Inorg. Chem. **2006**, *45*, 6467–6473

Inorganic Chemistry
Article

Structural Evolution in Polyoxometalates: A DFT Study of Dimerization Processes in Lindqvist and Keggin Cluster Anions

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Received January 19, 2006

Density functional theory (DFT) calculations are used to investigate dimerization, by acid condensation, between Lindvist and Keggin cluster anions. When specific addendum atoms are present (notably, Ti, V, Nb, and Cr), these clusters dimerize in the presence of acid via the formation of μ-O linkages. These processes may be viewed as molecular models for the formation of metal–oxygen bonds in the active sites of metalloenzymes, or in materials chemistry, and we here provide detailed information concerning these reactions. For this, DFT calculations are used to provide insight into the mechanism(s) associated with dimerization of Lindqvist clusters, $W_5MO_{19}{}^{n-}$ (M = W, Mo, V, Nb, and Ti) in acidic media. In full accord with experimental data, our calculations show that dimerization of Nb and Ti derivatives is thermodynamically favored and that this is not the case for dimerization between Mo, V, and W addendum atoms. In addition, dimerization of $PW_{11}TiO_{40}{}^{5-}$ and $SiW_{11}NbO_{40}{}^{5-}$ to give the corresponding dimers was also calculated to be exothermic. Two possible mechanisms, involved in two competing pathways, are evaluated and discussed. Conclusions are presented concerning the role played by the nature of the metal atoms taking part in M–μ-O–M bond formation. A correlation is established between the relative strengths of specific terminal M═O bonds in monomeric precursors and the tendency of these to form M–μ-O–M bonds.

Introduction

In recent years, the family of polyoxometalates (POMs) has captured the attention of scientists from many fields, having a growing impact on nanoscale chemistry.[1−3] These inorganic frameworks,[4] made primarily of O and early-transition-metal atoms (also called *addenda* atoms), have found applications in materials science, catalysis, and medicine, to mention just a few.[5,6] Relatively small POMs, such as Keggin anions, are typically formed through acid condensation, a self-assembly process that forms M−O linkages and water as a byproduct. Through further acid condensation processes, such as dimerization reactions, these cluster anions serve as building blocks for the construction of larger and more complex architectures. The first detailed description of dimerization between Keggin anions was reported in 1984 by Finke and Droege,[7] and Klemperer co-workers later synthesized other derivatives of the same family.[8−11] Dimers of the Lindqvist structure[12,13] as well as

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10.1021/ic060112c CCC: $33.50

other dimeric structures have also been described.[14] Notably, the intercluster linkages in all of these examples contain M−μ-O−M junctions, in which M = Nb, Ti, Cr, or Fe.[7−12,14,15−17] When present in POMs, these metals also form single bonds with either organic functional groups or metalloorganic fragments, whereas this is not commonplace for W and Mo addendum atoms.[18,19] As a result, in the formation of hybrid organic−inorganic POM-based materials and polymers, including functional gels, the above M elements are also used as attachment points for incorporation of organic linkers.[20]

Despite considerable synthetic work, the mechanisms that control these dimerization reactions (and, by implication, functionalization processes generally) are not fully understood. One reason for this is that intermediates are not easily observed. Recently, one of us used both ^{183}W and ^{29}Si NMR spectroscopy, and X-ray diffraction, to observe reversible, stepwise formation of individual Nb−μ-O−Nb linkages during acid condensation of 2 equiv of A-α-$[SiW_9Nb_3O_{40}]^{7-}$ to the tri-μ-oxo-bridged structure A-α-$[Si_2W_{18}Nb_6O_{77}]^{8-}$.[21] Even in this detailed study, however, the specific sites at which protonation by acid occurred to initiate M−O bond formation could not be identified. At the same time, correlations between the atoms susceptible to dimerization or functionalization, and calculations[22] of the electron density distributions in POM structures, suggest that whether these reactions occur or not depends on the relative basicities of the oxo sites on the cluster-anion surfaces. Using this observation, as well as additional experimental and theoretical data concerning the acid−base properties of POMs[22−25] as a starting point, we now provide detailed density functional theory (DFT) calculations of the relative energies of structures implicated as intermediates in the dimerization of Keggin and Lindqvist cluster anions while addressing a second point: why do only certain metal atoms appear to be involved in this chemistry?

First, we will discuss the relative energies computed for various $W_5MO_{19}^{n-}$ Lindqvist clusters, with M = W, Mo, V, Nb, and Ti. The choice of a medium-sized system allows the study of a larger series of compounds. Second, the larger $PW_{11}TiO_{40}^{5-}$ and $SiW_{11}NbO_{40}^{5-}$ anions, derivatives of the Keggin structure, are analyzed. In all of our calculations, we account for the solvent effects using a continuum model to obtain comparable energies in solution for the family of (differently charged) species treated.

Computational Details

We used the DFT implemented in the ADF 2004.01[26] package to study the molecules discussed in this work. The electron density is characterized by the local density approximation for the exchange electronic interactions, featuring the Xα model with Becke's gradient-corrected functional.[27] The correlation part is described by the Vosko−Wilk−Nusair parametrization[28] together with Perdew's corrections.[29] The valence electrons of all of the atoms are described with a set of Slater-type basis functions of triple-ζ + polarization quality. The innermost or *core* electrons (O, 1s; P, 1s 2s; Ti, V, 1s 2p; Nb, Mo, 1s 3d; W, 1s 4d) were kept frozen. We applied scalar relativistic corrections to them—*zeroth-order regular approximation* (ZORA)—via the core potentials generated with the

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program DIRAC.[26] All of the structures herein discussed were fully optimized in the presence of a model solvent, accounted for with the *conductor-like screening model* (COSMO)[30] implemented as part of the ADF code.[31] To define the cavity surrounding the molecules, we used the solvent-excluding-surface method and a fine tesserae. To obtain the electron density in solution, we first allowed the self-consistent field converge without solvent effects and, thereafter, the COSMO was turned on to include the solvent effects variationally. The ionic radii for the POM atoms, which actually define the size of the solvent cavity where the target molecule remains, were chosen to be 0.74 Å for all metal ions except V, for which we chose 0.68 Å. The radii for H and O are 1.20 and 1.52 Å, respectively. The dielectric constant (ϵ) utilized in the computations was set equal to 78 for modeling of water (calculations on Lindqvist anions) and 37 for modeling of the effects of acetonitrile (dimerization of $PW_{11}TiO_{40}{}^{5-}$).

Results and Discussion

The dimerization reaction in POMs has been reported to occur mostly in acidic media. Several authors have proposed the following general reaction mechanism,[15,16] herein referred to as dimerization of a Lindqvist anion:[32]

$$\underset{\mathbf{1}}{2W_5MO_{19}{}^{q-}} + 2H_3O^+ \rightarrow \underset{\mathbf{2}}{2HW_5MO_{19}{}^{(q-1)-}} + 2H_2O \quad (1)$$

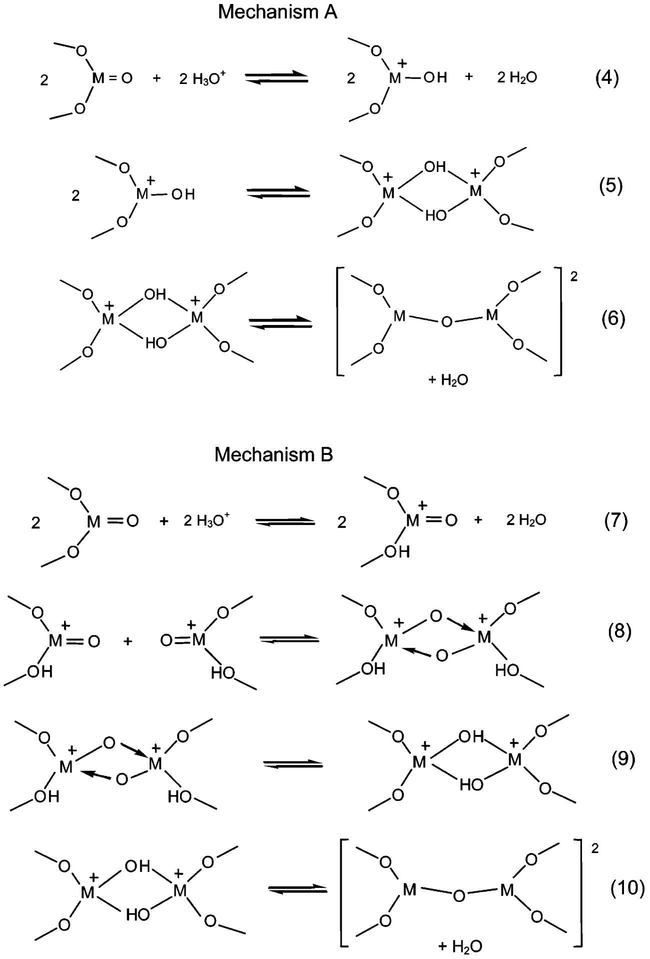
$$\underset{\mathbf{2}}{2HW_5MO_{19}{}^{(q-1)-}} \rightarrow \underset{\mathbf{3}}{[(HW_5MO_{18})_2(\mu\text{-}O)_2]^{2(q-1)-}} \quad (2)$$

$$\underset{\mathbf{3}}{[(HW_5MO_{18})_2(\mu\text{-}O)_2]^{2(q-1)-}} \rightarrow \underset{\mathbf{4}}{[(W_5MO_{18})_2\mu\text{-}O]^{2(q-1)-}} + H_2O \quad (3)$$

$$2W_5MO_{19}{}^{q-} + 2H_3O^+ \rightarrow [(W_5MO_{18})_2\mu\text{-}O]^{2(q-1)-} + 3H_2O$$

These equations (as well as those of Scheme 1) do not attempt to fully describe the elementary processes occurring during dimerization. They rather show key species proposed to play an important role in the dimerization process. In short, they denote the formation of a single μ-O linkage between the monomers, $W_5MO_{19}{}^{q-}$ (**1**), to give the $[(W_5MO_{18})_2\mu\text{-}O]^{2(q-1)-}$ dimer (**4**), as shown in the last equation. The first reaction corresponds to the protonation of the cluster, where the protonation site is, in principle, any external oxo site of the metal oxide structure. A second reaction can plausibly occur, namely, the condensation of two of such protonated monomers to form the doubly bridged $[(HW_5MO_{18})_2(\mu\text{-}O)_2]^{2(q-1)-}$ (**3**) intermediate. This might be the key step and, probably, is the most difficult to characterize theoretically or to detect experimentally. Equation 3 in the above reaction sequence is the loss of a water molecule to give the final product, the mono-oxo-bridged dimer **4**. Further steps can occur in some cases, that is, the formation of a second and even a third μ-O linkage. This is commonplace in some trisubstituted Keggin anions.[14,21]

Scheme 1



Upon closer analysis, two possible mechanisms (A and B in Scheme 1), both of which are consistent with eqs 1−3, can be identified. In mechanism A, the protonation site is the O atom of a terminal M═O bond (see Scheme 1, eq 4); in mechanism B, protonation occurs at a bridging O (eq 7), preferentially M−O−W.[24b] The two possible locations of the H atom were studied, leading to two protonated species **2** and two intermediates **3**. Each protonated monomer leads to a different intermediate in the condensation step (eqs 5 and 8, respectively). Finally, structure **4** corresponds to the product of the reaction, in which a single μ-O linkage remains after the loss of a water molecule.

The atom labeled M in eqs 4−10 stands in theory for any metal center. However, the synthesis of POM dimers concerns only some mixed-addenda anions as stated above, where the physical nature of the substituting metal atom would play a fundamental role in the characteristics of the POM monomer. One of the key factors associated with M is its effect upon the basicity of the O sites, which is still a debated question. In the past few years, several authors have studied theoretically the basicity of POMs. The first theoreti-

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(32) The complete process, represented by eqs 1−3, is mass and energy balanced. At each point of reaction, we account for *all* species, i.e., the POM species plus the corresponding H_2O or H_3O^+. Accordingly, *in terms of energies*, we refer likewise to species **1** or to point **1** as to $2W_5MO_{19}{}^{q-} + 2H_3O^+$, for point **2** as $2HW_5MO_{19}{}^{(q-1)-} + 2H_2O$; for point **3** as $[(HW_5MO_{18})_2(\mu\text{-}O)_2]^{2(q-1)-} + 2H_2O$, for point **4** as $[(W_5MO_{18})_2\mu\text{-}O]^{2(q-1)-} + 3H_2O$.

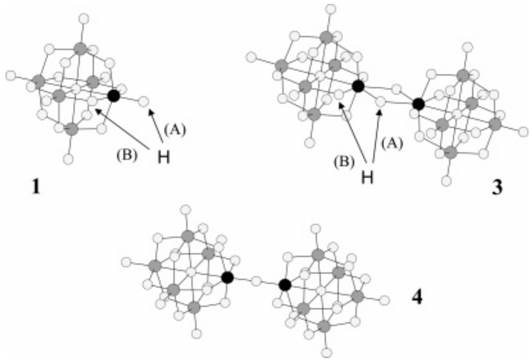

Figure 1. Ball-and-stick representation of the monomer (**1**), intermediate (**3**), and dimer (**4**) of the Lindqvist anion, $(W_5MO_{18})_2\mu$-O. Color code: W, gray spheres; M, black spheres. The arrows in structures I and II indicate, together with the associated mechanism, the possible locations of the H atoms, as shown in the general mechanisms A and B in Scheme 1.

Table 1. Relative Energies for Reactants, Intermediates, and Products Computed for the Dimerization of Lindqvist Anions (see Scheme 1)[a]

	W	Mo	Nb	V	Ti
			Mechanism A		
1	0.00	0.00	0.00	0.00	0.00
2	8.88	14.59	−27.84	−4.54	−53.61
3	16.41	22.63	−29.92	17.34	−42.45
4	6.87	12.31	−31.89	−8.07	−57.19
			Mechanism B		
1	0.00	0.0	0.00	0.00	0.00
2	−5.11	−6.53	−25.05	−24.91	−40.12
3	17.44	20.88	−18.96	24.06	−22.08
4	6.87	12.31	−31.89	−8.07	−57.19

[a] All of the values are in kcal mol^{-1}. Equations 1−3 and ref 32 show the species present at each point of the reaction.

cal attempt to classify the proton affinity of such molecules was carried out in the early 1990s by Bénard and co-workers, who discussed the basicity of the oxo sites in $V_{10}O_{28}{}^{6-}$ by analyzing the molecular electrostatic potential.[22] The group of Davis studied the protonation energies of single-addenda Keggin tungstates and molybdates.[23a] Our group has also reported studies on relative basicity scales for mixed-metal anions by comparing the protonation energies of terminal and bridging O atoms.[24] Most authors agree that bridging O atoms are, in general, the most basic sites in the external metal oxide structure of POMs. Moreover, cluster anions containing one or more Nb^{V}, V^{V}, or Ti^{IV} atoms are stronger Brønsted bases—mostly because of their higher negative charges—than their single-addenda oxotungsten(VI) counterparts.[12,18,22,24,33−37] However, more recently, a combined experimental/computational study[23b] showed that terminal O atoms could be the preferred sites for protonation in Keggin tungstates. Data based on molecular dynamics calculations[38] showed that the terminal sites are the most accessible to interact with solvent.

Lindqvist Anions. Calculations were first performed on the dimerization process for derivatives of the $W_5MO_{19}{}^{q-}$ Lindqvist anion, with M = W, Mo, V, Nb, and Ti, with water as the solvent. This relatively small POM is used here as a model for analysis of larger Keggin structures. The elementary reactions for a Lindqvist derivative are expressed in eqs 1−3. Figure 1 shows the structures of the monomer, the intermediate, and the dimer as well as the positions of the H atoms (as explained in Scheme 1) in the structures computed.

Table 1 shows the relative energies computed at each point of the reaction for both mechanisms. Let us start with the analysis of the dimerization energies for the nonsubstituted $W_6O_{19}{}^{2-}$ anion. The first step corresponding to the protonation of the monomer requires 8.9 kcal mol^{-1} at the terminal O and −5.1 kcal mol^{-1} at the bridging O; the subsequent intermediates **3** (in both mechanisms) appear at +16−18 kcal mol^{-1}, and the reaction product **4** is 6.9 kcal mol^{-1} above the reactants. It is clear from these values that the dimerization of $W_6O_{19}{}^{2-}$ is not thermodynamically favorable. To the best of our knowledge, there is no acid condensation reaction reported for a single-addenda polyoxotungstate. Our results also show that, similarly, acid condensation of $W_5MoO_{19}{}^{2-}$ is not expected to occur. Protonation at the terminal Mo═O oxo site is much less favored (+14.6 kcal mol^{-1}) than formation of Mo−OH−W (+6.5 kcal mol^{-1}). Both species **3** for the molybdate are quite high in energy. In the V derivative, the O atoms linked to the V ion are more basic than the O atoms only linked to W ions.[24b] The protonation of the vanadotungstate at the V−O−W oxygen (mechanism B) is strongly exothermic, −24.9 kcal mol^{-1}, but the corresponding intermediate **3**, $(HW_5VO_{18})_2(\mu\text{-}O)_2$, is 49 kcal mol^{-1} above species **2** and at +24.0 kcal mol^{-1} from the reactants. We observed qualitatively the same in the condensation reaction via mechanism A: the protonation at V═O is still exothermic, but the corresponding intermediate $(W_5VO_{18})_2(\mu\text{-}OH)_2$ is high in energy, lying at +17.3 kcal mol^{-1}. The final product is only 8 kcal mol^{-1} more stable than the reactants. These results are not as conclusive as those for W or Mo. From purely energetic considerations, $W_5VO_{19}{}^{3-}$ could self-assemble via acid condensation, although $[(W_5VO_{18})_2O]^{4-}$ has never been observed. We will further discuss its ability to dimerize. Figure 2 contains a graphical comparison of the values given in Table 1.

From the present calculations, the clusters containing Nb^{5+} or Ti^{4+} show species involved in the dimerization process lying in the region of strong exothermicity, in contrast to M = W, Mo, and V. When $M^{n+} = Nb^{5+}$, the protonation at Nb═O is largely exothermic and the relative energy of the protonated monomer is −27.8 kcal mol^{-1}. Meaningfully, the following steps, formation of intermediate **3** and water loss, are also favorable processes. Notice that the $W_5NbO_{18}(\mu\text{-}O)W_5NbO_{18}$ dimer is −31.9 kcal mol^{-1} more stable than 2 equiv of monomer, whereas for the hexatungstate, the energy of the hypothetical dimer is +6.9 kcal mol^{-1}. The process via mechanism B seems likely favorable because intermediate **3**, $HW_5NbO_{18}(\mu\text{-}O)_2W_5NbO_{18}H$, is also very stable (−19 kcal mol^{-1}). The most exothermic protonation step was found for

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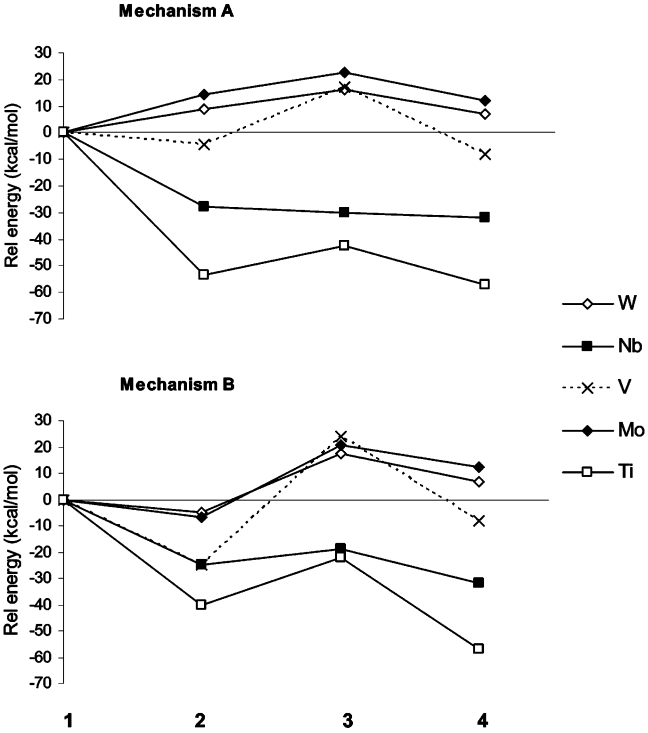

Figure 2. Relative energies computed (in kcal mol^{-1}) for species **1**−**4** involved in the dimerization process of Lindqvist anions (see ref 32 for details), listed in Table 1. We show the series of W_5MO_{19} (M = W, Mo, V, Nb, and Ti) for mechanisms A and B.

Table 2. Comparison of the Relative Energies (kcal mol^{-1}) for Intermediates **3** of the Lindqvist Ti Derivative

compound	energy
$[(W_5TiO_{18})_2(\mu\text{-}OH)_2]^{6-}$	11.2[a]
$[(W_5TiO_{18}H)_2(\mu\text{-}O)_2]^{6-}$	18.0[a]
$[(W_5TiO_{18})_2(\mu\text{-}O)(\mu\text{-}OH)]^{5-}$	18.9[b]
$[(W_5TiO_{18})(\mu\text{-}O)_2(W_5TiO_{18}H)]^{5-}$	15.9[b]

[a] Relative energy with respect to two protonated monomers **2**. [b] Relative energy to one protonated monomer **2** and one nonprotonated monomer **1**.

Ti^{4+} as expected because $W_5TiO_{19}{}^{4-}$ carries the highest negative charge. For the Ti derivative, the dimer is also much more stable than the monomer (−57.2 kcal mol^{-1}). The most significant difference between the Nb and Ti derivatives is that, for the latter, the condensation step (eq 2) is endothermic, requiring 11−12 kcal mol^{-1}. This fact comes from the high stability of the protonated monomer, **2**, especially in mechanism A.

Concerning the process of water loss (eq 3), nothing is known, while we expect this to be rather intricate. Even so, alluding to the very low energies of species **3** and **4** for M = Ti and Nb, we do believe that the trends found would not change upon further study of this issue.

At this point, one could ask if the reaction process could also take place via a single μ-hydroxo intermediate, which would involve the reaction of a protonated monomer **2** with a nonprotonated anion **1** to give intermediate **3**. To explore the viability of this mechanism, we have computed the structures $[(W_5TiO_{18})_2(\mu\text{-}O)(\mu\text{-}OH)]^{5-}$ and $[W_5TiO_{18}(\mu\text{-}O)_2W_5TiO_{18}H]^{5-}$. From the values in Table 2, it is clear that the reaction of two protonated Ti═OH monomers (mechanism A in Scheme 1) is thermodynamically more favorable than the reaction of an anion **1** with its protonated form **2**. Therefore, at low pH, the dimerization process should occur preferentially via the intermediate with two hydroxo bridges. However, at a less acidic pH, in which the concentrations of the protonated monomers are lower, the energies in Table 2 do not allow one to discard the formation of the intermediate $[(W_5TiO_{18})_2(\mu\text{-}O)(\mu\text{-}OH)]^{5-}$. The compound $[(W_5TiO_{18})(\mu\text{-}O)_2(W_5TiO_{18}H)]^{5-}$ could also be formed, but the protonation energy at a W−O−Ti oxygen is always smaller than that at a terminal Ti═O oxygen. As a matter of fact, this latter structure is less stable than the intermediate structure with one μ-hydroxo bridge by 6.7 kcal mol^{-1}. Finally, the term $T\Delta S$ has been estimated for the process $2[W_5O_{18}Ti{=}OH]^{3-}$ to give $[(W_5TiO_{18})_2(\mu\text{-}OH)_2\ ]^{6-}$ in a vacuum at room temperature. According to the bimolecular nature of the process, ΔS is negative and the entropic term amounts to $\sim$+15 kcal mol^{-1}. This value is expected to be significantly smaller in solution.[39] The entropic contribution for the global reaction $2[W_5O_{18}Ti{=}O]^{4-} + 2H_3O^+ \rightarrow [(W_5O_{18})_2Ti(\mu\text{-}O)]^{6-} + 3H_2O$ has been estimated to be almost zero.

M═O Bond Strengths. The dimeric species $[(W_5NbO_{18})_2O]^{4-}$ has been synthesized,[13] but the mechanism leading to the dimer is not fully understood. From the energies associated with the Nb and Ti derivatives in Figure 2, mechanism A appears to be clearly lower in energy than mechanism B, especially for $W_5TiO_{19}{}^{4-}$. In the case of Nb, both pathways are thermodynamically similar, although point **3A** is more than 10 kcal mol^{-1} below point **3B**. Therefore, although the dimer of $W_5NbO_{19}{}^{3-}$ could be formed through both mechanisms, $W_5TiO_{19}{}^{4-}$ forms the dimer probably via mechanism A. Moreover, the overall process is largely favored because the reaction energy is about −57 kcal mol^{-1}.

From the sets of relative energies discussed above, a first type of compound might be deduced: $W_6O_{19}{}^{2-}$, $W_5MoO_{19}{}^{2-}$, and $W_5VO_{19}{}^{3-}$, that is, those without computational or experimental verification of dimerization.[40] One evidence is the very poor basicity at the M═O sites, so the formation of **3** is invariably (in both mechanisms) endothermic. The reaction products **4** were also found at high energies in both mechanisms for W, Mo, and V derivatives, a symptom of the tendency of these W_5MO_{19} monomers to remain as such instead of dimerizing. Only the modest exothermicity of the dimerization reaction for $W_5VO_{19}{}^{3-}$ is quite controversial. Although the V═O bond is labile in many cases, our present results on the vanadate derivative would confirm the lack of information on its dimer partner. We tentatively propose that the reaction is not kinetically favored, in particular because of the relative instability of intermediate **3** and, probably, because of the hypothetical high-energy transition state associated with reaction **2** → **3**, not yet computed. Future work may clarify this point.

Because the possible mechanisms involved in acid condensation reactions require weakening of the terminal M═O

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(39) Vyboishchikov, S. E.; Buhl, M.; Thiel, W. *Chemistry* **2002**, *8*, 3962.
(40) This statement, although only proven here for monosubstituted W_5MO_{19} compounds, could be generalized to other $W_{6-x}M_xO_{19}$ clusters. Besides that, for higher values of *x*, a charge effect acting on the relative energies could exist. This interesting issue might be addressed in a future work.

bonds, we hypothesize a link existing between the strength of the terminal M═O bonds and the formation of a POM dimer. For this, we compare the energy of species **3A** with the available experimental M═O vibrational frequencies in POMs. The choice of **3** is not arbitrary because it invariably symbolizes the reaction intermediate of highest energy; thus, it represents how energetically accessible the overall process is. As a matter of fact, the IR spectra of POMs containing W, Mo, and V reveal the strongest terminal bonds among this class of metal oxides.[41] W═O and Mo═O have absorption bands at 1000−970 and 980−960 cm^{-1}, respectively.[42] Similarly, the terminal V═O stretching appears at 990−970 cm^{-1}.[43] On the other hand, for the species where exothermic protonation and condensation steps are herein reported, the M═O bond strengths behave differently; that is, the value for Nb═O is about 860−920 cm^{-1}.[44] For Ti═O groups, there is very scarce information because POMs containing titanyl moieties are very rare. This originates in the preferential formation of single Ti−O(R) bonds.[41,45,46] Other evidences for metal−oxo-containing systems show that the ability of TiO moieties to be protonated is much more important than that of, say, VO.[47]

We therefore have taken IR data from other species containing Nb═O and Ti═O. For the two isostructural inorganic compounds $Rb_2La_2M_3O_{10}$ (M = Ti and Nb), a full IR characterization has been reported.[48] Such crystalline compounds also contain octahedral MO_6 units featuring terminal M═O bonds. Although those crystals are different from our present clusters, their IR spectra are valuable for estimating the position of Ti═O bands in POM anions because the oxidation states of Nb and Ti as well as the number and nature of the coordinated ligands are the same in both cases. The authors of that study assigned the bands at 867 and 957 cm^{-1} to the stretching of Ti═O and Nb═O bonds, respectively. By comparison with IR spectra of Nb-containing POMs, we assume that typical Ti═O stretching bands in polyanions must appear at around 770−830 cm^{-1}, a very low value well correlated to the energetically advantageous dimerization in POM Ti derivatives. So, qualitatively, a relationship exists between the terminal M═O bond strengths and the ability to undergo dimerization processes.

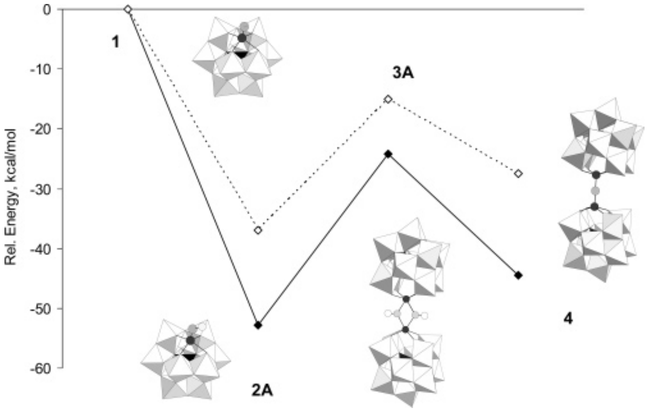

Figure 3. Relative energies (in kcal mol^{-1}) of species **1**−**4** computed for mechanism A of Keggin dimerization. Filled and empty diamonds represent species related to $PW_{11}TiO_{40}^{5-}$ and $SiW_{11}NbO_{40}^{5-}$, respectively.

Keggin Anions. In 2000, Kholdeeva et al. reported the dimerization of the monosubstituted $PW_{11}TiO_{40}^{5-}$ Keggin anion.[16] This was achieved under acidic conditions, and a single M−μ-O−M linkage was formed. Subsequent characterization showed that this linkage was a Ti−O−Ti bridge, with an overall reaction yield of 98%. This dimer has catalytic properties in the presence of H_2O_2, whereas, on the other hand, the monomer does not feature this activity. The authors of that study assumed protonation at the Ti−O_{term} site occurring prior to Ti−O−W. However, no strong evidence of the compounds formed at intermediate steps of the process is yet available. The reaction pathways one may tentatively suggest for this process are, in essence, equivalent to those discussed for Lindqvist species. We propose mechanisms A and B, as discussed in the previous section, for the dimerization of $PW_{11}TiO_{40}^{5-}$ and $SiW_{11}NbO_{40}^{5-}$. However, alluding to the differences found between both pathways for Lindqvist compounds, together with the very high computational cost associated with the present calculations, we only analyzed mechanism A. This one was, indeed, the most probable one thermodynamically for the smaller clusters analyzed.

The relative energies for each species **1**−**4** were computed equivalently to those carried out for Lindqvist anions[32] but setting $\epsilon = 37$,[49] to mimic the solvent used by the authors of the experimental study. If we focus on the relative energies computed for M = Ti in Figure 3, it is clear that the overall process is exothermic, as found for the formation of $(W_5TiO_{18})_2O$, because the reaction products **4** are about 47 kcal mol^{-1} more stable than the corresponding reactants. Also significant is the fact that the initial protonation step is also very exothermic, −55.6 kcal mol^{-1}, a value that is even larger than that for hexametalates. When W^{6+} is substituted by a metal with a lower oxidation state, the charge density of the anion increases and, therefore, the overall basicity of the

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(41) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(42) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

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(44) (a) Schwartz, C.; Klemperer, W. G. *Inorg. Chem*. **1985**, *24*, 4459. (b) Farrell, F. J.; Maroni, V. A.; SpiroInorg, T. G. *Inorg. Chem*. **1969**, *8*, 2638. (c) Santos, I. C. M. S.; Loureiro, L. H.; Silva, M. F. P.; Cavaleiro, A. M. V. *Polyhedron* **2002**, *21*, 2009.

(45) Literature related to titanyl-containing POMs reduces to a very few works. The Ti═O stretching bands in POMs are, in general, not observable or simply not clear. As a matter of fact, some authors have stated that "TiO_6 octahedra never contain Ti═O terminal bonds. Instead, they feature terminal Ti−OH bonds or are linked to other ligands".[46] Among the few works in which titanyl groups appear in POM clusters, we find: Campana, C. F.; Chen, Y.; Day, V. W.; Klemperer, W. G.; Sparks, R. A. *J. Chem. Soc., Dalton Trans*. **1996**, 691.

(46) Nyman, M.; Criscenti, L. J.; Bonhomme, F.; Rodriguez, M. A.; Cygan, R. T. *J. Solid State Chem*. **2003**, *176*, 111.

(47) Comba, P.; Merbach, A. *Inorg. Chem*. **1987**, *26*, 1315.

(48) Kim, H. J.; Byeon, S.-H.; Yun, H. *Bull. Korean Chem. Soc*. **2001**, *22*, 298.

(49) The value of ϵ in COSMO calculations affects very poorly the properties of POMs. This has been shown previously in: López, X.; Fernández, J. A.; Romo, S.; Paul, J. F.; Kazansky, L.; Poblet, J. M. *J. Comput. Chem*. **2004**, *25*, 1542.

POM also increases. In addition to the charge density, the basicity of a POM must be explained through the polarization of the anion. In general, the nucleophilicity of the substituted region is significantly greater than that of the nonsubstitued region. In the smaller Lindqvist anions this effect is less pronounced, and this allows an explanation as to why Keggin anions with lower charge densities can be more nucleophilic than Lindqvist anions.[50] The formation of intermediate species **3A** from **2A** requires +28 kcal mol^{-1}, a value that is higher than that obtained for the dimerization of $W_5TiO_{19}{}^{4-}$ (+11.2 kcal mol^{-1}). Also, the protonation at Ti−O−W to give species **2B** was computed to be ∼20 kcal mol^{-1} less favored than **2A**; thus, we ruled out the calculation of intermediate **3B** for its expected high energy (see also Figure 2). Thus, the relative energies calculated for the species leading to the formation of the two Ti-derived dimers, namely, $[(W_5TiO_{18})_2O]^{6-}$ and $[(PW_{11}TiO_{40})_2O]^{8-}$, are qualitatively similar, but the formation of **3A** is more energetic in the latter case. It is probably related to the fact that the Keggin framework is more rigid. Similar observations can be made from Figure 3 for M = Nb, but slightly energy upshifted.

Considering the data obtained for Lindqvist and Keggin anions together (Figures 2 and 3), we observe that the energies computed for the Ti and Nb intermediates and products are always found in the region of exothermicity, notably the final products, in contrast to M = W, Mo, and V. This suggests that the ability to under dimerization depends more on the nature of M than the shape or size of parent monomers. The behavior of Ti- and Nb-derived Lindqvist and Keggin anions indicates that $XW_{12}O_{40}$ and $XW_{12-x}M_xO_{40}$ (M = Mo and V) clusters are not expected to dimerize through acid condensation reactions. The most significant difference between the relative energies computed for Lindqvist and Keggin species resides in the larger energy difference found between species **2** and **3** in the latter case.

Conclusions

The present computational study reveals some key factors in the dimerization process of polyoxoanions: (i) the substitution of W^{6+} by M^{n+} ($n < 6$) in polyoxotungstates favors protonation in the O atoms adjacent to the M center(s), (ii) the nature of the substituting metal fully governs the ability to form *μ*-O junctions between monomers, (iii) species M−*μ*-(OH)$_2$−M is the intermediate of the reaction of highest energy, and (iv) among the metal elements studied (in agreement with experiments), acid condensation is favorable for M = Ti and Nb but not for M = W, Mo, and V. As a matter of fact, the dimerization of titanates is the most exothermic process computed. The substitution of W by Ti is a well-known technique for the formation of supramolecular structures.[51] The comparison of the data for $W_5TiO_{19}{}^{4-}$ and $PW_{11}TiO_{40}{}^{5-}$ suggests that the shape and size of POMs are less important than the nature of the addenda upon dimerization. The relationship observed between M═O IR bands and the energy of the dibridged (*μ*-O)$_2$ intermediate implies that terminal metal−oxo bond strengths are determinant in favoring or ruling out the acid condensation reaction.

Future work will concern the characterization of the transition states for two key steps, that is, the formation of the *μ*-(OH)$_2$ species and loss of water, the characterization of the structures involved in multiple linkages such as, for example, in $[SiW_9Nb_3O_{40}]^{7-}$, and the analysis of the possible relevance of the anion charge in these processes.

Acknowledgment. This work was supported by the Spanish MEC (Grant CTQ2005-06909-C02-01) and the CIRIT of the Autonomous Government of Catalonia (Grant 2005SGR00104). X.L. also thanks the Spanish MEC for a postdoctoral grant (Grant EX2004-0113). We thank the reviewers for comments and suggestions.

Supporting Information Available: Selected bond distances and *XYZ* coordinates for some optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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