

CHAPTER 1

Introduction to Polyoxometalates and Scope of the Work

The impact of polyoxometalate chemistry since the synthesis of the first derivative in 1826 is beyond all doubt. Experimentalists have studied these complexes for a long time and much is known about their behaviour and applications. Experimental techniques were used to study their properties and knowledge rapidly increased. The unprecedented properties and the virtually unlimited structural possibilities of these compounds have focused the attention of a large number of chemists for decades. Furthermore, the complex nature of metal-oxide frameworks and their associated phenomena created considerable interest amongst the community of theoretical chemists that, in the early 90s, started to apply modern computational techniques to explain the intricacies of polyoxometalate chemistry. The present chapter introduces the reader to the general characteristics of polyoxometalates: for example, the patterns governing their structure, their redox behaviour and the most important applications discovered to date. We pay particular attention to their structural characteristics, the main focus of the study. Finally, the last section shows the main aims of this thesis.

1.1. Introduction

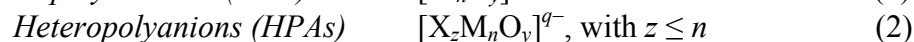
The great majority of inorganic compounds are constructed of metallic atoms as principal entities. This means that this subgroup of chemicals has considerable structural diversity, although it is still surpassed (in number of classified and characterised compounds) by organic compounds. However, inorganic molecules (a priori a much bigger field) have greater potential because the number of elements in *purely* inorganic molecules, combined with their structural diversity, make them more powerful, particularly as far as their applications are concerned. In fact, the search for new features puts more importance on the elements in a framework than on the structure itself. In the organic world, the principal variable that produces novel behaviour is the structure. In this sense, maybe the field of polyoxometalates (POMs) lies between the organic and the inorganic worlds.

Historical perspective

The first POM, the phosphomolybdate of formula $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, was reported by Berzelius¹ in 1826. Marignac² observed two isomeric forms of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$. In the early 1930s, Keggin solved the structure of the related anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$.³ Since then, countless structures have been synthesised and characterised. The turning point came when spectroscopic techniques were used for characterisation. The end of the 19th century and the early decades of the 20th century were fruitful in theories that explained coordination chemistry⁴ and, particularly, the chemistry of POMs.⁵ In the last 40 years, a lot of experimental information has been collected. Today, POMs constitute an immense class of polynuclear metal-oxygen clusters⁶⁻⁸ usually formed by Mo, W or V and mixtures of these elements. They have potential applications in many fields including medicine, catalysis, multifunctional materials, chemical analysis, etc. According to Katsoulis' compilation,⁹ in 1996 there were more than 700 communications (publications and patents) in the family of POMs. Most applications are related to their special ability to accept one or several electrons with minimal structural changes. Dozens of elements have been reported as taking part in POM compounds.⁶ In addition, beyond this chemical flexibility, they have an 'organic-like' structural diversity and the number of frameworks synthesised increases daily.

1.2. Structural Principles of Polyoxometalates

Polyoxometalates are one set of inorganic molecules in the vast field of coordination chemistry compounds. They are characterised by a metallic centre, M, which is surrounded by some atoms or groups of atoms. In POMs, ligands are normally oxygen atoms, although some derivatives with S,¹⁰⁻¹⁴ F,¹⁵ Br¹⁶ and other p-block elements are known. So, in general, we have MO_n units, where *n* indicates the coordination number of M. Usually, *n* = 6, although it can be 4, 5 or 7, as well. Apart from M and O, other elements, which are usually labelled as X, can be part of the POM framework. As a general rule, they are 4-fold- or 6-fold-coordinated and lie in the centre of the M_xO_y shell. Depending on whether X is present or not, we can distinguish two types of POM species. This classification is based on a purely structural criterion and this nomenclature will be used throughout the text:



There are no chemical limitations for X and M by definition. The X elements are the so-called primary, central or *heteroatoms*. In general, any element can participate as X in a POM cluster since there are no strict physical requirements for this position. On the other hand, M are the so-called secondary, peripheral or *addenda* atoms and only some M elements are typically found in such compounds (see text below in this section). In a few cases, this distinction may be confusing or uncertain, but in the clusters dealt with here the distinction is clear. Despite the simplicity of formulas (1) and (2) above, the composition of a cluster can be highly complex, with various M elements taking part in the structure. In anions in which more than one M addenda-type is present in the framework, the molecule is known as a *mixed-addenda* cluster. The study of mixed-addenda anions is a fundamental part of this thesis, and will be discussed at length in Part II.

Basic structural units

POMs are a family of medium-to-large-sized molecular (discrete) metal-oxides. Metal-oxide aggregates with fewer than 3–4 metal centres are traditionally *not* POMs. Nevertheless, due to the increasing diversity of

structures classified as such in the literature, the unequivocal definition of this group of compounds becomes gradually more and more diffuse. Be that as it may, countless reports,²¹ books¹⁷ and reviews¹⁸⁻¹⁹ have been published on this topic, showing an enormous molecular diversity amongst the inorganic family of molecules. This diversity is somehow a consequence of the rich, unprecedented and unusual properties associated to POMs. Many authors claim that they can be regarded as packed arrays of pyramidal MO_5 and octahedral MO_6 units (see Figure 1.1). These entities are, then, the fundamental structural units and are somewhat similar to the $-\text{CH}_2-$ unit in organic chemistry.

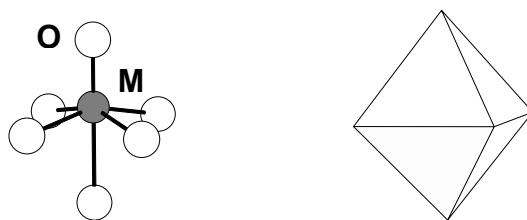
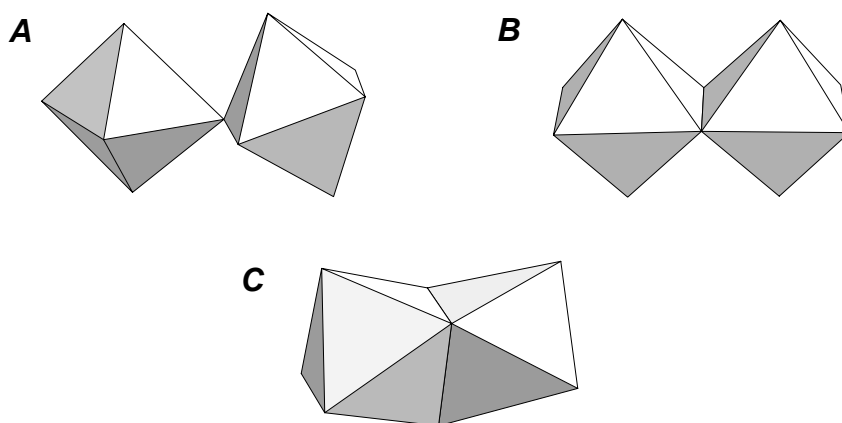


Figure 1.1. Ball-and-stick and polyhedral representations of the fundamental unit MO_6 . Note that the M atom is displaced off the geometrical centre of the octahedron towards one of the oxygens, thus giving rise to a distorted C_{4v} unit.

The very important MO_6 units (and the MO_5 partner as well but to a lesser extent) are, then, packed to form countless shapes. They join to one another, apparently, in accordance with a few simple rules (as $-\text{CH}_2-$ does in organic molecules). Observing a representative set of POM clusters, and identifying the MO_6 blocks, we notice that the molecule as a whole is built by edge- and/or corner-sharing MO_6 octahedra. Figure 1.2 shows these simple unions. The most stable unions between two octahedra are the corner- and edge-sharing models,²⁰ in which the M^{n+} ions are far enough from each other, and their mutual repulsion is modest (Table 1.1). In case C of Figure 1.2, the metallic centres are closer than in any of the other two cases (A, B) and, at such distances, the repulsion is not balanced by the stabilisation due to the chemical bonding in the 2-block unit. The latter form of union is uncommon and all the structures presented in this text only deal with derivatives containing combinations of pairs of types A and B.

Table 1.1. Selected M–M distances (in angstrom units) of corner- and edge-sharing octahedra in POMs.

<i>Metal(ON)</i>	<i>corner-sharing</i>	<i>edge-sharing</i>
W(VI)	3.7	3.4
Mo(VI)	3.7	3.5
V(V)	3.5	3.2

**Figure 1.2.** The polyhedral models represent the three possible unions between two MO_6 octahedral units. A) corner-sharing, B) edge-sharing and C) face-sharing. Each corner represents an oxygen position.

The clathrate-like structure

Clathrate-like systems are molecular or supramolecular arrangements in which an internal unit is encapsulated by an external core. In metal-oxide polynuclear clusters, it is a common phenomenon that has been discussed by experimentalists²¹⁻²⁴ and computational chemists.²⁵⁻²⁷ A formulation for molecules that accomplish the requirements of a clathrate-like system was introduced in the way I@E, in which I and E are the internal and the external *fragments* (see Figure 1.3). Keggin, Wells–Dawson and Lindqvist anions were also formulated as

$[\text{XO}_4]^{n-} @ \text{M}_{12}\text{O}_{36}$	Keggin,
$[\text{XO}_4]_2^{n-} @ \text{M}_{18}\text{O}_{54}$	Wells–Dawson,
$\text{O}^{2-} @ \text{M}_6\text{O}_{18}$	Lindqvist,

where the external M_xO_y core is free of metallic electrons if the cluster is fully oxidised. This assumption can be very advantageous in the study of complex phenomena like the isomerism, as shall be discussed in chapter 4.

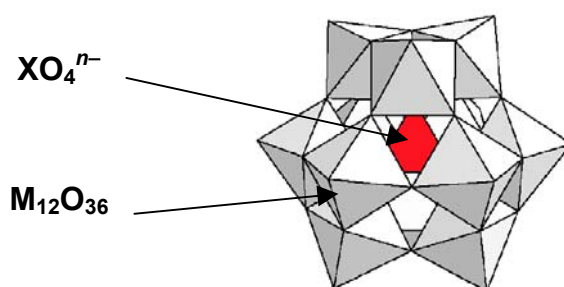


Figure 1.3. Polyhedral view of the clathrate-like structure of the Keggin anion. The external $\text{M}_{12}\text{O}_{36}$ core encapsulates the internal unit (represented as a red tetrahedron).

Chemical elements taking part in POMs

We have identified the addenda atom, M , as the most important entity in POMs. All the clusters included in this classification contain MO_n units, so the characteristics of M deserve further discussion. The fundamental structural block from which POM frameworks are built is the MO_6 unit,²⁸ where M is a transition-metal element. Many M elements are known to form six-fold, octahedral coordination compounds with oxygen, but not so many can take part, in MO_6 units, in a packed polynuclear metal-oxide aggregate. The structures of polyanions appear to be governed by the electrostatic and ionic radius principles of metal centres. That is, only selected values of the charge/radius ratio are observed in M^{n+} in combination with O^{2-} ligands, thus forming POMs. A few M s are commonly found or routinely included in a structure since these physical limitations control the stability of the metal-

oxide framework (see the values listed in Table 1.2). It only contains early transition metal elements, from the left of the periodic table. In fact, there are other ions that have values of q and r with limits similar to those shown in Table 1.2. So, apart from other transition metals, some p-block elements could be, at least in principle, good candidates for being included in MO_6 units as addenda.

However, charge and radius are not the only considerations to rule these assemblages of metal-centred units. Actually, an additional parameter to be considered, related to M , is the ability to form metal-oxygen π -bonds. This affects the stability of these clusters, as well. It was observed long ago that, in octahedral MO_6 blocks, the metallic centre is not in the very middle of the polyhedron, but somewhat displaced from the geometrical centre towards one of the corners (see Figure 1.1). More precisely, it is displaced towards the corner that does not share another octahedron, and the oxygen at this position usually forms a double bond with the metal (see the cluster in Figures 1.2 and 1.4). This is another of the requirements that the M centre should comply with. These $p\pi$ - $d\pi$ interactions are of the greatest importance in the stability of metal-oxide clusters,²⁹ and only the elements listed in Table 1.2 are suitable for this purpose. The reader shall see in future chapters that terminal (unshared) oxygens are, in general, essentially non-basic since there is a strong inward polarisation of the oxygen's electron density. This accounts for the molecular (discrete) metal-oxide arrays of MO_6 units, instead of extended, insoluble infinite layers or solids.

Table 1.2. List of common metal cations, M^{n+} , taking part in POM frameworks. We especially highlight W and Mo for being the most typical as addenda atoms.

<i>Metal ion</i>	<i>Octahedral radius (\AA)</i>	<i>Observed coordination numbers in POMs</i>
W^{6+}	0.74	6
Mo^{6+}	0.73	4, 6, 7
V^{5+}	0.68	4, 5, 6, 7
Ta^{5+}	0.78	6
Nb^{5+}	0.78	6

Table 1.2. Continued.

Tc ⁷⁺	0.70 ^a
Ti ⁴⁺	0.74 ^a
Sb ⁵⁺	0.74 ^a

a) Shannon–Prewitt effective ionic radii for sixfold coordination.

It is precisely the ability to form M=O double bonds that makes *small* POMs possible. Nevertheless, exceptions to this rule are discussed in chapter 6. Despite all of the above, after nearly two centuries of POM chemistry, almost all the elements of the periodic table have somehow been incorporated into a polyoxometalate framework.³⁰ This accounts for the chemical variability of this field.

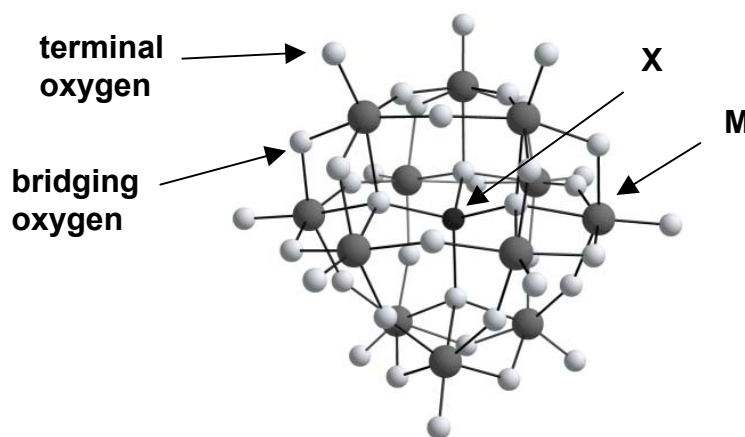


Figure 1.4. Ball-and-stick representation of the Keggin heteropolyanion. The terminal and bridging oxygen sites are indicated for further discussion.

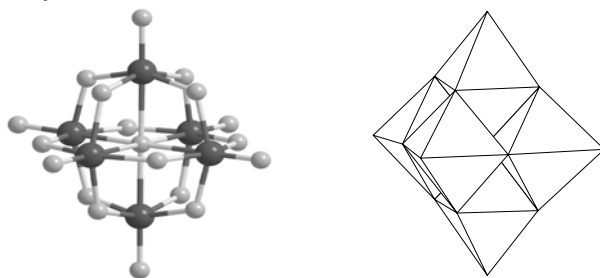
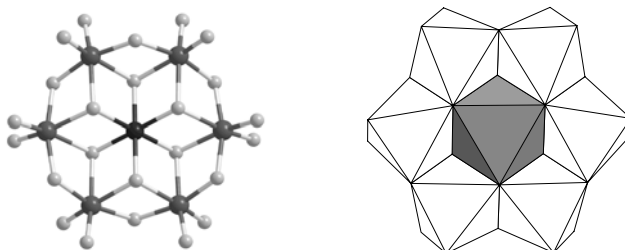
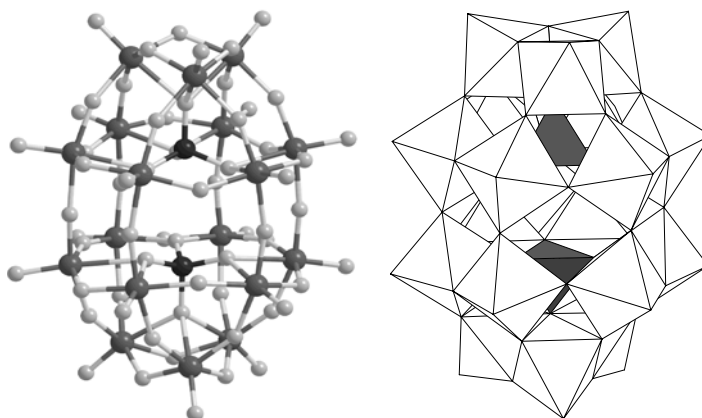
A. $M_6O_{19}^{n-}$ (Lindqvist)**B. $XM_6O_{24}^{n-}$ (Anderson)****C. $X_2M_{18}O_{62}^{n-}$ (Wells–Dawson)**

Figure 1.5. Ball-and-stick and polyhedral views of one isopolyanion (A) and two heteropolyanions (B, C). Dark grey spheres are metal centres, whereas light ones are oxygens. Black spheres (and the homologous dark polyhedra) contain the X heteroatom.

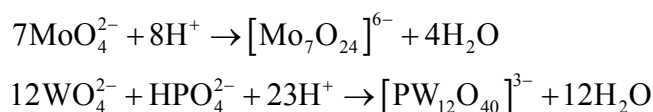
Fewer restrictions are found when the heteroatom X is part of a POM. Clusters with p-block elements (P, Si, Al, Ga, Ge...), transition metal elements (Fe(II/III), Co(I/II), Ni(II/IV), Zn(II)...), and even two H^+ have been synthesised. This position can be either tetrahedrally coordinated (as in Keggin and Wells–Dawson, or WD, anions) or octahedrally coordinated (as in the Anderson structure). Figure 1.5 shows a small collection of typical POMs including one isopolyanion (A) and two heteropolyanions (B and C). In B, atom X is surrounded by six oxo ligands in a pseudo-octahedral symmetry whereas, in C, two heteroatoms X are tetrahedrally coordinated. In Figure 1.4, only four oxygens surround the central atom. Form A only contains two structurally different atoms: M and O. However, the central atom (an oxygen) is chemically very different from the external ones since it is surrounded by six cations.



1.3. Features of Polyoxometalates

Preparation

Heteropoly- and isopolyanions are routinely prepared and isolated from both aqueous and non-aqueous solutions. The most common method of synthesis involves dissolving $[MO_n]^{m-}$ anions which, after acidification, assemble to yield a packed molecular array of MO_6 units. For example,



In general, care must be taken with pH conditions so that the reaction can be controlled. Sometimes, the sequence in which the reagents are added to the reaction media is important. One of the latest steps in synthetic procedures, and maybe the most important if POMs are to be completely characterised, is the isolation of crystals so that their features can be studied in greater depth. Clusters are precipitated by adding countercations (alkali metals, organic cations like TBA, ammonia, etc.) and subsequent separation. The crystals can then be fully characterised. As far as preparation and storage conditions are concerned, it is worth stressing that POMs are stable

in the presence of oxidising agents (air, water), and also at modestly high temperatures.

Redox properties

Addenda metals, M, are present in their highest oxidation state in all POMs, typically in d^0 or d^1 electronic configurations. They are also bonded to O^{2-} ligands, which produces very ionic structures. Formally, we have pairs like $W^{6+}-O^{2-}$ or $V^{5+}-O^{2-}$. They can be compared to metal-oxide crystals since the surface of molecular oxometal aggregates is similar to that of infinite surfaces. Thus, to what M_xO_y surfaces are interesting for, POMs can be as well with the great advantage of being soluble as discrete systems in liquid media. One can think in a powerful homogeneous catalyst with similar features to that of traditional crystalline surfaces.

There is little ligand-to-metal donation in their structure, so metal centres are willing to accept external electrons because their valence shell is empty. The overall charge of these anions depends on the heteroatom, X (formally P^{5+} , Al^{3+} , I^{7+} ...), and on the addenda metal. Fully oxidised M atoms in POMs usually have formal charges between 4+ and 6+. Obviously, the state of reduction of the molecules can vary this number. Even though they are negatively charged, reductions are common, and often accompanied by protonation. This is the principal feature of POMs: they are strong oxidising agents. The low-lying empty d-type orbitals of addenda atoms can accept numerous electrons with no major changes in their geometry. These extra electrons, located in d-metal orbitals, are called metallic or *blue* electrons. The latter term has its origin in the intense blue colour that can be observed when a few electrons reduce some common POMs. However, we will use the term *blue* regardless of the true colour of a reduced species it merely indicates the presence of metallic electrons. The localisation of metallic electrons is extensively studied throughout this text, and the relationship between the degree of localisation and the presence of different addenda atoms is stressed. The willingness of a given M atom to trap a metallic electron depends on its physical nature. There are many examples in the literature of POM clusters with a high number of metallic electrons (see chapter 7). This is why it is often said that they are a *reservoir* of electrons. An extensive study of reduced states can be found in reference.⁶ POMs, however, are stable in solution and in the solid state in their fully

oxidised forms, as well, obviously combined with counteranions balancing the negative charge that, in general, POMs carry.

Basicity

Another characteristic of POMs is their acid strength. Many acid-base equilibria in liquid media have been reported, in which POMs appear as polyacids.³¹ In most cases, their pK_a is lower than 0, which denotes strong acidity, although in very acidic media they can, of course, be protonated. Because of the chemical differences when POMs are bonded to M, not all oxygen sites in a POM framework are identically basic or acidic. This depends on the following parameters: the covalency/ionicity of the M–O bond, the number of neighbouring M atoms and the physical nature of M. This last point is especially important in the context of this thesis and will be dealt with in depth in the coming chapters. POMs are involved as catalysts in some organic reactions where proton transfer occurs. Incorporating a POM into acidic media can lead to polymerisation reactions, as well. Following similar chemical principles to those that govern the processes formulated in equations (1) and (2), molecular metal-oxides can self-assemble in the presence of protons and then produce larger oxometalates. The mechanics of this complex reaction are still not fully understood nowadays, although the parameters that govern the process are controlled quite well in solution. This phenomenon of polymerisation can, in principle, be attributed to many POMs in favourable conditions. After presenting the general results for the basicity of external oxo sites for a series of mixed-addenda Keggin anions, chapter 6 discusses the particular case of the Keggin dimerisation process.

Isomerism

The effect of isomerism on POMs is chemically subtle but it has been studied by both experimental and theoretical groups. The HPAs studied here have different isomeric forms: the Keggin and the Wells–Dawson anions (discussed in chapters 4 and 5). An assembly of four M_3O_{13} trimeric units forms the Keggin anion, $XM_{12}O_{40}^{n-}$ in general. Each of these trimers can be found in two possible orientations in the framework, thus giving five rotational isomers known as α , β , γ , δ and ε (see chapter 4). A similar rotational isomerism exists for the WD molecule. Differences in the

reduction potentials were found for different isomers of the same chemical formula, although the differences were smaller than those produced by changes in M. Isomers have some different properties, although in general they can be considered chemically similar. Nevertheless, the combination of isomerism and metal substitution make it possible for the properties of the cluster to be tuned.

1.4. Applications

All the value-adding properties presented above have many applications in the technological, chemical and medical fields. There are too many interesting applications to be listed here. At present, excluding medical and catalytic applications, there are nearly 20 categories in which POMs are attractive species.⁹ One of the traditionally reported applications concerns elemental analysis aided by POM chemistry. A large set of species, mostly metal elements, can be determined in solution. The reduction potentials in POM species vary considerably as a function of the geometrical characteristics of the cluster and the addenda atoms that take part. Redox potentials are affected by the overall charge of the species, too. So the reduction/oxidation properties can be *tuned* by choosing the heteroatom X, the addenda metal M and the framework.

Some brief comments should be made here, although they are far from exhaustive. POMs have been applied to medicine with considerable success and efficacy. Their oxidising ability is of particular interest. They catalyse many organic reactions and give high yields of reaction and good selectivity.³² Some POMs that contain vanadium centres have been investigated for environmental-friendly wood pulp bleaching.³³

The medical or biological/chemical principles governing the interactions between target biomolecules and drugs are

- redox potential,
- polarity,
- shape,
- surface charge distribution and
- acidity,

which are a set of attributes that chemists can skilfully control in POMs. So the features of POMs can be altered to fit the recognition rules for medical applications. An exhaustive compilation of the knowledge acquired in the field of medical applications of POMs can be found in the References.³⁴ The medical investigation of some oxometalates is promising although it is still in an initial stage. The *modus operandi* of POMs against viruses or tumoral agents, despite the amount of documentation on the subject, remains unclear. Some outlines of the mechanism have been proposed, though. In fact, POMs show high selectivity toward the target system, whether it is an enzyme or a membrane. The data collected over the years suggest that the overall charge and the charge density play a key role in the efficiency of the inhibition. Some reports have concluded that there is a lock-and-key mechanism between POMs and enzymes, so the size and the electrostatic properties of the oxometalate are determining factors for successful remedies.³⁴

1.5. Scope of the Thesis

The main goal of this thesis is to help rationalise the general physical basis of the chemical properties of POMs. The whole study is based on density functional theory calculations that have been proven to be appropriate for studying large molecular systems. Other mathematical tools are used and even introduced to the reader where needed. The theoretical details concerning the computation are discussed in length in chapter 2. The electronic properties of two well-known heteropolyanions —the Keggin ($\text{XM}_{12}\text{O}_{40}^{n-}$) and the Wells–Dawson ($\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$) anions— are the fundamental topic of the work. . A rather large set of compounds is presented, with variable X, M and the isomerism. So, the results are not limited to the compounds studied but can be extended to apply to all HPA behaviour. The data shall allow those interested in POM chemistry to find out about the origin of some properties. The main results will concern the following topics:

- The description of the structural features (geometry, clathrate-like framework, localisation of the charge, etc.) and the electronic properties of the Keggin and Wells–Dawson anions, as well as the redox chemistry associated to those clusters.

- The implications of the rotational isomerism in a series of HPAs, with different X and M, rationalised on the basis of their molecular orbitals' scheme. Changes in the MO sequence and energy can explain the reduction potentials observed experimentally.
- The chemical effects of the addenda substitution in HPA frameworks. A series of clusters (M = W, Mo, V, Nb, Ti) are analysed in terms of their protonation energies in different oxygen sites, and relative basicity scales are proposed.
- The dimerisation of mixed-addenda Keggin clusters. From the experimental information available, an attempt to unravel some aspects of the dimerisation process is made. The results combine protonation energies and Molecular Electrostatic Potential visualisation of the substituted Ti- and Nb-derivatives, as well as energy reaction profiles of possible dimerisation pathways.
- The influence of the solvent on the HPA's properties. A continuum model is used to show the effects of the solvent. Calculations carried out in this way show the downshift of the orbital energies accompanied by the stabilisation of the anions. An alternative study was made to give an approximate picture of the structure of a solvent surrounding a Keggin anion.

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