Inorg. Chem. **2002**, *41*, 6950–6952

Inorganic Chemistry

Communication

Stability and Structure in α- and *β*-Keggin Heteropolytungstates, $[X^{n+}W_{12}O_{40}]^{(8-n)-}$, X = p-Block Cation

Wade A. Neiwert, Jennifer J. Cowan, Kenneth I. Hardcastle, Craig L. Hill, and Ira A. Weinstock*

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received September 11, 2002

β-$[SiW_{12}O_{40}]^{4-}$ (C_{3v} symmetry) is sufficiently higher in energy than its α-isomer analogue that effectively complete conversion to α-$[SiW_{12}O_{40}]^{4-}$ (T_d) is observed. By contrast, β- and α-$[AlW_{12}O_{40}]^{5-}$ (β- and α-**1**; C_{3v} and T_d, respectively) are sufficiently close in energy that both isomers are readily seen in ^{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 $[AlO_4]^{5-}$ (T_d) moiety encapsulated within the polarizable, fixed-diameter β-$W_{12}O_{36}$ (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-$Cs_{4.5}K_{0.5}[Al^{III}W_{12}O_{40}]\cdot 7.5H_2O$; orthorhombic, space group $Pmc2_1$, $a = 16.0441(10)$ 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-$[SiW_{12}O_{40}]^{4-}$, and β_1-$[SiMoW_{11}O_{40}]^{4-}$.

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 O_2 oxidations in water,[2] we observed equilibria between β- and α-$[Al^{III}W_{12}O_{40}]^{5-}$ (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-$Cs_{4.5}K_{0.5}[Al^{III}W_{12}O_{40}]\cdot 7.5H_2O$, which, for the first time, provide accurate and precise atomic coordinates for a β-Keggin $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ 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 $[X^{n+}O_4]^{(n-8)-}$ tetrahedra increase, and increasing polarization of the X–O bonds shifts electron density toward the fixed-diameter α-$W_{12}O_{36}$ shell. The retention of tetrahedral (T_d) symmetry in $[XO_4]^{m-}$ and the absence of variation in the diameter of the $W_{12}O_{36}$ shell supported[3a] the clathrate structural model[6] of the Keggin ion: $[XO_4]^{m-}@W_{12}O_{36}$. 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 groups[8] involved in the still incipient use of DFT to model the physical properties of POMs, evaluated the relative energies of α- and β-$[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (X = P, Si, Al, etc.). In Poblet's model, isomerization from α to β was described by 60° rotation of a single W_3O_{13} 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 Poblet[4] was predicated on the clathrate structural model[6] described above. Accordingly, even when encapsulated within lower symmetry

---

* Author to whom correspondence should be addressed. E-mail: iaweinst@wisc.edu. Visiting scientist at Emory University. Permanent address: USDA Forest Service, Forest Products Laboratory, Madison, WI 53705.

[1] Tézé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2151–2154.

[2] Weinstock, I. A.; Barbuzzi, E. M. G.; Wemple, M. W.; Cowan, J. J.; Reiner, R. S.; Sonnen, D. M.; Heintz, R. A.; Bond, J. S.; Hill, C. L. *Nature* **2001**, *414*, 191–195.

[3] (a) Weinstock, I. A.; Cowan, J. J.; Barbuzzi, E. M. G.; Zeng, H.; Hill, C. L. *J. Am. Chem. Soc.* **1999**, *121*, 4608–4617. (b) Cowan, J. J.; Bailey, A. J.; Heintz, R. A.; Do, B. T.; Hardcastle, K. I.; Hill, C. L.; Weinstock, I. A. *Inorg. Chem.* **2001**, *40*, 6666–6675. (c) Cowan, J. J.; Hill, C. L.; Reiner, R. S.; Weinstock, I. A. *Inorg. Synth.* **2002**, *33*, 18–26.

[4] Lopez, X.; Maestre, J. M.; Bo, C.; Poblet, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 9571–9576.

[5] Davidson, E. R., Ed. *Chem. Rev.* **2000**, *1000*, 351–818.

[6] Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533–541.

[7] (a) Kepert, D. L. *Inorg. Chem.* **1969**, *8*, 1556–1558. (b) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794–3797. (c) Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2008–2010. (d) Robert, F.; Tézé, A.; Hervé, G.; Jeannin, Y. *Acta Crystallogr.* **1980**, *B36*, 11–15. (e) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34–48.

10.1021/ic026023r CCC: $22.00

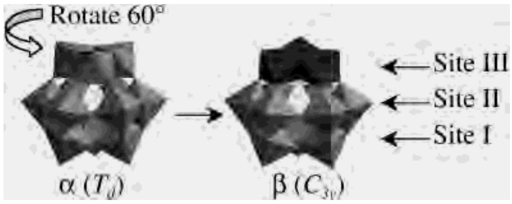

Figure 1. Isomerization of α- to β-$[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (in polyhedral notation). The 60°-rotated W_3O_{13} triad is shown in dark gray.

(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$-\mu_4$-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-$Cs_{4.5}K_{0.5}[Al^{III}W_{12}O_{40}]\cdot 7.5H_2O$ (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-$[SiW_{12}O_{40}]^{4-}$ (β-**2**), have been reported[13] 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—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).

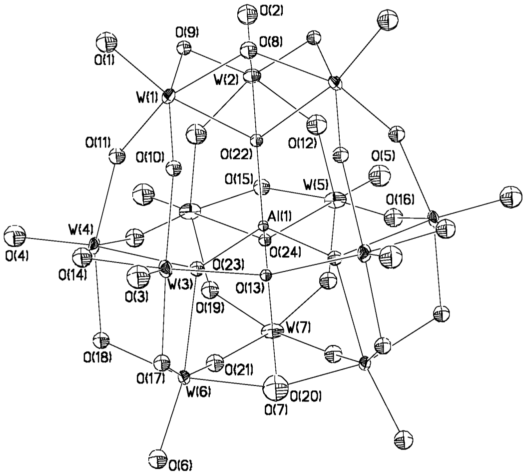

Figure 2. Thermal ellipsoid plot of β-**1** (ellipsoids shown at 50% probability).

Given these uncertainties, the α- and β-**1** isomer pair is more defensibly evaluated by comparison with α-**2** and β_1-$K_4[SiMoW_{11}O_{40}]$ (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-$[SiW_{11}O_{39}]^{8-}$ (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$-\mu_4$-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-$[PW_{12}O_{40}]^{3-}$ is included[18] to reveal trends). Four conclusions

---

(8) (a) Rohmer, M. M.; Bénard, M.; Blaudeau, J.-P.; Maestre, J. M.; Poblet, J. M. *Coord. Chem. Rev.* **1998**, *178−180*, 1019−1049. (b) Maestre, J. M.; Poblet, J. M.; Bo, C.; Casan-Pastor, N.; Gomez-Romero, P. *Inorg. Chem.* **1998**, *37*, 3444−3446. (c) Maestre, J. M.; Lopez, X.; Bo, C.; Poblet, J.-M.; Casañ-Pastor, N. *J. Am. Chem. Soc.* **2001**, *123*, 3749−3758. (d) Maestre, J. M.; Lopez, X.; Bo, C.; Poblet, J. M. *Inorg. Chem.* **2002**, *41*, 1883−1888. (e) Bardin, B. B.; Bordawekar, S. V.; Neurock, M.; Davis, R. J. *J. Phys. Chem. B* **1998**, *102*, 10817−10825. (f) Bardin, B. B.; Davis, R. J.; Neurock, M. *J. Phys. Chem. B* **2000**, *104*, 3556−3562. (g) Duclusaud, H.; Borshch, S. A. *Inorg. Chem.* **1999**, *38*, 3489−3493. (h) Duclusaud, H.; Borshch, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 2825−2829. (i) Bridgeman, A. J.; Cavigliasso, G. *Inorg. Chem.* **2002**, *41*, 3500−3507. (j) Bridgeman, A. J.; Cavigliasso, G. *J. Phys. Chem. A* **2002**, *106*, 6114−6120.

(9) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236.

(10) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558−1565.

(11) The X-ray quality crystals of β-$Cs_{4.5}K_{0.5}[Al^{III}W_{12}O_{40}]\cdot 7.5H_2O$ were grown from an aqueous solution of β-K_5**1** (ref 3a) and CsCl. The crystal system is orthorhombic, space group $Pmc2_1$, $Z = 4$, $\rho_{calcd} = 5.488$ Mg m^{-3}, $a = 16.0441(10)$ Å, $b = 13.2270(8)$ Å, $c = 20.5919(13)$ Å, $V = 4369.9(5)$ Å^3. The final statistics based on F^2 are GOF = 1.166, R1 = 0.0554 and wR2 = 0.1231 for $I > 2\sigma(I)$. (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.

(13) (a) Yamamura, K.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* **1973**, *18*, 648−649. (b) Matsumoto, K. Y.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3146−3151. (c) Fuchs, J.; Thiele, A.; Palm, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 161−171.

(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$-\mu_4$-O distances were relatively small: 2.41(3), 2.32(2), 2.28(2), 2.36(3), 2.36(2), and 2.39(3) Å.

(17) Structures of α$-\beta$ 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-$PMo_3W_9O_{40}$); see Table S1.

Table 1. Mean[a] Distances (Å) and Angles (deg) for α- and β-$[X^{n+}W_{12}O_{40}]^{(8-n)-}$, 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 (1σ) 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-$[X^{n+}W_{12}O_{40}]^{(8-n)-}$, X = Si(IV), Al(III)

	Δ(W···W) distances (Å)			Δ(W−O−W) angles (deg)		
X	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 $[XO_4]$ 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 XO_4 and $W_{12}O_{36}$ 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 W_3O_{13} triad (Figure 1) and provide further support for the clathrate[6] structural model, $[XO_4]^{m-}$@$W_{12}O_{36}$, the two assumptions on which the fragment interaction method applied by Poblet[4] 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 nonbonded 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, $[X^{n+}W_{12}O_{40}]^{(8-n)-}$, 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 $[AlO_4]^{5-}$ (T_d) moiety encapsulated within the polarizable, yet fixed-diameter, β-$W_{12}O_{36}$ (C_{3v}) shell.

Acknowledgment. We thank the DOE (DE-FC36-95GO10090) (I.A.W. and C.L.H.) and the NSF (CHE-9975453) (C.L.H.) for support, Ankit Patel, and Marike Herold.

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-$Cs_{4.5}K_{0.5}[AlW_{12}O_{40}]\cdot 7.5H_2O$, β-$Cs_{3.5}K_{1.5}[AlW_{12}O_{40}]\cdot 5H_2O$, and β-$K_5[AlW_{12}O_{40}]\cdot 8H_2O$ (PDF), and CIF files for each; a discussion of crystallographic data reported for β-$[SiW_{12}O_{40}]^{4-}$; 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.

IC026023R

---

(18) Spirlett, M. R.; Busing, W. R. *Acta Crystallogr. B* **1978**, 907−910.

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