General Introduction

In 21st century, Green and Sustainable Chemistry has emerged as a new concept and scientific area in both academia and industry with the aim of providing environmentally friendly option for hazardous synthetic pathways to achieve clean sustainable environment, maintaining the health and safety of people. Almost all chemical processes, through beneficial, leads unwanted wastes. The in-efficient recovery of organic solvents and their disposal are problems which damage environment.

Catalysis is a key technology to provide realistic solutions to such environmental issues [1]. The central tasks of catalysts are to lower the raw material and energy requirement of chemical reactions, the diminution of side products/waste products, as well as the control of hazardous effects of chemical substances for the sound establishment of chemical science and technology. To cope up with the problems, the development and implementation of ecofriendly as well as environmentally benign innovative catalysts as well as catalytic processes with high efficiency, simple operations, and simple work-up procedures are desirable and is the prime objective for chemists and scientists.

In this context, the uses of Polyoxometalates **(POMs)** and POMs based compounds as catalysts have become a very important field of research, industrially as well as academically [2-11]. They 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. They provide good basis for the molecular design of mixed oxide catalyst and have high capability in practical uses.

What are Polyoxometalates (POMs)?

POMs are a distinctive class with unique properties of topology, size, electronic versatility as well as structural diversity. Due to the combination of their added value properties such as redox properties, large sizes, high negative charge, nucleophilicity they play a great role in various fields such as medicine, material science, photochromism, electrochemistry, magnetism as well as catalysis.

POMs are a rich class of inorganic metal- oxide cluster compounds with transition metals in their highest oxidation state and have general formula $[X_xM_mO_y]^{n-}$, in which X is the hetero atom, usually a main group element (e.g. P, Si, Ge, As), and M is the addenda atom, being a d-block element in high oxidation state, usually V^V, Mo^{VI} or W^{VI} [11,12]. These compounds are always negatively charged, although the negative density is widely variable depending on the elemental composition and the molecular structure.

The free acids or acidic forms of POMs are known as heteropolyacids **(HPAs)**.

History of POMs

- The POMs have been known since the first report by Berzelius (1826). He described the yellow precipitate (ammonium 12-molybdophosphate) that is produced when ammonium molybdate is added in excess to phosphoric acid. [13].

After the discovery of this first POM, the field of POM chemistry progressed significantly [14].

- About 20 years later, Svanberg and Struve showed that the insoluble ammonium salt of this complex could be used for the gravimetric analysis of phosphate [15].
- However, the first polyoxotungstates were discovered and characterized by Marignac in 1862 [16]. He prepared and analyzed two isomers of 12-tungstosilicic acid viz. tungstosilicic acid and silicotungstic acid now known as α and β isomers.

During the next 70 years, POMs were rigorously investigated and over 60 different types of heteropoly acids (giving rise to several hundred salts) had been described by the end of first decade of the century.

- In 1908, according to A. Miolati hypothesis for heteropoly compounds, the heteroatom was considered to have octahedral coordination with MO_4^{2-} or $M_2O_7^{2-}$ ligands, based on coordination theory [17].
- In the mid 1930's, A. Rosenheim had given a laboratory perspective for the synthetic and descriptive research of Miolati [18].
- In 1929, L. C. Pauling [19] proposed a structure for 12:1 complexes based on an arrangement of twelve MO_6 octahedra surrounding a central XO_4 tetrahedron, which was a key step towards understanding the structure of POM anions. Pauling He proposed the structure of 12-tungstoanions based on the central PO_4 or SiO_4 tetrahedrons surrounded by WO_6 octahedrons. In order to minimize electrostatic repulsions, he proposed that all the polyhedral linkages involved sharing of vertices rather than edges. As a result the resulting formula required 58 oxygen atoms i.e. $[(PO_4)W_{12}O_{18}(OH)_{36}]^{3-}$. The structures he elaborated turned out to be incorrect because he did not consider the possibility of edge-sharing between MO_6 octahedra.
- After Pauling's proposal, in 1933 Keggin [20,21] solved the structure of $[H_3PW_{12}O_{40}].5H_2O$ by powder X-ray diffraction and showed that the anion was indeed based on WO6 octahedral units. These octahedra being linked by shared edges as well as corners. The application of X-ray crystallography to the determination of POM structures accelerated the development of POM chemistry.
- In 1934, Signer and Gross demonstrated that $H_4SiW_{12}O_{40}$, $H_5BW_{12}O_{40}$ and $H_6[H_2W_{12}O_{40}]$ were structurally isomorphous with Keggin's structure [22].
- Bradley and Illingworth confirmed Keggin's work in 1936, by studying the crystal structure of $H_3PW_{12}O_{40}.29H_2O$ [23].
- In 1977, Brown and co-workers largely supported the results of Bradley's and Illingworth's by the single crystal experiments [24].

With the development of POMs chemistry various types of structures were discovered. Polyhedral representations of various types of POMs are presented in Figure 1.

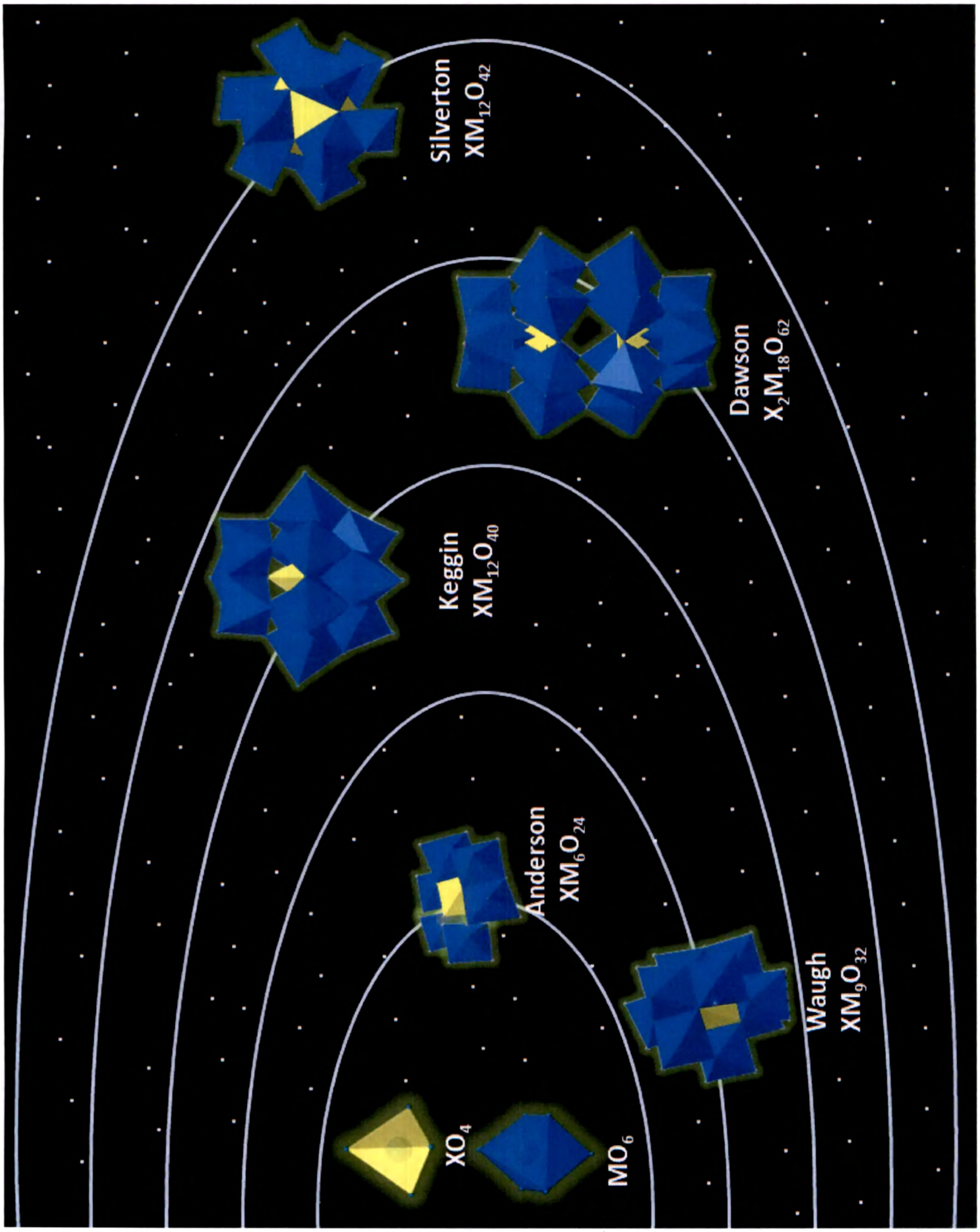
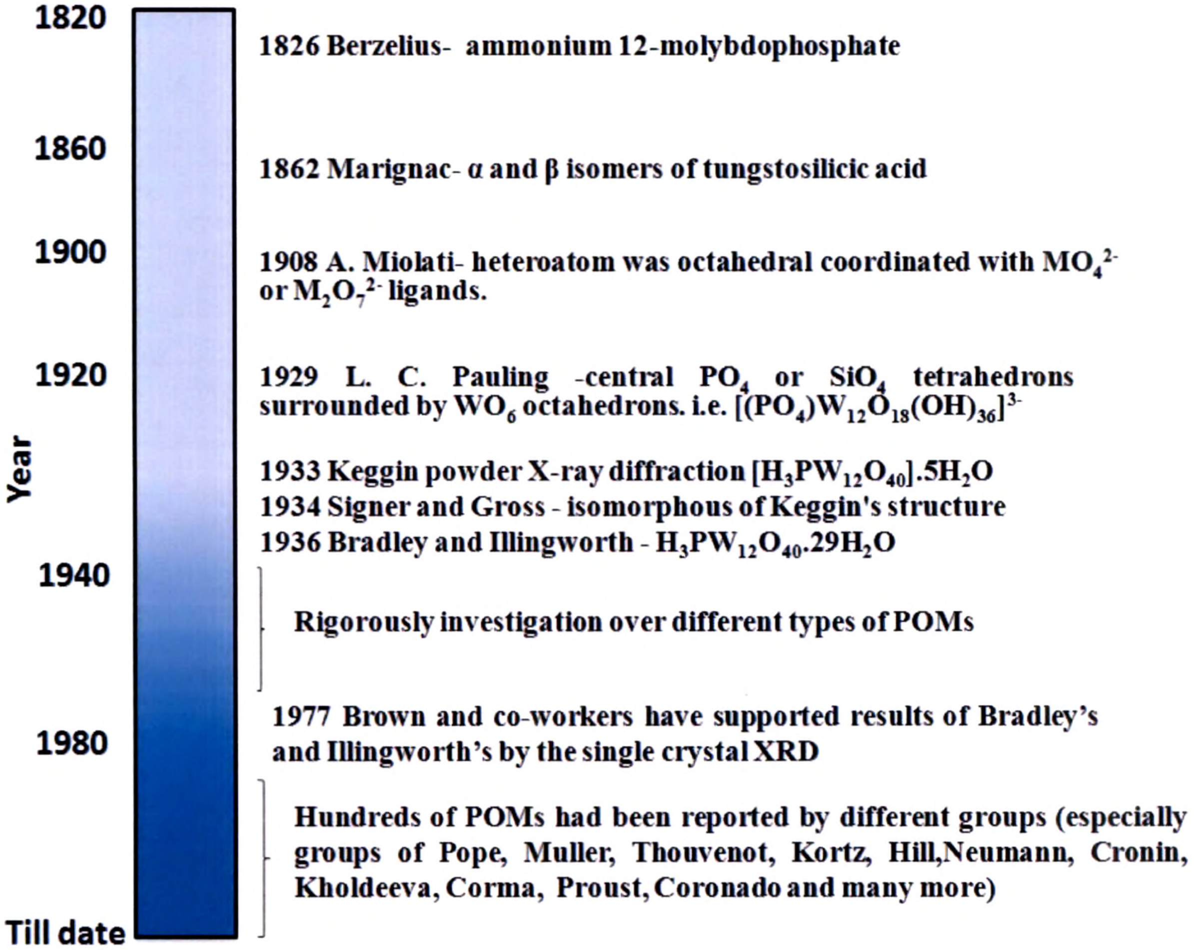


Figure 1. POMs family (Polyhedral representation)

After that, an extensive literature on their synthesis and structure has been accumulated and summarized in the form of reviews as well as books namely:

1. M. T. Pope, "Heteropoly and Isopoly Oxometalates" (Eds.) C. K. Jorgensen, Springer-Verlag, Berlin (1983)
2. Issue on Polyoxometalates, Eds. C. L. Hill, *Chem. Rev.*, 98, 1, (1998)
3. J. B. Moffat, "Metal-oxygen clusters: The surface and catalytic properties of heteropolyoxometalates", (Eds.) M. V. Twing, M. S. Spencer, Kluwer Academic plenum, New York, (2001)
4. "Polyoxometalate chemistry: From topology via self assembly to applications" (Eds.) M. T. Pope and A. Mucler, Kluwer Academic, (2001)
5. "Polyoxometalate Molecular Science", M. T. Pope, A. Muller, Kluwer Academic Publishers, (2003)
6. Polyoxometalate clusters, nanostructures and materials: From self assembly to designer materials and devices, D-L Long, E. Burkholder, L. Cronin, Chem. Soc. Rev., 36, 105, (2007).
7. Hybrid Organic−Inorganic Polyoxometalate Compounds: From Structural Diversity to Applications, A. Dolbecq, E. Dumas , C. R. Mayer, P. Mialane, Chem. Rev., 110 (10), 6009, (2010)
8. Polyoxometalates containing late transition and noble metal atoms, P. Putaj, F. Lefebvre, Coord. Chem. Rev., 255, 1642, (2011)
9. Theme issue: Polyoxometalate cluster science, Edited by L. Cronin, A. Muller, Chem. Soc. Rev., 41, 7325, (2012)
10. Polyoxometalate Chemistry: Some Recent Trends, Francis Secheresse, World Scientific Publishing Company (2013).

Among different POMs, Keggin type POMs are investigated extensively because of their easy synthesis as well as stability [12]. Chart 1 represents progress in Keggin POMs chemistry.



1826 Berzelius- ammonium 12-molybdophosphate

1862 Marignac- α and β isomers of tungstosilicic acid

1908 A. Miolati- heteroatom was octahedral coordinated with MO_4^{2-} or $M_2O_7^{2-}$ ligands.

1929 L. C. Pauling -central PO_4 or SiO_4 tetrahedrons surrounded by WO_6 octahedrons. i.e. $[(PO_4)W_{12}O_{18}(OH)_{36}]^{3-}$

1933 Keggin powder X-ray diffraction $[H_3PW_{12}O_{40}].5H_2O$
1934 Signer and Gross - isomorphous of Keggin's structure
1936 Bradley and Illingworth - $H_3PW_{12}O_{40}.29H_2O$

Rigorously investigation over different types of POMs

1977 Brown and co-workers have supported results of Bradley's and Illingworth's by the single crystal XRD

Hundreds of POMs had been reported by different groups (especially groups of Pope, Muller, Thouvenot, Kortz, Hill,Neumann, Cronin, Kholdeeva, Corma, Proust, Coronado and many more)

Chart 1. Progress in POM (Keggin) chemistry with respect to time

Structure of Keggin type POM

The ideal Keggin structure, $[XM_{12}O_{40}]^{3-}$ of α-type has T*d* symmetry and consists of a central XO_4 tetrahedron (X = heteroatom or central atom) surrounded by twelve MO_6 octahedra (M = addenda atom). The twelve MO_6 octahedra comprise four groups of three edge-shared octahedra, the M_3O_{13} triplet [19, 20], which have a common oxygen vertex connected to the central heteroatom. The oxygen atoms in this structure fall into four classes of symmetry-equivalent oxygens: X-O_a-$(M)_3$, M-O_b-M, connecting two M_3O_{13} units by comer sharing; M-O_c-M, connecting two M_3O_{13} units by edge sharing; and O_d-M, where M is the addenda atom and X the heteroatom. The schematic representation of Keggin type is shown in Figure 2.

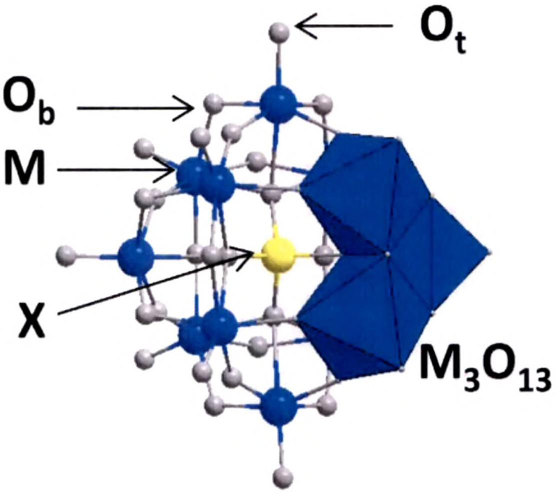


Figure 2. Keggin type $[XM_{12}O_{40}]$

POM compounds, in the solid state, are composed of polyoxoanions, cations such as protons, metals or onium ions and water of crystallization. Sometimes in additions they contain neutral organic molecules. From the view point of catalysis based on POMs, it is very important to distinguish between the primary, secondary and tertiary structure [2, 25-28]. It has also been realized that, in addition to these structures, tertiary and higher-order structures influence the catalytic function [28]. The different types of structures for the polyoxoanion are represented in Figure 3.

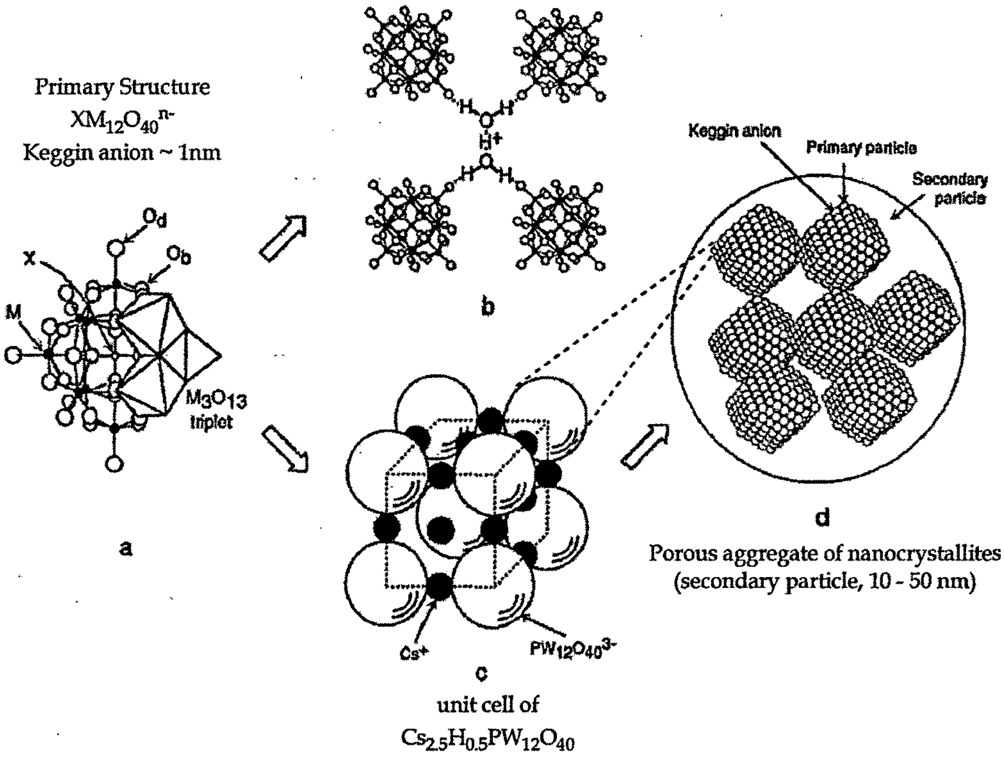


Figure 3. Primary, secondary, and tertiary structures of Keggin type POM; (a) Primary structure (Keggin structure, $XM_{12}O_{40}$); (b) secondary structure ($H_3PW_{12}O_{40}.6H_2O$); (c) secondary structure for unit cell of ($Cs_3PW_{12}O_{40}$); (d) tertiary structure with porous aggregates [$Cs_{2.5}H_{0.5}PW_{12}O_{40}$]; {Taken from "Advances in Catalysis", by M. Misono and N. Mizuno, 41, 113, (1996)}

The basic structure of a polyoxoanion molecule itself is called a "primary structure" and is formed from the condensation of oxoanions.

The secondary structure of the solid POM is formed from the coordination of the polyoxoanion with acidic protons, other cations and/or water molecules of hydration. A stable form contains six water molecules of hydration per Keggin unit, forming a body centered cubic (bcc) structure with Keggin units at the lattice points and $H_5O_2{}^+$ bridges along the faces. Each terminal oxygen atom is bound to a hydrogen atom of an $H_5O_2{}^+$ bridge. In this structure, the acidic protons are located in the $H_5O_2{}^+$ bridges between lattice points. If less than six water molecules are present, acidic protons may be located in remaining $H_5O_2^+$ bridges, in H_3O^+ or may be directly coordinated to oxygen atoms of the Keggin unit. The tertiary structure is the structure of solid POMs as assembled. The size of the particles, pore structure, distributions of protons in the particle etc. is the elements of the tertiary structure (Figure 3c).

Properties of POMs

POMs have usually low surface area (1-10 m^2/g) reflecting their high solubility in water. The pores of POMs are inter-particle, not intra-crystalline. Considering the size and shape of the Keggin anion and the crystal structure, there is no open pore through which nitrogen molecule can penetrate.

Thermal Stability

There are various kinds of stabilities, for example, thermal stability and hydrolytic stability in solution, and those stabilities change very much depending on the kind of POMs [25-27]. Some solid POMs in acidic form are thermally stable and applicable to vapor phase reactions conducted at high temperatures. The thermal stability of these POMs changes with heteroatom, polyatom and polyanion structure as follows:

$$PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-} > SiMo_{12}O_{40}^{4-}$$

But the thermal stability of mixed addenda heteropolyanions is generally low. The thermal stability of POM type compounds is studied extensively by TGA, DTA, XRD, etc.

DTA results of different POMs shows an endotherm at lower temperature and an exotherm at higher temperature (Table 1).

Table 1 DTA results of different HPAs:

Heteropolyacid	**Endotherm (K)**	**Exotherm (K)**
$H_3PW_{12}O_{40}$	448-569	853-868
$H_4SiW_{12}O_{40}$	413-551	743-773
$H_3PMo_{12}O_{40}$	336-432	663-681
$H_4SiMo_{12}O_{40}$	337-453	609-628

Herve et al. investigated the thermal changes of structures by means of XRD, TGA and DTA for Keggin type HPAs.

The low temperature endotherm is due to removal of water. The high temperature exotherm is ascribed to the decomposition of cage like structure of heteropolyanion compound to yield a more compact crystalline product consisting largely of oxides of Mo(VI) and W(VI).

From TGA and DTA two types of water are observed in heteropoly compounds i. e., water of crystallization and constitutional water molecules. The former usually lost at temperature below 473 K. The constitutional water molecules (acidic protons bound to oxygen of the polyanion) of $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ are lost at 623 K and 543 K respectively.

In situ XRD, ^{31}P NMR and thermoanalysis, it was concluded that thermolysis of $H_3PMo_{12}O_{40}$ proceeds in two steps, as shown below:

$$H_3PMo_{12}O_{40}.nH_2O \xrightleftharpoons[nH_2O]{473-623\,K} H_3PMo_{12}O_{40} \xrightleftharpoons[-1.5H_2O]{658\,K} H_xPMo_{12}O_{38.5+\frac{x}{2}(x=0.01)}$$

The MoO_3 phase appears at temperature higher than 573 K.

Acidic properties [29]

It was proved that acidic forms of POMs (HPAs) in the solid state are pure Bronsted acids and are stronger acids than the conventional solid acids such as SiO_2-Al_2O_3, H_3PO_4/SiO_2, HX and HY zeolites [8, 30]. HPAs are much stronger than the oxoacids of constitute elements and ordinary mineral acids. The strong acidity is caused by:

1. Dispersion of the negative charge over many atoms of the polyanion
2. The fact that the negative charge is less distributed over the outer surface of the polyanion owing to the double-bond character of the M=O bond, which polarizes the negative charge of O_t to M.

The dissolution constants of POMs along with mineral acids are presented in Table 2.

Table 2 Dissociation Constants of various acids and acidic form of POMs [29]

Dissociation Constants of acids and acidic form of POMs in Acetone at 25°C				
Sr. No.	**Acids**	**pK_1**	**pK_2**	**pK_3**
1	$H_3PW_{12}O_{40}$	1.6	3.0	4.0
2	$H_4PW_{11}VO_{40}$	1.8	3.2	4.4
3	$H_3PMo_{12}O_{40}$	2.0	3.6	5.9
4	$H_4SiMo_{12}O_{40}$	2.1	3.9	5.9
5	H_2SO_4	6.6	-	-
6	HCl	4.3	-	-
7	HNO_3	9.4	-	-

The acid strength is found to follow the order

$$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3AsW_{12}O_{40} > H_4GeW_{12}O_{40}$$

Redox properties

The addenda metal atoms in most POMs are in their highest oxidation states (d^0) and it is therefore clear that these complexes are in general capable of acting as oxidizing agents [13]. It was noted that certain polyanions, especially the 12-molybdo Keggin type species were readily reduced to form blue species more commonly known as "heteropoly blues" or "molybdenum blues". In most of the POM structures the addenda (i.e. metal) atoms occupy "octahedral" sites with either one or two terminal oxygen atoms. As a result, they can undergo facile reversible reduction to yield species of the type $\{MOL_5\}$ in which one or more of the metal centers has a reduced i.e. d^1 configuration.

Depending on the solvent, the acidity of the solution and the charge of the polyanion, the reductions involve either single electron or multi electron steps often accompanied by protonation. The oxidation potential is strongly dependent on the addenda atom and is not much influenced by central hetero atom. The oxidation potentials of polyanions containing Mo and V are high as these ions are easily reduced. It has been reported that oxidative ability decreases in the order V - > Mo - > W - containing heteropolyanion.

Redox properties of dodecapolyoxoanions depend on both the constituent elements of polyanions and counter cations. The oxidizing ability (or reducibility) has been estimated from the reduction of heteropoly compounds by H_2, CO and organic compounds. The methods involve measurements of the reduction rate at a constant temperature, the temperature-programmed reduction and the EPR signal formed by the reduction. Also the binding energy of the XPS peaks has been examined. Although the orders of oxidizing ability observed differ a little for the various methods adopted and the investigators, the following trends have been observed:

When the activation of a reducing agent proceeds easily, the reduction rate of polyanions approximately parallels the oxidation potential in solution. For example, in the case of heteropolyanions mixed with Pd / carbon powders, the order for the reduction by H_2 was

$$PMo_{12}O_{40}^{3-} > SiMo_{12}O_{40}^{4-} > PW_{12}O_{40}^{3-} > SiW_{12}O_{40}^{4-}$$

Oxidation reactions in which heteropoly compounds are efficient solid catalysts are oxidative dehydrogenation of aldehydes, carboxylic acids, ketones, nitriles, etc., to form C=C bonds at α position to a C=O or C=N group; and dehydrogenation of alcohols and amines to form C=O and C=N bonds, as well as oxidation of aldehydes to produce carboxylic acids.

Apart from these, the use of POMs in oxidation catalysis is much more complicated and diverse. The basic importance of using POMs in various homogeneous as well as heterogeneous oxidation catalysis is due to their inherent stability towards strong oxidants as well as their ability to retain their structures at high temperatures.

The advantage of POMs as catalysts [4]:

1. Catalyst can be designed at molecular levels based on the followings

I. Acidic and redox properties
   These properties of catalyst can be controlled by choosing appropriate elements (type of polyanion, heteroatom counter cation etc.)

II. Multi-functionality
   Acid-Redox, Acid-Base, multielectron transfer etc.

III. Tertiary structure, bulk type behavior etc for solid state:
   These are well controlled by counter cations

2. Molecularity-metal oxides cluster

I. Molecular design of catalyst

II. Cluster models of mixed oxide catalyst and relationships between solution and solid catalyst

III. Description of catalytic processes at atomic/molecular level.
Spectroscopic study and stoichiometry are realistic

3. Unique reaction field

I. Bulk type catalysis
"Pseudo-liquid" and bulk type-II behavior provide unique there dimensional reaction environment for catalysis

II. Pseudo-liquid behavior
This makes spectroscopic and stoichiometric studies feasible and realistic.

III. Phase transfer catalysis

IV. Shape selectivity.

4. Unique basicity of polyanion

I. Selective co-ordination and stabilization of reaction intermediates in solution and in pseudo-liquid phase, possibly also on the surface.

II. Ligands and supports for metals and organometallics.

Applications of POMs

Since the discovery of POMs, they found significant importance in various fields of science and technology. The field of POM chemistry is about more than two centuries old but still they are a large and rapidly growing class of compounds, especially because of their large domains of applications (Table 3).

Table 3 Areas of applications involving acidic form of POMs

Sr. No.	POMs	Application field	Reference
1	$H_4PMo_{11}VO_{40}$ $K_xH_{4x}PMo_{11}VO_{40}$ $H_5PMo_{10}V_2O_{40}$	modification of carbon electrodes, capacitors	31
2	$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$	electrolytic capacitors	32,33
3	$H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$	colorants for pigmenting paints, printing inks and plastics	34
4	$H_4SiMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$	dyes for polyester and polyacrylonitrile fibers	35
5	$H_3PW_{12}O_{40}$	electrochromic-ion conducting gels, films, xerogels; photochromic coatings for copiers	36-40
6	$H_4SiW_{12}O_{40}$	treatment of cathode electrodes (vitreous C and graphite) dopant of polyaniline and polypyrrole	41
7	$H_3PMo_{12}O_{40}$	dopant of poly(*N*-methylpyrrole)	42
8	$H_3PW_{12}O_{40}nH_2O$	liquid H_2-O_2 fuel cell	43
9	$H_4SiW_{12}O_{40}$	Au/*n*-Sb_2S_3 Schottky barrier solar cells	44

Thus, as mentioned above, in last two decades POMs have attracted significant interest in variety of fields.

Apart from these applications, POMs have played an important role in the field of acid as well as oxidation catalysis due to their high Bronsted acidity as well as their tendency to exhibit fast reversible multi-electron redox transformations under rather mild conditions and their inherent stability towards strong oxidants.

Hence they are widely used as a model system for fundamental research providing unique opportunities for mechanistic studies on the molecular level. At the same time they become increasingly important for applied catalysis. They provide good basis for the molecular design of mixed oxide catalyst and they have high capability in practical uses.

The first attempts to use POMs as catalysts were tracked way back in the 19th century. Systematic investigation of catalysis by POMs began in the early 1970's. Some of the major achievements of POM based compounds in the field of catalysis have been reviewed by number of groups.

1. Use of heteropolyacid compounds in acid catalyzed hydrocarbon reactions had studied by A. Corma, Chem. Rev., 559, (1995).
2. The catalytic properties of heteropoly compounds have been studied and reviewed by T. Okuhara, N. Mizuno, M. Misono, Adv. Catal., 41, 113, (1996).
3. Different reactions such as hydration, esterification, condensation, miscellaneous reactions, polymerization, alkylation, oxidation of various organic compounds has been studied and reviewed by I. V. Kozhevnikov, Chem. Rev., 171, (1998).
4. Structural and catalytic properties of heteropolyacids have also been studied and reviewed by N. Mizuno and M. Misono, Chem. Rev., 199, (1998).
5. "Catalysts for fine chemical synthesis: Catalysis by polyoxometalates", I. V. Kozhevnikov, Vol. 2, Wiley (2002).

6. Use of different heteropolyacids for oxidation of alcohols using molecular oxygen has been demonstrated by T. Mallat, Chem. Rev., 104, 3037, (2004)
7. "Green chemistry and catalysis", by R. A. Sheldon, Ch 2 Solid acids and bases as catalysts, Wiley (2007)
8. "Mechanisms in homogeneous and heterogeneous epoxidation catalysis", (Eds) S. Ted Oyama, Ch 4 "Activation of hydrogen peroxide by polyoxometalates" , N. Mizuno, Elsevier Publications, (2008)
9. "Modern heterogeneous oxidation catalysis, Edited by N. Mizuno, Ch 6 Liquid-Phase Oxidations with Hydrogen Peroxide and Molecular Oxygen Catalyzed by Polyoxometalate-Based Compounds". N. Mizuno, Wiley (2009).
10. Catalytic evaluation of different organic substrates over supported polyoxometalates has been studied by Y. Ren, B. Yue, M. Gu, H He, Materials, 3, 764, (2010)
11. Liquid Phase Oxidation Via Heterogeneous Catalysis: Organic Synthesis and Industrial Applications, Edited by M. G. Clerici, O. A. Kholdeeva, John Wiley & Sons (2013)
12. Environmentally benign catalysts for cleaner organic reactions, Edited by A, Patel, Springer (2013)

Apart from these, a number of patents describing use of POMs based compounds in catalysis are also available

1. Method of preparing heteropolyacid catalysts by Lyons et al, US Patent No.4916101, (1990)
2. Use of supported heteropolyacids for one step production of alkylphenol from olefins under adiabatic conditions by J. F. Knifton, US Patent No. 5300703, (1994)
3. Alkylation of isoparaffin with olefins to produce alkylate using heteropolyacids supported onto MCM-41 by Kresge et al., US Patent No. 5324881, (1994).

4. Zirconium hydroxide supported metal and heteropolyacid catalysts by Soled et al., US Patent No. 5391532, (1995).
5. Heteropolyacid supported onto sulfated zirconia as heterogeneous catalyst for alkylation of isoparaffins by Angstadt et al., US Patent No. 5493067, (1996).
6. Alkylation of aromatic amines using heteropolyacid catalyst by Rhubright et al., US Patent No. 5817831, (1998).
7. Polyoxometallate catalysts and catalytic processes by Davis et al., US Patent No 6914029 B2, (2005).
8. Oxidation of methanol and /or dimethyl ether using supported molybdenum containing heteropolyacid catalysts by Liu et al., US Patent No 6956134 B2, (2005).
9. Silica support, heteropolyacid catalyst produced there from and ester synthesis using the silica supported heteropolyacid catalyst by Bailey et al., US Patent No. 2008/004466 A1, (2008).
10. Process for alkylation of phenol by N. Bhatt et al., US Patent No. 7692047 B2, (2009).
11. Process for production of alkenes from oxygenases by using supported heteropolyacid catalysts by Gracey et al., US Application No. 2010/0292520A1, (2010).
12. Materials for degrading contaminants by Hill et al., US 7655594 B2 (2010).
13. Method for the breakdown of lignin by Voitl et al., US 7906687 (2011).
14. Method for producing phenolphthalein suing heteropolyacid catalyst by Bolta et al., US Patent No 7868190 B2, (2011).
15. Process for oxidizing alkylaromatic compounds by Jaensch et al., US 7906686 B2 (2011).

A literature survey shows that plenty of studies have been carried out on **unsupported (homogeneous) as well as supported (heterogeneous)** POMs by different groups in the field of acid as well as oxidation catalysis. The world of catalysis by POMs is largely expanded and it would be difficult to mention all references. Hence, in the present thesis, **we would like to restrict ourselves to**

supported POMs, especially for oxidation catalysis. We would also like to excuse us if some of the references are missing as it is quite difficult to summarize such a huge number of available references for the same.

Oxidation catalysis over supported POMs

A detailed survey of literature shows that Venturello and coworker in 1983 carried out epoxidation of electron poor terminal alkenes in presence of phase transfer catalysts over tungstate and phosphate salts [45]. Later on, in 1987 Ishii and coworkers carried out same process of epoxidation of relatively electron poor terminal olefins by utilizing the more environmentally and economically significant oxidant, H_2O_2 and $H_3PW_{12}O_{40}$, in presence of a phase transfer catalyst **(PTC)** such as cetyl pyridinium chloride (CPC) or Arquad [46]. After Ishii's work, HPAs attracted much attention and have been used as catalytic systems in presence of a PTC (CPC) in biphasic medium for oxidation of a large number of organic substrates [47-57].

Oxidation of methyl alcohol using $H_4SiMo_{12}O_{40}$ supported onto silica [58,59] was studied by M. Fournier and coworkers as well as by C. Rocchiccili and group. A. Molinari and coworkers carried out oxygenation of cyclohexane using $H_3PW_{12}O_{40}$ supported onto silica [60], R. A. W. Johnstone's group carried out oxidation of alkenes using $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ supported onto aluminum, zinc and magnesium oxide [61], Xi Chen group performed studies on oxidation of propylene to acetone using $H_3PMo_{12}O_{40}$ supported onto silica [62], J. L. G. Fierro and coworkers have carried out oxidation of methyl alcohol using $H_3PMo_{12}O_{40}$ supported onto ZrO_2-SiO_2 [63], W. Y. Lee and group carried out oxidation reactions with supported $H_3PW_{12}O_{40}$ [64]. One-stage Wacker-Type oxidation of C2-C4 Olefins [65], biphasic oxidation of arenes with oxygen [66], epoxidation of oleic acid [67] was also evaluated by Kozhevnikov's group. The same group also reported the oxidation of 2,3,6-trimethylphenol [68] using supported $H_3PW_{12}O_{40}$.

J. B. Moffat studied oxidation of methane [69] using silica supported different $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$. E. R. Herrero and L. R. Pizzio studied limonene epoxidation [70] using carbon and alumina supported $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$. Edyta-Stochmal-Pomarzanska and group carried out oxidation of propylene with polymer supported $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ [71]. Yong-Gun Shul and coworkers carried out oxidation of ethanol with silica supported $H_3PW_{12}O_{40}$ [72]. Michel Fournier and group carried out oxidation of methanol with silica supported $H_3PMo_{12}O_{40}$ [73]. Kyu Song and coworkers carried out methacrolein oxidation with polystyrene supported $H_3PMo_{12}O_{40}$ [74]. P. S. Sai Prasad and his group studied ammoxidation of 2-methylpyrazine with zirconium dioxide supported $H_3PMo_{12}O_{40}$ [75]. M. Naik et al. reported the use of $H_3PMo_{12}O_{40}$ supported on Al-pillared clay for benzoxanthenes synthesis [76]. Recently, J. Ferrell et al. reported the use of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$ dispersed over Nafion coated with Pt/C for oxidation of dimethyl ether to be used in fuel cells [77]. Kholdeeva et al. reported H_2O_2-based alkene epoxidation over $PW_{12}O_{40}$/MIL-101 [78]. All reported oxidation reactions have been carried out in presence of organic solvents such as acetone, acetonitrile, hexane as well as PTC.

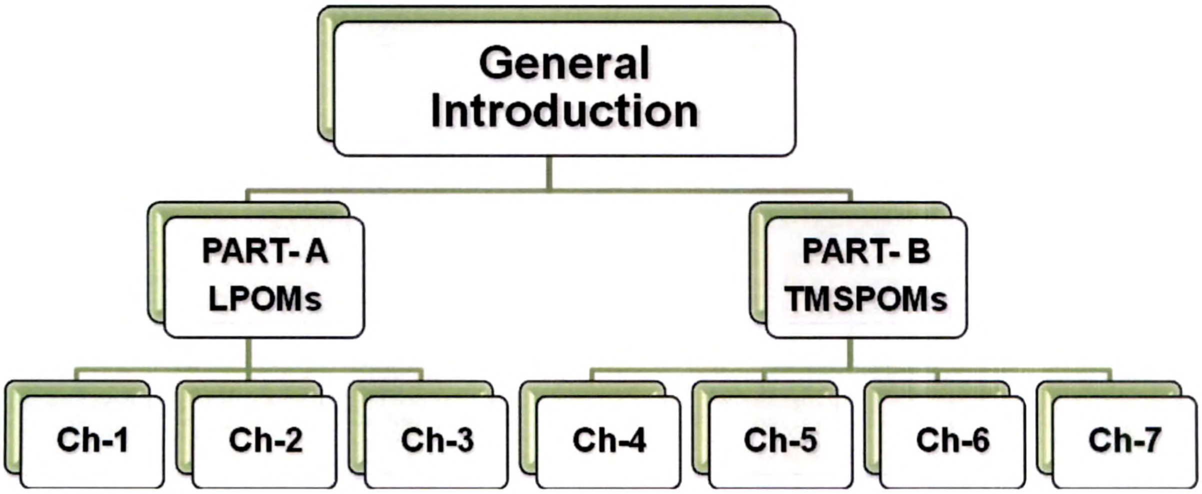
As discussed earlier, the redox properties of POMs can be tuned at molecular level which can lead to development of a new class of materials with unique structural as well as electronic properties. One of the most significant properties of modified precursors is their ability to accept and release specific numbers of electrons reversibly, under marginal structural rearrangement [79-81]. As a result, they are expected to play an important role in catalysis. Thus, the modification of parent POMs are likely to help in development of new generation catalysts with enhanced redox properties as well as stability.

The modification of properties can be basically done by tuning the structural properties at the atomic or molecular level in two ways (i) By creating defect (lacuna) in parent POM structures (i.e. Lacunary Polyoxometalates, LPOMs) and (ii)

Incorporation of transition metal ions into the defect structures (i.e. Transition Metal Substituted Polyoxometalates, TMSPOMs).

A literature survey shows that almost all work have been carried out on polyoxotungstates. At the same time, similar reports on analogous **polyoxomolybdates** are scanty. Keeping these in mind, present work aims to design catalytic materials based on polyoxomolybdate, as well as to explore their use as stable, recyclable and sustainable catalysts, especially for oxidation reactions.
The thesis is divided into two parts (A) Lacunary Polyoxometalates and (B) Transition Metal Substituted Polyoxometalates.

ORGANIZATION OF THE THESIS



Chapter 1 consists of detailed introduction of the LPOMs. Special attention was given to the history of LPOMs as well as need for developing the novel catalytic materials based on the same.

Chapter 2 describes synthesis and physicochemical characterization of mono lacunary molybdophosphate (undecamolybdophosphate; PMo_{11}), supported PMo_{11} i.e. PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3; Hydrous Zirconia and neutral alumina were used as supports.

Chapter 3 describes the catalytic activity of PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3 for solvent free liquid phase oxidation of alcohols and alkenes using environmentally benign oxidants viz. O_2 and 30% aqueous H_2O_2.

Kinetic study for oxidation of styrene with H_2O_2 over supported catalysts was studied.

A comparative study of supported catalysts was also studied for oxidation reactions.

Chapter 4 consists of introduction of Transition metal substituted phosphomolybdate and their importance in oxidation catalysis. By proper selection of the redox active transition metal ion and substituting them into the polyanions can lead to development of active and selective oxidation catalysts. As Co, Mn and Ni have good redox properties, they were chosen for substitution.

Chapter 5 consists of one pot *in situ* synthesis of cesium salt transition metal (Co, Mn, Ni)- substituted phosphomolybdate; $PMo_{11}M$ (M= Co, Mn, Ni). The synthesized complexes were systematically characterized by various spectroscopic techniques as well as Single-crystal X-ray diffraction.

Chapter 6 describes the catalytic activity of $PMo_{11}M$ (M= Co, Mn, Ni) for solvent free liquid phase oxidation of alcohols and alkenes using environmentally benign oxidants viz. O_2 and 30% aqueous H_2O_2. Comparison of catalytic activity of $PMo_{11}M$ (M= Co, Mn, Ni) was studied. Kinetic study for oxidation of styrene with H_2O_2 was also studied.

Chapter 7 describes use of $PMo_{11}Ni$ as a sustainable catalyst for C-C coupling.

REFERENCES

1. G. Centri, P. Ciambelli, S. Perathoner, P. Russo, Catal. Today, 75, 3, (2002).
2. M. T. Pope, Inorganic Chemistry Concepts Vol. 8: Heteropoly and Isopoly Oxometalates, Springer, Berlin, (1983).
3. C. L. Hill, C. Chrisina, M. Prosser-McCartha, Coord. Chem. Rev., 143, 407, (1995).
4. T. Okhuhara, N. Mizuno, M. Misono, Adv. Catal., 41, 113, (1996).
5. R. Neumann, Prog. Inorg. Chem., 47, 317, (1998)
6. N. Mizuno, M. Misono, Chem. Rev., 98, 199, (1998).
7. I. V. Kozhevnikov, Chem. Rev., 98, 171, (1998).
8. I. V. Kozhevnikov, Catalysis by Polyoxometalates, Wiley, Chichester, (2002).
9. C. L. Hill in Comprehensive Coordination Chemistry II, Vol 4 (Eds.: J. A McCleverty, T. J. Meyer), Elsevier Pergamon, Amsterdam, 679 (2004).
10. N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev., 249, 1944, (2005).
11. N. Mizuno, S. Hikichi, K. Yamaguchi, S. Uchida, Y. Nakagawa, K. Uehara, K. Kamata, Cat. Today., 117, 32, (2006).
12. M. T. Pope, A. Muller (Eds.), Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications, Kluwer, Dordrecht, (2001).
13. J. J. Berzelius, Pogg. Ann. Phys. Chem., 6, 369, (1826).
14. "Polyoxometalate Molecular Science", M. T. Pope, A. Muller, Kluwer Academic Publishers, (2003).
15. L. Svanberg, H. Struve, J. Prakt. Chem., 44, 257, 291, (1848).
16. C. Marignac. Ann. Chim., 25, 362, (1862).
17. A. Miolati, R. Pizzighelli, J. Prakt. Chem., 77, 417, (1908).
18. A. Rosenheim, H. Jaenicke, Z. Anorg. Allg. Chem., 100, 304, (1917).
19. L. C. Pauling. J. Am. Chem. Soc., 51, 2868, (1929).
20. J. F. Keggin. Nature, 131, 908, (1933).
21. J. F. Keggin. Proc. Roy. Soc. A, 144, 75, (1934).
22. R. Signer, H. Gross, Helv. Chim. Acta, 17, 1076, (1934).
23. A. J. Bradley, J. W. Illingworth, Proc. R. Soc., A157, 113, (1936).

24. G. M. Brown, M.-R. Noe-Spirlet, W.R. Busing, H.A. Levy, Acta Crystallogr., B33, 1038, (1977).
25. M. Misono, K. Sakata, Y. Yoneda, W. Lee, in "Proc. 7th Int. Congr. Catal., Tokyo, 1980, 1047; Kodansha, Tokyo, Elsevier, Amsterdam, (1981).
26. M. Misono, Catal. Rev.-Sci. Eng., 29, 269 (1987).
27. M. Misono, Catal. Rev.-Sci. Eng., 30, 339 (1988).
28. M. Misono, in "Proc. 10th Int. Congr. Catal., Budapest, 1992," p. 69. Elsevier, Amsterdam, and Akademiai Kiado, Budapest, (1993).
29. M. Furuta, K. Sakata, M. Misono, Y. Yoneda, Chem. Lett., 31, (1979).
30. M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara, Y. Yoneda, Bull. Chem. Soc. Jpn., 55, 400, (1982).
31. J. Calahan, E. Cueller, M. Desmond, J. Currie, U.S. Patent 4633372 A, (1986).
32. T. Morimoto, T. Matsubara, Y. Hamaya, N. Iwano, Japanese Patent JP 62114207 A2, (1987).
33. R. S. Alwitt, German Patent DE 2618616, (1976); (English equivalent, U.S. Patent 4031436).
34. F. Closs, B. Albert, H. Wienand, European Patent EP 619346, (1994).
35. R. A. Clarke, U.S. Patent 3387916, (1968).
36. D. E. Katsoulis, J. R. Keryk, Abstract ACS National Meeting, Inorganic Chemistry Section, Aug 20-24, Chicago, (1995).
37. M. Tasumisago, H Honjo, Y. Sakai, T. Minami, Solid State Ionics, 59, 171, (1993).
38. B. Orel, U. Lavrencic-Stangar, M. G. Hutchins, K. J. Kalcher, Non-Cryst. Solids, 175, 251, (1994).
39. A. Averbach, U.S. Patent 3623866, (1971).
40. A. Averbach, U.S. Patent 3687672, (1972).
41. L. Nadjo, B. Keita, French Patent FR 2573779 A1, (1986).
42. G. Bidan, E. Genies, M. Lapkowski, European Patent EP 323351 A1, (1989).
43. N. Giordano, P. Staiti, S. Hocevar, A. S. Arico, Electrochim. Acta., 41, 397, (1996).
44. O. Savadogo, K. C. Mandal, Electron. Lett., 28, 1682, (1992).

45. C. Venturello, E. Alneri, M. Ricci, J. Org. Chem., 48, 3831, (1983).
46. Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, J. Org. Chem., 52, 1868, (1987).
47. C. Venturello, R. D. Aloisio, J. Org. Chem., 53, 1553, (1988).
48. Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T, Yoshida, M. Ogawa, J. Org. Chem., 53, 3587, (1988).
49. Y. Ishii, T. Yoshida, K. Yamawaki, M. Ogawa, J. Org. Chem., 53, 5549, (1988).
50. T. Oquchi, Y. Sakata, N. Takeuchi, K. Kaneda, Y. Ishii, M. Ogawa, Chem. Lett., 2053, (1989).
51. F. P. Ballistreri, S. Failla, E. Spina, G. A. Tomaselli, J. Org. Chem., 54, 947, (1989).
52. Y. Ishii, Y. Sakata, J. Org. Chem., 55, 5545, (1990).
53. C. Aubry, G. Chottard, N. Platzer, J. M. Bregeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Inorg. Chem., 30, 4409, (1991).
54. A. C. Dengel, W. P. Griffith, B. C. Parkin, J. Chem. Soc. Dalton Trans., 2683, (1993).
55. S. Sakaguchi, S. Watase, Y. Katayama, Y. Sakata, Y. Nishiyama, Y. Ishii, J. Org. Chem., 59, 5681, (1994).
56. A. J. Bailey, W. P. Griffith, B. C. Parkin, J. Chem. Soc. Dalton Trans. 1833, (1995).
57. L. Salles, J-Y Piquemal, R. Thouvenot, C. Minot, J-M. Brequeault, J. Mol. Catal., 117, 375, (1997).
58. J. M. Tatibouet, M. Che, M. Amirouche, M. Fournier, Claude Rocchiccioli-Deltcheff, J. Chem. Soc. Chem. Comm., 1260, (1988).
59. C. Rocchiccioli-Deltcheff, M. Amirouche, M. Fournier, J. Catal., 138, 445, (1992).
60. A. Molinari, R. Amadelli, L. Andreotti, A. Maldotti, J. Chem. Soc. Dalton Trans., 1203, (1999).
61. C. D. Brooks, L-chu Huang, M. Mc Carvon, R. A. W. Johnstone, J. Chem. Soc. Chem. Comm., 37, (1999).
62. M. Li, J. Shen, X. Ge, Xi Chen, Appl. Catal. A: Gen., 206, 161, (2001).

63. L. M. Gomez Sainero, S. Damyanova, J. L. G. Fierro, Appl. Catal. A: Gen., 208, 63, (2001).
64. S. S. Lim, Gyo Ik Park, In Kya Song, W. Y. Lee, J. Mol. Catal. A: Chem., 182, 175, (2002).
65. A. Lambert, E. G. Derouane, I. V. Kozhevnikov., J. Catal., 211, 445, (2002).
66. H. A. Burton, I. V. Kozhevnikov. J. Mol. Catal. A: Chem., 185, 285, (2002).
67. I. V. Kozhevnikov, G. P. Mulder, M. C. Steverink-de Zoete, M. G. Oostwal, J. Mol. Catal. A: Chem., 134, 223, (1998).
68. O. A. Kholdeeva, A. V. Golovin, R. I. Maksimovskaya, I. V. Kozhevnikov., J. Mol. Catal., 75, 235, (1992).
69. S. Kasztelan, J. B. Moffat, J. Catal., 106, 512, (1987).
70. S. G. Casuscelli, M. E. Crivello, C. F. Perez, G. Ghione, E. R. Herrero, L. R. Pizzio, P. G. Vazquez, M. N. Blanco, Appl. Catal. A: Gen., 274, 115, (2004).
71. W. Turek, E. S. Pomarzanska, A. Pron, J. Haber, J. Catal., 189, 297, (2000).
72. H. J. Kim, Y. G. Shul, H. Han, Appl. Catal. A: Gen., 299, 46 (2006).
73. C. Rocchiccioli-Deltcheff, A. Aouissi, S. Launay, M. Fournier, J. Mol. Catal. A: Chem., 114, 331, (1996).
74. H. Kim, J. C. Jung, S. H. Yeom, K. Y. Lee, I. K. Song, J. Mol. Catal. A: Chem., 248, 21, (2006).
75. K. N. Rao, K. M. Reddy, N. Lingaiah, I. Suryanarayana, P. S. S. Prasad, Appl. Catal. A: Gen., 300, 139, (2006).
76. M. Naik, S. Samantaray, B. Mishra, A. Dubey, Reac. Kin. Catal. Lett., 98, 125, (2009).
77. J. Ferrell, M. Kuo, A. Herring, J. Pow. Sources, 195, 39, (2010).
78. N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin, O. A. Kholdeeva, Inorg. Chem., 49 (6), 2920, (2010).
79. I. A. Weinstock, Chem. Rev., 98, 113, (1998).
80. M. Sadakane and E. Steckhan, Chem. Rev., 98, 219, (1998).
81. R. Thouvenot, A. Proust, P. Gouzerh, Chem. Comm., 1837, (2008).

PART
A

Lacunary Polyoxometalates

Chapter

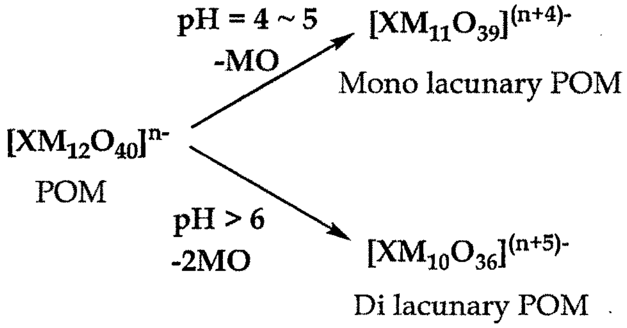
1

Introduction

What are Lacunary Polyoxometalates?

Lacunary Polyoxometalates **(LPOMs)** are a sub class of POMs with a set of unique properties such as multidenticity, rigidity, thermal and oxidative stability [1-3]. They represent an important class of compounds due to their unique structural as well as chemical properties. Controlled treatment of heteropoly/polyoxo species with base can produce "lacunary" heteropoly/polyoxo species wherein one or more addenda atoms have been eliminated from the structure along with the oxygens [4]. Due to the structural diversity as well as the unique electronic properties, LPOMs are of potential importance.

Removal of one or two MO units from the fully occupied POMs, $[XM^{VI}_{12}O_{40}]^{n-}$, gives rise to mono- or di- lacunary POMs, $[XM^{VI}_{11}O_{39}]^{(n+4)-}$ and $[XM^{VI}_{10}O_{36}]^{(n+5)-}$. When the solution of $[XM_{12}O_{40}]^{n-}$ are treated with base (pH 4~5), a series of hydrolysis reactions occurs leading to the formation of mono and di lacunary POMs (Scheme 1).



Scheme 1. Formation of LPOMs

Classification and Properties of LPOMs

The structures of the lacuna obtained with the LPOMs are mainly dependent on the number of vacancies generated in the parent 'saturated' POMs structure. The classical examples of geometries observed in LPOMs are shown in Figure 1.

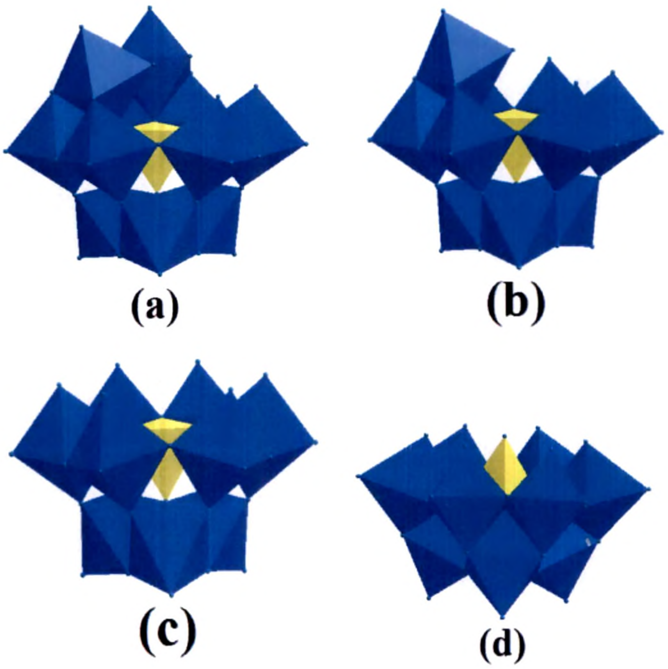


Figure 1. Different types of LPOMs structures derived from parent Keggin unit (a) $[XM_{11}O_{39}]^{n-}$ (b) $[XM_{10}O_{36}]^{n-}$ (c) A-$[XM_{9}O_{34}]^{n-}$ (d) B-$[XM_{9}O_{34}]^{n-}$

In monovacant species, total five oxygen atoms are available, of which four oxygen atoms are accessible at the surface of the lacuna. These four oxygen atoms present a slightly distorted square geometry. In divacant species, γ-$[XM_{10}O_{36}]^{n-}$, the four nearly coplanar oxygen atoms of the lacuna define a rectangular geometry. In trivacant, $[XM_{9}O_{34}]^{n-}$, six nearly coplanar oxygen atoms define a distorted hexagon. For trivacant species, the nature of the isomer (A- or

B-$[XM_9O_{34}]^{n-}$) and the nature of the hetero element are crucial parameters that will influence the type of derivatization that can occur at the vacant site. In A-$[XM_9O_{34}]^{n-}$ a void space is present in the middle of the hexagon, while an oxygen atom of the central XO_4 tetrahedron points toward the middle of the hexagon in B-$[XM_9O_{34}]^{n-}$. The lacunary species derived from the parent Keggin type structure, are obtained from the three Baker-Figgis (α, β and γ) isomers by means of the elimination of a variable number of octahedral. [5]. The structural rearrangement of one of the 4 triads leads to the formation of different types of LPOMs.

Formation of mono, di or tri lacunary species is mainly pH dependent, each possessing its own reactivity and stability trend. Hence, synthetically, special attention is paid to fine changes in reaction conditions such as pH, temperature, buffer capacity, ionic strength, and cation size: all having the potential to exert a considerable effect on the polyanion equilibria and formation of products [6, 7].

Among the large variety of LPOMs, the mono lacunary Keggin type POMs form the most versatile class of LPOMs. As mentioned earlier, the removal of one MO at suitable pH from parent POMs leads to the formation of mono LPOMs (Figure 2).

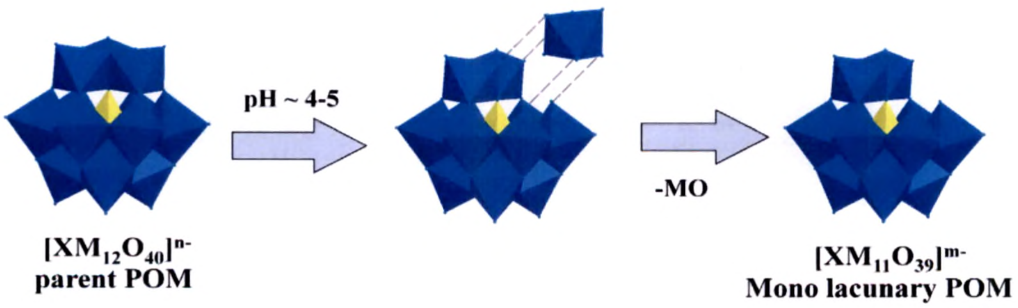


Figure 2. Formation of Mono LPOMs

A list of mono LPOMs are represented in Table 1

Table 1 Different LPOMs with variable heteroatoms [1]

	X	**Isomer**
	P, As	α
	Si, Ge	α, β_1, β_2, β_3
$[XW_{11}O_{39}]^{n-}$	B	-
	Al, Ga, Fe(III), Co(III)	α
	Co(II), Zn	α*
	Sb(III), Bi(III)	-
$[XMo_{11}O_{39}]^{n-}$	P, As, Si, Ge	α

* Free ligand structure not known

The first report on synthesis of mono lacunary silicotungstates was reported by Marignac in 1864 [8]. After this report, there was no significant contribution in the field of lacunary silicotungstates upto century. In 1976, Matsumoto et al. reported the first crystal structure analysis of $K_8SiW_{11}O_{39}$ species [9]. In 1983, Brevard et al. came up with the synthesis as well as characterization of the sodium salt of mono lacunary phosphotungstate [10]. The first crystal structure of mono lacunary phosphotungstate $[PW_{11}O_{39}]^{7-}$, was reported by Ozeki and coworkers in 2002 [11]. A literature survay shows that system based on lacunary polyoxotungstates, $[XW_{11}O_{39}]^{n-}$ (X= Si, P) are well documented [8-15]. At the same time, reports on the analogous compounds based on monolacunary molybdophosphate, $[PMo_{11}O_{39}]^{7-}$ are scarce. Therefore, we have selected $[PMo_{11}O_{39}]^{7-}$ for study.

First, attention was given to molybdophosphates by Berzelius [16]. He described the yellow precipitate (ammonium 12-molybdophosphate) that is produced when ammonium molybdate is added in excess to phosphoric acid.

Since then the system has been currently studied and a variety of compounds with many different Mo/P ratios have been reported. Many research groups had made considerable contributions to the chemistry of the molybdophosphates.

In 1978, molybdophosphates species including $PMo_{11}O_{39}^{7-}$, generated during the pH-dependent decomposition of 12-molybdophosphoric acid in aqueous solution have been studied with the Raman spectroscopy by starr et al. [17]. In 1982, Crouch et al. evaluated formation of constants of 9-, 11-, and 12-molybdophosphates in strong acidic solutions with spectrophotometrically and computer simulation experiments [18]. In 1983, Murata et al. has identified two kinds of yellow molybdophosphates in acidic solutions, 12-molybdophosphoric and 11-molybdophosphoric acid with the help of laser raman spectroscopy. They also found that both these species are in equilibrium in solution at pH 1-2 [19]. In 1984, Black et al. reported use of ^{31}P NMR spectroscopy as a characterisation tool for a number of molybdophosphates species formed during the degradation of $PMo_{12}O_{40}^{3-}$. During their experiments they found that the preparation of pure $PMo_{11}O_{39}^{7-}$ is quite difficult and it is present as impurities [20]. In 1986, for the identification of molybdophosphate species, aqueous solutions containing sodium phosphate and sodium molybdate ([P] = 0.01-0.07 mol l^{1-}, [Mo] : [P] = 1.25-1.5) were acidified with concentrated HCl and the formation of molybdophosphate anions has been investigated with ^{31}P NMR spectroscopy, Raman spectroscopy and differential pulse polarography by Rob van Veen et al. [21]. They observed that the molybdophosphate was present in different type of species, i.e. $[P_2Mo_5O_{23}]^{6-}$, $[PMo_6O_{25}]^{9-}$, $[PMo_9O_{31}.(OH)_3]^{6-}$, $[PMo_{10}O_{34}]^{3-}$, $[PMo_{11}O_{39}]^{7-}$ and $[PMo_{12}O_{40}]^{3-}$, in the acidified aqueous solution. The presence of different species was found to be dependent on Mo: P ratio as well as pH of the solution. It was also found that, because of high decomposition and equilibrium rate, the isolation of $[PMo_{11}O_{39}]^{7-}$ from aqueous solution of phosphate-molybdate is quite difficult. In the same year, speciation in the molybdophosphate system has been studied by a combination of potentiometric and ^{31}P NMR measurements by Pettersson et al. [22].

Thus, all reports described the generation and characterization of undecamolybdophosphate, $[PMo_{11}O_{39}]^{7-}$ in the solution. It was also found that, the isolation of $[PMo_{11}O_{39}]^{7-}$ from aqueous solution is quite difficult. Beside these, few more reports are available citing $[PMo_{11}O_{39}]^{7-}$ insitu [23-31] which also suggested that $[PMo_{11}O_{39}]^{7-}$ compound decomposes or equilibrates at rates too rapid to permit isolation and purification.

In 1991, isolation and purification of $[PMo_{11}O_{39}]^{7-}$ as tetrabutyl ammonium salt was successfully achieved by Hill et al. [32]. The synthesized material was well characterized by FT-IR, UV-visible spectroscopy, ^{31}P NMR and cyclic voltametry studies. However, knowledge about the number, composition, and the structures of various species formed especially mono lacunary seemed incomplete. In addition, a literature survey also shows that no study has been carried out in last two decades on the $[PMo_{11}O_{39}]^{7-}$ due to the difficulty in isolation, and poor thermal as well as kinetic stability of the same.

So, keeping these as target, in the present work, an attempt was made to isolate and stabilize $[PMo_{11}O_{39}]^{7-}$ species by use of a suitable support. Supports provide large surface area for dispersion, and hence can be used as heterogeneous catalysts for organic transformations. The catalyst molecule gets dispersed on the surface of the support and thus available for the combination with reactant as in homogenous catalyst. The resulting heterogeneous catalyst can function mechanically as if it was in solution but it would operate as a separate immobile phase. Thus the advantages of both homogenous catalysts are retained and at the same time the advantages of heterogeneous catalyst is obtained.

The supported molybdophosphates can be advantageous for:

1. Thermal stability is increased
2. Surface area is increased
3. They have high catalytic activity and selectivity
4. Separation from a reactions mixture is easy
5. Repeated use is possible

Choice of the support

The choice of support is a crucial step in heterogeneous catalysis. The most important is stability. The support must be stable up to high temperature, under reaction condition and regeneration conditions. It should also not interact with solvent, reactants or reaction products. A support must be easily available, either commercially or should be easily synthesized.

Critical properties of a support include surface area and the ability to give rise to catalyst-support interactions.

Dispersing of POMs on solid supports with high surface areas is important for catalytic application. In general, POMs strongly interact with supports at low loading levels, while the bulk properties of POMs prevail at high loading levels. Acidic or neutral substances such as ZrO_2, SiO_2, active carbon, acidic ion exchange resin are suitable supports. Enhanced catalytic activity of POMs was found when they were supported on to strongly acidic support. The higher activity was explained by the synergism due to the interaction of the heteropolyanion and protons of the support.

As mentioned when POMs are supported onto acidic supports, strong interaction is expected between oxygens of POM and protons of the supports.

Keeping in mind these aspects, in the present study hydrous zirconia was chosen as a support.

It is very interesting and important to note that support does not play always merely a mechanical role but it can also modify the catalytic properties of the catalyst. A support can affect catalyst activity, selectivity, recyclability, material handling and reproducibility. It is well known that basic support cannot be used for supporting POMs, since it gets decomposed on the same. So, in the present work an attempt was made to use neutral support, in addition to acidic support, neutral alumina was selected for the same.

Based on the available literature as well as keeping in mind the demands of the society for sustainable heterogeneous catalysts, the following work was planned. For the first time an attempt was made to develop heterogeneous catalysts by supporting $[PMo_{11}O_{39}]^{7-}$ onto suitable supports.

OBJECTIVES OF THE WORK

1. To synthesize and isolate mono lacunary molybdophosphate i.e. undecamolybdophosphate (**$[PMo_{11}O_{39}]^{7-}$ =PMo_{11}**).
2. To stabilized PMo_{11} by supporting onto different metal oxides (acidic and neutral) and detailed characterization of supported materials by various physico-chemical techniques.
3. To establish the use of synthesized materials as sustainable heterogeneous catalysts, especially for oxidation reactions under mild solvent free reaction conditions.
4. To carry out kinetic study for the same.
5. To study the effect of the supports and effect of oxidants on the catalytic activity.

The following two chapters (Chapter 2 and Chapter 3) describe the details for the same.

Chapter 2 consists synthesis as well as detailed characterization of PMo_{11} and supported PMo_{11} (PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3).

Chapter 3 consists use of PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3 as sustainable heterogeneous catalysts for solvent free oxidation of alkenes and alcohols with environmentally benign oxidant (H_2O_2 and O_2) under mild reaction conditions. It also consists comparative study as well as kinetic study of oxidation of styrene with H_2O_2 over PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3.

REFERENCES

1. M. T. Pope, Heteropoly and Isopoly Oxometalates, Springer- Verlag, Berlin, (1983)
2. M. T. Pope, A. Müller, Angew. Chem. Int. Ed. Engl., 30, 34, (1991)
3. J. J. Borras-Almenar, E. Coronado, A. Müller, M. T. Pope (Eds.), Polyoxometalate Molecular Science, Kluwer Academic Publisher, Dordrecht, (2003)
4. L. C. W. Baker, D. Glick, Chem. Rev., 98, 3, (1998)
5. F. Hussain, Ph. D Thesis, International University Bermen, (2006)
6. N. H. Nsouli, A. H. Ismail, I.S. Helgadottir, M.H. Dickman, J. M. Clemente-Juan, U. Kortz, Inorg. Chem., 48, 5884, (2009)
7. S. G. Mitchell, H. N. Miras, D. Long, L. Cronin, Inorg. Chim. Acta, 363, 4240, (2010)
8. C. Marignac, Ann. Chim. Phys., 3, 5, (1864)
9. K. Matsumoto, Y. Sasaki, Bull. Chem. Soc. Jpn., 49, 156, (1976)
10. C. Brevard, R. Schimpf, G. Tourne, C. Tourne, J. Am. Chem. Soc., 105, 7059, (1983)
11. N. Honma, K. Kusaka, T. Ozeki, Chem. Comm., 2896, (2002)
12. P. Souchay, A. Teze, G. Herve, C. R. Acad. Sci. Paris Ser. C, 275, 1013, (1972)
13. D. Laurencin, A. Proust, H. Gerard, Inorg. Chem., 47, 7888, (2008)
14. P. shringarpure, A. Patel, Dalton Trans., 3953, (2008)
15. S. Pathan, A Patel, J. Coord. Chem., 63, 4041, (2010)
16. J. J. Berzelius, Pogg. Ann. Phys. Chem., 6, 369, (1826)
17. M. S. Kasprzak, S. R. Crouch, G. E. Leroi, Appl. Spectrosc, 32, 527, (1978)
18. C. C. Kircher and S. R. Crouch, Anal. Chem., 54, 879, (1982).
19. K. Murata, S. Ikeda, Polyhedron,. 2, 1005 (1983).

20. J. B. Black, N. J. Clayden, L. Griffiths, J. D. Scott, J. Chem. Soc. Dalton Trans., 2765, (1984).
21. J. A. R. Van Veen, O. Sundmeijer, C. A. Emeis, H. J. De Wit, J. Chem. Soc., Dalton Trans., 1825, (1986).
22. L. Pettersson, I. Andersson, L-O Ohman Inorg. Chem., 25, 4726, (1986).
23. C. Tourne, G. Tourne, Bull. Soc. Chem Fr., 4, 1124, (1969).
24. C. Tourne, G. Tourne, S. A. Malik, T. J. R. Weakley, J. Inorg. Nucl. Chem., 32, 3875, (1970)
25. M. Leyrie, M. Fournier, R. C. R. Massart, Acad. Sci. Ser. C, 273, 1569, (1971).
26. C. Rocchiccioli-Deltcheff, R. Thouvenot, J. Chem Res., Synop. 2, 46, (1977).
27. M. S. Kasprzak, S. R. Crouch, G. E. Leroi, Appl. Spectrosc. 32, 537, (1978).
28. K. Nomiya, M. Sugaya, M. Miwa, Bull. Chem. Soc. Jpn., 52, 3107, (1979).
29. K. Murata, S. Ikeda, Anal. Chim. Acta., 151, 29, (1983).
30. K. Nomiya, R. Kobayashi, M. Miwa, T. Hori, Polyhedron, 3, 1071, (1984).
31. G. M. Maksimov, L. I. Kuznetsova, K. I. Matveev, R. I. Maksimovskaya, Koord. Khim., 11, 1353, (1985)
32. L. A. Combs-Walker and C. L. Hill, Inorg. Chem., 30, 4016, (1991).