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Theoretical Study of the Relative Stabilities of the α/β_3-$[XW_{11}O_{39}]^{m-}$ Lacunary Polyoxometalates (X = P, Si)

Danielle Laurencin,[†,‡] Anna Proust,[‡] and Hélène Gérard*[,§]

*Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UPMC, Universitè Paris 06,
UMR 7071, F-75005 Paris, France, and Laboratoire de Chimie Théorique, UPMC,
Universitè Paris 06, UMR 7616, F-75005 Paris, France*

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A computational study of the relative stability of the monolacunary Keggin polyoxotungstates α and β_3-$[XW_{11}O_{39}]^{m-}$ (X = P, *m* = 7; X = Si, *m* = 8) was performed. The influence of the nature of different grafted cations and of the central anion XO_4^{n-} on the relative stabilities of the lacunary isomers was analyzed. From these results, an interpretation of the structural difference in the metallic frameworks of α-$[PW_{11}O_{39}\{Ru(DMSO)_3(H_2O)\}]^{5-}$, α-$[PW_{11}O_{39}\{Ru(C_6H_6)(H_2O)\}]^{5-}$, and β_3-$[SiW_{11}O_{39}\{Ru(DMSO)_3(H_2O)\}]^{6-}$ is proposed, and conclusions are drawn as to how to favor the formation of β_3 derivatives in future syntheses.

Introduction

Among the numerous different polyoxometalate structures, Keggin anions, of the general formula $[XW_{12}O_{40}]^{n-}$ [X = P, *n* = 3; X = Si, *n* = 4; further referred to as **1(X)**], have been widely studied from both experimental[1] and theoretical[2] points of view. Five different isomers of **1(X)** (referred to as α, β, γ, δ, and ε), which differ in the arrangement of their oxometallic frameworks and in their physicochemical properties, have been described.

The monolacunary derivatives of **1(X)**, of the general formula $[XW_{11}O_{39}]^{m-}$ [X = P, *m* = 7; X = Si, *m* = 8; further referred to as **2(X)**], have also been extensively used, in particular as robust ligands for various transition metals.[1] Several isomers of **2(X)** have been described[3] (see Figure 1); however, much less is known on the importance of the

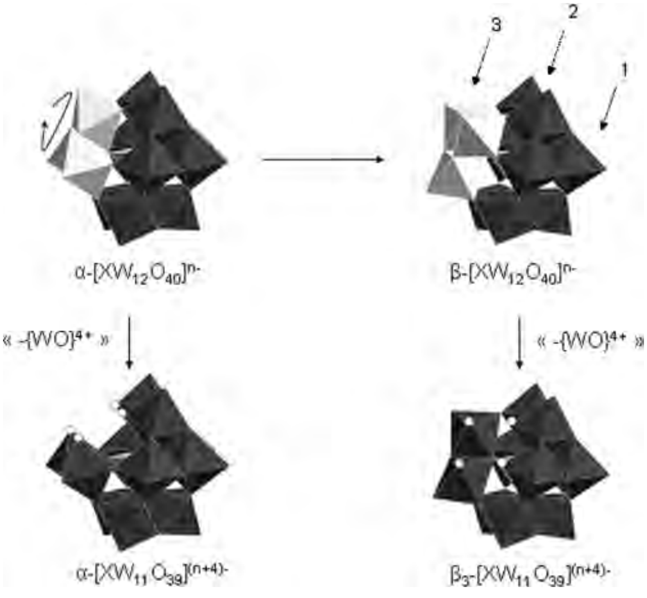

Figure 1. Polyhedral representations of the α (left) and β (right) isomers of $[XW_{12}O_{40}]^{n-}$ (the β form derives from the α one by a 60° rotation of the gray triad about one of the 3-fold axes of α-$[XW_{12}O_{40}]^{n-}$) and of the corresponding α and β_3 isomers of $[XW_{11}O_{39}]^{(n+4)-}$ (with a schematic explanation of the peculiarity of the β_3 form).

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* To whom correspondence should be addressed. E-mail: helene.gerard@upmc.fr.

[†] Current address: Department of Physics, University of Warwick, CV47AL Coventry, U.K.

[‡] Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UPMC, Universitè Paris 06, UMR 7071.

[§] Laboratoire de Chimie Théorique, UPMC, Universitè Paris 06, UMR 7616.

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(3) For a complete description of the α and β isomers of the full polyoxometallates and their monolacunary derivatives, see the Supporting Information.

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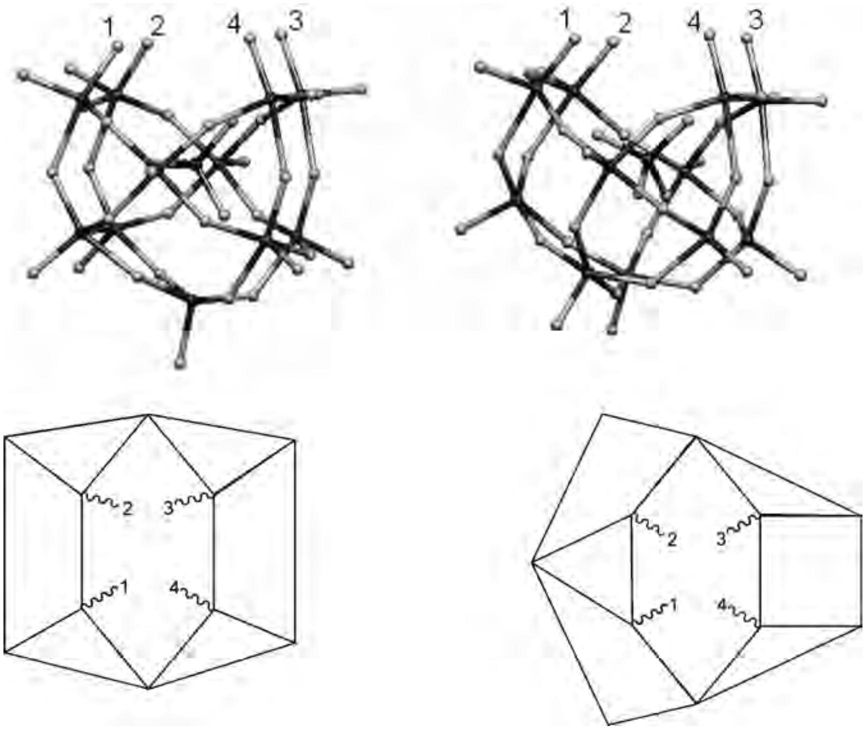

Figure 2. Structures of the α (left) and β_3 (right) isomers of $[XW_{11}O_{39}]^{m-}$ (**2(X)**). A schematic representation of the environment of the lacuna is given below, using zigzag lines to represent the pending W−O bonds and solid lines to represent WOW entities. On this scheme, the solid triangles correspond to the $\{W_3O_9\}$ "triads".

structural arrangement of the oxometallic framework on their relative stability and reactivity, and this issue has never been addressed from a theoretical point of view. One of the reasons for this is probably related to the fact that the vast majority of the **2(X)** structures found in the literature are α-$[XW_{11}O_{39}]^{m-}$ isomers and that very few derivatives of the other **1(X)** isomers have been reported.[4,5] However, among these exceptions, the synthesis of the β_3-$[SiW_{11}O_{39}\{Ru(DMSO)_3(H_2O)\}]^{6-}$ complex [**β_3-3(Si,DMSO)**; DMSO = dimethyl sulfoxide], recently published by Kortz et al.,[5] caught our attention. Indeed, its oxometallic framework contrasts with that of the closely related α-$[PW_{11}O_{39}\{Ru(DMSO)_3(H_2O)\}]^{5-}$ and α-$[PW_{11}O_{39}\{Ru(C_6H_6)(H_2O)\}]^{5-}$ anions [further referred to as **α-3(P,DMSO)** and **α-3(P,C_6H_6)**, respectively],[6,7] which we obtained quasi-simultaneously. Two major factors can be proposed to explain the origin of the skeletal difference. First, the central anion XO_4^{n-} is different (X = P or Si), which could be of importance, given that for complete polyoxotungstates like the Keggin ions **1(X)** the nature of the XO_4^{n-} ion has been shown to have a major impact not only on the stability of the outer $\{W_{12}O_{36}\}$ cage but also on its electronic properties and thus most probably on its grafting abilities.[2,8] Second, the experimental procedures were very different because **α-3(P,DMSO)** and **α-3(P,C_6H_6)** were obtained by grafting of a ruthenium cation on a preformed α-$[PW_{11}O_{39}]^{7-}$ lacunary anion, whereas **β_3-3(Si,DMSO)** was synthesized by self-assembly of smaller sized fragments. However, these hypotheses deserve to be further studied, in order to allow, in the future, the rational preparation of one of the isomers.

The present work thus aims at theoretically investigating the relative stabilities of the α and β_3 isomers of $[XW_{11}O_{39}]^{m-}$, depicted in Figure 2. In a first part, the study focuses on the phosphorus-containing oxoanions α-$[PW_{11}O_{39}]^{7-}$ and β_3-$[PW_{11}O_{39}]^{7-}$ [further referred to as **α-2(P)** and **β_3-2(P)**, respectively], yielding a simple model to understand the impact of different grafted cations on the relative stabilities of the two lacunary isomers. Then, the influence of the central anion XO_4^{n-} is systematically studied by comparing phosphorus-containing species to silicon-containing ones. Finally, a conclusion is drawn on the origin of the structural differences between the oxometallic frameworks of **β_3-3(Si,DMSO)** and **α-3(P,DMSO)** [or **3(P,C_6H_6)**], and the current study is put into perspective with synthetic strategies.

Results and Discussion

Relative Stability of the α and β_3 Skeletons of $[PW_{11}O_{39}]^{7-}$. First, the complete Keggin polyoxotungstates **α-1(P)** and **β-1(P)** were computed. The α isomer is found to be the

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Table 1. Influence of the Nature of the Grafted Fragment on the Energy Difference between the α and β_3 Derivatives, Either in the Gas Phase (Left) or by Modeling Solvation Using a Continuum Model (Right; See the Computational Details Section for References)

			$E(\alpha) - E(\beta_3)$ (kcal·mol^{-1})			
			gas phase		continuous water	
no.	corresponding structure reference	fragment coordinated to the lacuna of $[XW_{11}O_{39}]^{m-}$	P	Si	P	Si
1	**1(X)**	η^4-$\{WO\}^{4+}$	−7.7	−6.9	−7.5	−6.7
2	**2(X)**		−0.1	+2.9	−3.0	+0.2
3	**2′(X,H$_2$O)**	H_2O	+0.6	+2.3	−0.8	+0.3
4	**2′(X,Na)**	η^4-$\{Na\}^+$	−2.1	−2.9	−2.9	−6.0
5	**4(X,DMSO)**	η^4-$\{Ru(DMSO)\}^{2+}$	−3.1	−0.5	−3.3	−1.3
6	**3(X,C$_6$H$_6$)**	η^2-$\{Ru(C_6H_6)(H_2O)\}^{2+}$	−3.9	−2.3	−3.7	−0.6
7	**3(X,DMSO)**	η^2-$\{Ru(DMSO)_3(H_2O)\}^{2+}$	+1.2	+4.6	+2.1	+5.0

Table 2. Evaluation of the Size of the Lacuna of $[XW_{11}O_{39}]^{m-}$ from Average Values of the O···O Distances between the Neighboring Pending O Atoms of the Lacuna

			⟨O···O⟩ distance (Å)			
			α		β_3	
no.	corresponding structure reference	fragment coordinated to the lacuna of $[XW_{11}O_{39}]^{m-}$	P	Si	P	Si
1	**1(X)**	η^4-$\{WO\}^{4+}$	2.65	2.66	2.65	2.67
2	**2(X)**		3.55	3.56	3.70	3.72
3	**2′(X,H$_2$O)**	H_2O	3.60	3.61	3.69	3.73
4	**2′(X,Na)**	η^4-$\{Na\}^+$	3.22	3.24	3.28	3.27
5	**4(X,DMSO)**	η^4-$\{Ru(DMSO)\}^{2+}$	2.92	2.92	2.93	2.93
6	**3(X,C$_6$H$_6$)**	η^2-$\{Ru(C_6H_6)(H_2O)\}^{2+}$	3.13	3.08	3.09	3.10
7	**3(X,DMSO)**	η^2-$\{Ru(DMSO)_3(H_2O)\}^{2+}$	3.31	3.31	3.37	3.34

more stable (Table 1, entry 1), and the energy difference between the α and β isomers amounts to 7.7 kcal·mol^{-1} in the gas phase, which is in agreement with already published results.[2e] Including solvation implicitly via a continuum model does not alter significantly the energy difference, which decreases by only 0.2 kcal·mol^{-1}.[9] Previous studies have suggested that the energy difference between the α and β isomers of **1(X)** anions results from the balance between the intrinsic larger stability of the α-$\{W_{12}O_{36}\}$ cage and the larger polarizability of the β-$\{W_{12}O_{36}\}$ cage.[2c]

When considering the lacunary phosphorus-containing anions **2(P)** (Table 1, entry 2), the energy difference is nearly fully canceled in the gas phase [$E(\alpha) - E(\beta_3) = -0.1$ kcal·mol^{-1}], meaning that α and β_3 frameworks are quasi-isoenergetic. In order to interpret this, the geometries of the lacuna in the complete Keggin anions **1(P)** and the monovacant derivatives **2(P)** were compared. As evidenced in Table 2 (entries 1 and 2), the formation of the lacuna can be associated with the relaxation of the oxometallic framework:[6] the average distance between the neighboring O atoms of the lacuna (i.e., atoms 1 to 4 in Figure 2, further referred as O_{lac} in the text) increases by ca. 1 Å. This relaxation is found to be larger for the β_3 isomer (increase by 1.05 Å) than for the α one (increase by only 0.90 Å), which could thus explain the greater stabilization of the initially more constrained[2] β framework.

However, from an experimental point of view, the β_3 isomers of **2(P)** and **2(Si)** are unstable in solution and convert into the much more stable α isomer.[4a–d] The fact that **α-2(P)** and **β_3-2(P)** have almost the same energy in the gas phase thus tends to show that it is absolutely necessary to take into account the reaction medium in order to better evaluate the relative stability of the two isomers. First, the impact of the solvent itself was considered by introducing it implicitly using a continuum.[2a,e,10] In these conditions, the relative stability of the α species is increased by 2.9 kcal·mol^{-1} (Table 1, entry 2). A second solvent model was considered by including the coordination of one explicit water molecule to the lacuna [yielding structures **2′(P,H$_2$O)** represented in the case of the α isomer in Figure 3].[11] This water molecule is found to be strongly bound to the polyoxometallic framework, since the binding energy in the gas phase is of 21.9 kcal·mol^{-1} for **α-2′(P,H$_2$O)** and 22.9 kcal·mol^{-1} for the β_3 isomer. However, its inclusion in the lacuna does not lead to an increase in the stability of the α form. As a consequence, given the very small variations in the energy difference observed here, including solvation by both one explicit water molecule on the lacuna *and* implicit hydration by a continuum does not alter significantly the relative energy of the α and β_3 isomers, which remain quasi-isoenergetic.

This result cannot fully reproduce the experimental observation of a very strong stability in solution of the α isomer of $[PW_{11}O_{39}]^{7-}$. Given that numerous experimental studies evidence the important role of the counterions in the structural stabilization of polyoxometalates,[4a,b,12,13] inclusion of the effect of the counterions also associated in solution was thus carried out by coordinating a Na$^+$ cation at the center of the lacuna. This leads to stabilization of the α isomer relative to the β_3 one by more than 2 kcal·mol^{-1}, both in the gas phase and in the presence of the continuum model of the solvent (Table 1, entry 4). Even though small

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[9] It is noteworthy that this is significantly smaller than what was obtained in a previously published study, using a different solvation model (see refs 2b and 2f), most probably because of basis set differences.

[10] López, X.; Bo, C.; Poblet, J. *J. Am. Chem. Soc.* **2002**, *124*, 12574.

[11] For an example of explicit water solvation of a complete Keggin anion, see: López, X.; Nieto-Draghi, C.; Bo, C.; Bonet Avalos, J.; Poblet, J. M. *J. Phys. Chem. A* **2005**, *109*, 1216.

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[13] Guo, S.-X.; Mariotti, A. W. A.; Schlipf, C.; Bond, A. M.; Wedd, A. G. *Inorg. Chem.* **2006**, *45*, 8563.

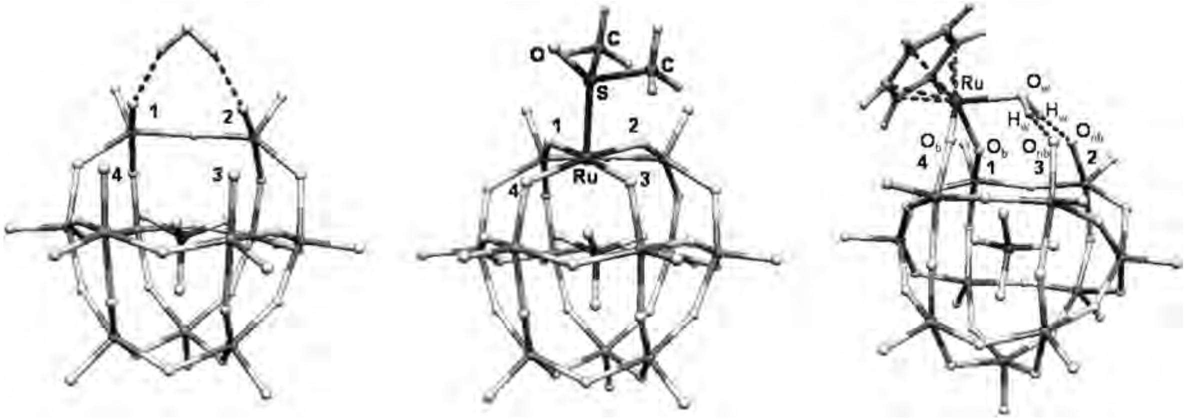

Figure 3. Optimized structure of α-$[PW_{11}O_{39}(H_2O)]^{7-}$ [**α-2′(P,H$_2$O)**] on the left, α-$[PW_{11}O_{39}\{Ru(DMSO)\}]^{5-}$ [**α-4(P,DMSO)**] in the center, and α-$[PW_{11}O_{39}\{Ru(C_6H_6)(H_2O)\}]^{5-}$ [**α-3(P,C$_6$H$_6$)**] on the right, including the numbering of the O atoms, which delimit the lacuna.

and thus not fully satisfying in the absence of vibrational correction, an origin to this effect can be proposed by looking at the values of $O_{lac}\cdots O_{lac}$ average distances, namely, $\langle O_{lac}\cdots O_{lac}\rangle$ (Table 2, entry 4). Indeed, the coordination of Na^+ decreases the distances between neighboring O atoms of the lacuna, with the decrease being more pronounced for the β_3 isomer. The average $O_{lac}\cdots O_{lac}$ distances for both the α and β_3 isomers actually become very similar (3.22 vs 3.28 Å), thus suggesting that the oxoanionic framework adapts the size of the lacuna to the presence of the grafted fragment. As a consequence, the tensions on the β-type framework are partly rebuilt, leading to destabilization of this structure with respect to the α one.

This effect is likely to play an important role during the grafting of metallic fragments on the lacunary Keggin polyoxotungstates: the relative stability of the complexes formed could, at least in part, depend on the amount of constraint that the grafted fragment will impose on the α or β_3 oxometallic framework. This is well evidenced when the α/β_3 energy difference and the values for $\langle O_{lac}\cdots O_{lac}\rangle$ distances in the $[PW_{11}O_{39}]^{7-}$ frameworks grafted by either Na^+ [i.e., structure **2′(P,Na)**], $\{Ru(DMSO)\}^{2+}$ [i.e., structure **4(P,DMSO)**, represented in Figure 3], or $\{WO\}^{4+}$ [i.e., in the complete Keggin anion **1(P)**] are compared. Indeed, when following this series, the average $O_{lac}\cdots O_{lac}$ distance within the lacuna is reduced from 3.22 to 2.92 Å and then 2.65 Å (in the case of the α isomer, with the distances for the β_3 isomer being very close), whereas the energetic preference for the α isomer increases from −2.1 to −3.1 kcal·mol^{-1} and finally −7.7 kcal·mol^{-1} (Tables 1 and 2, entries 1, 4, and 5).

This order of stability, described so far for η^4-coordinated fragments, is also obtained when grafting the $\{Ru(C_6H_6)(H_2O)\}^{2+}$ fragment in a η^2 mode by coordinating the ruthenium to two nonequivalent O atoms of the lacuna (e.g., atoms 1 and 4 in Figure 2 and structure in Figure 3). Indeed, the α isomer is found to be more stable by 3.9 kcal·mol^{-1}, in agreement with the experimental results[6,7] and in line with the decrease in $\langle O_{lac}\cdots O_{lac}\rangle$ distances down to 3.13 Å in the α isomer and 3.09 Å in the β_3 one (Tables 1 and 2, entry 6). However, most surprisingly, a different order of stability of the two isomers is obtained when the isolobal $\{Ru(DMSO)_3(H_2O)\}^{2+}$ fragment is grafted onto the $[PW_{11}O_{39}]^{7-}$ framework. Indeed, the β_3 form is found in this case to be more stable than the α one by 1.2 kcal·mol^{-1}, and this energy preference is increased to 2.1 kcal·mol^{-1} when implicit hydration is included (Table 1, entry 7), which corresponds to an overall relative destabilization of the α isomer by more than 5 kcal·mol^{-1} with respect to the β_3 one.[14]

Because the size of the lacuna in the bidentate grafted species **3(P,DMSO)** is significantly larger compared to **3(P,C$_6$H$_6$)** (Table 2, entries 6 and 7), the increase in the relative stability of the β_3 isomer of **3(P,DMSO)** seems reasonable. However, in order to fully justify why the β_3 isomer of **3(P,DMSO)** actually becomes more stable than the α form and why the a priori similar $\{RuL_3(H_2O)\}^{2+}$ fragments behave differently, other explanations must be sought. To this respect, we can compare more closely the respective structures and spectroscopic characteristics of **3-α(P,DMSO)** and **3-α(P,C$_6$H$_6$)**. Indeed, on the one hand, after geometry optimization in the gas phase, the $Ru\cdots O_b$ distance (see Figure 3 for atom labels) in the DMSO complex **3-α(P,DMSO)** is larger by 0.07 Å than that in the arene (Table 3 and Figure 3). This increase could be due to the larger steric constraints imposed by three DMSO ligands compared to benzene, which force the ruthenium to move away from the polyoxoanionic framework. On the other hand, from an experimental point of view, whereas in the case of the α-$[PW_{11}O_{39}\{Ru(arene)(H_2O)\}]^{5-}$ species free rotation of the aromatic ligand around its C_6 axis is observed in solution by ^{1}H NMR,[6] six distinct signals are observed for the methyl protons of the DMSO ligands in the case of α-$[PW_{11}O_{39}\{Ru(DMSO)_3(H_2O)\}]^{5-}$,[7] meaning that the rotation of the DMSO ligands around the Ru−S axes is significantly hindered. This is all the more noteworthy because free rotation of the DMSO ligand around the Ru−S axis is observed in the case of α-$[PW_{11}O_{39}\{Ru(DMSO)\}]^{5-}$,[15] and clearly confirms that the steric

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[14] The stability of the β_3 isomer is additionally most probably underevaluated because one may expect the less symmetric β_3 structure to have higher entropy than the α one: inclusion of a vibrational correction to the free energy would favor even more the β_3 isomers.

[15] Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932.

Table 3. Distances and Average (⟨···⟩) Distances (in Å) Characteristic of the Coordination of the $\{RuL_3(H_2O)\}^{2+}$ (L_3 = C_6H_6, $(DMSO)_3$) Fragments to the α and β_3 Isomers of the $[XW_{11}O_{39}]^{m-}$ (X = P, *m* = 7; X = Si, *m* = 8)[a]

	α				β_3			
	L = DMSO		$L_3 = C_6H_6$		L = DMSO		$L_3 = C_6H_6$	
	P	Si	P	Si	P	Si	P	Si
⟨Ru···O_b⟩	2.07	2.03	2.01	1.99	2.06	2.05	1.99	1.99
Ru···O_w	2.08	2.07	2.10	2.12	2.09	2.08	2.12	2.11
⟨O_w···O_{nb}⟩	2.48	2.46	2.58	2.61	2.50	2.48	2.62	2.60
⟨H_w···O_{nb}⟩	1.46	1.40	1.58	1.62	1.49	1.46	1.64	1.62
⟨W···O_b⟩	1.83	1.84	1.83	1.85	1.83	1.84	1.83	1.85
⟨W···O_{nb}⟩	1.78	1.78	1.76	1.75	1.78	1.78	1.76	1.76
⟨Ru···L⟩	2.33	2.34	2.19	2.20	2.33	2.33	2.20	2.20

[a] Ru···L represents the distance between the ruthenium center and the binding atoms of the L ligand (i.e., S for DMSO and C for C_6H_6), and the various types of O atoms are defined in Figure 3.

constraints created by three DMSO ligands are much larger than those resulting from a single arene.

The consequence of the difference in steric hindrance of both $\{RuL_3(H_2O)\}^{2+}$ fragments on the relative stability of the α and β_3 isomers can now be examined in more detail by analyzing the environment at the ruthenium center after bidentate coordination to the lacuna. First, it should be noted that, from an experimental point of view, for both β_3-$[SiW_{11}O_{39}\{Ru(DMSO)_3(H_2O)\}]^{6-}$ and α-$[PW_{11}O_{39}\{Ru(L)_3(H_2O)\}]^{5-}$ [L_3 = C_6H_6, $(DMSO)_3$], the grafting of the cation on the lacuna is regiospecific: the ruthenium is coordinated to the O atoms 1 and 4 (or 2 and 3 if the other enantiomer is considered; see the scheme in Figure 2). This can be explained by thermodynamic considerations because we have shown that, of the three possible isomers of α-$[PW_{11}O_{39}\{Ru(C_6H_6)(H_2O)\}]^{5-}$, the asymmetrically grafted one is slightly more stable.[7] It is noteworthy that this asymmetric grafting mode actually corresponds, for both the α and β_3 isomers, to the binding of the ruthenium between O atoms 1 and 4 (or 2 and 3), which are separated by a long W−O−W−O−W bridge, and not between O atoms 1 and 2 (or 3 and 4), which are only separated by a much smaller and thus much less flexible W−O−W bridge. Following the same idea, an explanation of the difference in the stability of **α-2(P)** and ***β*$_3$-2(P)** can now be proposed. Indeed, as it appears by looking at the scheme in Figure 2, once coordinated between O atoms 1 and 4 (or 2 and 3), the metal will occupy a binding site that bridges two directly connected triads in the case of the **α-2(P)** isomer. This center is thus probably more constrained than that in the case of ***β*$_3$-2(P)**, where only one of the two W−O−W entities belongs to a triad, with the other one being part of a larger four-sided oxotungstic structure. Because of this, the interactions between the bidentate grafted fragment and the polyoxotungstic framework should be more important in the α isomer than in the β_3 one. In other words, the α polyoxometalate will appear as a more bulky ligand than the β_3 one for a metallic fragment grafted in an asymmetric−bidentate mode. As a result, this could explain why the energy of the α isomer becomes higher than that of the β_3 species after grafting of a sterically hindered cation like $\{Ru(DMSO)_3(H_2O)\}^{2+}$.

Impact of the Central Anion: P vs Si. Given that, from an experimental point of view, the β_3 isomer ***β*$_3$-3(Si,DMSO)** had been isolated in the case of a silicon-containing polyoxometalate, the systems described previously were also optimized with a SiO_4^{4-} core. Several of the conclusions drawn for the phosphorus-containing anions are still valid: the α isomer is more stable for the complete $[XW_{12}O_{40}]^{n-}$ structure, as well as the lacunary one coordinating Na^+ [**2′(Si,Na)**] in the lacuna (Table 1, entries 1 and 4). Furthermore, it is especially noteworthy that the geometrical parameters of the lacuna are quasi-similar in the silicon- or phosphorus-containing species (Table 2, entries 1, 4, and 5).

However, two major differences appear when both systems are compared. First, in the case of isolated $[SiW_{11}O_{39}]^{8-}$ anions **2(Si)** (Table 1, entry 2), the β_3 isomer is systematically more stable than the α one, thus showing once more the importance of the counterions in solution [and thus the use of the **2′(Si,Na)** model] to interpret the experimentally observed instability of β_3-$[SiW_{11}O_{39}]^{8-}$. Second, in the case of the $\{Ru(C_6H_6)\}^{2+}$ derivatives **3(Si,C$_6$H$_6$)**, the energy difference between the α and β_3 isomers becomes much smaller compared to that in the phosphorus system.[14] In parallel, in the case of the $\{Ru(DMSO)_3(H_2O)\}^{2+}$ derivatives **3(Si,DMSO)**, the stability of the β_3 form is enhanced. The changes in $E(\beta_3) - E(\alpha)$ observed upon switching from phosphorus to silicon cannot be justified by simply looking at the changes in the values of ⟨O_{lac}···O_{lac}⟩ because the distances in the silicon derivatives are systematically almost equal to those observed in the case of the phosphorus species (Table 2). However, the influence of the charge of the central anion on the relative stability of grafted monolacunary isomers is not surprising and is a well-documented effect in the case of the naked lacunary structures. For instance, in the case of $[PW_{11}O_{39}]^{7-}$, the α isomer is the only stable species in solution, whereas in the case of $[AlW_{11}O_{39}]^{9-}$, it has been shown experimentally that the α and β_3 isomers can coexist, with the energy preference for the α form being only of 0.3 kcal·mol^{-1}.[16]

Conclusion

In this paper, a computational study of the relative stabilities of the monolacunary Keggin anions α-$[XW_{11}O_{39}]^{m-}$ and β_3-$[XW_{11}O_{39}]^{m-}$ (X = Si, P) and of their grafted derivatives was performed, leading to the following conclusions. First, the presence of the environment, and more specifically of the countercations in solution, plays a major role in the relative stabilization of the α isomer with respect to the β_3 one. In particular, the interaction of one Na^+ cation with the four O atoms of the lacuna creates stronger constraints in the case of the β_3 cage. Binding of alkali cations in solution had already been proposed,[17] but no definitive experimental evidence had been given in that connection.[16] Though we have only computationally addressed this issue in the case of sodium, it is likely that any cation binding inside the lacuna will destabilize the β_3 cage in a similar way. On the other hand, the relative stability of

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the α and β_3 isomers for cationic fragments bound in a η^2 mode is influenced by two competitive factors: the destabilizing tensions created in the β_3-oxotungstic framework and the larger steric repulsion between the grafted fragment and the α-oxotungstic framework. Finally, the central anion (PO_4^{3-} or SiO_4^{4-}) was shown to have an impact on the relative stability of the two isomers, with the β_3 structure being more favored in the case of SiO_4^{4-}.

From the computational study performed here, an explanation of the structural differences of **3-β₃(Si,DMSO)**, **3-α-(P,DMSO)**, and **3-α(P,C₆H₆)** can now be proposed. Whereas **3-α(P,C₆H₆)** could be described as the thermodynamic product, **3-α(P,DMSO)** appears to be a kinetic product.[14] This compound forms by reaction between a ruthenium precursor and the α-$[PW_{11}O_{39}]^{7-}$ anion, which is stabilized in solution by alkali cations. Once the ruthenium is bound to the lacuna, **3-α(P,DMSO)** cannot rearrange into the thermodynamic compound **3-β₃(P,DMSO)** because of the strong binding energy of the metallic fragment. All the same, it appears that the **3-β₃(Si,DMSO)** compound prepared by Kortz et al. is the most stable of the α and β_3 isomers and thus the thermodynamic product, which is not fully surprising given that this compound has formed by self-assembly in solution.[18]

Finally, from this work, the following proposals can be made as to how to favor the formation of β_3 structures in future syntheses. First, the use of anions of higher charge, such as SiO_4^{4-}, GeO_4^{4-}, or AlO_4^{5-}, will increase the stability of β-type metallic frameworks, as was already shown in the litterature.[2] Second, the synthetic procedure to follow will need to be chosen carefully. Indeed, when self-assembly syntheses are relied upon, given that nonbulky cations tend to favor the formation of α-type frameworks,[19] sterically demanding fragments should be privileged in order to form β isomers because they are more likely to strongly interact with the oxometallic cage and destabilize α skeletons. On the other hand, in the case of a "grafting" synthetic strategy, the use of preformed β_3-$[XW_{11}O_{39}]^{m-}$ anions as starting materials appears necessary. This can be seen as a challenge because it is well-known that the α isomer is generally more stable for the full **1(X)** compounds and that experimental self-assembly procedures have mainly led to the formation of **α-2(X)** species.[15] Additionally, because our results have shown that the strong coordination of cations inside the lacuna destabilizes β_3 frameworks, it appears necessary to avoid it, either by using less coordinating ions such as tetrabutylammonium or by adding crown-ether-type ligands to the mixture in order to complex the maximum of alkali cations.

Computational Details

Calculations on the lacunary polyoxometalates $[XW_{11}O_{39}]^{7-}$ (X = P, Si) and on their ruthenium(II) derivatives were carried out using the Jaguar 6.0 release 11 set of programs,[20] within the framework of the density functional theory using the B3PW91 functional. The LANL2DZ effective core potentials were used to replace the 60 innermost electrons of W, the 28 innermost electrons of Ru, and the 10 innermost electrons of P, Si, and S. The associated double-ζ basis set was used for these atoms, and a 6-31+G* basis set was used for the other atoms. No symmetry constraints were used in the calculations. Full geometry optimization was carried out, except when otherwise specified. Because no vibrational correction to the reaction energy could be added, the obtained energy differences are subject to systematic errors due to the entropy difference of the α and β_3 cage. As a result, only trends within the relative energies of the isomers are analyzed here, and they are systematically discussed in view of structural properties of the compounds.

Solvation was taken into account by using the Jaguar self-consistent reaction field continuum dielectric;[21] parameters were chosen in order to model water (dielectric constant equal to 80.37). Geometry optimization in the presence of the dielectric medium was carried out for selected systems, namely, **4(P,DMSO)** and **3-(X,C₆H₆)** (for both X = P and Si; see the Supporting Information for full data). In all cases, the $\langle O_{lac}\cdots O_{lac}\rangle$ value within the lacuna is found to be altered by no more than 0.05 Å. An overall slight increase of the distances around the ruthenium is observed. Nevertheless, the variations are of the same order of magnitude for both isomers. Despite these small geometrical changes, which are consistent with those reported previously,[7] no significant variation in the energy difference between the two isomers is obtained. For instance, upon optimization with the continuum, structure **α-4(P,DMSO)** is found to be 3.8 $kcal\cdot mol^{-1}$ more stable than the β_3 isomer, compared to 3.3 $kcal\cdot mol^{-1}$ for gas-phase optimization followed by continuum incorporation (Table 1, entry 5). For **3(X,C₆H₆),** α and β_3 isomers are found to be isoenergetic in the case of both X = Si and P species. As a result, because neither the geometry of the compounds nor the energy differences between the two isomers are significantly altered when a dielectric medium is added, no geometry optimization in the presence of the continuum is reported in the results given in the core of this study.

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Supporting Information Available: Polyhedral representations of the four different isomers of $[XW_{11}O_{39}]^{n-}$ and characteristic distances in the structures optimized in presence of a continuum. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) It is noteworthy that the energy of the other β isomers **3-β₁(Si,DMSO)** and **3-β₂(Si,DMSO)** has not been computed. However, because of their strong instability in solution (see ref 3), we believe that their formation would be highly disfavorable, even through self-assembly procedures, and that the **β₃-3(Si,DMSO)** complex is thus the thermodynamic product.

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