 isomer pair is more defensibly evaluated by comparison with α -2 and β -1-K₄[SiMoW₁₁O₄₀] (β -1-3), an isoelectronic derivative of β -2. A reliable X-ray crystal structure^{7d} of β -1-3 (R1 value of 5.2), in which a vacant site in β -1-[SiW₁₁O₃₉]⁸⁻ (site I at the lower right in Figure 1) is occupied by Mo(VI), was obtained by Jeannin and co-workers. Apart from 60° rotation of the W_3O_{13} unit (site III), no significant distortion of the $[SiO_4]^{4-}$ tetrahedron was observed: Si- μ_4 -O distances ranged from 1.61 to 1.66 Å and O-Si-O angles from 109° to 112° .¹⁶ On the basis of close *compositional* and *electronic* similarity to β -2, as well as the quality of the crystallographic data (three requisite and defensible criteria), β -1-3 was selected from all available possibilities (see Table S1) as suitable for use in evaluating the structural changes that occur upon isomerization of α - to β -2.¹⁷

From comparison of both processes and all four structures involved in isomerization of α - to β -1 and of α - to β -2 (represented by β -1-3), it is clear that β -1 is not uniquely distorted. Mean bond distances and angles for the $[X^{n+}O_4]^{(8-n)-}$ moieties in α and β isomers are listed in Table 1 (α -[PW₁₂O₄₀]³⁻ is included¹⁸ to reveal trends). Four conclusions

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- (11) The X-ray quality crystals of β -Cs_{4.5}K_{0.5}[Al^{III}W₁₂O₄₀]·7.5H₂O were grown from an aqueous solution of β -K₅1 (ref 3a) and CsCl. The crystal system is orthorhombic, space group *Pmc*2₁, *Z* = 4, ρ_{calcd} = 5.488 Mg m⁻³, *a* = 16.0441(10) Å, *b* = 13.2270(8) Å, *c* = 20.5919(13) Å, *V* = 4369.9(5) Å³. The final statistics based on *F*² are GOF = 1.166, *R*₁ = 0.0554 and *wR*₂ = 0.1231 for *I* > 2 σ (*I*). (See SI for full details.)
- (12) In all, crystallographic data were acquired using four crystals of β -1 from four different solutions. Data for two of these crystals are included as SI. While both of these are higher in quality than any β - $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ structure previously published, they are, by some indices, poorer in quality than that shown in Figure 2. Nonetheless, the bond lengths and angles, and their uncertainties, are very close to those of the structure shown in Figure 2.; see Table S12 in SI.

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- (17) Structures of α - β isomer pairs involving other heteroatoms, X, such as P, As, or Ge, have either not been reported (As, Ge, or others), or fail to meet the criteria needed for reliable comparison to α - and β -1 (e.g., β -PMo₃W₉O₄₀); see Table S1.

Table 1. Mean^a Distances (Å) and Angles (deg) for α - and β -[Xⁿ⁺W₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻, X = P(V), Si(IV), Al(III)

X	isomer	X- μ_4 -O	μ_4 -O-W	sum of X- μ_4 -O and μ_4 -O-W	O-X-O
P	α	1.526(1) ^b	2.438(3) ^b	3.964(3) ^b	109.5(2) ^b
Si	α	1.63(2)	2.35(2)	3.98(3)	109.5(4) ^b
	β^c	1.64(1) ^b	2.34(2)	3.98(2) ^b	109.5(7) ^b
Al	α	1.742(8)	2.265(8)	4.007(11)	109.5(6)
	β	1.760(17)	2.245(14)	4.00(2)	109.5(7)

^a Average values with uncertainties (1 σ) in parentheses. ^b Uncertainties calculated from scatter in reported data. ^c Data for β_1 -3.

Table 2. Changes^a in Angles (deg) and Nonbonding Distances (Å) upon Isomerization from α - to β -[Xⁿ⁺W₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻, X = Si(IV), Al(III)

X	Δ (W $\cdots$ W) distances (Å)			Δ (W-O-W) angles (deg)		
	sites III-II ^b	site II ^b	site II ^c	sites III-II ^b	site II ^b	site II ^c
Si ^d	-0.027(4)	+0.058(4)	-0.07(1)	-9.2(16)	+4.0(17)	-3.7(13)
Al	-0.047(4)	+0.040(11)	-0.046(9)	-6.2(9)	+7.7(11)	-2.1(9)

^a Uncertainties calculated from observed scatter in data or published uncertainties (where available). ^b Intertriad. ^c Intratriad. ^d β -Isomer data are from β_1 -3.

emerge. In every structure, regular [XO₄] tetrahedra are observed. Moreover, during both isomerization processes (X = Si and Al), X- μ_4 -O bond lengths, μ_4 -O-W bond lengths (distances between XO₄ and W₁₂O₃₆ fragments), and the sums of X- μ_4 -O and μ_4 -O-W bond lengths all remain constant. These data confirm that *both* α - β pairs are related to one another by 60° rotation of one W₃O₁₃ triad (Figure 1) and provide further support for the clathrate⁶ structural model, [XO₄]^{m-}@W₁₂O₃₆, the two assumptions on which the fragment interaction method applied by Poblet⁴ was predicated.

We now consider additional subtle changes that accompany isomerization from α to β (Table 2).¹⁹ While small, these are all statistically significant. (Note that all changes in nonbonding distances are accompanied by expected changes in bond angles.) Importantly, these changes are

identical (within 3 σ) for both **1** and **2**. The changes entail a slight decrease in nonbonded W $\cdots$ W distances between the three W atoms in the rotated triad (site III in Figure 1) and the six “belt” W atoms (site II), accompanied by a slight decrease in the six associated W- μ -O-W bond angles. Within site II, the three *intertriad* W $\cdots$ W distances increase slightly, while the three *intratriad* distances decrease. As expected, the corresponding W- μ -O-W bond angles increase and decrease, respectively, by a few degrees each. Although these subtle changes are not included in Poblet’s model, the fact that they accompany isomerization in both α - β pairs (X = Si and Al) clearly demonstrates the close similarity between the two isomerization processes.

We herein report the first precise structure of a β -Keggin dodecatungstate heteropolyanion, [Xⁿ⁺W₁₂O₄₀]⁽⁸⁻ⁿ⁾⁻, and show that, as predicted by DFT calculations, the unprecedented stability of β -**1** (X = Al(III)) appears entirely an electronic consequence of the large, highly electron donating [AlO₄]⁵⁻ (*T_d*) moiety encapsulated within the polarizable, yet fixed-diameter, β -W₁₂O₃₆ (*C_{3v}*) shell.

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Supporting Information Available: A catalog of 142 Keggin heteropolytungstates structurally characterized by X-ray crystallography; tables of crystal data, structure solution and refinement, atomic coordinates, selected bond lengths and angles, and experimental procedures for three β -**1** structures, β -Cs_{4.5}K_{0.5}[AlW₁₂O₄₀]·7.5H₂O, β -Cs_{3.5}K_{1.5}[AlW₁₂O₄₀]·5H₂O, and β -K₅[AlW₁₂O₄₀]·8H₂O (PDF), and CIF files for each; a discussion of crystallographic data reported for β -[SiW₁₂O₄₀]⁴⁻; a table comparing selected bond lengths and angles from crystallographic data acquired using three different crystalline salts of β -**1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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