CHAPTER 4

Electronic Properties of Keggin anions

The Keggin anion, of general formula $XM_{12}O_{40}^{n-1}$, has been the focus of much effort for the understanding of the chemistry of POMs. A simple synthetic route as well as the flexibility of its chemical composition makes this compounds the main reference for the knowledge of the general behaviour of metal-oxide clusters and, especially, heteropolyanions. Since 1933, when J. F. Keggin resolved for the first time the X-ray structure of such a molecule, many experiments have detached all the properties and characteristics of this framework. In this chapter we focus on a couple of subjects intimately related to the electronic structure of these anions. Firstly, the structural isomerism occurring in $XM_{12}O_{40}^{n-}$ compounds and the relative stability of the most common forms, namely, α and β . These two isomers are ancient subjects in the literature, and it was established an order of stability for them, although it was shown recently that, in some cases, an inversion of this trend can be observed. We provide here general guidelines to unravel when and why this inversion can take place. The second part of the chapter concerns the chemical effects of metal substitution, one of the most exploited ways to vary the properties of POMs. The main goal here is to connect the features of trisubstituted Keggin anions, SiM₃W₉O₄₀^{*m*-}, with the physical nature of M. For this purpose, the molecular orbitals interpretation is a useful tool that provides complementary information for experimentalists about the affinity to extra electrons and their localisation in the metal-oxide framework.

4.1. Study of the Relative Stability of Single-addenda α/β-Keggin Anions

Historical perspective

The general features of the Keggin anion, $[XM_{12}O_{40}]^{n-}$, were introduced in the previous chapter, stressing on the electronic structure, the composition of the frontier Molecular Orbitals and the clathrate-type structure of the framework. We only were concerned with the α form of the molecule, of T_d symmetry, in which all the metal centres are equivalent. Baker and Figgis¹ proposed that the β structure might be derived from 60° rotation of one of the M₃O₁₃ triad about a 3-fold axis of the α anion. Three additional isomers, γ , δ and ε , were postulated resulting from 60° rotation of the remaining triads (Figure 4.1).²

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 isomerisations on Keggin heteropolytungstates and -molybdates all occur in the $\beta \rightarrow \alpha$ direction.^{3a-c} Starting from the highly-symmetric α form, the other four isomers are formally obtained by successive 60° rotations of the four M₃O₁₃ triads about the three-fold axis of symmetry of the α structure. Amongst these five rotational isomers of the Keggin anion, α and β are the most common in the literature as a consequence of their major stability. Conventionally, the α structure appears to be the most stable. The first X-ray characterisation for a β isomer was reported in 1973 for the potassium salt of $[SiW_{12}O_{40}]^{4-.4}$ Later, Matsumoto *et al.*⁵ showed that this compound is kinetically stable. Even though, Weinstock and co-workers⁶ reported a detailed study on the equilibrium between α and β isomers for several fully oxidised Keggin anions. 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 conditions of the solution. A relevant ordering of these β -polyanions stability with X = Al(III) > Si(IV) > P(V) is found, confirming Pope's hypothesis.⁷ Previous theoretical calculations carried out by our group⁸ on α -Keggin anions supported the hypothesis⁹ that a Keggin anion may also be viewed as a neutral M₁₂O₃₆ cage that encapsulates the internal charged $[XO_4]^{n-}$ subunit.



Figure 4.1. Polyhedral representation of the five rotational isomers of the Keggin anion. Shaded are the edge-sharing octahedra involved in the isomerism, which rotate 60° about the four 3-fold axis of the α form.

In the present section we make use of the clathrate model introduced in chapter 1 to study the Keggin molecule. The discussion is addressed to know in which situations this inversion of the traditional stability can occur and what are the factors governing it. The DFT calculations shown were carried out on a series of Keggin anions to analyse the different factors that govern the relative stability of its α and β isomers.

To our knowledge, only a few more β structures have been characterised by X-ray: the fully oxidised tungstates $[GeW_{12}O_{40}]^{4-,10}$ $[AIW_{12}O_{40}]^{5-6}$ and the four-times reduced molybdates $[PMo_{12}O_{40}]^{7-11a}$ and $[AsMo_{12}O_{40}]^{7-.11b}$ Somewhat more abundant are the structures for β mixed-

addenda complexes.¹² An interesting point concerning structures with only one addenda metal type is that reduced β isomers can be more stable than the corresponding α isomers, because β structures reduce at slightly more positive potentials than α structures.^{5,7} Tézé *et al.*¹³ showed that there is a direct relationship between the oxidising character of Keggin POMs and the number of rotated triads in the M₁₂O₃₆ framework: that is to say the reducibility increases in the order $\alpha < \beta < \gamma$. Related to this point, Sécheresse and co-workers reported hydrothermal preparations of reduced β -SiMo₁₂ derivatives in low reduction states.¹⁴

DFT study of fully oxidised clusters

Geometry optimisations under T_d and $C_{3\nu}$ 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, Ga and M = W, 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 stabilises in the order Al(III) > Si(IV) > P(V) and Ga(III) >Ge(IV) > As(V) for both W and Mo addenda atoms (Table 4.1). The largest stability in favour 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 aluminium and gallium tungsto-derivatives, in which the stability is inverted by $-0.34 \text{ eV} (-7.8 \text{ kcal mol}^{-1})$ and by $-0.18 \text{ eV} (-4.2 \text{ kcal mol}^{-1})$. respectively. Only the values for the silico- and germano-tungstates 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.⁶ 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 isomerisation processes are dependent upon the temperature, the solvent, the ionic strength and the nature of the countercation. Therefore, this suggests that absolute Gibbs isomerisation energies in solution and the computed beta-alpha energies, based on isolated anions, are not directly comparable.

X	М	Isomer	$d(X-O_4)$	$d(O_4-M)$	d(M-M)	$q(XO_4)$	ΔE	$\beta - \alpha^{a}$
Р	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		

Table 4.1. Relevant mean distances, (XO₄) Mulliken charges and $\beta - \alpha$ energy differences calculated for a series of Keggin heteropolyanions.

a) Values in parentheses are for monoreduced species.

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 0.07eV 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 4.1 show that the total charge on the [XO₄] 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 according to Mulliken analysis only ~0.5 electrons are added to [XO₄]^{*n*-}, while the remaining half electron is expected to be over the outer sphere. This general behaviour 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}W₁₂O₄₀]⁵⁻ and [Co^{III}W₁₂O₄₀]⁵⁻ and of -4.5 e in [Co^{III}W₁₂O₄₀]^{6-.8}

In order 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.*,¹⁵ that is an adaptation of Morokuma's¹⁶ wellknown decomposition scheme.

$$E(Keggin) = E(M_{12}O_{36}) + E(XO_4^{n}) + FIE$$

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:

$$FIE = SR + OI$$

(see chapter 2 for further details). The contributions to the *FIE* are shown in Table 4.2.

		Steric	Orbital	Total	Sum of	
Isomer	X	Repulsion	Interactions	Interactions	fragments	
α	Р	-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	Р	+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	

Table 4.2. Energy decomposition for a series of Keggin molecules α/β - $[XW_{12}O_{40}]^{n-}$. Absolute values for α isomers and relative values for β isomers are listed in eV.

An analysis restricted to *FE* shows that this term always slightly favours 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 Energy¹⁷ (*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 beta cages. Such notable *DEs* originate in the change in the cage geometry when the relaxed M₁₂O₃₆ 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 -W₁₂O₃₆ 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 organisation of M and O atoms in the M₁₂O₃₆ cage.

FEs by themselves cannot explain the trend of the α/β relative stability in the series in Tables 4.1 and 4.2. 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 favours the α isomer. Only for the Ga derivative the SR contribution was found slightly less repulsive for the β isomer. The orbital interaction (OI) term, which represents the stabilising energy when the electron density relaxes, is, therefore, the only contribution that is always more stabilising for the β isomer. This term, as well as the Pauli and electrostatic contributions to the SR term, increase 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 polarisation 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 polarisation) 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.¹⁸ 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 behaviour cannot be assumed in POMs because of the delocalised nature of metallic orbitals.⁸

Alternatively, the polarisation 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 polarisation 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.¹⁹ Polarisation energies computed with this model are given in Table 4.3.

Table 4.3. Comparison of the total Orbital Interaction (*OI*) term with the cage $(M_{12}O_{36})$ polarisation energy for the series of X = P, Si and Al. The cage polarisation terms were computed substituting the internal tetrahedron by a set of point charges in the positions of the nuclei. Three types of charges were taken into account for more generality of the results.

	Isomer	OI	Cage Polarisation ^{a)}		
			Formal	Mulliken	CHelpG
$\left[PW_{12}O_{40}\right]^{3-}$	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
[A]W ₁₂ O ₄₀] ⁵⁻	α	-43.0	-37.6	-35.4	-38 3
	β	-44.0	-38.1	-35.7	-38.6

a) Cage polarisation energies correspond to the stabilisation 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.

Several conclusions emerge from the values in this table.

- (*i*) the three sets of point charges give similar polarisation energies,
- *(ii)* the cage polarisation energy is heavily dependent on the anion charge and
- (*iii*) for all three sets of point charges, the polarisation energies are slightly greater for β than for α cages and this difference is larger for the aluminium derivative.

Moreover, the parallel behaviour of the *OI* term and the cage polarisation contribution and the small difference between these two terms

suggest that the cage polarisation is, very probably, the dominant contribution in the OI term. An equivalent analysis for $[XO_4]^{n-}$ polarisation shows that the energies involved are clearly smaller: they range between 3-4 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 non-negligible 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 $[XO_4]^{n-}$ $(a)M_{12}O_{36}$ and, second, the higher polarizability of the β framework. The distinct polarizability of α and β neutral M₁₂O₃₆ cages is directly related to the different H-L gap for the two clusters (Figure 4.2), which makes the orbital mixing and further cluster stabilisation 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 $C_{3\nu}$ point group the symmetries of these molecular orbitals are e and $e + a_2$. The combination of these two e orbitals stabilises one of them (LUMO) by 0.20 eV, and slightly destabilises the other by 0.14eV. 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 . Summarising, two opposing forces compete in the formation of Keggin anions: the major intrinsic stability of the α organisation, which favours 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 oxidised anions.

α/β Stability in Reduced Clusters

Let us now analyse 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^{7a} 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 $\Delta E_{\beta-\alpha}$ is more favourable to the β isomer than in the oxidised 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 X = Si, the reduction also increased the stability of the β isomer quite considerably but the α form was still more stable. This considerable stabilisation of β isomers can also be explained by the lower energy of their LUMO (Figure 4.2).



Figure 4.2. Symmetry descent representation from T_d to $C_{3\nu}$ point groups for the frontier orbitals region of the α and β isomers of $[SiW_{12}O_{40}]^{4-}$. The values are relative to the energy of the HOMO.

In order to determine the factors affecting the stability inversion in the addenda- we calculated the parameter $\Delta E_{\beta-\alpha}$ 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 4.3 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 favours 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 PW₁₂O₄₀ framework occurs for I = 2 but the energy difference is only 0.04 eV.



Figure 4.3. Representation of the computed $\Delta E_{\beta-\alpha}$ values for a series of Keggin anions and cages in several reduction states. **1**: Mo₁₂O₃₆, **2**: W₁₂O₃₆, **3**: PO₄³⁻@Mo₁₂O₃₆, **4**: PO₄³⁻@W₁₂O₃₆, **5**: SiO₄⁴⁻@Mo₁₂O₃₆.

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 in the smaller slope in Figure 4.3. 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 Mo₁₂O₃₆ cage. The H-L energy gap also makes it possible to rationalise the different behaviour of molybdates and tungstates. Although the descent from T_d to $C_{3\nu}$ 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 eV and 0.18 eV for W and Mo cages, respectively. It is worth noting from Figure 4.3 that the encapsulation of a $[PO_4]^{3-}$ produces almost exactly the same stabilisation 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 eV 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 beta phosphotungstate Keggin cluster has not been reported yet. However, the structure of α -[PMo₁₂O₄₀]⁷⁻ has been characterised by X-ray spectroscopy.²¹ From the structural properties of this cluster, Pope and co-workers proposed no localisation of the four metal electrons.^{11a} Present calculations confirm this interpretation since the degenerate e orbital, which accommodates the four additional electrons, is delocalised over the twelve 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 coworkers¹⁴, 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 $[AIO_4]^{5-}$ the beta isomer is more

stabilised than the beta isomer in the analogous silicon derivative ($\Delta E_{\beta-\alpha} = -0.1 \text{ eV}$). But both compounds require one-electron reduction undergo inversion of stability. This behaviour 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 4.3 were computed retaining T_d and $C_{3\nu}$ symmetries for α and β isomers, respectively. The partial occupation of the doubly degenerate orbitals (Figure 4.2) might yield, however, a Jahn-Teller (J-T) distortion for oneand three-times-reduced anions in both isomers. Keggin clusters are rigid molecules and, in general, J-T distortions are quite small. Previous calculations on α -[Co^{III}W₁₂O₄₀]⁵⁻, a cluster with a paramagnetic heteroatom, showed that the distortion of the geometry from T_d to D_{2d} only stabilises the anion in 1.4 kcal mol^{-1.8} We have checked the eventual importance of J-T distortions in the α/β equilibrium of heteropolyblues performing geometry optimisations 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,²² we got consistent energies for the various points on the adiabatic potential surface associated with the J-T distortions. The orbital of e symmetry in T_d splits into a_1 and b_1 in D_{2d_2} 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 optimising these configurations were 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 beta form the same process can be followed and the stabilisation 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 4.3 will remain almost unchanged if heteropolyblues with unpaired electrons are optimised with lower symmetry than that of the fully oxidised 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, which are centred in the outer metal-oxide core. For example, for $[PW_{12}O_{40}]^{4-}$ the unpaired electron is completely localised on the outer sphere and, consequently, the net charge on the internal tetrahedron is only 0.03 e larger than in the parent oxidised cluster. Therefore, according to the clathrate model, fully oxidised 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.

As concluding remarks, we claim that the hypothesis⁹ that a fully oxidised 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 rationalise 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 oxidised anions the α isomer is, in most cases, the most stable due to the greater intrinsic stability of the α organisation of d⁰ metals and oxo ligands,
- *ii)* the relative stability of the β isomer increases as the charge of the cluster localised in the internal tetrahedron increases. This behaviour 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 -molybdoderivatives are always more similar than the energies of homologous tungstates,
- *v)* the 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 oxidised systems $[AIW_{12}O_{40}]^{5-}$ 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 isomerise to β but α reduced tungstates do not. It is likely that this behaviour will only be understood by taking kinetic considerations into account.

4.2. Mixed-addenda Keggin Anions: A Study of the Redox Properties

Experimental studies

At the end of the 1960's, the work of C. Tourné and G. Tourné²³ created interest in how addenda substitution can affect POMs. Their work permitted a rapid growing of the research in this field in the subsequent decades. Klemperer and co-workers,^{9,24} with the aim of obtaining suitable polyoxometalate-supported organometallic derivatives, carried out most research on the Lindqvist isopolyanion. Mixed-addenda HPA research is even more extensive since Keggin- and Dawson-type derivatives can give rise to a greater number of stoichiometries, shapes and aggregates. The addenda W^{VI}, Mo^{VI}, V^V and Nb^V and the main group heteroatoms P and Si are the most common metal ions in Keggin and W-D HPAs, but other fourth (Ti,^{35e,25} Zr²⁶), fifth (Ta)²⁷ and sixth (Cr)²⁸ row transition metal elements have been incorporated into the POM framework. Lanthanides, actinides²⁹ and non-transition metal derivatives have also been reported.^{35b,g,30} A considerable number of traditionally paramagnetic atoms have been included in the framework of Keggin and W-D anions, as well as in the sandwich-type molecules³¹ derived from them. This is a growing area in which rational methods for systematically modifying POM structures have still to be fully developed.³²

In this section, the general properties of $[SiM_3W_9O_{40}]^{n-}$ Keggin clusters is discussed. A family of compounds with M = Mo, V and Nb were computed and their redox properties analysed. Firstly, the structural characteristics and qualitative results on the electronic structure are discussed. For a quantitative description of the redox properties of this family of molecules, we studied the reduced clusters. Fundamentally, the goal of this section is to discuss the energies of reduction in relation to the substituting element, M. Another relevant feature of these anions is the basicity of their external oxygens. Calculations aimed at describing the

basicity of Keggin anions are presented in chapter 6. The reader shall meet the relationship between the basicity and the ability to dimerise that some clusters have.

Analysis of the geometry and electronic structure of SiM_3W_9 anions

In previous sections we showed that quantum chemistry calculations based on the DFT formalism can be very useful for understanding and rationalising the electronic and magnetic properties of Keggin anions.^{8,33} The systematic study of $[XM_{12}O_{40}]^{n-}$ clusters correctly described the redox properties and their magnetic features.³⁴



Figure 4.4. Polyhedral representation of the mixed-addenda anion, A- α -SiM₃W₉O₄₀, and the parent lacunary form, A- α -SiW₉. The blue polyhedra share corners and contain the M atoms. In the series of molecules discussed here, white polyhedra contain tungsten ions.

Figure 4.4 shows a polyhedral view of a three-times-substituted Keggin tungstosilicate. The chemical composition of the cluster and the shape of the framework define the properties of a POM. For example, the improvement in the catalytic activity of polyanions is closely related to addenda substitution.³⁵ Like in single-addenda clusters, formally two sets of orbitals are identifiable in substituted clusters without paramagnetic ions: a set of doubly occupied MOs, delocalised over the oxo ligands, and a set of unoccupied d-like addenda orbitals that conform the metallic band. For the present discussion about A- α -SiM₃W₉ systems, with M = Mo, V and Nb,

full geometry optimisations were carried out under $C_{3\nu}$ symmetry constraints. We assume that present DFT calculations reproduce the geometry of the heteropolyanions well enough for the purpose of the discussion (see Table 4.4).

	[SiMo ₃ W ₉ O ₄₀] ⁴⁻	$[SiV_{3}W_{9}O_{40}]^{7-}$	$[SiNb_{3}W_{9}O_{40}]^{7-}$
distance			
M-O _{term}	1.74	1.65	1.81
M–M	3.73	3.54	3.77
$M-O_{brid}(M)$	1.91	1.83	1.96
M-O _{brid} (W)	1.93	1.99	2.09
Si–M	3.58	3.58	3.72
M-O _{tetra}	2.39	2.48	2.56
angle			
M-O _{brid} -M	154.5°	150.8°	148.1°

Table 4.4. Structural parameters computed for the SiM_3W_9 clusters discussed in this section. Distances are in angstrom units.

In fact, with the exception of the metal-terminal oxygen bond lengths, that are computed systematically ~ 0.04 Å longer than the experimental ones, the deviations are in average small. They seem to depend on the net charge in the internal tetrahedron, indeed.

From the DFT results obtained for various SiM₃W₉, the empty set of dmetallic orbitals appears, after the addenda substitution, as a mixture of d-W and d-M orbitals. The order, energy and composition of the molecular orbitals strongly depend on M. There is no doubt that the redox properties of the substituted cluster will be governed by the nature of M. Let us analyse the results concerning the H-L gaps in this series of compounds. In the α -XW₁₂, the H-L gap was computed to be ~2.8 eV at the DFT level (section 4.1). This energy decreases to ~2.0 eV in the homologous molybdates. The lower H-L gap in molybdates means that they are, in general, more easily reduced. Hence, for instance, SiMo₁₂ and GeMo₁₂ are more powerful

oxidising agents than the corresponding tungstates by ~ 0.5 V.³⁶ The other fundamental variable that plays an essential role in the oxidant power is the total negative charge of the anion. Pope and Varga³⁷ rationalised the first cathodic potential dependence with the negative charge for Keggin anions (Figure 4.5), where the internal atom X fixes the charge. The potential to be applied for reducing a Keggin anion is linearly dependent with the charge of the anion. Thus, the higher the charge, the stronger the potential. This is an important point to be taken into account when calculating and comparing reduction energies for a set of POMs.



Figure 4.5. Dependence of the first reduction potentials of non-protonated α - $[XW_{12}O_{40}]^{n-}$ clusters (V vs sce) with the charge of the anion. Data extracted from references 7a and 37.

Thus, starting from the single-addenda dodecatungstate, the substitution of three tungsten ions by three molybdenum ions modifies the relative energy of the LUMO from 2.8 eV to 2.5 eV in $A-\alpha$ -SiMo₃W₉ (Figure 4.6). In the mixed-addenda SiMo₃W₉, the LUMO is a degenerate orbital of e symmetry with a larger participation of d-molybdenum orbitals. Since the total charge of the anion does not change, the simple substitution of tungsten by molybdenum increases the oxidising power of the anion. In particular, present DFT calculations indicate that the monoreduction of A- α -SiMo₃W₉

is ~0.4 eV more favourable than that of α -SiW₁₂, a value comparable to the previously reported 0.54 V obtained experimentally.³⁸



Figure 4.6. Energy-scaled MO diagram for α -[SiW₁₂O₄₀]⁴⁻ and the series of A- α -[SiM₃W₉O₄₀]^{*n*-} anions computed for this section. The labelled molecular orbitals are the unoccupied metallic ones. The H-L gaps are showed in eV.

In this series of substituted Keggin anions, the group 5 derivative, A- α -SiV₃W₉, has an H-L gap of 2.21 eV. This is even a lower gap than that computed for A- α -SiMo₃W₉. The LUMO in the vanadium derivative, which is a degenerate orbital of e symmetry, and the LUMO+1, which appears ~2.9 eV from the HOMO, are d_{xy} -orbitals essentially localised on the vanadium centres. This means that the vanadotungstate might preferentially be reduced in the vanadium centres, that is, $V^V \rightarrow V^{IV}$ processes would occur before $W^{VI} \rightarrow W^V$. This result is consistent with the electrochemical data obtained by Hervé and co-workers.³⁹⁻⁴⁰ Results concerning the important matter of the reduction sites in mixed-addenda clusters is also discussed in chapter 5 with the Wells–Dawson anion, in which mixed Mo/V

centres compete for the metallic electrons. Another paradigmatic case is shown in chapter 7, where the localisation of the metallic electrons in a capped system containing V and Mo is studied in deep. It shall be shown that the problems of orbital quasi-degeneration need more complicated ways to be solved.

Finally, the analogous niobium derivative has an H-L gap of 2.92 eV (Figure 4.6), which is somewhat larger than the single-addenda dodecatungstate. This behaviour combined with the higher negative charge of the Nb-substituted derivative means that the substitution of W by Nb always decreases the oxidising power of the anion.

the series of fully oxidised A- α -[SiM ₃ W ₉ O ₄₀] ^{<i>n</i>-} anions computed.				
Anion		% Contribution ^{a)}		
	LUMO	LUMO+1	LUMO+2	
$A-\alpha-[SiV_3W_9O_{40}]^{7-}$	65/10	64/7	69/5	
$A-\alpha-[SiMo_3W_9O_{40}]^{4-}$	46/20	7/57	0/65	

1/63

17/48

7/59

Table 4.5. Percentile contributions to the first three unoccupied metallic orbitals of the series of fully oxidised A- α -[SiM₃W₉O₄₀]^{*n*-} anions computed.

a) In the format (%M)/(%W).

A- α -[SiNb₃W₉O₄₀]⁷⁻

The relative energy and composition of the LUMO is quite well correlated to the electron affinity of each *isolated* M^{n+} ion, which is in the order $Mo^{6+} > V^{5+} > W^{6+} >> Nb^{5+}$. The first reduction potentials are -68.10 eV (Mo^{6+}), -65.72 (V^{5+}), -63.95 eV (W^{6+}) and -49.96 (Nb^{5+}) at the present level of theory. Nb is systematically less willing to gain electrons than any other metal of this series. Figure 4.7 shows the series of reductions starting from the maximum oxidation numbers to the metallic state.



Figure 4.7. First to sixth energies of reduction, in eV, for the addenda cations discussed in this section. The reference oxidation numbers are W^{6+} , Mo^{6+} , V^{5+} and Nb^{5+} . Thus, the x-axis represents the reduction processes *lst*.: $W^{6+} \rightarrow W^{5+}$, *2nd*.: $W^{5+} \rightarrow W^{4+}$, or *lst*.: $V^{5+} \rightarrow V^{4+}$, and so on.

In agreement with these reduction energies, present DFT calculations gave the following LUMO compositions (see Table 4.5): for the niobotungstate, only 7% of Nb and 59% of W contribution. When M = Mo, the sharing of the LUMO is 46/20% for Mo/W and, finally, the LUMO has the largest heteroatom participation, 65%, for SiV₃W₉. The tungsten contribution is 10%. This mixed cluster has the lowest H-L gap.

Unrestricted calculations of single-reduced Keggin anions were performed in order to confirm the predictions made by orbital analysis. J–T effects might take place in monoreduced species since a degenerate e orbital is populated with one electron. Nevertheless, previous calculations on single addenda Keggin anions³³ showed that the stabilisation due to the J–T effect is very small and it has not been considered here.

anions.		
Anion	Spin pole	arisation ^{a)}
	W_9	M_3
$[SiV_{3}W_{9}O_{40} \ 1e]^{8-}$	0.15	1.04
$[SiW_9Mo_3O_{40} \ 1e]^{5-}$	0.20	0.72
$[SiW_9Nb_3O_{40} \ 1e]^{8-}$	0.87	0.13

Table 4.6. Spin polarisations for the series of single-reduced $A-\alpha$ -[SiM₃W₉O₄₀]^{*n*-} anions.

a) $\alpha - \beta$ electrons for nine tungstens and three heteroatoms

Spin polarisation given in Table 4.6 reinforce the qualitative predictions based on the molecular orbitals of the oxidised species, which suggest that the additional electron in the monoreduced species A- α -SiW₉V₃ is delocalised over the three vanadium atoms (0.35 spin alpha electrons per V). Some extra polarisation in the molecule yields a population of 0.012 spin alpha electrons per W. In the analogous molybdate, 70% of the additional electron is distributed among the three Mo centres. Finally, when the substituting addenda is the Nb⁵⁺ ion, the orbitals of the substituting addenda do not participate in the LUMO and the spin density is localised in the W centres in 87%. Although the ionisation energies of isolated metal ions would suggest that the reduction of mixed vanadomolybdates would take place at the molybdenum centres, the extra electron mostly goes to a vanadium atom.^{8,39} Notice in Figure 4.5 that the V orbital is the lowest of the four LUMO. The particular behaviour of the Mo^{6+} and V^{5+} pair arises from the different electronic population of d orbitals in fully oxidised clusters, which is larger for Mo atoms.

We conclude, from the results of this section, that two factors govern the redox properties of a POM: the energy and composition of the lowest unoccupied orbitals, being formally symmetry-adapted d_{xy} -type orbitals developed on the addenda atoms and the total charge of the anion. In the α -XM₁₂ anion, all metals are equivalent and so they all have the same probability of trapping the additional electron when the cluster is reduced. When the ion W⁶⁺ in the 1:12 tungstate is substituted by a more electronegative Mo⁶⁺ ion, the energy of the LUMO decreases and the cluster is more easily reduced, the additional electron going to a Mo orbital. The

same phenomenon takes place when a V⁵⁺ replaces a W⁶⁺: the extra electron goes to the vanadium center. Mixed niobotungstates behave differently since niobium orbitals are energy high lying. They are inserted into the tungsten band and the reduction of SiNb₃W₉ for example, yields the *blue* species SiNb₃W₉1e and not the cluster SiNb^V₂Nb^{IV} W₉.

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