β-[SiW\textsubscript{12}O\textsubscript{40}\textsuperscript{4-}] (C\textsubscript{6}v symmetry) is sufficiently higher in energy than its α-isomer analogue that effectively complete conversion to α-[SiW\textsubscript{12}O\textsubscript{40}\textsuperscript{4-}] (T\textsubscript{d}) is observed. By contrast, β- and α-[AlW\textsubscript{12}O\textsubscript{40}\textsuperscript{5-}] (β- and α-1; C\textsubscript{m} and T\textsubscript{d}, respectively) are sufficiently close in energy that both isomers are readily seen in \textsuperscript{27}Al 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 [AlO\textsubscript{4}\textsuperscript{5-}] (T\textsubscript{d}) moiety encapsulated within the polarizable, fixed-diameter β-W\textsubscript{12}O\textsubscript{40} (C\textsubscript{6}v) 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\textsubscript{4.5}K\textsubscript{0.5}[Al\textsubscript{III}W\textsubscript{12}O\textsubscript{40}]\textsuperscript{7-}·7H\textsubscript{2}O; orthorhombic, space group Pmc\textsubscript{2}1, 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-[SiW\textsubscript{12}O\textsubscript{40}\textsuperscript{4-}], and β\textsubscript{1}[SiMoW\textsubscript{11}O\textsubscript{40}\textsuperscript{4-}].

Until recently, the relative instability of β isomers of Keggin anions was accepted as a general rule.\textsuperscript{1} In 1999, however, as part of an ongoing effort to develop Keggin tungstoaluminates as catalysts for O\textsubscript{2} oxidations in water,\textsuperscript{2} we observed equilibria between β- and α-[Al\textsubscript{III}W\textsubscript{12}O\textsubscript{40}\textsuperscript{5-}] (β- and α-1).\textsuperscript{3} The basis for the small difference in energy between these isomers was recently investigated by Poblet and co-workers.\textsuperscript{4} Based on density-functional-theory (DFT) calculations,\textsuperscript{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\textsubscript{4.5}K\textsubscript{0.5}[Al\textsubscript{III}W\textsubscript{12}O\textsubscript{40}]\textsuperscript{7-}·7H\textsubscript{2}O, which, for the first time, provide accurate and precise atomic coordinates for a β-Keggin [X\textsuperscript{n+}W\textsubscript{12}O\textsubscript{40}\textsuperscript{(8−n-)−}] heteropolyanion (X = main-group or transition-metal cation).

In water (pH 0, 200 °C), β-1 is only 2.1 kcal mol\textsuperscript{-1} higher in energy than is α-1.\textsuperscript{3a} Concerning this unique property of 1, five lines of evidence\textsuperscript{3a} indicated a clear trend: As X is varied from P(V) to Al(III), X−μ\textsubscript{5}O bond distances in [X\textsuperscript{n+}O\textsubscript{(8−n)−}] tetrahedra increase, and increasing polarization of the X−O bonds shifts electron density toward the fixed-diameter α-W\textsubscript{12}O\textsubscript{36} shell. The retention of tetrahedral (T\textsubscript{d}) symmetry in [XO\textsubscript{4}]\textsuperscript{m-} and the absence of variation in the diameter of the W\textsubscript{12}O\textsubscript{36} shell supported\textsuperscript{3a} the clathrate structural model\textsuperscript{6} of the Keggin ion: [XO\textsubscript{4}]\textsuperscript{m-}@W\textsubscript{12}O\textsubscript{36}. Still missing, however, was a causative relationship between the indicated trend in electronic properties and differences in energy between β and α isomers.\textsuperscript{1,6,7}

In 2001, however, Poblet and co-workers,\textsuperscript{4} one of several groups\textsuperscript{6} involved in the still incipient use of DFT to model the physical properties of POMs, evaluated the relative energies of α- and β-[X\textsuperscript{n+}W\textsubscript{12}O\textsubscript{40}\textsuperscript{(8−n-)−}] (X = P, Si, Al, etc.). In Poblet’s model, isomerization from α to β was described by 60° rotation of a single W\textsubscript{13}O\textsubscript{41}, triad,\textsuperscript{7b} and by attendant reduction in symmetry of the anion from T\textsubscript{d} to C\textsubscript{3v} (Figure 1).

The fragment interaction method\textsuperscript{9,10} used by Poblet\textsuperscript{4} was predicated on the clathrate structural model\textsuperscript{6} described above. Accordingly, even when encapsulated within lower symmetry

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(CIo) β-W2O36 shells, coordination about X in [XO4]m−n was presumed to remain tetrahedral (T0). 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 ([XO4]m−n → W12O40) 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 19993a 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–μ3-O and μ3-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-C5M5K3[AlIII(W12O40)]7.5H2O (β-1) (Figure 2)11,12 so that α3– and β-1 could be compared with other α- and β-[Xn+1W12O40]m−(n−1)+ pairs.

While numerous α-Keggin anions have been structurally characterized, until now, crystallographic data for only one β-[Xn+1W12O40]m−(n−1)+ anion, β-[SiW11O39]16– (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 comprehensive annotated catalog of 142 Keggin heteropolytungstates—main-group or transition-metal heteroatom-structured chemical entities that can be 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 definitively examined by comparison with α-2 and β1-K2[SiMoW11O40] (β1-3), an isoelectronic derivative of β-2. A reliable X-ray crystal structure7d of β1-3 (R1 value of 5.2), in which a vacant site in β1-[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 W12O43 unit (site III), no significant distortion of the [SiO4]4− tetrahedron was observed: Si–μ4-O distances ranged from 1.61 to 1.66 Å and O–Si–O angles from 109.9 to 112.9°. 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), β1-3 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 β1-3), it is clear that β-1 is not uniquely distorted. Mean bond distances and angles for the [Xn+1O4]m−(n−1)+ moieties in α and β isomers are listed in Table 1 (α-[PW12O40]3− is included18 for reveal trends). Four conclusions

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(11) The X-ray quality crystals of β-C5M5K3[AlIII(W12O40)]7.5H2O were grown from an aqueous solution of β-KI (ref 3a) and CsCl. The crystal system is orthorhombic, space group Pmnc21, Z = 4, a = 4.0441 (10) Å, b = 13.2270 (8) Å, c = 20.5919 (13) Å, V = 5469.9 (5) Å3. The final statistics based on F2 are GOF = 1.166, R1 = 0.0554 and wR2 = 0.1231 for I > 2σ(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-[Xn+1W12O40]m−(n−1)+ 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.


(14) Cambridge Crystallographic Data Center (CCDC), Cambridge, U.K.

(15) Fiz-Karlsruhe, Karlsruhe, Germany (via STN International).

(16) Uncertainties in these values were not reported. Significantly, however, reported uncertainties associated with adjacent W–μ4-O distances were relatively small: 2.41(3), 2.52(2), 2.28(2), 2.36(3), 2.36(2), and 2.39–3.3 Å.

(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-PMo6W10O40); see Table S1.
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Table 1. Mean* Distances (Å) and Angles (deg) for α- and β-[X⁺₄W₁₂O₄₀]³⁻⁻, X = P(V), Si(IV), Al(III)

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>P α</td>
<td>1.526(1)</td>
<td>2.438(3)</td>
<td>3.964(3)</td>
<td>109.5(2)</td>
</tr>
<tr>
<td>Si α</td>
<td>1.63(2)</td>
<td>2.35(2)</td>
<td>3.98(3)</td>
<td>109.5(4)</td>
</tr>
<tr>
<td>Al β</td>
<td>1.64(1)</td>
<td>2.34(2)</td>
<td>3.98(2)</td>
<td>109.5(7)</td>
</tr>
</tbody>
</table>

* Average values with uncertainties (1σ) in parentheses.

Table 2. Changes* in Angles (deg) and Nonbonding Distances (Å) upon Isomerization from α- to β-[X⁺₄W₁₂O₄₀]³⁻⁻, X = Si(IV), Al(III)

<table>
<thead>
<tr>
<th>X sites III–II⁺</th>
<th>site II⁺</th>
<th>site II⁻</th>
<th>site III–II⁺</th>
<th>site II⁺</th>
<th>site II⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>+0.07(4)</td>
<td>+0.58(4)</td>
<td>−0.07(1)</td>
<td>−9.2(16)</td>
<td>+4.0(17)</td>
</tr>
<tr>
<td>Al</td>
<td>−0.047(4)</td>
<td>+0.04(11)</td>
<td>−0.046(9)</td>
<td>−6.2(9)</td>
<td>+7.7(11)</td>
</tr>
</tbody>
</table>

* Uncertainties calculated from observed scatter in data or published uncertainties (where available).

emerge. In every structure, regular [XO₄] tetrahedra are observed. Moreover, during both isomerization processes (X = Si and Al), X–μ–O bond lengths, μ–O–W bond lengths (distances between XO₄ and W₁₂O₃₆ fragments), and the sums of X–μ–O and μ–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 W₁₂O₃₆ triad (Figure 1) and provide further support for the clathrate⁶ structural model, [XO₄]ₙ⁻⁻@W₁₂O₃₆, the two assumptions on which the fragment interaction method applied by Poblet¹ 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 3σ) for both 1 and 2. The changes entail a slight decrease in nonbonding W···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···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, [X⁺₄W₁₂O₄₀]³⁻⁻, 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]¹⁻– (T₃) moiety encapsulated within the polarizable, yet fixed-diameter, β-W₁₂O₃₆ (C₃₀) 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-C₅₃₆K₉₃₅[AlW₁₂O₄₀]·7.5H₂O, β-C₅₃₆K₉₃₅[AlW₁₂O₄₀]·5H₂O, and β-K₉₃[AlW₁₂O₄₀]·8H₂O (PDF), and CIF files for each; a discussion of crystallographic data reported for β-[SiW₁₂O₄₀]¹⁻⁻; 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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