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Electronic Properties of Polyoxometalates: A DFT Study of α/β-$[XM_{12}O_{40}]^{n-}$ Relative Stability (M = W, Mo and X a Main Group Element)

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Abstract: Keggin heteropolyanions $[XM_{12}O_{40}]^{n-}$ have various isomeric structures, α and β being the most common. Conventionally, the α structure appears to be the most stable, but calculations carried out at the DFT level for X = P(V), Si(IV), Al(III), As(V), Ge(IV), and Ga(III) and M = W(VI) and Mo(VI) show that this stability depends on several factors, particularly on the nature of the heteroatom (X) and the total charge of the cluster. In this paper, we apply the clathrate model to the Keggin molecule to carry out a fragment-interaction study to elucidate when and why the traditional relative stability of various isomers can be inverted. The fully oxidized anions that have inverted the traditional stability trend in this series are $[AlW_{12}O_{40}]^{5-}$ and $[GaW_{12}O_{40}]^{5-}$, both of which contain a third-group heteroatom and an overall charge of −5. β-isomers are always more easily reduced than α-isomers. This experimental observation suggests that reduction favors the stability of β-isomers and one of the most important results of this study is that the α/β inversion is achieved in most cases after the second reduction. The α- and β-isomers may have different properties because the energy of the LUMO, a symmetry-adapted d_{xy}-metal orbital, is different.

Introduction

Keggin anions, $[XM_{12}O_{40}]^{n-}$ (X = a main group or a transition metal ion and M = transition metal ion), comprise an extensive group of molecules in shape and chemical composition, in which 12 MO_6 octahedra encapsulate a central tetrahedron (XO_4).[1] The first polyoxometalate (POM), the phosphomolybdate $[PMo_{12}O_{40}]^{3-}$, was reported by Berzelius[2] in 1826 and, in 1864, Marignac[3] observed two different forms of the acid $[H_4\text{-}SiW_{12}O_{40}]$, later named α and β (Figure 1). Keggin[4] solved the α-isomer structure of $[PW_{12}O_{40}]^{3-}$ in 1933. Nowadays, α-Keggin anions are known for a wide range of heteroatoms, X (e.g., X = P^{V}, Si^{IV}, Al^{III}, Ge^{IV}, Fe^{III}, Co^{II}, Co^{III}, Cu^{I}, Cu^{II}, $2H^{+}$, etc.), and addenda, M (e.g. M = W^{VI}, Mo^{VI}, etc.). In contrast, β-Keggin anions are less common. The first X-ray characterization for a β-isomer was reported in 1973 for the potassium salt of $[SiW_{12}O_{40}]^{4-}$.[5] Later, Matsumoto et al.[6] showed that this compound is kinetically stable. To our knowledge, only a few more β-structures have been characterized by X-ray: the fully oxidized tungstates $[GeW_{12}O_{40}]^{4-}$ [7] and $[AlW_{12}O_{40}]^{5-}$ [8] and the four-times-reduced molybdates $[PMo_{12}O_{40}]^{7-}$ [9a] and $[AsMo_{12}O_{40}]^{7-}$.[9b] Somewhat more abundant are the structures for β-mixed-addenda complexes.[10] Baker and Figgis[11] proposed that the β-structure might be derived from 60° rotation of one of the M_3O_{13} triad about a 3-fold axis of the α-anion. Three additional isomers, γ, δ, and ϵ, were postulated to result from 60° rotation of the remaining triads. It is accepted that these latter structures are less stable than α and β, which are supposed to have similar energies, although the α-isomer is probably somewhat more stable since isomerizations on Keggin heteropolytungstates and heteropolymolybdates all occur in the $\beta \rightarrow \alpha$ direction.[12a−c] An interesting point concerning structures with only one addenda metal type is that

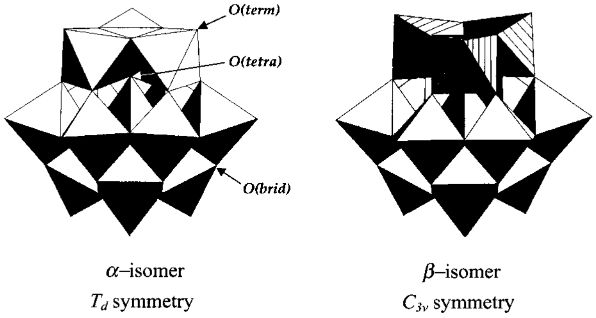

Figure 1. Polyhedral representation of α- and β-isomers of the Keggin anion. Point groups are showed in parentheses. The hatched triad of the β-isomer has been rotated 60° about a 3-fold axis of the α-isomer.

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reduced β-isomers could be more stable than the corresponding α-isomers, because β-structures reduce at slightly more positive potentials than α-structures.[6,13] Tézé et al.[14] showed that there is a direct relationship between the oxidizing character of Keggin POMs and the number of rotated triads in the $M_{12}O_{36}$ framework: that is to say the reducibility increases in the order $\alpha < \beta < \gamma$. Related to this point, Sécheresse and co-workers reported hydrothermal Keggin POM preparations of reduced β-derivatives of the 12-molybdosilicate in low reduction states.[15]

Recently, Weinstock and co-workers[8] reported a detailed study on the equilibrium between α- and β-isomers for several fully oxidized heteropolytungstates. They quantify the relative kinetic and thermodynamic stability of β-isomers in relation to the α-isomers, and it appears to depend on such factors as the heteroatom and the environment. A relevant ordering of β-polyanion stability with X = Al(III) > Si(IV) > P(V) is found, confirming Pope's hypothesis.[1] Previous theoretical calculations carried out by our group[16] on α-Keggin anions supported the hypothesis[17] that a Keggin anion may also be viewed as a neutral $M_{12}O_{36}$ cage that encapsulates the internal $[XO_4]^{n-}$ subunit. The ab initio and density-functional theory (DFT) modeling of polyoxoanions is still incipient[18] but, in the past decade, it has been shown that it is suitable for the understanding of questions concerning the acidity and basicity of POMs,[19] the localization or delocalization of metal electrons in reduced species[20,21] and substituted ions,[22] the identification of host and guest subunits in a cage complex,[23] and the electronic characterization of Keggin oxothio polyanions.[24] Here, we report DFT calculations carried out on a series of Keggin anions to analyze the different factors that govern the relative stability of α/β-isomers of these important compounds.

Theoretical Details

The calculations were carried out by using the DFT methodology with the ADF2.3 program.[25] Gradient corrections were included. LDA approximation characterized by the electron gas exchange (Xα with $\alpha = 2/3$) together with Vosko–Wilk–Nusair[26] (VWN) parametrization for correlation were used. Becke[27] and Perdew[28] nonlocal corrections were added to the exchange and correlation energy, respectively. Triple-ζ + polarization Slater basis sets were used to describe the valence electrons of main group atoms whereas, for transition metal atoms, a frozen core composed of 1s to 3spd shells for molybdenum and 1s to 4spd for tungsten was described by means of single Slater functions. *n*s and *n*p electrons were described by double-ζ Slater functions, *n*d and (n+1)s by triple-ζ functions and (n+1)p by a single orbital.[29] Quasirelativistic corrections for the core electrons were employed by using the Pauli formalism with corrected core potentials. The quasirelativistic frozen core shells were generated by using the auxiliary program DIRAC.[25] We made unrestricted calculations for open shell configurations.

Results and Discussion

Fully Oxidized Clusters. Complete geometry optimizations under T_d and C_{3v} symmetry constraints for α- and β-isomers, respectively, were carried out for the $[XM_{12}O_{40}]^{n-}$ series, with X = P, Si, Al, As, Ge, and Ga and M = W and Mo. No significant differences were observed between the computed and experimental geometries for the clusters with a known X-ray structure. The calculations show that the β-isomer gradually stabilizes in the order Al(III) > Si(IV) > P(V) and Ga(III) > Ge(IV) > As(V) for both W and Mo *addenda* atoms (Table 1). The largest stability in favor of the α-isomer was found for X = P(V) and M = W with an energy difference of 0.28 eV (+6.5 kcal·mol^{-1}). On the other hand, the greater the charge of the cluster, the more stable the β-isomer is, particularly for aluminum and gallium tungsto derivatives, in which the stability is inverted by −0.34 (−7.8 kcal·mol^{-1}) and by −0.18 eV (−4.2 kcal·mol^{-1}), respectively. Only the values for the silico- and germanotungstates seem to fall outside the expected range of energies for which the difference in energy is slightly above the general tendency. These results are in accordance with the recent studies of Weinstock et al.,[8] who found that the thermodynamic stability of β-isomers in Keggin polytungstates increases in the same order Al(III) > Si(IV) > P(V). However, ΔG for $\alpha \rightarrow \beta$ $[AlW_{12}O_{40}]^{5-}$ isomerization was estimated from kinetic measurements to be positive, +2.1 kcal·mol^{-1}. The same authors pointed out that the Gibbs energies for these isomerization processes are dependent upon the temperature, the solvent, the ionic strength, and the nature of the countercation. Therefore, this suggests that absolute Gibbs isomerization energies in solution and the computed $\beta-\alpha$ energies, based on isolated anions, are not directly comparable.

For molybdates, the same trend was observed. Nevertheless, the energies range between smaller values. As for the tungstate series, the largest positive $\Delta E_{\beta-\alpha}$ was found for X = P(V) with a value of 0.21 eV, an energy that is 0.07 eV smaller than that of the homologous tungstate. In contrast, for X = Al(III), the β-isomer becomes more stable but the α-isomer is still the most stable by 0.08 eV. For the gallium derivative, the other group 15 heteroatom considered, both isomers have approximately the same energy. The Mulliken population values in Table 1 show that the total charge on the $[XO_4]$ subunit increases as the total charge of the molecule goes from −3 to −5. This increase almost parallels the formal increment except for X = Al, where

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Table 1. Relevant Mean Distances, (XO_4) Mulliken Charges, and $\beta-\alpha$ Energy Differences Calculated for a Series of Keggin Heteropolyanions

X	M	isomer	$d(X-O_{tetra})$	$d(O_{tetra}-M)$	$d(M-M)$	charge XO_4	$\Delta E_{\beta-\alpha}$ [a]
P	W	α	1.53	2.35	3.44−3.71	−1.66	+0.28 (+0.13)
		β	1.58	2.43	3.38−3.71	−1.61	
	Mo	α	1.58	2.46	3.47−3.75	−1.90	+0.21
		β	1.59	2.45	3.42−3.80	−1.86	
Si	W	α	1.64	2.33	3.35−3.70	−2.59	+0.26 (+0.11)
		β	1.67	2.33	3.32−3.74	−2.63	
	Mo	α	1.67	2.37	3.41−3.75	−2.68	+0.14
		β	1.68	2.37	3.41−3.79	−2.63	
Al	W	α	1.74	2.26	3.32−3.73	−3.09	−0.35 (−0.57)
		β	1.81	2.24	3.29−3.75	−3.19	
	Mo	α	1.81	2.27	3.35−3.77	−3.53	+0.08
		β	1.81	2.28	3.33−3.80	−3.59	
As	W	α	1.75	2.35	3.44−3.74	−1.95	+0.16
		β	1.75	2.35	3.44−3.80	−1.93	
	Mo	α	1.75	2.37	3.47−3.78	−2.19	+0.11
		β	1.76	2.37	3.42−3.82	−2.17	
Ge	W	α	1.82	2.26	3.36−3.73	−3.26	+0.21
		β	1.83	2.26	3.33−3.76	−3.38	
	Mo	α	1.84	2.30	3.42−3.79	−3.34	+0.01
		β	1.84	2.30	3.37−3.83	−3.27	
Ga	W	α	1.92	2.19	3.33−3.76	−3.53	−0.19
		β	1.93	2.19	3.30−3.77	−3.77	
	Mo	α	1.93	2.22	3.36−3.80	−3.80	−0.02
		β	1.93	2.23	3.34−3.84	−3.82	

[a] Values in parentheses are for 1-electron reduced species.

according to Mulliken analysis only ~0.5 electron is added to $[XO_4]^{n-}$, while the remaining half electron is expected to be over the outer sphere. This general behavior is also observed in clusters containing paramagnetic heteroatoms. Negative charges of −4.0 e were estimated for the internal tetrahedron in the highly charged clusters $[Fe^{III}W_{12}O_{40}]^{5-}$ and $[Co^{III}W_{12}O_{40}]^{5-}$ and of −4.5 e in $[Co^{II}W_{12}O_{40}]^{6-}$.[16]

To get a better understanding of the electronic effects involved in Keggin clusters, we decomposed the interaction energy between the two subunits $[XO_4]^{n-}$ and $M_{12}O_{36}$ by means of the transition state (TS) method developed by Ziegler et al.,[30] which is an adaptation of Morokuma's[31] well-known decomposition scheme. Once the Fragment Energies (FE) for the isolated $[XO_4]^{n-}$ and $M_{12}O_{36}$ units (for M = W) in the geometry they adopt in the cluster are calculated, the Fragment Interaction Energy (FIE) analysis accounting for the interactions between the two fragments is made. The FIE itself can be decomposed in two terms:

$$\mathrm{FIE} = \mathrm{SR} + \mathrm{OI}$$

where SR, the steric repulsion, consists of two components: the classical electrostatic interaction between two unperturbed charge distributions of the interacting fragments and the so-called exchange or Pauli repulsion. This latter term comprises the 4-electron destabilizing interactions between occupied orbitals in the fragments and is responsible for SR. In addition to the steric interaction there are the orbital interactions, OI, which account for the charge transfer between fragments and the mutual polarization of each fragment. These contributions are shown in Table 2.

An analysis restricted to FE shows that this term always slightly favors the α-isomer, while the energy of the tetrahedral fragment is, in practice, identical for α- and β-isomers. In addition, the energy change associated to deformation is fairly dependent on the total charge of the cluster for the geometry of the cage but is small for the tetrahedron. We found that the Deformation Energy[32] (DE) of neutral α-cages is 2.37 eV for X = P, a value that increases to 4.91 eV for X = Si and to 7.46 eV for X = Al. These energies are very similar to those for β cages. Such notable DEs originate in the change in the cage geometry when the relaxed $M_{12}O_{36}$ encapsulates the anion. The major variations occur in the $W-O_{term}$ bond distances, which increase consistently with the net charge of the anion. Thus, for example, the bond distance between the tungsten atom and the terminal oxygen is 1.727 Å for $[PW_{12}O_{40}]^{3-}$, whereas the corresponding values for the anions $[SiW_{12}O_{40}]^{4-}$ and $[AlW_{12}O_{40}]^{5-}$ are 1.743 and 1.763 Å, respectively. Differences were smaller for the bridging bonds. On average, the α-$W_{12}O_{36}$ cage is ~0.3 eV more stable than the β-cage, a value that is quite similar to the energy difference between the *relaxed* α- and β-structures. Therefore, the present calculations confirm the assumed *major intrinsic stability* of the α organization of M and O atoms in the $M_{12}O_{36}$ cage.

Table 2. Energy Decomposition for a Series of Keggin Molecules α/β-$[XW_{12}O_{40}]^{n-}$ with Absolute Values for α-Isomers and Relative Values for β-Isomers Listed in eV

isomer	X	steric repulsion	orbital interactions	total interactions	sum of fragments
α	P	−10.23	−14.61	−24.84	−429.6
	Si	−13.62	−26.30	−39.92	−414.0
	Al	−8.34	−43.03	−51.37	−395.9
	As	−7.69	−15.78	−23.47	−425.1
	Ge	−9.28	−29.33	−38.61	−409.9
	Ga	−5.54	−44.38	−49.92	−391.1
β	P	+0.12	−0.29	−0.17	+0.44
	Si	+0.26	−0.03	+0.24	+0.02
	Al	+0.35	−1.02	−0.67	+0.33
	As	+0.12	−0.19	−0.07	+0.23
	Ge	+0.28	−0.20	+0.08	+0.14
	Ga	−0.05	−0.72	−0.78	+0.59

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(32) The Deformation Energy (DE) is defined as the energy difference between the fragment energy and the energy of the corresponding subunit in its optimal, fully relaxed conformation. The DE for $M_{12}O_{36}$ therefore represents the energy required for transforming this cage from its hypothetical equilibrium structure to the geometry it has in the Keggin anion.

Table 3. Comparison of the Orbital Interaction (OI) Term and the $M_{12}O_{36}$ Cage Polarization Energy

			cage polarization[a]		
	isomer	OI	formal	Mulliken	CHelpG
$[PW_{12}O_{40}]^{3-}$	α	−14.6	−13.9	−12.2	−12.4
	β	−14.9	−14.2	−12.5	−12.5
$[SiW_{12}O_{40}]^{4-}$	α	−26.3	−24.2	−22.3	−22.8
	β	−26.3	−24.4	−22.7	−23.0
$[AlW_{12}O_{40}]^{5-}$	α	−43.0	−37.6	−35.4	−38.3
	β	−44.0	−38.1	−35.7	−38.6

[a] Cage polarization energies correspond to the stabilization energy of $M_{12}O_{36}$ when this cage encapsulates an $[XO_4]^{n-}$ anion, which atoms were replaced by point charges, Mulliken, formal, or CHelpG.

FEs by themselves cannot explain the trend of the α/β relative stability in the series in Table 1. The inversion in the stability of these two isomers has to be actually due to the FIE. For all the systems studied, the steric component of this term is dominated by the attractive electrostatic interaction that always overcomes the Pauli repulsion. Neither is the SR term responsible for the α/β inversion since in general it favors the α-isomer. Only for the Ga derivative was the SR contribution found slightly less repulsive for the β-isomer. The orbital interaction (OI) term, which represents the stabilizing energy when the electron density relaxes, is, therefore, the only contribution that is always more stabilizing for the β-isomer. This term, as well as the Pauli and electrostatic contributions to the SR term, increases monotonically with *n*, the negative charge of the anion $[XM_{12}O_{40}]^{n-}$. For X = P ($n = 3$) the SR term is −10.2 eV. Despite being very large, this energy is smaller than the energy that results from orbital mixing (OI energy), which reaches values of up to −14.6 eV, and increases by more than 10 eV when $n = 4$ and by more than 25 eV for $n = 5$. It has been mentioned above that the OI term includes the $[XO_4]^{n-} \rightarrow M_{12}O_{36}$ charge transfer (CT) and the polarization of both fragments. The electronic transfer from the neutral cage to the central tetrahedron can be neglected. It is not easy to separate these two terms (CT and polarization) in the TS energy decomposition scheme. Some authors have estimated the charge transfer between fragments by selectively removing the virtual orbitals from the molecular orbital fragment set.[33] This method cannot be applied here since it implicitly accepts that the charge is only transferred from the highest occupied orbitals of one of the fragments to the LUMO of the other. Such behavior cannot be assumed in POMs because of the delocalized nature of metallic orbitals.[16]

Alternatively, the polarization energy for cage and tetrahedral fragments can be estimated, substituting the atoms of one or the other fragment by point charges. Three sets of atomic charges (formal, Mulliken, and CHelpG) were used to evaluate the cage polarization by the presence of an $[XO_4]^{n-}$ in its interior. CHelpG charges were calculated to simulate the electrostatic potential generated by the tetrahedral fragment anion.[34] Polarization energies computed with this model are given in Table 3. Several conclusions can be drawn from the values in this table:

(i) the three sets of point charges give similar polarization energies,

(ii) the cage polarization energy is heavily dependent on the anion charge,

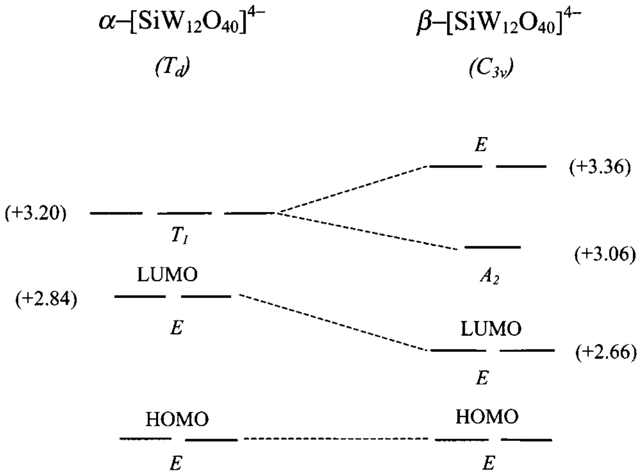

Figure 2. Symmetry descent representation from T_d to C_{3v} point group for the frontier molecular orbitals for α- and β-species of $[SiW_{12}O_{40}]^{4-}$. The lowest (empty) metal orbitals of a fully oxidized Keggin anion are symmetry-adapted d_{xy}-like orbitals of the $M_{12}O_{36}$ framework.[16] Values (in eV) are relative to the HOMO energy.

and (iii) for all three sets of point charges, the polarization energies are slightly greater for β- than for α-cages (this difference is larger for the aluminum derivative).

Moreover, the parallel behavior of the OI term and the cage polarization contribution and the small difference between these two terms suggest that the cage polarization is, very probably, the dominant contribution in the OI term. In fact, an equivalent analysis for $[XO_4]^{n-}$ polarization shows that the energies involved are clearly smaller: they range between 3 and 4 eV for X = P and Si. The corresponding computed value for $[AlO_4]^{5-}$ is very high, about 18 eV. This considerable amount of energy originates in the intrinsic instability of $[AlO_4]^{5-}$ as a free anion. A symptom of this instability is the small energy gap between occupied and unoccupied sets of orbitals for the free $[AlO_4]^{5-}$ anion, which allows these two sets of orbitals to mix easily when the fragment supports an external perturbation such as the electric field generated by the cage. An analysis of the molecular orbitals in the complex does not suggest that there are strong charge transfers from occupied tetrahedron orbitals to the virtual cage orbitals. It is worth mentioning that for X = Al there is a *nonnegligible mixing* between orbitals of both fragments. However, the charge transfer appears in multiple small contributions and this phenomenon is difficult to quantify. All these results seem to confirm, first, the validity of the clathrate model for the Keggin anion, which can therefore also be formulated as $[XO_4]^{n-}@M_{12}O_{36}$ and, second, the higher polarizability of the β-framework. The distinct polarizability of α- and β-neutral $M_{12}O_{36}$ cages is directly related to the different HOMO-LUMO (H-L) gap for the two clusters (Figure 2), which makes the orbital mixing and further cluster stabilization greater for the β-isomer. The H-L gap is smaller when going from the α- to the β-form because of a symmetry reduction; the LUMO and LUMO+1 in the T_d symmetry belong to the E and T_1 irreducible representations, respectively, while in the C_{3v} point group the symmetries of these molecular orbitals are E and E + A_2. The combination of these E symmetry orbitals stabilizes one of them (LUMO) by 0.20 eV, and slightly destabilizes the other by 0.14 eV. These values correspond to the silicotungstate anion but the same tendency was found for the other systems. The computed gap is ~2.8 eV for α-tungstates, on average 0.18 eV higher than in the β isomer. For molybdates, the gap is notably smaller for both isomers, on average 2.0 eV for α and 1.85 eV for β. Summarizing, two opposing forces compete in

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(33) See for example: Gonzalez-Blanco, O.; Branchadell, V. *Organometallics* **1997**, *16*, 475. Gonzalez-Blanco, O.; Branchadell, V. *Organometallics* **1997**, *16*, 5556. Gonzalez-Blanco, O.; Branchadell, V.; Gree, R. *Chem. Eur. J.* **1999**, *5*, 1722−1727. Gonzalez-Blanco, O.; Branchadell, V. *Organometallics* **2000**, *19*, 4477−4482.

(34) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

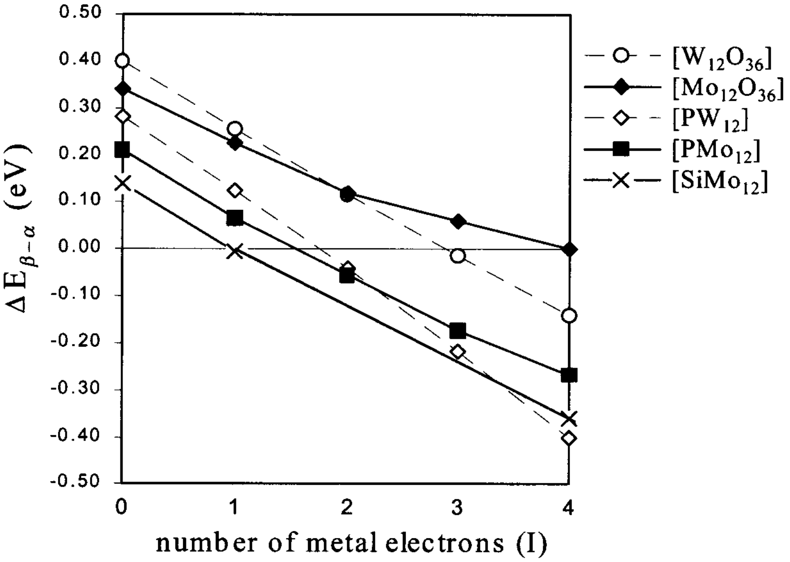

Figure 3. Computed $\beta-\alpha$ energies (in eV) for a series of Keggin anions and cages in several reduction states.

the formation of Keggin anions: the major intrinsic stability of the α-organization, which favors the α-isomer, and the greater polarizability of the β-cage during the process of building the Keggin framework. This latter factor is probably responsible for the greater stability of the β-isomer in highly charged, fully oxidized anions.

α/β-Stability in Reduced Clusters. Let us now analyze the role of metallic electrons in the α/β-equilibrium. A Keggin framework has a special ability to accept electrons without decomposing. Actually, the Keggin core is a *reservoir* of electrons that can undergo many electron reduction processes without significantly deforming the framework.[20] It is well-known that the β-isomer reduces at more positive potentials[13] and, consequently, reduced β-isomers increase their relative stability in relation to α-isomers. Calculations carried out on the single-reduced anions $[XW_{12}O_{40}]^{(n+1)-}$, X = P, Si, and Al, completely agree with this observation since the computed $\Delta E_{\beta-\alpha}$ are more favorable to the β-isomer than in the oxidized parents. Thus, for X = Al, the reduction increased the relative stability of the β-isomer by 0.22 eV and the $\Delta E_{\beta-\alpha}$ for this reduced species was −0.57 eV. For X = P and Si, the reduction also increased the stability of the β-isomer quite considerably but the α-form was still more stable. This considerable stabilization of β-isomers can also be explained by the lower energy of their LUMO (Figure 2).

To determine the factors that affect stability inversion in reduced species—that is, the number of metal electrons, the central ion, and the addenda—we calculated $\Delta E_{\beta-\alpha}$ for a series of reduced Keggin anions and $M_{12}O_{36}$ cages as a function of the number I of metal electrons, where I was between 0 and 4. Figure 3 shows this dependence for the clusters studied. Let us look first at $W_{12}O_{36}$. Although in the neutral cluster the α-isomer is initially the most stable by 0.4 eV, after the third reduction both clusters have similar energies ($\Delta E_{\beta-\alpha} = -0.02$ eV). And when the orbital of E symmetry is filled ($I = 4$), the stability of the β-cage is 0.14 eV higher. There is almost a linear dependence between this energy difference and the number of metal electrons. When a $[PO_4]^{3-}$ is encapsulated in the interior of the cage, the $\Delta E_{\beta-\alpha}$ values shift toward lower energies, which confirms once again that the presence of an anion inside the cage favors the stability of the β-isomer. Thus, for the four-times-reduced $[PW_{12}O_{40}]^{7-}$ complex, the β-isomer is more stable by 0.40 eV. In fact, the α/β-inversion in the $PW_{12}O_{40}$ framework occurs for $I = 2$ but the energy difference is only 0.04 eV.

In general, reduced molybdates behave like their corresponding tungstates but there are some significant differences. Perhaps the greatest of these is that *absolute* energy differences between the two isomers are smaller. This can be seen by the smaller slope in Figure 3. Let us take $Mo_{12}O_{36}$; for $I = 0$, the α-form is, as in the homologous tungstate, the lowest in energy, but in the molybdate cluster the energy difference between the two forms is 0.06 eV smaller ($\Delta E_{\beta-\alpha} = 0.34$ eV). The reduction increases the relative stability of the β-isomer. However, the increase in stability of this isomer is not enough to induce an inversion of the α/β-stability in the isolated $Mo_{12}O_{36}$ cage. The H-L energy gap also makes it possible to rationalize the different behavior of molybdates and tungstates. Although the descent from T_d to C_{3v} symmetry lowers the H-L gap by 0.14 eV for $W_{12}O_{36}$ and by 0.13 eV for the molybdate cage—a smaller but very similar value—this difference tends to be larger between tungstates and molybdates when metallic electrons are added. For the 4-electron-reduced cages, the H-L gaps are 0.28 and 0.18 eV for W and Mo cages, respectively. It is worth noting from Figure 3 that the encapsulation of a $[PO_4]^{3-}$ produces almost exactly the same stabilization in both cages. Therefore, as in the isolated cage, the values for $\Delta E_{\beta-\alpha}$ vary less in the phosphomolybdate cluster than in the analogous tungstate (between +0.21 and −0.27 eV for M = Mo and between +0.28 and −0.40 eV for M = W). To our knowledge, the four-times-reduced β-phosphotungstate Keggin cluster has not been reported yet. However, the structure of α-$[PMo_{12}O_{40}]^{7-}$ has been characterized by X-ray spectroscopy. From the structural properties of this cluster, Pope and co-workers proposed no localization of the four metal electrons.[9a] Present calculations confirm this interpretation since the degenerate E orbital, which accommodates the four additional electrons, is delocalized over the 12 molybdates.

The case in which $Mo_{12}O_{36}$ encapsulates a $[SiO_4]^{4-}$ should be mentioned in particular. The larger negative charge in the internal tetrahedron increases the relative stability of the β-isomer by shifting the $\Delta E_{\beta-\alpha}$ energies toward even lower values. A direct consequence is that, for $[SiMo_{12}O_{40}]$, the α/β-inversion occurs for $I = 1$. This result completely agrees with the recent study reported by Sécheresse and co-workers,[15] who provided evidence for the greater thermodynamic stability of the β-[$SiMo_{12}O_{40}$] isomer even when the cluster has *one* or *two* metallic electrons. When the internal tetrahedron contains a [AlO_4]$^{5-}$ the β-isomer is more stabilized than the β-isomer in the analogous silicon derivative ($\Delta E_{\beta-\alpha} = -0.1$ eV). But both compounds require one-electron reduction undergo inversion of stability. This behavior is slightly different from that of the homologous tungstate for which the inversion occurs for $I = 0$.

It should be remarked that all the energies shown in Figure 3 were computed retaining T_d and C_{3v} symmetries for α- and β-isomers, respectively. The partial occupation of the doubly degenerate orbitals (Figure 2) might yield, however, a Jahn–Teller (JT) distortion for one- and three-times-reduced anions in both isomers. Keggin clusters are rigid molecules and, in general, JT distortions are quite small. Previous calculations on α-[$Co^{III}W_{12}O_{40}$]$^{5-}$, a cluster with a paramagnetic heteroatom, showed that the distortion of the geometry from T_d to D_{2d} only stabilizes the anion in ~500 cm^{-1}.[16] We have checked the eventual importance of JT distortions in the α/β-equilibrium of heteropolyblues performing geometry optimizations for the single reduced [$PW_{12}O_{40}$]$^{4-}$ cluster, under D_{2d} and C_s symmetry restrictions for α- and β-isomers, respectively. By means of the strategy suggested by Daul and co-workers,[35] we got consistent energies for the various points on the adiabatic potential surface associated with the JT distortions. The orbital of *e* symmetry in T_d splits into a_1 and b_1 in D_{2d}, therefore there are two ways for accommodating one electron, $a_1^1\ b_1^0$ and $a_1^0\ b_1^1$. The result of optimizing these configurations was two slightly distorted structures, in which the most stable is ~1.1 kcal mol^{-1} lower in energy than the T_d geometry. For the β form the same process can be followed and the stabilization reached is ~1.3 kcal mol^{-1}. Furthermore, for two-times-reduced structures, even a minor distortion should occur. Thus, it can be concluded that the $\Delta E_{\beta-\alpha}$ values of Figure 3 will remain almost unchanged if heteropolyblues with unpaired electrons are optimized with lower symmetry than that of the fully oxidized parents.

Finally, we would like to point out that the reduction of the cluster does not change the net charge on the internal tetrahedron since the additional electrons go to addenda symmetry-adapted orbitals. For example, for [$PW_{12}O_{40}$]$^{4-}$ the unpaired electron is completely localized on the outer sphere and consequently the net charge on the internal tetrahedron is only 0.03 e larger than in the parent oxidized cluster. Therefore, according to the clathrate model, fully oxidized Keggin anions may also be formulated as [XO_4]$^{n-}$@$M_{12}O_{36}$ and the associated reduced clusters as [XO_4]$^{n-}$@[$M_{12}O_{36}$]$^{I-}$, where I is the reduction state.

Conclusions

We performed DFT calculations on a series of Keggin anions [$XM_{12}O_{40}$]$^{n-}$, where M = W or Mo and X is a main group element, to determine which factors govern the relative stability of α- and β-isomers in Keggin structures. The hypothesis[17] that a fully oxidized Keggin anion may be viewed as a [XO_4]$^{n-}$ ion encapsulated by a neutral $M_{12}O_{36}$ was fully confirmed by the calculations, and this model, together with an energy partitioning analysis, enabled us to rationalize the thermodynamic α/β-stability in these important compounds. Although the relative stability of these isomers is governed by a variety of factors, this study illustrates that most of them are related to the relative energy of metallic $M_{12}O_{36}$ orbitals. The calculations led us to formulate the following general rules: (i) In fully oxidized anions the α-isomer is, in most cases, the most stable due to the greater intrinsic stability of the α-organization of d^0 metals and oxo ligands. (ii) The relative stability of the β-isomer increases as the charge of the cluster localized in the internal tetrahedron increases. This behavior originates in the higher polarizability of β-cage. (iii) There is a strong relationship between the presence of metallic or blue- electrons in the addenda and the increase in the β-isomer stability. (iv) The energies of α- and β-molybdo derivatives are always more similar than the energies of homologous tungstates. (v) Energy differences between both isomers are larger when X is a third row element.

The α-isomer, therefore, displays the largest stability for X = P, M = W, and $I = 0$ (I is the number of metal electrons). $\Delta E_{\beta-\alpha}$ for this cluster was computed to be +0.28 eV. This energy becomes negative for the highly charged fully oxidized systems [$AlW_{12}O_{40}$]$^{5-}$ and [$GaW_{12}O_{40}$]$^{5-}$ (−0.35 and −0.19 eV, respectively). For the four-times-reduced clusters [$PW_{12}O_{40}$]$^{7-}$ and [$SiMo_{12}O_{40}$]$^{8-}$, the β-isomer is ~0.4 eV more stable. Although the largest relative stability of the β-isomer was found for the single reduced cluster of the tungstoaluminate derivative (−0.57 eV), successive reductions of this cluster should increase this energy. All these different properties can be inferred from the symmetry reduction when going from α to β and the subsequent decrease in energy of the LUMO, which is responsible for the changes in the relative stability for these two isomers. Current calculations, however, cannot explain why α-reduced molybdates tend to isomerize to β but α-reduced tungstates do not. It is likely that this behavior will only be understood by taking kinetic considerations into account.

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