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Relative Energies of α and β Isomers of Keggin Dodecatungstogallate

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The relative energies of β Keggin heteropolytungstates, $X^{n+}W_{12}O_{40}{}^{(8-n)-}$, decrease as X^{n+} is varied within period 3, from P^{5+} to Si^{4+} to Al^{3+}. With heating of α-$H_5Ga^{3+}W_{12}O_{40}$ at 200 °C in water, an equilibrated mixture of α (T_d; one ^{183}W NMR signal) and β (C_{3v}; three signals; 1:2:1 ratio) isomers is obtained. From $\Delta G_{exp} = -RT \ln K_{\beta\rightarrow\alpha}$, in which (from ^{71}Ga NMR spectra) $K_{\beta\rightarrow\alpha}$ ($= [\alpha]/[\beta]$) $= 5.0$, β-$GaW_{12}O_{40}{}^{5-}$ is 0.65 kcal mol^{-1} higher in energy than α-$GaW_{12}O_{40}{}^{5-}$. This finding is evaluated by analysis of the X-ray crystal structure α-$K_2Na_3[GaW_{12}O_{40}]\cdot 9.3H_2O$ [trigonal, space group $P3_221$, $a = 18.9201(13)$ Å, $b = 18.9201(13)$ Å, $c = 12.5108(12)$ Å, $Z = 3$, $T = 100(2)$K], comparison of the Shannon and Prewitt radii and Pauling electronegativities of Al^{3+} and Ga^{3+}, and insight from density functional theory calculations, which predicted $E_\beta - E_\alpha = 0.32$ kcal mol^{-1}.

Until recently, the relative instability of β isomers of Keggin cluster anions was accepted as a general rule. In all documented cases involving fully oxidized Keggin anions in water, effectively complete conversions to α-isomer analogues were observed.[1] In 1999, however, as part of an effort to prepare Keggin tungstoaluminate catalysts for O_2 oxidations in water,[2] we observed equilibria between β- and α-$[Al^{3+}W_{12}O_{40}]^{5-}$ (β- and α-**1**).[3–6] Using ^{27}Al NMR spectroscopy, we found that, at 200 °C, β-**1** was only 2.1 kcal mol^{-1} higher in energy than α-**1**.[3] An X-ray crystal structure of α-**1** showed that, as in α-$PW_{12}O_{40}{}^{3-}$ (heteroatom, $X^{n+} = P^{5+}$) and α-$SiW_{12}O_{40}{}^{4-}$ ($X^{n+} = Si^{4+}$), the central $[X^{3+}O_4]^{5-}$ moiety in **1** ($X = Al^{3+}$) resided within a $W_{12}O_{36}$ shell, whose diameter remained constant as X^{n+} was varied from P^{5+} to Si^{4+} to Al^{3+}. This lent support to the clathrate structural model[7] of the Keggin cluster: $[XO_4]^{(8-n)-}@W_{12}O_{36}$. We also observed[3] that, as X^{n+} varied from P^{5+} to Si^{4+} to Al^{3+}, $X-\mu_4$-O bond distances in $[X^{n+}O_4]^{(8-n)-}$ tetrahedra increased and increased polarization of the X−O bonds (away from the less electronegative main-group cations and toward oxygen) shifted electron density toward the fixed-diameter $W_{12}O_{36}$ shell. We noted a correlation between increase in the relative stabilities of β isomers and this shift in electron density toward the $W_{12}O_{36}$ shell.

Using the clathrate model,[7] Poblet and co-workers[8] subsequently performed density functional theory (DFT) calculations[9] that evaluated electronic interactions between the encapsulated (XO_4) and shell ($W_{12}O_{36}$) "fragments". They showed that the unprecedented stability of β-**1** was due to encapsulation of a larger, more electron-donating $Al^{3+}O_4{}^{5-}$ (T_d) moiety within a polarizable, fixed-diameter β-$W_{12}O_{36}$ (C_{3v}) shell. This conclusion, while consistent with the correlations noted above,[3] was predicated on the assumption that the encapsulated $AlO_4{}^{5-}$ oxoanion in β-**1** was indeed tetrahedral in structure, such that no unexpected distortion was involved in stabilization of the β isomer. To verify this assumption, we obtained a high-quality X-ray crystal structure of β-**1**[6] and found no structural distortion.

Poblet also predicted[8] that β-$Ga^{3+}W_{12}O_{40}{}^{5-}$ (β-**2**) should be relatively close in energy to α-$Ga^{3+}W_{12}O_{40}{}^{5-}$ (α-**2**). Using ^{71}Ga and ^{183}W NMR spectroscopy and X-ray crystallography, we now show this prediction to have been correct.

Crystalline α-$K_2Na_3GaW_{12}O_{40}$ was prepared in 21% yield by modification of a literature method[10] (see the Supporting Information, SI). The α structure was determined by ^{71}Ga and ^{183}W NMR spectroscopy and confirmed by single-crystal X-ray crystallography (vide infra). The Fourier transform

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(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) Weinstock, I. A.; Cowan, J. J.; Barbuzzi, E. M. G.; Zeng, H.; Hill, C. L. *J. Am. Chem. Soc.* **1999**, *121*, 4608−4617.

(4) 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.

(5) Cowan, J. J.; Hill, C. L.; Reiner, R. S.; Weinstock, I. A. In *Inorganic Synthesis*; Coucouvanis, D., Ed.; John Wiley & Sons: New York, 2002; Vol. 33, pp 18−26.

(6) Neiwert, W. A.; Cowan, J. J.; Hardcastle, K. I.; Hill, C. L.; Weinstock, I. A. *Inorg. Chem.* **2002**, *41*, 6950−6952.

(7) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533−541.

(8) Lopez, X.; Maestre, J. M.; Bo, C.; Poblet, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 9571−9576.

(9) Davidson, E. R. *Chem. Rev.* **2000**, *100*, 351−352.

(10) Fedotov, M. A.; Kazanskii, L. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, *9*, 2000−2003.

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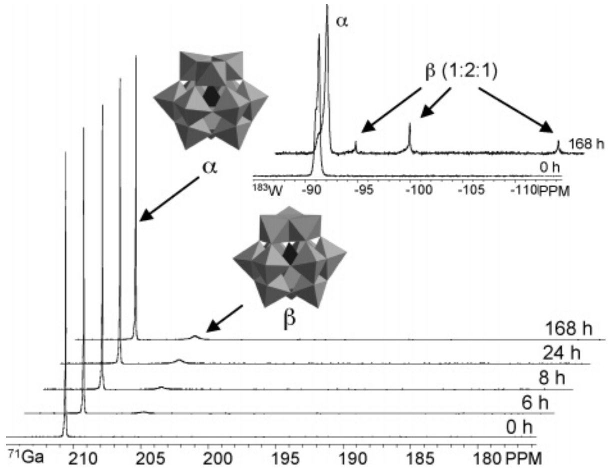

Figure 1. ^{71}Ga and ^{183}W NMR (inset) spectra before, during, and after conversion of a 0.1 M aqueous solution of α-$H_5[GaW_{12}O_{40}]$ (α-H_5**2**) to an equilibrated mixture of α and β isomers at 200 °C.

infrared (FTIR) spectrum (Figure S1 in the SI) includes a strong band at 729 cm^{-1}, assigned to the central Ga$-\mu_4$-O_4 moiety, and the UV−vis spectrum (Figure S2 in the SI) features a broad absorption with a maximum at 266 nm, typical of α-Keggin dodecatungstate anions.[4] The first and second one-electron-reduction potentials of **2** (−0.35 and −0.57 V vs Ag/AgCl; Figure S3 in the SI) are similar to those of α-**1**.[11]

Isomerically pure α-$H_5GaW_{12}O_{40}$ was obtained by dissolution of crystalline α-$K_2Na_3GaW_{12}O_{40}$ in water, the addition of concentrated H_2SO_4, and extraction with diethyl ether. After drying and precipitation from warm water, the free acid, an amorphous white solid, was obtained in 69% yield. When dissolved in D_2O, one singlet at $\delta = 211.1$ ppm ($\nu_{1/2} = 110$ Hz) was observed by ^{71}Ga NMR spectroscopy (Figure 1; $t = 0$ h). As expected for an α isomer (T_d symmetry), the ^{183}W NMR spectrum featured a single signal (12 equivalent W atoms; see $t = 0$ h in the inset of Figure 1).

The relative energies of β- and α-**2** were measured by equilibration of α-$H_5GaW_{12}O_{40}$ (0.10 M in water), for 7 days at 200 °C in a 25-mL Teflon-lined bomb. These conditions are identical with those used in previous work,[3] in which equilibria between β- and α-**1** was observed. Aliquots were removed periodically, and ^{71}Ga NMR spectra were acquired (Figure 1). Within 6 h, a new signal, assigned to the β isomer, was observed at 207 ppm ($\nu_{1/2} = 340$ Hz). After 24 h, no further changes were observed. To ensure that equilibrium had been reached, the experiment was continued for an additional 6 days. The presence of three new signals in the ^{183}W NMR spectrum of the solution (intensity ratio of 1:2:1)[3,4,6,12] confirmed that the ^{71}Ga NMR signal at 207 ppm was due to β-**2** (C_{3v} symmetry) now present in equilibrium with α-**2** (Figure 1, inset).[13]

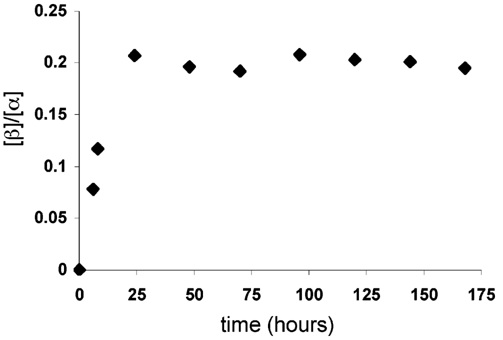

Figure 2. Equilibration of α- and β-**2** (0.1 M) in water at 200 °C. The molar ratios of β to α isomers, obtained by integration of ^{71}Ga NMR spectra, are plotted as a function of time from $t = 0$ h (no β isomer present) to $t = 168$ h (7 days). The reported equilibrium constant, $K_{\beta\rightarrow\alpha}$ (the average of all seven mole ratio values after equilibration), is 1/0.2, or 5.0.

Table 1. Relative Energies of α and β Keggin Isomers of $X^{n+}W_{12}O_{40}{}^{(8-n)-}$, where $X^{n+} = Ga^{3+}$, Al^{3+}, Si^{4+}, and P^{5+}

	DFT COSMO[a]		experiment[b]	
X^{n+}	$E_\beta - E_\alpha$, kcal mol^{-1}	$K_{\text{calculated}}(\beta\rightarrow\alpha)$	$\Delta G_\beta - \Delta G_\alpha$, kcal mol^{-1}	$K_{\text{observed}}(\beta\rightarrow\alpha)$
Ga^{3+}	0.32	1.7	0.65	5.0
Al^{3+}	2.37	55	2.1	9.1
Si^{4+}	3.82	633	NA[c]	NA[c]
P^{5+}	4.57	2248	NA[c]	NA[c]

[a] Values calculated for $X^{n+}W_{12}O_{40}{}^{(8-n)-}$ in a dielectric continuum ($\epsilon = 78$), at 25 °C. [b] Values for $X^{n+} = Ga^{3+}$ and Al^{3+} refer to 0.1 M aqueous solutions of the free acids, $H_5X^{n+}W_{12}O_{40}$, equilibrated at 200 °C. [c] Not reported. To our knowledge, fully oxidized β isomers have not been observed by ^{29}Si or ^{31}P NMR in *equilibrated* aqueous solutions.

Isomer ratios of β- to α-H_5**2** were calculated by integration of the ^{71}Ga NMR signals (6.5-μs pulse width and a 1-s delay). From these data (Figure 2), the equilibrium constant, $K_{\beta\rightarrow\alpha}$, for isomerization of β-**2** to α-**2** at 473 K ($K_{\beta\rightarrow\alpha} = [\alpha]/[\beta]$) is 5.0 ± 0.2. Using $\Delta G = -RT \ln K_{\beta\rightarrow\alpha}$, the β isomer is 0.65 kcal mol^{-1} (0.028 eV) higher in energy than the α isomer. This value is similar to that observed for solutions of **1** ($X^{n+} = Al^{3+}$), equilibrated under identical conditions.[3] There, ^{27}Al NMR spectra indicated that $K_{\beta\rightarrow\alpha} = 9.1$, such that β-**1** is higher in energy than the α isomer by 2.1 kcal mol^{-1} (0.09 eV).

In 2001, Poblet and co-workers reported DFT results for the relative energies of the α and β isomers of **1** and **2** in vacuo.[8] They calculated that $E_{\beta-\mathbf{1}} - E_{\alpha-\mathbf{1}} = -7.8$ kcal mol^{-1} (−0.35 eV) and that $E_{\beta-\mathbf{2}} - E_{\alpha-\mathbf{2}} = -4.19$ kcal mol^{-1} (−0.18 eV). In both cases, they found the β isomers to be lower in energy than their α analogues.

In 2004, however, Poblet and Lopez calculated updated $E_\beta - E_\alpha$ values for $X^{n+}W_{12}O_{40}{}^{(8-n)-}$ anions ($X^{n+} = Al^{3+}$, Si^{4+}, and P^{5+}).[14,15] Rather than vacuum values, they now used a "conductor-like screening model" (COSMO),[16] in which the solvent dielectric constant was set at $\epsilon = 78$ (water at 25 °C). For α- and β-**1** (X = Al^{3+}), these calculations gave $E_{\beta-\mathbf{1}} - E_{\alpha-\mathbf{1}} = 2.37$ kcal mol^{-1} (0.104 eV), a value much closer to the experimental value of 2.1 kcal mol^{-1} (0.09 eV), observed by ^{27}Al NMR at 200 °C.[3] For α- and β-**2**, their

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(11) Geletii, Y. V.; Hill, C. L.; Bailey, A. J.; Hardcastle, K. I.; Atalla, R. H.; Weinstock, I. A. *Inorg. Chem.* **2005**, *44*, 8955−8966.

(12) Lefebvre, J.; Chauveau, F.; Doppelt, P.; Brevard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589−4591.

(13) These spectra are very similar to those shown in ref 10 (although α and β isomers are not mentioned there).

(14) Lopez, X.; Poblet, J. M. *Inorg. Chem.* **2004**, *43*, 6863−6865.

(15) Poblet, J. M.; López, X.; Bo, C. *Chem. Soc. Rev.* **2003**, *32*, 297−308.

(16) Klamt, A. *J. Phys. Chem.* **1995**, *99*, 2235.

Table 2. Radii[a] and Electronegativities[b] of Heteroatoms X^{n+} and Mean[c] Bond Distances (Å) and Angles (deg) for α-$X^{n+}W_{12}O_{40}{}^{(8-n)-}$

X^{n+}	radius, Å	electronegativity	$X-\mu_4$-O	μ_4-O$-$W	sum of $X-\mu_4$-O and μ_4-O$-$W	O$-$X$-$O	ref
Ga^{3+}	0.61	1.81	1.799(7)	2.205(7)	4.004(9)	109.1(3)	this work
Al^{3+}	0.53	1.61	1.742(8)	2.265(8)	4.007(11)	109.5(6)	3
Si^{4+}	0.40	1.90	1.63(2)	2.35(2)	3.98(3)	109.5(4)[b]	14
P^{5+}	0.31	2.19	1.526(1)[b]	2.438(3)[d]	3.964(3)[d]	109.5(2)[b]	14

[a] Shannon and Prewitt radii for the four-coordination X^{n+} cations. [b] Pauling electronegativities of the main-group elements. [c] Average values with uncertainties (1σ) in parentheses. [d] Uncertainties not reported; values shown were calculated from scatter in published data.

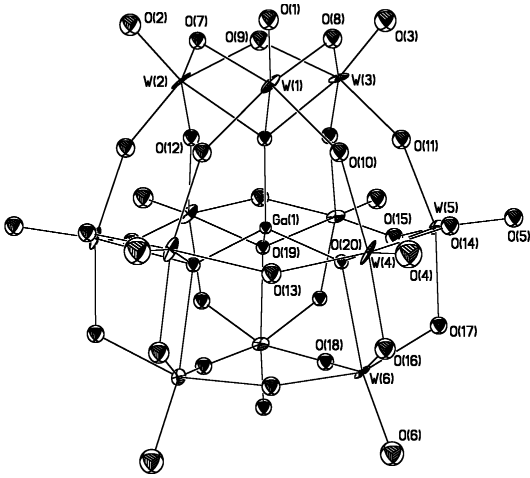

Figure 3. Thermal ellipsoid plot (50% probability) of α-**2**.

COSMO calculation[17] ($\epsilon = 78$) gave $E_{\beta-\mathbf{2}} - E_{\alpha-\mathbf{2}} = 0.32$ kcal mol^{-1} (0.014 eV), again much closer to the value provided by ^{71}Ga NMR (this work).[18] These results are summarized in Table 1, along with data for $X^{n+}W_{12}O_{40}{}^{(8-n)-}$ anions containing Si^{4+} and P^{5+} heterotaoms.

The DFT calculations[8] show that β-$W_{12}O_{36}$ shells are more polarizable than their α-isomer analogues (α-$W_{12}O_{36}$) and, as a result, are stabilized to a greater extent by electron donation from $X^{n+}O_4{}^{(8-n)-}$ "fragments". The close agreement between theory and experiment in the data in Table 1 thus suggests that the electron-donating ability of the encapsulated $X^{n+}O_4{}^{(8-n)-}$ oxoanions generally increases as X^{n+} is varied from P^{5+} to Ga^{3+}.

At the same time, the experimental results show that a change in X^{n+} from Al^{3+} to Ga^{3+} has a relatively small effect on the relative energies of the respective β and α isomers. To investigate this in more detail, we obtained an X-ray crystal structure of α-$K_2Na_3GaW_{12}O_{40}$.[19]

The structure of the α-$GaW_{12}O_{40}{}^{5-}$ anion is shown in Figure 3. In Table 2, key bond lengths and angles are compared with analogous data from the series: α-$X^{n+}W_{12}O_{40}{}^{(8-n)-}$, where $X^{n+} = Al^{3+}$, Si^{4+}, and P^{5+}. Included in Table 2 are Shannon and Prewitt cationic radii[20] of the heteroatoms X^{n+} and Pauling electronegativities[20] of the corresponding main-group elements, X.

In all cases, the $X-\mu_4$-O and μ_4-O$-$W bond distances sum to ca. 4.0 Å and the central $X^{n+}O_4{}^{(8-n)-}$ oxoanion is a nearly ideal tetrahedron (O$-$X$-$O angles are all close to 109.5°).[21] As X^{n+} is varied within the third period from P^{5+} to Si^{4+} to Al^{3+}, cationic radii (Table 2; coordination number $= 4$) increase in increments of 0.09 and 0.13 Å and electronegativities decrease from 2.19 to 1.61. Moving down group IIIA from Al^{3+} to Ga^{3+}, the cationic radius increases by 0.08 Å, while the electronegativity now *increases* from 1.61 for Al to 1.81 for Ga. This simultaneous increase in both the cation size *and* the electronegativity explains why the increase in the $X-\mu_4$-O bond distance observed upon replacement of Al^{3+} by Ga^{3+} (+0.06 Å) is smaller than the 0.09 and 0.13 Å increments observed when X^{n+} is varied from P^{5+} to Si^{4+} to Al^{3+}.

In addition, the larger electronegativity of Ga attenuates the extent to which an increase in the radius of X^{n+}, and, thus, in the size of the central $X^{n+}O_4{}^{(8-n)-}$ oxoanion, is able to stabilize the β isomer by delivery of electron density to the polarizable β-$W_{12}O_{40}$ shell. As a result, the equilibrium constant, $K_{\beta\rightarrow\alpha}$, and the difference in energy between β- and α-**2** ($X^{n+} = Ga^{3+}$, $K_{\beta\rightarrow\alpha} = 5.0$; $\Delta G = 0.65$ kcal mol^{-1}) are only slightly smaller than those for $X^{n+} = Al^{3+}$ ($K_{\beta\rightarrow\alpha} = 9.1$; $\Delta G = 2.1$ kcal mol^{-1}).

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Supporting Information Available: Optimized syntheses of α-$K_2Na_3[GaW_{12}O_{40}]$ and α-$H_5[GaW_{12}O_{40}]$; FTIR and UV$-$vis spectra and a cyclic voltammogram of α-$K_2Na_3[GaW_{12}O_{40}]$ (Figures S1$-$S3); experimental details, crystal data, and structure refinement parameters for α-$K_2Na_3[GaW_{12}O_{40}]\cdot 9.3H_2O$ (Table S1); select bond lengths and angles (Table S2); ratios of the average errors in the crystal structures of $H_5[GaW_{12}O_{40}]$ and α-$K_2Na_3[GaW_{12}O_{40}]\cdot 9.3H_2O$ (Table S3); full structural data in CIF format; and a discussion of the structure reported in ref 21. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Poblet, J. M., private communication.

(18) At 200 °C (15.5 bar), the dielectric constant of water is ca. 38: Shock, E. L.; Oelkers, E. H.; Johnson, J. W.; Sverjensky, D. A.; Helgeson, H. *Faraday Trans.* **1992**, *88*, 803$-$826.

(19) The X-ray-quality crystals of α-$K_2Na_3[GaW_{12}O_{40}]\cdot 9.3H_2O$ were grown by adding KCl to an aqueous solution of α-**2**, prepared by modification of the procedure in ref 10. The crystal system is trigonal, space group $P3_221$, $Z = 3$, $\rho_{calcd} = 4.150$ g cm^{-3}, $a = 18.9201(13)$ Å, $b = 18.9201(13)$ Å, $c = 12.5108(12)$ Å, and $V = 3878.5(5)$ Å^3. The final statistics based on F^2 are R1 $= 0.0380$ and wR2 $= 0.0917$ for $I > 2\sigma(I)$.

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

(21) See the SI for discussion: Niu, J.-Y.; Li, M.-X.; Wang, J.-P.; Bo, Y. *J. Chem. Cryst.* **2003**, *33*, 799$-$803 (X-ray structure of $GaW_{12}O_{40}{}^{5-}$).

(22) A new DFT study of α- and β-**1** appeared (on the web) after submission: Zhang, F. Q.; Wu, H. S.; Qin, X. F.; Li, Y. W.; Jiao, H. *J. Mol. Struct.* **2005**, *755*, 113$-$117.