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The "Alternate" Keggin Ion: A Theoretical Study of the Stability Factors for the β-Keggin Ion in Comparison with the Corresponding α-Keggin Ion

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The syntheses and chemical properties of geometrical isomers of 12 tungstopolyoxyanions have been studied for several decades. These materials are utilized in multiple commercial catalytic processes and many experimental and theoretical initiatives have been directed at understanding and enhancing their stability. In our previous work, we have discovered that competing bonding interactions help to establish limits in stability. These effects include substitution of the metal ion in the oxide shell and coordination effects with the central tetrahedral oxyanion. Here, we focus on the central oxyanion effect and the electronic stability of the β-Keggin ion in comparison with its α-isomer. It is obvious that the β-Keggin ion is less thermally stable than its α-isomer. Electronic indicators help to establish the stability limits and characterize spectral and physical properties.

Introduction

The geometrical isomers of 12-tungstopolyoxyanion, a well-known oxidation and acid catalyst, have been confirmed and identified.[1−3,5−12] The α-Keggin ion is constructed through the assemblage of edge- and corner-sharing octahedra into an arrangement of interconnecting trimers and tetramers as shown in Figure 1. In this work, we focus on the β-isomer of the well-known Keggin unit which acquires its structure by rotating one of the edge-sharing trimers of α-12-tungstopolyoxyanion by 60° along its C_3 axis,[1,5,8,13] producing adjacent trimers and tetramers around the shell. This rotated trimer is distorted but remains "attached" to the shell through corner-shared, bridging oxygens. This assembly is unique to the β-Keggin ion and lowers its symmetry from T_d in the α-isomer to C_s.[1] For the α-Keggin unit, the trimeric/tetrameric connectivity is always alternating; however, for the β-Keggin unit, pairs of trimers/tetramers are observed as shown in Figure 1.

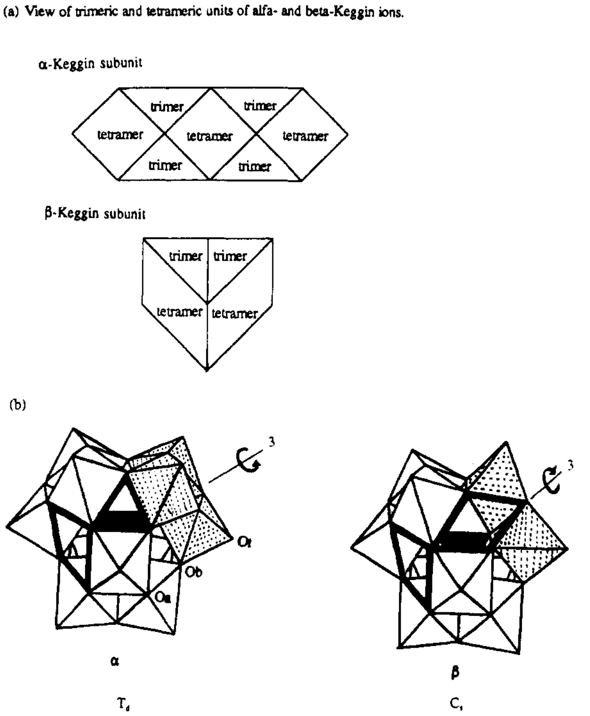

Figure 1. (a) Views of trimers ($W_3O_{13}^{8-}$) and tetramers ($W_4O_{18}^{12-}$) of tungsten-based α- and β-Keggin ions. (b) The structures of α- and β-$X^nW_{12}O_{40}^{(8-n)-}$ Keggin ions with oxyanion, $X^nO_4^{(8-n)-}$. The unique subunit between α- and β-Keggin ions is a "dotted" trimer which is rotated 60° along its C_3 axis, which is the local symmetry element as indicated. The tetramer (◇) and the trimer (△) are outlined.

To better understand the structure, it is necessary to decompose the cluster into its atomic constituents. There are 12 terminal oxygen (O_t), four apical oxygens (O_p), and 24 bridging oxygens which can be further identified as corner- (O_b) and edge- (O_a) shared oxygens, that is, the "corner" oxygens are shared between the adjacent trimers and the "edge" oxygens are shared between two octahedra of a trimer; the apical oxygens are shared between one trimer and the central heteroatom (X) and the terminal oxygens are unshared with any atoms.[1,2,4] These definitions are taken from the α-Keggin ion. This is shown in Figure 1 as well.

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Although the chemical and physical properties of β-Keggin ions are not as well established as those of the α-isomers, the β-Keggin ions are less stable and are more easily reduced than the corresponding α-Keggin ions.[1,2,13] The tendency of transformation of unreduced isomers from β to α has been studied and it has been determined that the β → α isomerization can be retarded by contact or coordination with organic solvents. In aqueous solution, this transformation is accelerated by the addition of a small amount of base. A few stability generalizations for the α- and β-isomers have been obtained from solution chemistry and thermal gravimetric analysis. Differences in stability are related to central oxyanion, hydration state or anion-anion interaction in the crystal. In addition, the aqueous solubility of β-Keggin ion is slightly greater than that of α-Keggin ion.[1] The solubility difference of the α- and β-Keggin ions may be attributed to the hydration lattice. In these materials, cubic lattices of Keggin oxide clusters are observed. These clusters are "interconnected" by many water(s) of crystallization. The number of water(s) of crystallization varies with crystal group; however, the average number of water molecules per unit cell is greater for the β-isomer.[5b] It is believed that the hydrogen bonding between the water and Keggin ion helps to stabilize the extended solid-state structure and promote the solubility. Insoluble salts of Keggin ions frequently contain few water(s) of crystallization and large inorganic or organic cations link the oxide clusters together.

The primary differences between α- and β-Keggin ions can be classified into categories based on their electrochemical and spectroscopic properties.[2] Electrochemically, the β-Keggin ion tends to undergo one-electron reduction more easily than its α-isomer and even though their polarograms look similar, the half-wave reduction potentials are less positive for the α-isomers. Similarly, the absorption spectra of both unreduced isomers are similar but the extinction coefficients are smaller for the α-isomers. The major difference in the vibrational spectra of α- and β-isomers in the infrared and Raman spectra are attributed to the variation in the charge distribution that destabilizes the β-Keggin ion with respect to that of the other isomers; however, the detailed comparisons of vibrational characteristics are complicated by the cluster size and symmetry differences. In this work, we focus only on the component interactions that help to define the electronic properties of this unique isomer.

Results and Discussion

In this analysis, a crystal/band calculation based on the extended Hückel method[14,15] is applied. The coordinates of α-[16] and β-[1]Keggin ions are taken from X-ray crystallographic data and the central heteroatom is set as the origin of the Cartesian coordinates for convenience. The β-Keggin ion possesses a single symmetry plane which passes through one of the edge-shared octahedral pairs of the rotated trimer with the average bond distance of four $X-O_p$ 1.62 Å and an average bond distance of 12 $W-O_t$ 1.68 Å, while its α-isomer is nearly tetrahedral with a bond distance for $X-O_p$ of 1.53 Å and an average bond distance of $W-O_t$ 1.65 Å. The Coulomb integrals (Hii) and Slater-type orbital (STO) exponents[17−22] of the framework metal, oxygen, and the central heteroatoms are listed in Table 1. The parameters selected were developed by Hoffmann et al.[17−22] for metal oxides and metal carbides. These are charge-iterated parameters selected to produce more accurate HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels in clusters and Fermi levels in the solid state. These parameters have been used successfully for vanadium and molybdenum oxides, titanium carbides, and many metal surfaces. In this work, the model used is that of the complete metal oxide cluster, extracted from the X-ray data.[1] A full band calculation is precluded by the size of the unit cell. Molecular calculations were performed on the full Keggin ion clusters to produce interaction diagrams. The density of states (DOS) and weighted orbital overlap population (WOOP)[4] or crystal orbital overlap population (COOP) curve were generated by application of the band component of EHMACC (extended Hückel molecular and crystal calculation). However, the construct utilized is one in which the translation distance between units exceeds any potential orbital overlap >20 Å. This is a standard computational approach and allows for the generation of the overlap population curves and the DOS for the noninteracting clusters. The energies and orbital vectors are identical to those obtained from the molecular calculation. Owing to the cluster size, analysis of the WOOP and DOS provides a useful and convenient tool. We have used the acronym WOOP here as the full crystal is not analyzed, and the interactions are those within the clusters.

Table 1. Hückel Parameters

atom	orbital	H_{ii} (eV)	ζ_1	c_1
Si	3s	−16.3	1.383	
	3p	−8.5	1.383	
Ge	4s	−16.0	2.16	
	4p	−9.0	1.85	
P	3s	−14.5	1.6	
	3p	−9.7	1.6	
O	2s	−27.61	2.28	
	2p	−11.01	2.275	
W	6s	−6.26	2.34	
	6p	−3.17	2.34	0.6685
	5d	−8.37	4.98	0.5424

The stability effects of the central oxyanion $(X^nO_4^{(8-n)-})$ and the isomerism (α and β) can be interpreted through analysis of the binding energy, overlap populations, orbital energy diagrams, and DOS of the cluster in both the α- and β-forms. To assist with the analysis, the cluster has been decomposed into trimeric and tetrameric structural units and into fragments.[4] Each of these components of the Keggin ion demonstrates characteristic bonding due to differences in metal and oxygen coordination. The identification of the character

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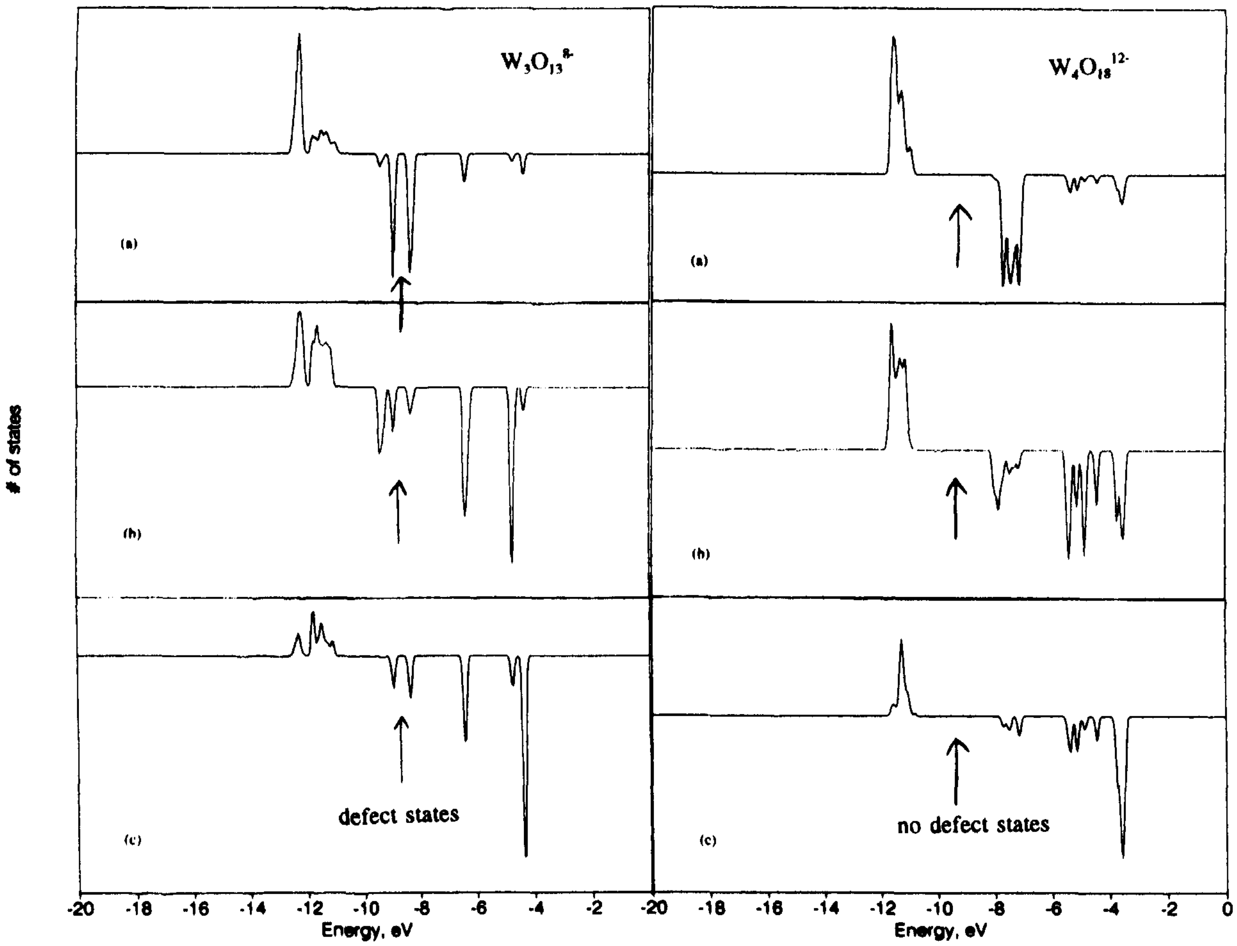

Figure 2. WOOP or COOP curves, normalized to the same scale, for $W_3O_{13}^{8-}$ and $W_4O_{18}^{12-}$: W to O distance of (a) $W-O_t$, (b) $W-O_a$ and $W-O_b$, and (c) $W-O_p$, among the trimer or tetramer.

of the unique states of the trimer and tetramer will rely on analysis of the DOS of the cluster. The fragments are the central oxyanion and the metal oxide shell. In this work, the binding or stabilization energy refers to the energy difference between the cluster and its two fragments: $X^nO_4^{(8-n)-}$ central oxyanion and $W_{12}O_{36}$ shell. The discussion of the stability will be divided into two interrelated components. The first will focus on stability effects in the tetrameric and trimeric fragments. The second will be the fragment analysis and considerations of related homologs.

Analysis of Stability of Trimeric and Tetrameric Fragments. The DOS analysis allows insight into the changes in the local bonding that influence the cluster stability. Since this is a cluster calculation, the DOS is really a histogram of molecular states.[4] As shown in previous work,[4,7,12] the stability of the metal oxide shell arises from bonding in the two structural components: the trimer and the tetramer. The tetrameric structure is a harbinger of the parent metal oxide and the trimer forms upon "condensation". In the α-Keggin ion, the trimers and tetramers are satisfied by the coordination with the central oxyanion. The DOS shows no intrusion of defect states between the HOMOs and the LUMOs.[4] However, in th β-Keggin ion the trimer coordination is not satisfied. In fact, Figure 2 shows that the "observed" defect states can be traced to unsatisfied interactions within the trimer, not the tetrameric unit of the cluster. To understand this decomposition of the Keggin ion, the coordination in the trimeric and tetrameric models should be established. The trimer is $W_3O_{13}^{8-}$ and the tetramer is $W_4O_{18}^{12-}$. In these units, each metal is six-coordinate with the relevant symmetry elements of the Keggin ion preserved in the unit, i.e., the local symmetry of the trimer is C_3 and that of the tetramer is C_2 or approximately C_4. An orbital-by-orbital decomposition of these trimeric and tetrameric states clearly shows that activation of the W–O bonds can be directly attributed to the coordination effects in the trimer; in other words, the bonding produced from interaction with the O_p atom of the central oxyanion is not sufficient to stabilize the trimer in the clusters and thus defects in the trimer persist in the β-isomer. It is this softening or weakening in bonding that may contribute to the observed structural lability. Furthermore, it has been shown that substitution of the β-Keggin ion with dissimilar metals in the affected trimer sites helps to stabilize the β-isomer. Finke et al.,[23] Wassermann et al.,[24] and Peng et al.[25,26] have prepared the $SiV_3W_9O_{40}^{7-}$, $SiCr_3W_9O_{40}^{10-}$, and $SiFe_3W_9O_{40}^{13-}$ clusters, respectively. In such a material, the defect states, i.e., the corresponding V–O, Cr–O, and Fe–O antibonding states will be located at a significantly higher energy with the overall V, Cr, and Fe contributions to these states

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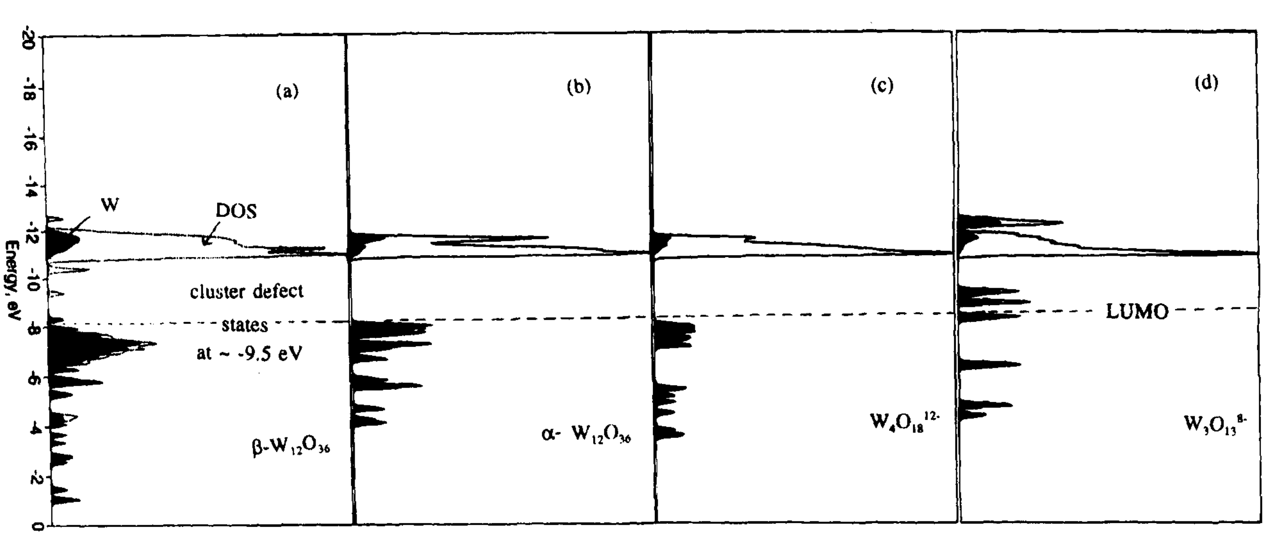

Figure 3. Density of states of the α- and β-Keggin shells, $W_{12}O_{36}$, and the subunits: $W_3O_{13}^{8-}$ and $W_4O_{18}^{12-}$.

dependent on the relative energy of the metal d orbitals and that of the oxygen p states. Thus, the reduction that promotes isomerization is more difficult to achieve and the cluster enjoys greater stability. Lability at the bridging oxygen sites may promote isomerism and change catalysis, while weakening of the $W-O_p$ linkage may lead to decomposition of the cluster to the corresponding metal oxide. Analysis of the WOOP and DOS (Figures 2 and 3) shows the origins of the weakening of these bonds through the defect states. Here, WOOP is the cluster equivalent of COOP which really shows the local bonding effects.[4]

Shown in Figure 3a, the first defect state, located at an energy of about −9.5 eV, is an antibonding state within the trimeric subunit. An orbital decomposition shows that this state is an antibonding π-state for $W-O_b$ interactions. For the α-isomer, this state is at a considerably higher energy and does not intrude between the HOMO and LUMO states. This can be seen by comparing Figure 3a with Figure 3b. These antibonding $W-O_b$ π states of the trimer are stabilized slightly by W−W interactions of π symmetry. These states are predominantly W−O antibonding. Under the normal preparative conditions of β-Keggin ion, these states are not occupied. Thus, no formal double bond is observed. However, π bonds are observed over similar distances in tungsten carbonyls.[27] For typical carbonyls, W−W distances range between 3.0 and 3.60 Å. In $[H_2W_2(CO)_8]^{2-}$,[28] for example, a double bond or four-center bonding stabilizes the binuclear cluster. Here, the W−W distance is about 3.1−3.2 Å. This orbital overlap can easily occur over 3.2 Å as this distance is well within the van der Waals limit for W which exceeds 5 Å.

The W atoms have a through-atom interaction as seen in Figure 4a while the W−O interaction is simply antibonding, and the O-to-O interaction occurs through an antibonding link also. The corresponding interaction is not observed in the tetramer for two reasons: the W−W distance and the orbital symmetry. The primary influence appears to be the symmetry effects of the coordinations as seen in Figure 4. Furthermore, the distance over which the interaction occurs is longer and thus limits the extent to which bonding may occur. In the trimer, the W−O−W distance is shorter and O_p is roughly centered in the metal trimer and more significant antibonding combinations of the $W-O_b$ π-bonding combinations of the W−W π-through-atom interactions occur. As the distance constraint is somewhat diminished, these interactions become significant and the "defect" state is created. Other defect states noted at higher energy are secondary, as the isomerization appears dependent on population of the first defect state only. In fact, it has been observed experimentally that a one-electron reduction produces the β → α conversion experimentally. The higher energy states at ~−9.0 and ~−8.5 eV contain $W-O_p$ antibonding and $W-O_t$ as shown in Figure 2. Interestingly, these defects persist and contribute to the electronic character of the metal oxide cluster. In the β-Keggin ion, the cluster assembly, e.g., connection of trimers unique to this isomer as shown in Figure 1, does not significantly effect the orbital composition of the trimer states at the "rotated" site. This can be seen in Figure 4. The adjacent trimer does not significantly alter the W−W π bonding or the $W-O_b$ antibonding interactions as the additional W site is noded in the relevant orbital states. In the α-Keggin ion, the trimer is adjacent to a tetramer and the orbital contributions are quite different, as seen in Figure 4. The W−O antibonding character is actually increased between trimer and tetramer, and thus this orbital is shifted to higher energy. It no longer appears as a "defect" between the HOMO−LUMO gap. The higher energy defect states are comprised of antibonding $W-O_p$ and $W-O_t$ character to a large degree. Though these are not shown in Figure 4, they can be inferred from those diagrams. Clearly, the states initially affected by reduction contribute to the bridging linkages in the trimer and thus reduction will significantly compromise the stability of the trimer. In the β-isomer, the one-electron reduction which is known to promote isomerization should cause population of $W-O_b$ antibonding states in the trimeric unit. Thus the mechanism of isomerization appears to rely on population of these so-called trimeric, defect states activating the W−O bond.

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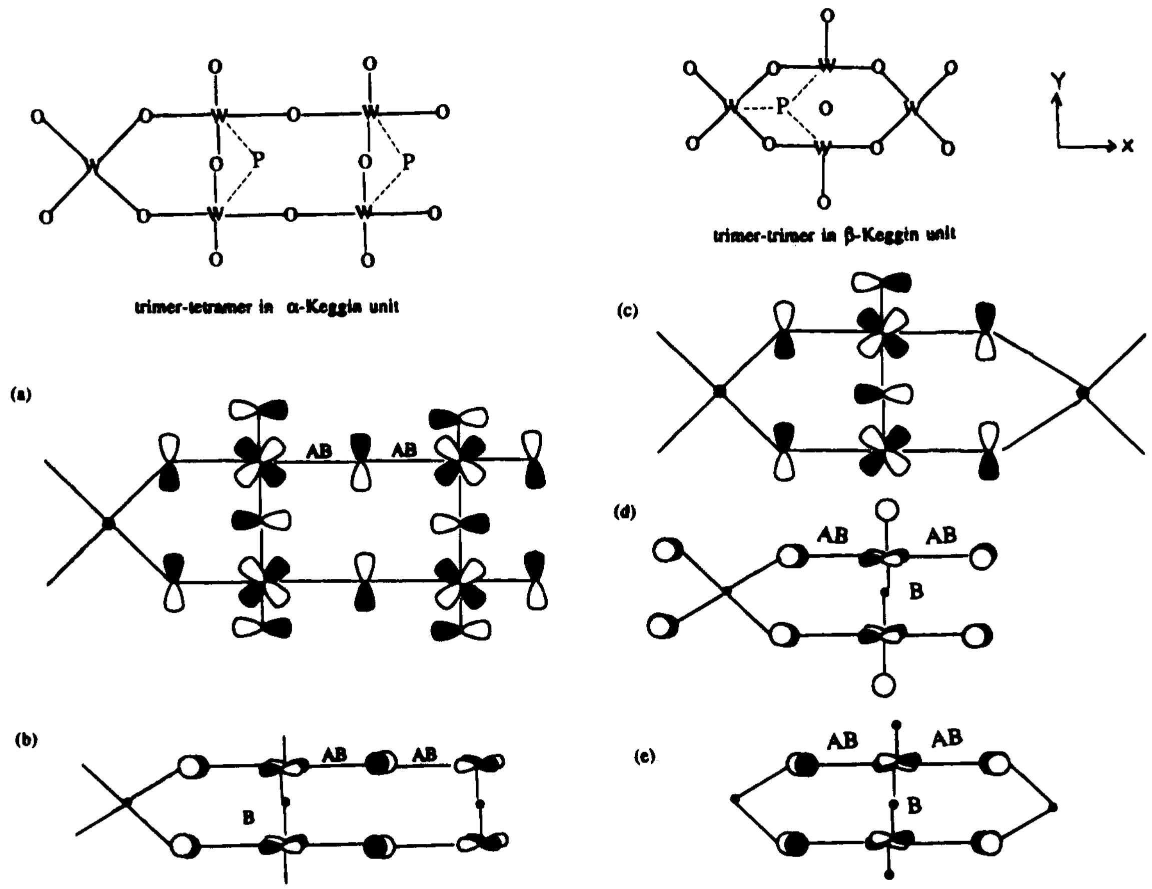

Figure 4. Orbital interaction diagram of $W_3O_{13}^{8-}$ and $W_4O_{18}^{12-}$ in α- and β-Keggin shells: (a) and (b) are the bonding interactions between W−W and antibonding interactions between W−O in the trimer−tetramer linkage of the α-Keggin shell. Here, AB and B represent antibonding and bonding interactions, respectively. (c) to (e) are the bonding interactions between W−W and the antibonding interactions between W−O in the trimer−trimer linkage of the β-Keggin shell. The W atoms of two adjacent trimers, which create "defect" states in the β-Keggin shell can π bond to each other due to the "shorter" distance, 3.2 Å. This interaction occurs by a through-atom interaction.

In the α-Keggin ion, no defects in the trimeric unit are observed. This is likely due to the stronger antibonding character of W−O states between the trimeric and tetrameric linkage of the α-isomer, and better bonding between O_p and the central ion leading to the establishment of more true tetrahedral states in the oxyanion which in turn lessens the interaction with the W−W π states. (Recall the average X−O_p distance is about 0.1 Å shorter for the α-Keggin ion[4] relative to the β-isomer.[1])

Fragment Analysis and Stabilization of the Homologs of the β-Keggin Ion. The fragment analysis and DOS decomposition for the α- and β-Keggin isomers provide several indicators of electronic interaction. A consideration of binding energy allows for simple comparison of bonding stability. Analysis of the DOS in terms of atomic constituents helps to establish the relative contributions of the metal, oxide, and heteroatom states to the important states of the polyanion. Analyses of the fragment molecular orbital states of the oxyanion and their relative interaction help to establish limits of bonding between fragments which are further reinforced by the overlap population, a measure of bond strength, between states in the oxyanion tetrahedron and the metal oxide shell. The following discussion will focus on these factors to complete the analysis of the stability of the Keggin ion.

Table 2. Binding Energy of Keggin Ions

species	total energy (eV)	binding energy (eV)
β-$W_{12}O_{36}$	−4446.1955	
β-$SiW_{12}O_{40}^{4-}$	−4941.7178	2.4082
β-$GeW_{12}O_{40}^{4-}$	−4950.9122	−5.1102
β-$PW_{12}O_{40}$	−4948.9223	−4.1455
α-$W_{12}O_{36}$	−4442.7650	
α-$SiW_{12}O_{40}^{4-}$	−4946.0514	−5.0190
α-$GeW_{12}O_{40}^{4-}$	−4948.1030	−5.4106
α-$PW_{12}O_{40}^{3-}$	−4947.2074	−5.4455
	α	β
SiO_4^{4-}	−498.2755	−497.9305
GeO_4^{4-}	−499.9274	−499.6065
PO_4^{3-}	−498.9969	−498.5813

Assessment of stability can be obtained through a comparison of the binding energy of the cluster which results from bonding between the fragments. Since this energy uses two cluster fragments, differences in the local bonding in the central oxyanion and in the metal oxide shell are computed through comparison of the total cluster energy to that of its two primary constituents. Table 2 suggests that the structural distortion in the isolated central oxyanion corresponding to that induced in the complete cluster through "rotation" of the trimer does not significantly alter the energy of the oxyanion. However, this distortion does affect the total energy of the β-Keggin ion, −4941.7 vs −4950.9 eV. One contribution to the stabilization in the β-Keggin ion is the stabilization of the central oxyanion in the metal oxide shell. This coordination occurs as a consequence of the fact that the oxygen atoms of the oxyanions must satisfy the coordination of the metal oxide octahedra in the trimer. The calculated stability order of the β-Keggin ion with X = Si, Ge and P is Ge > P > Si. This differs from the trend of the aqueous stability,[1] and that of α-Keggin ions is P > Ge > Si.[4] The relative stability of the β-Keggin ions obtained through a comparison of isomerization kinetics has been measured only in solution. The extent of solvation and relative electron affinities of the solvent and β-Keggin ion affect the rate of isomerization. Thus, the data in Table 2 cannot be directly compared with experimental data presently available; however, the experimentally measured stability tends for the β-Keggin ions are reproduced in this work. The corresponding data for the α-Keggin ions reliably follows experimental trends,[7] however. A comparison of the total energies between α- and β-Keggin ions is not valid as significant differences in local bonding affects the total energy of the cluster. However, the binding energies suggest that the β-Keggin ions are considerably less stable than the α-Keggin ions. Furthermore, it seems that the stability trend observed in the β-isomer follows the total energy trend of the isolated central oxyanion as the coordination effects are similar for all of the oxyanions considered. This trend is also demonstrated in the overlap population in that the extent of overlap population of O−X is almost identical to the trend observed for the stabilities of the oxyanions in the β-Keggin ions. The greatest overall stability is observed for X = Ge. For the α-Keggin ion, two effects define the stability of the isolated oxyanion in its undistorted structure and the stabilization of the oxyanion in the cluster.[7] Though the isolated oxyanion of Ge is calculated to be the most stable, it is the least affected upon coordination in the cluster. The same "trade off" factors favor phosphate coordination in the α-Keggin ion.[7,12]

Incomplete or poor coordination produces "defect states" in the β-Keggin ion and leaves the cluster more redox active and perhaps a potential semiconductor precursor. Furthermore, this implies that changes in the electrical or a photo properties as well as changes in the chemical properties such as solubility and oxidation−reduction of the cluster may occur as a result of the defect states existing at the orbital frontier. A sizable component of the defect states of a β-Keggin ion originate from $W-O_t$ and $W-O_p$ linkages and the development of the $W-O_p-X$ linkage is critical for the stability of α- and β-Keggin ions. However, these states lie at a higher energy than the $W-O_b$ defect states described previously.

An analysis of DOS for the three homologs provides a comparison of the relative contribution of the defect states to the overall electronic structure. Here, DOS refers to a histogram[4] of molecular states within an energy increment versus energy. The DOS, through atomic orbital projections of the α- and β-Keggin shells, shows different limits in bonding. The number of states per energy interval of an α-isomer is much greater than that of a β-isomer due to the more narrow bands or reduced dispersion of the DOS. In a β-Keggin ion, the rotated trimer provides better local bonding interactions in some cases. The broadening in the O_p region of the DOS is noted in the oxide region of the DOS at approximately −11.5 eV because stronger local interactions occur within the trimer; therefore, the "bandwidth" of a β-Keggin shell spreads and thus reduces the intensity of each band shown in the DOS which in turn results in fewer states per energy interval. In this text, "band" refers to the numerous states of very close energy in the cluster. This use of "band" is borrowed from solid-state terminology but here refers to the rather significant concentration of states in an energy interval for the Keggin ion. It is obvious that the bonding p band contains more oxygen character and in the β-isomer it is further dispersed, contributing to the defect states and demonstrating the competing bonding/antibonding interactions between the oxyanion and the shell metal states. Similarly, the antibonding band located at −7.00 eV of W 5d character is also more dispersed in the β-isomer and the bandgap of ~3.00 eV observed for the α-Keggin shell vanishes in the β-Keggin shell. Thus these intrinsic defects should make the β-Keggin ion a better oxidant than the α-Keggin ion in catalytic oxidation reactions.

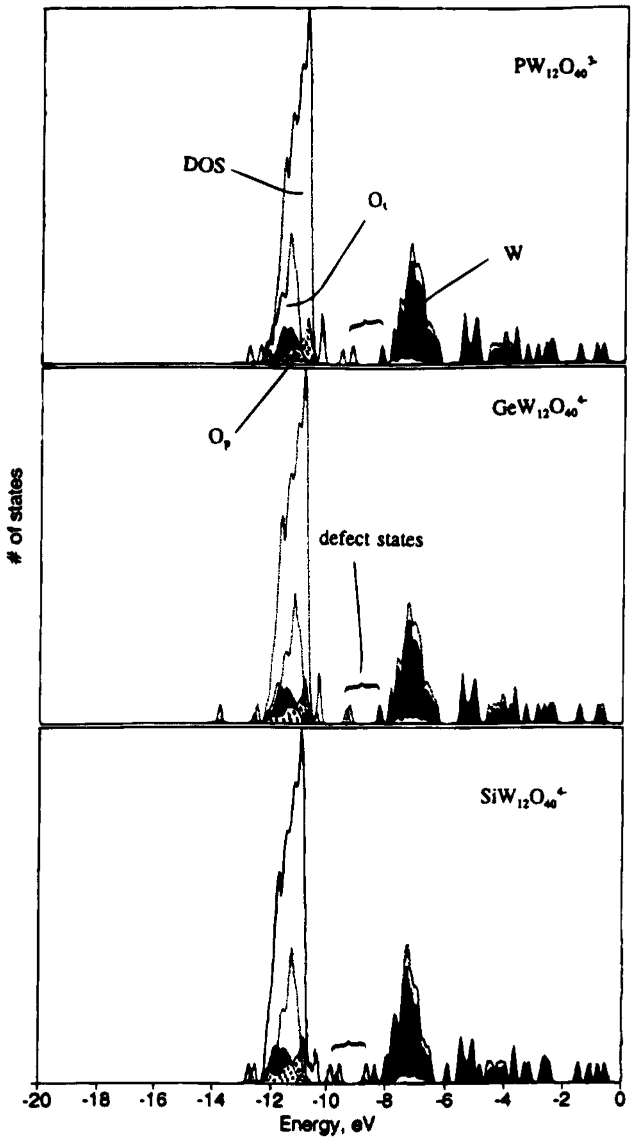

Figure 5. Density of states of β-Keggin ions: $SiW_{12}O_{40}^{4-}$, $GeW_{12}O_{40}^{4-}$, and $PW_{12}O_{40}^{3-}$.

In addition to the electronic structural differences between the two unique isomers, subtle but important differences are observed in the homologous series of the β-Keggin ions. Figure 5 shows that the DOS of β-$GeW_{12}O_{40}^{4-}$ and β-$PW_{12}O_{40}^{3-}$ are similar to that of the β-$W_{12}O_{36}$ shell while that of β-$SiW_{12}O_{40}^{4-}$ shows more defect states within the gap. Figure 6 is the energy

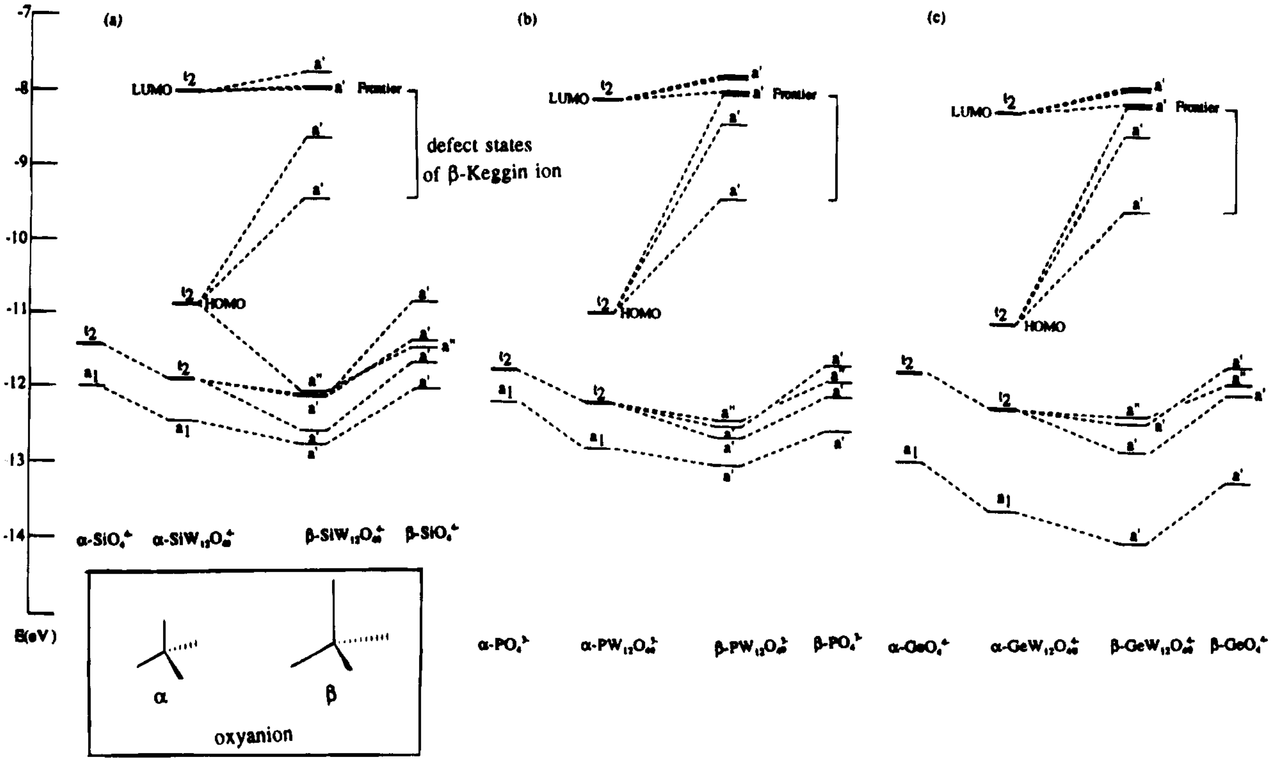

Figure 6. Energy diagrams of α- and β-central oxyanions and polyanions: (a) SiO_4^{4-} and $SiW_{12}O_{40}^{4-}$, (b) PO_4^{3-} and $PW_{12}O_{40}^{3-}$, and (c) GeO_4^{4-} and $GeW_{12}O_{40}^{4-}$.

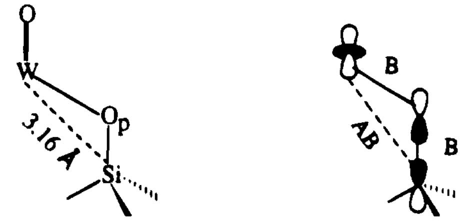

Figure 7. Three-way-interaction between W, O_p, and Si. The W d_{z^2}–O_p p_z interaction and the Si p_z–O_p p_z interaction are bonding while the W d_{z^2}–Si p_z interaction is antibonding.

diagram of β-$SiW_{12}O_{40}^{4-}$ which is somewhat unique from its two isostructural homologs. The "defect" character provides a rationale for the increased instability of β-$SiW_{12}O_{40}^{4-}$.[1,2] For Si, the W–O–Si interaction is strongly affected by the electronegativity of atoms. As reported in other work,[7,12] a three-way interaction can occur as the energy of the Si p states is close to that of W. Since the defects involve W–O_p- - -O_p–Si interactions, it is not surprising to see a greater contribution in the Si homolog. The primary W–O_p interaction occurs at the top of the O_p band, with a defect state at about −8.0 eV. For the SiO_4^{4-} unit, the HOMO contains a sizable contribution from Si and thus Si–O_p contribution through the W–O_p interactions are bonding and a W–Si, through atom, antibonding interaction occurs. The distance between Si and W is well within the van der Waals limit. One such interaction is shown in Figure 7. The extent of this interaction is dependent on the Si and W contributions to the W–O or Si–O states. Here, these contributions are at a relative maxima and thus the Si–W antibonding interaction becomes notable. In addition, it is important to note that 12 such interactions can occur.

A closer analysis of the orbital interactions of the α- and β-Keggin ions with the oxyanions will help to illustrate the differential stabilization of the oxyanions in the clathratic oxide shell. Recall Figure 6 which shows the correlation of states of α- and β-Keggin ions arising from the symmetry change at the trimeric site. The degenerate p-π (t_2) states in an α-isomer appear to be less stable than the a′ and a″ analogs of the β-isomer. The t_2 states of the α-isomer are split into a′, a′, and a″ orbitals. The bonding states labeled a′, a′, a″, and a′ are located at an energy lower than that of the corresponding α-isomer. This might suggest a greater stabilization of the β-Keggin ion. However, some antibonding combinations of these states are occupied in the β-isomer. This suggests lower or weaker bonding of the central oxyanion to the $W_{12}O_{36}$ shell: for the β-isomer, the defect states fall between the "HOMO–LUMO" states of the related α-isomer. The energy diagrams of central oxyanions and Keggin ions in α- and β-isomers are similar respectively when X = Ge or P. It is obvious that the bonding states of β-isomers are more stabilized than the corresponding α-isomers but the competition between W–O_p and W–O_t bonding and the destabilization of W–O_b π states lead to the greater destabilization in β-isomers.

The redox characteristics described in the introduction can be understood in terms of the frontier orbital energies. For the β-isomer, the "defect" states sit in the frontier region between the HOMO and the LUMO of the normal Keggin shell. The defect states shown in Figure 6 of the β-Keggin ion are composed of three a′ states which are derived from the degenerate t_2 HOMO states of the α-Keggin ion. For a closer look, the energy of the third a′ state derived from the t_2 HOMO of the α-Keggin ion is almost identical to the first a′ state derived from the t_2 LUMO states of the α-Keggin ion. Although the "HOMO" and "LUMO" of the β-Keggin ion are nondegenerate by symmetry, the calculated energies shown in nature can be treated as "degenerate" with

Table 3. Overlap Population between Atoms of O_p−X Bond

	isolated			Keggin		
O/X	Si	Ge	P	Si	Ge	P
β-						
O-0301	0.5294	0.5545	0.5480	0.5839	0.6006	0.5932
O-0302	0.5294	0.5539	0.5475	0.5837	0.6004	0.5930
O-1101	0.7364	0.8041	0.8130	0.7833	0.8430	0.8480
O-1701	0.4109	0.4113	0.4044	0.4425	0.4386	0.4288
av	0.5515	0.5810	0.5782	0.5984	0.6207	0.6158
α-						
O-0401	0.5766	0.6105	0.6076	0.6239	0.6487	0.6450
O-0402	0.5766	0.6105	0.6076	0.6238	0.6486	0.6449
O-0403	0.5766	0.6105	0.6076	0.6237	0.6485	0.6447
O-0404	0.5766	0.6105	0.6076	0.6234	0.6482	0.6444
av	0.5766	0.6105	0.6076	0.6237	0.6485	0.6448

respect to redox processes, and thus we include these states with frontier states. There are two distinct a′ orbitals of nearly the same energy which comprise the frontier states and thus the reduction of β-isomer is expected to occur readily. Reduction of the β-isomer is expected to decrease the interaction of the central oxyanion in the cluster and at the same time assist the oxidative process by activating the W−O_b bond. The most stable oxidation state of the cluster may require the loss of four electrons as the antibonding states between the $X^nO_4^{(8-n)-}$ and $M_{12}O_{36}$ shell are completely depopulated.

The intrinsic defects in the β-Keggin ion are produced by rotating or twisting the trimer which locally improves the orbital overlap but at the same time it compromises the overall bonding of the cluster. The data in Table 3 support this conclusion suggesting that the β-shell, $W_{12}O_{36}$, is more stable than the α-shell. In the β-isomer, more W−O short contacts occur, thus increasing the average effective coordination number of W though the formal coordination number is the same in the α- and β-isomers.

Another interesting feature is observed in this analysis. The silicate Keggin ion appears to show a different limit of stability in the β-isomer. This instability may be caused by an unusual orbital segregation of "HOMO", of which the a′ component is deeply buried at the lower level of bonding states and the other two components, a′ and a′, are lifted to the energy levels close to pure Si 3p states. Due to electronegative differences, the Si contribution is at a relative minimum for these states, and thus the average bonding within the SiO_4^{4-} is a minimum for the isolated and complexed ions. Therefore, the instability in the cluster is attributed to a large extent to the weaker Si−O bonding.

These effects can be seen in Table 4 which shows the overlap population between O and X (=Si, Ge, P) of isolated α- and β-central oxyanions and Keggin ions. It is obvious that the overlap populations in β-isomers are not the same. This is because the overall symmetry is reduced in the β-isomer and differences in bond length occur; however, a comparison can be made by considering the average overlap populations. The average overlap population in the β-Keggin ion or central oxyanion is smaller than that in an α-Keggin ion or central oxyanion. This is due in part to the longer X−O average bond distances in the β-isomer but also due to stabilization in the oxyanion imparted upon complexation with the clathratic shell when compared to overlap populations reported in Table 3. A comparison of the average stabilization for β-$PW_{12}O_{40}^{3-}$, β-$SiW_{12}O_{40}^{4-}$, and β-$GeW_{12}O_{40}^{4-}$ shows that the oxyanion is stabilized to approximately the same extent in the metal oxide shell for the β-Keggin ion, i.e., ~7%. The stability of the oxyanion in the α- isomer varies from ~5% to 9% with the differences attributed to the orbital composition of a_1 and t_2 bonding states of the corresponding tetrahedral ion. These stabilization comparisons are based on overlap population only. The differences in binding energies should only be compared within the series, i.e., a comparison of data for α- and β-isomers is not valid as significant differences occur in the bonding within the cluster. In addition, these stabilities are critically dependent on the redox states of the ion with, and that multiple redox states are common. All reported data provided are for the "normal" electron count. Recall the tradeoff effect between W−O_p and X−P_p bonds from our previous work[4] that the stability of a Keggin ion depends on the balance of forming W−O_p bonds and weakening X−O_p bonds. The driving force of stability is generally the formation of W−O_p bonds together with limited destruction of X−O_p bonds and W−O (bridging: a and b). The overlap population of W−O_p bonds in α- and β-Keggin ions are very close (~0.1470), and thus the net tradeoff effect favors and stabilizes the α-Keggin ions.

Conclusion

Although the chemistry of β-Keggin ions is not yet well defined, from this work we are able to understand trends in the stability and redox behavior. The decomposition of the two isomers into trimeric and tetrameric units and oxyanion and metal oxide shell fragments has allowed for a characterization of stability effects. Substitution of the central oxyanion affects the stability of the Keggin ion, and this can be explained in terms of electron density effects: the more electronegative X, the more stabilized the shell. This is the reason that β-$GeW_{12}O_{40}^{4-}$ and β-$PW_{12}O_{40}^{3-}$ possess similar stabilization energies and demonstrate similar electronic character. It seems that the electronic and photo character of these two Keggin ions should be similar. However, to date, little experimental evidence of such effects has been reported. The twisting of the trimer creates defects comprised of W−O_b states which are responsible for the chemical and physical differences between α- and β-Keggin ions; these defects have been identified and appear critical in the isomerization process. The former isomer is more stable and can be oxidized while the latter is reduced readily; thus it may be a more active oxidation catalyst. Further exploration of the defect states and redox stability of these materials may yield as new semiconductor precursors and extremely sensitive color sensors.