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Razi university

Faculty of Science  
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M.Sc. Thesis

**Synthesis of Bisnaphtholes with HPA  
&  
Synthesis of Spirans through Oxidation of Bisnaphtholes with  
 $H_2O_2/MoO_3$**

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**July 2008**

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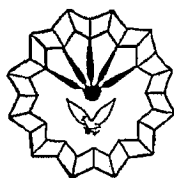
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*Dedicated to:*

*My Family*

**Abstract:**

In this thesis at first, synthesis of bisnaphtholes compounds with heteropoly acid catalyst were investigated in various conditions.

Bisnaphtholes compounds are produced with aromatic aldehydes and 2-naphtholes in the presence of heteropoly acid in solvent conditions and time of this reaction is shorter relative to similar reactions.

Corresponding bisnaphtholes are produced at low temperature and with good efficiency.

Because of availability, ease of usage and being eco-friendly, the group of Heteropoly acids applications has been increasing and is developing and they are interested in wide bases of research of catalyst and medicine.

Finally bisnaphtholes are oxidized using  $\text{H}_2\text{O}_2/\text{MoO}_3$  oxidizing conditions in solvent conditions and spiranes compounds were obtained in excellent yields in mild conditions.

Low cost, availability and easy use are advantages of  $\text{H}_2\text{O}_2/\text{MoO}_3$  oxidizing system.

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# **CHAPTER ONE**

## Introduction

## 1.1. Heteropoly acids

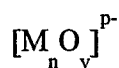
Polyoxometalates (POM), which include the compounds historically known as "heteropoly acids" (HPAs), have been investigated for well over a century. These compounds have attracted the interest of a significant number of researchers, due to the wide range of properties, such as a considerable structural versatility, accompanied by a large number of physicochemical properties<sup>1</sup>, like catalytic, magnetic and optical properties.<sup>2</sup>

Arguably no other class of compounds, inorganic or organic, displays more versatility with respect to electronic and molecular structures, properties and applications of this compound. POM is the field which currently attracts wide academic and industrial attention, especially with respect to catalysis and medicine (antiviral and anti-retroviral activity). Chemistry of these compounds serves as inexhaustible source for molecular models for different aspects, especially due to their versatile redox chemistry.

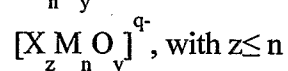
Many heteropoly compounds are highly coloured and the colours ranging through the spectrum and occurring in many shades. Also POM is a metallate containing anion or molecule consisting of transition metal ions bonded to other ligands, generally oxygen atoms, though some derivatives might contain nitrogen or sulfur. Furthermore POMs are anionic metal-oxygen clusters as the basic structural unit.<sup>3</sup>

Inorganic cluster anions form a class of compounds that is unique in its topological and is important in several disciplines. Isopoly anions (IPAs) and heteropoly anions are the classes that belong to POM. The general formulas which these complexes represented with them are shown below:

(1) Isopoly anions (IPAs)



(2) Heteropoly anions



## 1.2. Perspective

In 1826, Berzelius<sup>4</sup> published the first account of a compound that we now call a heteropoly salt. This was ammonium 12-molybdophosphate, "the yellow precipitate", which, produced when ammonium molybdate is added to phosphoric acid.

This compound now known as ammonium 12-molybdophosphate  $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$  beginning with the work of Svanberg and Struve<sup>5</sup>, became famous in analytical chemistry as the eventual basis for both gravimetric and volumetric determinations of phosphorus.

However it was not until the discovery of tungstosilicic acids (SiW) and their salts by Marginac in 1862 that the analytical compositions of such HPAs were precisely determined. Thereafter the field was developed rapidly, so that by the first decade of this century about 60 different types of HPAs had been described.<sup>6</sup>

In 1892, Blomstrand proposed the structure of phosphomolybdic acid (PMo) and other poly-acids as a chain or ring configuration.<sup>7</sup>

The first attempt to understand the composition of HPAs were based on Werner's coordination theory (1907).<sup>8</sup> Werner, using the coordination compounds ideas of Copaux attempted to explain the structure of SiW. He assumed a central group,  $[\text{SiO}_4]^{4-}$  ion, enclosed by four  $[\text{RW}_2\text{O}_6]^+$ , where R is a unipositive ion. The  $[\text{RW}_2\text{O}_6]^+$  are linked to the central group by primary valences.

A hypothesis advanced by Miolati and Pizzighelli in 1908 was adopted and developed by Rosenheim. During the subsequent 25-30 years Rosenheim was probably the most productive and influential researcher in the field of poly anion chemistry. According to the Miolati-Rosenheim (MR) theory HPAs were based on six coordinate hetero atoms with  $\text{MO}_4^{2-}$  or  $\text{M}_2\text{O}_7^{2-}$  anions as ligands or bridging groups.<sup>8</sup>

In 1928, Pauling<sup>9</sup> proposed the structure for the  $\alpha$ -Keggin anions with tetrahedral central ion,  $[\text{XO}_4]^{n-8}$ , caged with twelve  $\text{WO}_6$  octahedral. In this proposed structure, three of four oxygens on each of the octahedral shared electrons with three neighboring octahedral. As a result, 18 oxygen atoms were used as bridging atoms between the metal atoms. The remaining oxygen atoms bonded to protons. This structure explained many characteristics that were observed such as basicities of alkali metal salts and the hydrated of some of the salts. However the structure could no explain the structure of dehydrated acids.

While accepting the Rosenheim structure for 6:1 complex, Pauling noted that molybdenum(VI) and tungsten(VI) had crystal radii appropriate for octahedral coordination by oxygen and proposed a structure for the 12:1 complex based on an arrangement of twelve molybdenum(VI) or tungsten(VI) octahedra surrounding a central  $XO_4$  tetrahedron. The resulting formula were written as  $H_4[SiO_4W_{12}(OH)_{36}]$ , and these predicted the correct (observed) basicities. The structure was ultimately shown to be wrong in detail, since Pauling considered only the corner sharing between the  $MO_6$  octahedra.<sup>10</sup>

After four years, Keggin<sup>11</sup> using X-ray diffraction experimentally determined the structure of  $\alpha$ -Keggin anions. The Keggin structure accounts for the hydrated  $\alpha$ -Keggin anions as well as the dehydrated without significant structural changes. Keggin structure is the widely accepted structure for the  $\alpha$ -Keggin anions.

Keggin showed that the anion was indeed based on  $WO_6$  octahedra units as suggested, but these octahedra were linked by shared edges as well corners. Anions were confirmed shortly afterwards by Bradley and Illingworth's investigation of  $H_3[PW_{12}O_{40}] \cdot 29H_2O$ . Structure determination was based on powder photographs.<sup>12</sup>

After the papers on  $H_3[PW_{12}O_{40}]$  (PW), there followed a number of reports of isomorphous complexes, but the next new poly anion structure did not appear until 1948 when Evans<sup>13</sup> reported the structure of  $[TeMo_6O_{24}]^{6-}$ . The structure had, in fact, been suggested by Anderson twelve years previously as a possibility for the 6:1 heteropoly anions and for para(hepta)molybdate anion  $[Mo_7O_{24}]^{6-}$ . The different structure of the latter anion was finally reported by Lindqvist<sup>14</sup> in 1950.

In 1952, the formula indicated for the tungstate complex by Wells' proposed structure,  $[P_2W_{18}O_{62}]^{6-}$ , was established for the molybdo complex by Tsigdinos. Dawson in 1953 [19], determined by a single-crystal X-ray study that the positions of the W atoms in  $[P_2W_{18}O_{62}]^{6-}$  were as postulated by Wells. Since 1970 there has been a great expansion of work in the field of POMs, many papers have been published about these compounds.<sup>15</sup>

Where M is usually molybdenum or tungsten, less frequently vanadium, niobium or tantalum, or mixtures of these elements, in their highest ( $d^0, d^1$ ) oxidation states.<sup>12</sup> Such

POM anions form a structurally distinct class of complexes based predominantly although not exclusively, upon quasi-octahedrally-coordinated metal atoms.

A large part of the known heteropoly anions containing inorganic anionic ligands, comprise of tetrahedral phosphate groups, due to the amazing electronic and structural properties of POM-phosphates.

Although the elements that can function as addenda atoms, M, in heteropoly anions or IPAs, appear to be limited to those with both a favorable combination of ionic radius, charge and the ability to form  $d\pi-p\pi$  M–O bonds, whereas there is no such restriction on the heteroatom, X.<sup>10</sup> Over 60 other elements including most nonmetals and transition metals can function as heteroatoms.<sup>15</sup> Taking into account those species with different m/x ratios, with more than one type of heteroatom and with mixtures of addenda atoms, the resulting field of heteropoly anions is enormous.<sup>10</sup>

Polyoxo anions are important models for elucidating the biological and catalytic action of metal-chalcogenide clusters, since metal-metal interactions in the oxo clusters range from very weak (virtually none) to strong (metal-metal bonding) and can be controlled by choice of metal (3d, 4d, 5d), electron population (degree of reduction), and extent of protonation. Mixed-valence vanadates, in particular, show novel capacities for unpaired electrons, and the magnetic properties of these complexes may be tuned in a stepwise manner.

Metal-oxygen clusters are also present in the geosphere and possibly in the biosphere. The mixed-valence vanadates contribute to an understanding of the extremely versatile geochemistry of the metal. The significant differences between the chemistry of the polyoxo anions and that of the thio anions of the same elements are of relevance to heterogeneous catalysis, bioinorganic chemistry, and veterinary medicine. They also have found applications in analytical and clinical chemistry, catalysis (including photocatalysis), medicine (antitumoral, antiviral, and even anti-HIV activity), and solid-state devices. These fields are the focus of much current research.<sup>16</sup>

### 1.3. Structure of Polyoxometalates

The structures of heteropoly and isopoly anions appear to be governed by the well-known electrostatic and radius-ratio principles observed ionic lattices. It is therefore customary, and often convenient, to describe these structures in terms of assemblages of metal centered.

In every case the metal ion does not lie at the center of its polyhedron of oxide ions but it is displaced strongly toward the exterior of the poly anion structure, i.e., toward a vertex or edge of its own polyhedron.<sup>10</sup>

As it shown by various researchers, the metal atom displacement is in the directions predicted. Backer has argued that polarization of oxygen atoms by the small highly charged addenda results in the strong ion induced dipole forces that are responsible for atom displacements. Exterior terminal oxygens are polarized, in one direction only by a layer of addenda atoms just beneath the surface.

These addenda have moved from center of the anion and have interior oxygen atoms, with positive atoms on all sides, less polarized in any one direction. The surface oxygens, as a result of the inward polarization, are not easily protonated.<sup>17</sup>

On the following section, our focused is in some detail on common poly anion structures which illustrate most of the important structural features and isomerism to be found in the field of POMs.<sup>17</sup>

### **1.3.1. Isopoly Anions**

Traditionally, IPAs are poly anions containing only transition metals. Main group elements may appear but they are considered as ligands only, not as a part of the framework. Many IPAs are known today and the number of published structures increases rapidly with synthesis in nonaqueous solvents and with the use of ligands other than oxo ligands. IPAs may be based upon various metallic frameworks with a number of metal centers varying from 2 up to over 150. Involved metals are vanadium, niobium, tantalum, molybdenum, tungsten, and more seldomly some others. There are mixed species involving several types of metal atoms. It is also possible to have POMs in which other ligands having incorporated, for instance thio, or nitrosyl, or various organic moieties, all of them replacing oxo ligand(s) of a parent structure. Finally mixed species in which the same metal species occurs under various oxidation states are known. In summary IPA subclasses include<sup>17</sup>:

- A) The Anderson structure and derived compounds
- B) Isopoly Anions with five metal centers
- C) Isopoly anions with a larger number of metal centers

#### **1.3.1.1. The Anderson Structure and Derived Compounds**

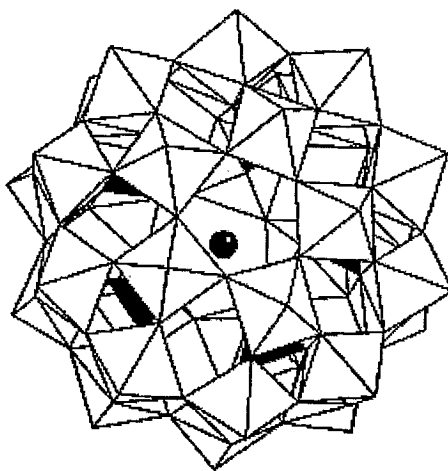
The Anderson structure may be described as an isopolyoxometalate containing a crown of six octahedrons sharing edges. The center may be occupied or not. Oxo ligands and mixed-ligand compounds are Anderson structure derivative.<sup>17</sup>

### 1.3.2. Heteropoly Anions

Heteropoly anions are those poly anions and their derivatives made of an assembly of fused  $\text{MO}_6$  octahedrons more or less completely wrapped around a tetrahedron containing traditionally a main group element, more seldomly a transition metal. In the following section some of heteropoly anions have been brought.

#### 1.3.2.1. Heteropoly Anions Containg a Large Number of Tungsten Atoms

$[\text{P}_5\text{W}_{30}\text{O}_{110}]^{15-}$  is the fusion of five  $\text{PW}_6\text{O}_{22}$  groups which are joined together, forming a doughnut shaped compound which has a 5-fold axis of symmetry (Scheme 1.1).<sup>18</sup> Each



Scheme 1.1.  $[\text{P}_5^{\text{V}}\text{W}_{30}\text{O}_{110}]^{15-}$  has molecular 5-fold axis of symmetry with anion encapsulated into this doughnut shaped compound as a black circle; it may be sodium or europium or others. The five phosphorus-containing tetrahedrons are black.

group has two such neighboring groups and it shares four oxygen atoms with each of them, so that there are 20  $\mu$ -oxo bridges in the whole structure interconnecting five  $\text{PW}_6\text{O}_{14}$  groups.



Other derivatives from heteropoly anions contain: reduced compounds, mixed-metal heteropoly anion, compounds with one vacant metal site, a heteropoly anion with an eight metal atom skeleton.

## 1.4. Applications of Polyoxometalates

The field of POMs, although a mature field, continues to attract significant attention. The number of publications and patents continues to grow and also new researchers are entering in this field.

The applications of POMs are centered primarily on their redox properties, photochemical response, ionic charge, conductivity and ionic weights.<sup>10</sup> Furthermore the wide range of applications of POMs, are based on their unique properties which include size, mass, electron and proton transfer (storage abilities), thermal stability, lability of "lattice oxygen" and high Brønsted acidity of the corresponding acids.

There are more commercial applications of POMs than other class of cluster compounds and promise for additional application in areas from catalysis and medicine to materials and micro device technology is substantial. POMs have long been used for detection, separation and quantitation based on properties like their high molecular weight, their electrochemical activity and reducibility to form coloured species and the fact that a wide variety of elements can be incorporated in the poly anion framework.

In 1996, according to Chemical Abstracts, nearly 600 refereed publications and over 120 patents were issued in reference to the POM chemistry and technology.<sup>19</sup>

The majority of the patent and applied literature is devoted to the applications of the Keggin type HPAs and their salts. Primarily  $\text{PMo}$ ,  $\text{PW}$ ,  $\text{H}_4\text{SiMo}_{12}\text{O}_{40}$  ( $\text{SiMo}$ ) and  $\text{SiW}$  are used as the main examples for many applications. Their popularity can be attributed to a large extent to the enormous volume of literature over several decades that describes their fundamental chemistry and to their commercial availability, which makes them convenient starting materials.

### 1.4.1. Catalysis

The high acid strength of HPAs makes them excellent catalysts for a wide variety of acid catalyzed reactions. Catalysis by HPAs and related POM compounds is a field of increasing importance.<sup>20</sup>

HPAs have several advantages as catalysts which make them economically and environmentally attractive.<sup>17</sup> On the one hand, HPAs have a very strong, approaching the superacid region, Brønsted acidity and also they are efficient oxidants, exhibiting fast reversible multielectron redox transformations under rather mild conditions. In acid catalysis the Brønsted acidity plays an important role. HPAs are active catalysts in solution compared to the conventional catalysts such as the mineral and organic acids.

Literature is rich in reports with the utility of heteropoly compounds as acid catalysts.<sup>17</sup> About 80-85% of patent and applied literature claims or investigates POMs for their catalytic activity. The remaining 15-20% of the applications can be grouped in the categories of Table A.<sup>21</sup>

**Table A.** Categories of applications for POMs (Derived from patent literature; excluding catalysis and medicine).<sup>22</sup>

1. Coatings	10. Electrochemistry/electrodes
2. Analytical chemistry	11. Capacitors
3. Processing radioactive waste	12. Dopants in nonconductive polymers
4. Separations	13. Dopants in conductive polymers
5. Sorbents of gases	14. Dopants in sol-gel matrixes
6. Membranes	15. Cation exchangers
7. Sensors	16. Flammability control
8. Dyes/pigments	17. Bleaching of paper pulp
9. Electro optics	18. Clinical analysis

Molar catalytic activity of acids is often 100-1000 times higher than that of mineral acids. Thus it is possible to carry out the catalytic process at a lower catalyst concentration and at a lower temperature.<sup>23</sup> Their acid-base and redox properties can be varied over a wide range by changing the chemical composition.

Great advantages of heterogeneous catalysts are easy separation and reusability. Furthermore HPAs and salts have been used as heterogeneous catalysts for a wide variety of reactions, and compilations up to 1973 are available. Examples include: oxidation of propylene and isobutylene to acrylic and methacrylic acids, and ammoxidation of

acrylonitrile, oxidation of aromatic hydrocarbons, olefin polymerization and epoxidation and hydro desulphurization.

HPAs are widely used as model systems for fundamental research, providing unique opportunities for mechanistic studies on the molecular level. At the same time, they become increasingly important for applied catalysis.<sup>17</sup> Most of the pioneering work has been done since the 1970s mainly by Japanese and Russian research groups. In the last two decades, the broad utility of HPA and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic substances.<sup>17</sup>

Several new industrial processes based on HPA catalysis, such as oxidation of methacrolein, hydration of olefins (propene and butenes), acylation of anisole with acetic anhydride<sup>24</sup>, polymerization of tetrahydrofuran, polycondensation of benzyl alcohols, and Friedel – Crafts type alkylation, acylation and sulphonation of aromatics, methyl tertiary butyl ether synthesis, oxidation of butadiene to furan, and dehydration of alcohols have been developed and commercialized.<sup>23</sup> There are no side reactions observed with the HPAs. Reduction of silver, copper and nickel salts of heteropoly anions with molecular hydrogen and carbon monoxide occurs at lower temperature than for the acids, indicating possibilities for improved catalyst design.<sup>25</sup>

The transition metal substituted compounds are active as oxidation catalysts with a wide range of organic / inorganic substrates and are operable with a wide variety of oxygen donors in various solvents.<sup>26</sup> Mixed addenda system coupled with Pd (II) salts are known to effectively catalyze aerial oxidation of olefins.

Catalytic processes involving heteropoly anions in homogeneous solution have received considerable attention by Russian workers, and they catalyze a wide variety of reactions in homogeneous liquid phase offering strong options for more efficient and cleaner processing compared to conventional mineral acids.<sup>27</sup> Being stronger acids, HPAs will have significantly higher catalytic activity than mineral acids.<sup>28</sup>

### **1.4.1.1. Acid Catalysis by Heteropoly Acids**

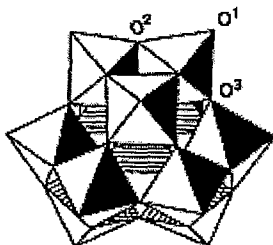
#### **1.4.1.1.1. Structure**

HPAs are complex proton acids that incorporate POM anions (HPAs) having metal-oxygen octahedra as the basic structural units.<sup>28</sup> The first characterized and the best known of these is the Keggin heteropoly anion typically represented by the formula

$\text{XM}_{12}\text{O}_{40}^{x-8}$  where X is the central atom ( $\text{Si}^{4+}$ ,  $\text{P}^{5+}$ , etc.), X is its oxidation state, and M is the metal ion ( $\text{Mo}^{6+}$  or  $\text{W}^{6+}$ ).<sup>29</sup>

Among a wide variety of HPAs, the Keggin's are the most stable and more easily available; these are the most important for catalysis. Solid HPAs possess a discrete ionic structure, comprising fairly mobile basic structural unit heteropoly anions and counter cations ( $\text{H}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ , etc.) unlike the network structure of, e.g., zeolites and metal oxides.

The crystal structure of HPAs depends on the amount of hydration water.<sup>30</sup> Unlike the rigid network structure of zeolites, in HPA crystal the Keggin anions are quite mobile.



**Scheme 1.2.** The Keggin structure of the  $\text{XM}_{12}\text{O}_{40}^{x-8}$  anion (R-isomer): terminal ( $\text{O}^1$ ), edge-bridging ( $\text{O}^2$ ) and corner bridging ( $\text{O}^3$ ) oxygen atoms

## ii) Proton Structure

HPAs are strong Brønsted acids.<sup>31</sup> Structural characterization of the HPA proton sites is an important step toward understanding the catalytic activity.<sup>32</sup> Keggin anions have three types of outer oxygen atoms as potential protonation centers: terminal oxygens  $\text{M}=\text{O}$  and two types of bridging oxygens  $\text{M}-\text{O}-\text{M}$ , edge sharing and corner sharing (Scheme 1.2).

Bond length-bond strength correlations<sup>38</sup> as well as  $^{17}\text{O}$  nuclear magnetic resonance (NMR) data<sup>34</sup> indicate that in the free poly anions (e.g.,  $\text{V}_{10}\text{O}_{28}^{6-}$ ) in solution, the bridging oxygen atoms, having a higher electron density than the terminal oxygen atoms, are protonated. Hypothetically, in the free Keggin anion in the gas phase, edge bridging  $\text{M}-\text{O}-\text{M}$  oxygens may be assumed to be the predominant protonation sites. In solid HPAs, the protons take part in the formation of the HPA crystal structure, linking the neighboring heteropoly anions. In this case the more accessible terminal oxygens can be protonated. Thus, from single-crystal X-ray and neutron diffraction data,<sup>35</sup> the crystal