

HISTORICAL DEVELOPMENT, SYNTHETIC VARIABLES, CLASSIFICATION AND CHARACTERIZATION TECHNIQUES OF POLYOXOMETALATES

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ABSTRACT

Polyoxometalates represent a diverse family of metal oxide clusters having well defined structures with a large variation in size, metal-oxygen framework, elemental composition and unmatched properties. They are considered as one of the most attractive and growing area of research and development especially in the field of catalysis, material chemistry and biochemistry.

This review paper starts with a brief introduction of POMs along with many reports and historical aspects. This also summarizes the synthetic and design approaches of various POM building- units encompassing the important synthetic variables like concentration of cation, pH, reaction temperature etc. On the development, it highlights the different sub-class of POMs along with their fundamental structural types with special focus on Keggin and Lindqvist structure. The final section is devoted for discussing the various cutting edge techniques and precise tools which enables the complete characterization of newly synthesized POM clusters.

Keywords: *Polyoxometalates, Building-units, Synthetic Variables, Keggin Structure, Lindqvist Structure, Characterization techniques.*

1. INTRODUCTION

The term polyoxometalates refer to an extensively large group of structurally well – defined infrastructure of anionic clusters built from transition metal oxoanions which are linked via oxide ions. POMs are macromolecules (species with high molar mass), having more solubility in solvent of high dielectric constant (polar solvent). In broader aspect we can say that these are distinct assemblies of early transition element oxide $[MO_x]$ where $x = 4 - 7$ ^[1] and M is transition metal especially vanadium, molybdenum and tungsten in their highest oxidation state. Mo, W and V are the foremost component in POM clusters due to favourable combination of the ionic radius, charge and availability of vacant d-orbitals for metal oxygen π bonding^[2]. Since addenda atoms are present at their maximum oxidation state hence metal-metal bonding is not possible due to lack of electron. So the structure are linked together by metal-oxygen bonds.

Polyoxometalates may contain a number of metal atom that reach to a nuclearity as high as 368 metal atoms in one single cluster molecule, forming nanoparticle^[3]. They show a large variety of shapes, elemental composition and size which may vary from small $[Mo_6O_{19}]^{n-}$ ^[4] to nanosized

species like $[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-15}$. For the better understanding of POM sub-units, metal-oxo building-units are represented as polyhedral units, (for example MO_6 octahedron) in which the O-atoms are present at the vertices and short terminal $M=O$ bonds tend to lead to the consequence of closed discrete structure with such bonds projected outward^[6]. The terminal oxo-ligands are strong and effective π -electron donors so that lone pair of O-atoms forms very firm bond to main group transition metal ion. POM clusters are formed when three polyhedra are linked by the edge and / or by the corners or face sharing modes.

Chemistry of polyoxometalates is an important subarea of contemporary inorganic chemistry. They have gained much attention by becoming a centre of modern chemical research not only because of their diverse structure and versatile physical & chemical properties but also due to their potential application in various fields such as catalysis, analytical chemistry, nanotechnology, chemical sensing, biochemical and geochemical process, medicine and material science. Among various applications of POMs, catalysis & material science^[7] are two main fields.

A new area of research called Polyoxometalate-Organic-Frameworks (POMOFs), has been emerged after getting inspiration from metal-organic framework (MOF) materials. POMOFs are formed by the combination of polyoxometalates building units with organic/metal species which act as linkers^[8-9]. Hence POMOFs are also called POM based inorganic-organic hybrids.

2. HISTORY AND GROWTH OF POLYOXOMETALATES

In 1783, D'Elhuyar brothers discovered that a yellow salt having bitter taste is obtained by the reaction of ammonium molybdate with a quantitatively excess of phosphoric acid. This salt is now known as ammonium 12-phosphomolybdate, $(NH_3)_4[PMo_{12}O_{40}]^{10}$, the first example of polyoxometalates, reported by Berzelius in 1826^[11]. In 1892 Blomstrand proposed the chain or ring structure of phosphomolybdic acid and other polyacids. Using the idea of coordination compounds by Copaux a German scientist Alfred Werner explained the structure of silicotungstic acid. Another American chemist Linus Carl Pauling along with Werner explored these molybdates and tungsten based compounds in seeking to study and understand the detailed structure and composition of the material^[12-14]. This requisites for a magnificent scientific insight to fully elucidate the nature of the reaction product. For instance, crystal structure determination by X-ray diffraction methods, which was first conceptualized by Laue in 1912 and innovated by Bragg and Bragg.^[15] This method permitted the monosemous identification and structural characterization of these cluster compound. The time taken for data collection and initial structure determination can be reduced by using fast and single crystal x-ray diffraction method which allows an accelerated and accurate structure refinement and characterization of a number of new compounds. Rosenheim was the first person to start characterization & systematic study of the properties of POM in early 20th century. Souchay was the first to implement polarography in the study of solutions of POMs. In 1928, Linus Pauling proposed a structure for α -keggin anion consisting of a tetrahedral central ion, $[XO_4]^{n-8}$ caged by twelve WO_6 octahedron. Later on, in 1934 the renowned J. K. Keggin experimentally determined the structure of hydrated and dehydrated 12-phosphotungstic acid using x-ray diffraction images^[16-17]. Hence these structures are called Keggin structures for their discoverer^[18]. Pope et al^[19] reported the characterization of the formations of unsymmetrical polyoxotungstate via transfer of POM building units. Bruedgam

et. al. reported a $[W_{24}]$ isopolyoxotungstate $Cs_{24}(W_{24}O_{84})(H_2O)_{26}$. A novel 3d metal hybrid compound is reported by Mialane et al^[20] by combining the various carboxylic acid derivatives and 3d transition metal ions (Ni, Co & Cu). The first example of TRIS [(tris-hydroxymethyl) aminomethane] functionalized Mn – Anderson cluster is reported by Hasenknopf et al.^[21].Kortz and pope reported the structure of non-conventional Dawson cluster $\alpha - [Mo_{18}O_{54}(P_2O_7)_2]$. A cigar shaped 30-molybdobispyrophosphate $[(P_2O_7)(Mo_{15}O_{45})_2]^{8-}$ was also reported recently. A method to anchor both silver and gold nanoparticles and preyssler type polyoxometallates in a silica matrix is recently developed by Wu et al.

After its advancement and popularity, the evolution of POMs has received a massive input like the publication of heteropoly and isopolyoxometalates by pope in 1983^[22]. The indispensable analization by pope and Muller in 1991 anticipated the current trend. In 1998,^[23-28]Crarg Hill documented the extensive growth and prolonged range of applications in a special discourse of POMs by chemical review. A few new interesting structures have been reported recently. For examples a novel three – dimensional frame work formed by $[GdMo_{12}O_{42}]^{9-}$ anions with 9 coordinated Gd(III) centres was discovered by Wu et al^[29] and a basket shaped three – electron reduced heteropoly blue $[PMo_{18}O_{73}]^{11-}$ has also been reported. Also a number of dioxouranate complexes of polyoxotungstate is reported by Kim^[30] and Pope.

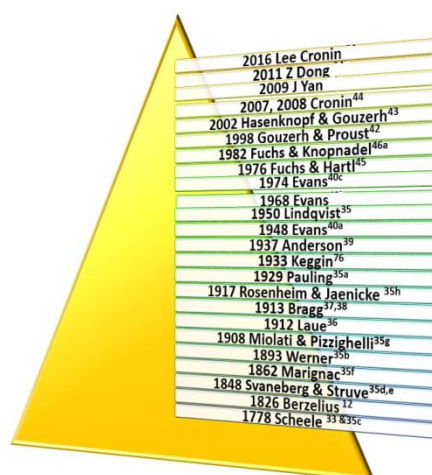
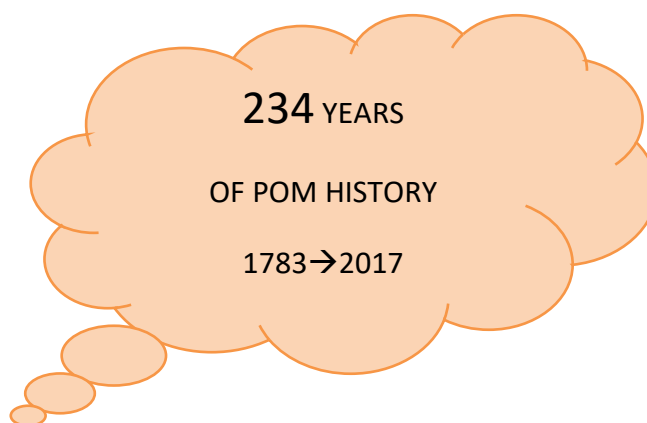


Table-I Showing a historical time line of important discoverer and publisher of POM-chemistry

It is frequently been observed that the molecules enclosed within the area of POM chemistry oven an unparallel range of physical and chemical characteristics along with transferable building units which can be reliably availed in the configuration of new materials. Now a days many area of interest has been emerged out in POM chemistry such as:-

- (i)The potential to develop sophisticated designer molecule based materials and devices that bridge several length scales, exploiting the progress made in instrumentation, nano-science and material fabrication methods.
- (ii)Potential medicinal applications especially with anti – tumoral and anti-viral agent^[43].
- (iii)POM cores, containing numerous hybrid organic and inorganic materials etc.

In chemistry laboratory, POM have been known and used for nearly two hundred years, but due to their structural diversity, distinct physical properties, applications and potential for new development POMs have become so attractive compounds and have gained lots of attention ,after the second half of 20th century .In new century an extensive progress has been achieved in the novelty and variety of structures and properties like magnetic ^[44-45] , electronic ^[46-48], catalytic ^[49-51] and optical ^[50-52] properties of POMs. Ofcourse, the inspiration for much of these concepts comes from previous work, which demonstrates the fundamental idea that polyoxometalates based nonosystem with well-defined functionality could be possible. Every year more than 500 papers have been published on POM related topics. Numerous review addressing different aspects of POM science, for example – new structures, analytical methods, biomedical applications, catalysis, theoretical calculations as well as perspectives for new material have been published. The essential properties and potential of POMs have shown an extensive accomplishment till now, which has made all the difference in scientific advancement.



3. GENERAL PROPERTIES OF POMS

Generally polyoxometalates are macromolecular (species having high molar mass), large sized species. They are non-sensitive to water and air and are more stable (having low dissociation constant) in aqueous acidic solution while dissociation of POM cluster takes place in presence of hydroxide (OH⁻) ion , as shown below :-



The exact pH at which decomposition starts, depends upon the nature of polyanion. The discrete polyanions of POMs are water soluble, highly symmetrical ions with charge ranging from -3 to -14. They have different degree of thermal stability, depending on the nature of heteroatom, polyatom and polyanions ^{53(a,b&c)}. For example the order of thermal stability among the three polyanions is - $[\text{SiMo}_{12}\text{O}_{40}]^{4-} < [\text{PMo}_{12}\text{O}_{40}]^{3-} < [\text{PW}_{12}\text{O}_{40}]^{3-}$. Generally polyoxometalates containing “mixed addenda cluster” have less thermal stability.

One of the most significant properties of POMs is their ability to gain & loss a specific number of electrons without changing their structural arrangement ^[54-56] or without decomposing. The other radically distinct and remarkable property of this class of compound is their ability to

undergo condensation reaction under aqueous acidic condition, where they form water soluble crystalline compounds called heteropolyacids. Due to their bigger size, the charge density at the surface O-atoms of POMs is insufficient. Hence (i) it is difficult to form covalent linkage with more than one chemical groups, (ii) the surface basicity is weak, (because most of the charge concentrated on oxygen atoms, below the surface^[57]) and (iii) they are soluble in various organic solvents like dimethyl sulfoxide, benzene^[58] etc.

There are two possible ways to activate (that is to increase surface charge or to increase basicity) the surface O-atoms of POMs, including heteropolyoxometalates^[59] (i) by reducing the metal from higher oxidation state to lower oxidation state {Eg- Mo(VI) to Mo(V)} by using strong reducing agent, but this strategy is challengeable because the highly reduced POMs are unstable and get oxidized in ambient atmosphere and (ii) by substituting the higher valence metal by a lower valence metal { Eg- Mo(VI) by V(IV)}.

POMs have abundant physical & versatile chemical properties like catalytic activity, ion exchange, reversible redox behaviour and photochromic or electrochromic response^[60-62], which makes them a unique class of inorganic metal oxide cluster. The lower charge density possessed by the POMs than the traditional anions (eg- ClO_4^- , NO_3^-) make them an ideal candidate for outer-sphere electron transfer reagent. Due to their bifunctional behaviour that is acidic nature as well as redox behaviour, heteropolycompounds have received much attention by researchers.

4. STRUCTURE & CLASSIFICATION OF POLYOXOMETALATES

The polyoxometalates defines a broader class of compounds made up of metal-oxide building -units. They are represented as $[\text{MO}_x]$, where O represents oxide ion and M is the metal atom that build up the framework and is called addendum atom. Most common addenda are Mo, W or V at their highest oxidation state. The oxide ions act as ligands and are co-ordinated to the metal atoms to give a bridged framework. Some other ligands like nitrosyl, alkoxy, S or Br can substitute the oxide ions (S substituted POMs are often termed as polyoxothiometalates). When more than one metallic elements are present in the cluster then it is called "mixed addenda cluster". All POM clusters are anionic and thus can be convoluted (complexed) with an additional cation called heteroatom. The heteroatom can be either primary or secondary. Presence of primary heteroatom is indispensable to the POM structure. Generally the heteroatom is present at the centre of anion (as in case of Keggin structure) or in the structure framework (as in Dawson structure – two P atoms are present at the centre of two symmetric fragments) and acts as template during the synthesis of POM clusters. The nature of the heteroatom does not show any confinement as shown by the addendum atom. It can be generally an element with co-ordination number of 4, 6, 8 or 12^[63].



Figure1. - showing the position of heteroatom (a) in Keggin structure (one P-atom) and (b) two P-atoms (yellow colour) in Dawson structure.

In order to better contrived and comprehended understanding POMs can be classified into different categories on various basis.

4.1. Classification of Poms on the basis of linkage between metal ions

4.1.1 plenary structure: - The POM structures in which metal cations are linked through surface terminal and bridging oxygen are called plenary structure. An example of this class is weak and labile complex of Eu^{3+} ion with $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$. Here the metal ions are linked via a single terminal oxygen of monodentate ligands. Plenary structures are stable at acidic pH and their degradation (occurs in presence of hydroxide) results into the formation of lacunary structure.

4.1.2 lacunary structure:-The defective structure obtained when one or more addenda atoms along with their attendant oxide ions are removed from the plenary structure, is called lacunary structure. It means that the degraded derivative of Plenary structure is called lacunary structure^[64]. For example Dawson lacunary structure is $\text{As}_2\text{W}_{15}\text{O}_{56}$. They connect metal ions by enclosing them in a vacant site formed by four exterior oxygen. When the size of metal cation is small enough (for example d-block metal ions) to be enclosed in the vacant or defect site then they are isolated as 1:1 complex with solvent molecule present as ligand in the co-ordination sphere such as $[(\text{SiW}_{11}\text{O}_{39})\text{Co}(\text{H}_2\text{O})]^{6-}$ and when the metal ion is larger with high charge density (for example f-block metal ions) then they sandwiched between the vacant site of two ligands and are isolated as 1:2 complex such as $[\text{Pr}(\text{SiW}_{11}\text{O}_{39})_2]^{13-}$. Lacunary structure can further give rise to high concentration of daughter lacunary structure by the addition of calculated amount of base (this process is called controlled degradation).

4.2. Classification on the basis of nature of central core

On the basis of type of central core POM structures^[65] can be classified into four sub-groups:-

4.2.1 Structures containing tetrahedral central core-These structure consist of tetrahedrally coordinated heteroatom with co-ordination number 4 such as P, Si, Ge, Bi etc. The central core consisting of one or two tetrahedron XO_4 unit(s) (where X is hetero atom) and is surrounded by highly symmetrical assembly of MO_6 octahedra (where, M is addendum & may be Mo(VI), W(VI), V(V), Nb(V) or Ta(V)). This group includes Lindqvist structure, Keggin structure, Dawson structure. Eg- $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ etc.

4.2.2 Structure containing octahedral central core- These structure consist of octahedrally co-ordinated heteroatom with co-ordination number 6 such as Al. These structures have a central core of transition metal octahedron XO_6 units (where $X = Mo(VI), Mn(II)$ etc.). The co-ordination number around heteroatom is 6. For example – Anderson structure. Eg- $[Mn^{II}Mo_9O_{32}]^{6-}$, $[Te^{VI}Mo_6O_{24}]^{6-}$

4.2.3 Structure containing square-antiprism central core- This group includes those POM cluster where central core has square antiprism core and co-ordination number around heteroatom is 8. Eg- $[(CeO_8)W_{10}O_{28}]^{8-}$.

4.2.4 Structure containing icosahedral central core -These structure have an icosahedrally co-ordinated central core (face shared octahedra with Mo atoms at the vertices of an octahedron) and the co-ordination number around the heteroatom is 12.

Eg- $[(UO_2)Mo_{12}O_{30}]^{8-}$, $[Ce^{VI}Mo_{12}O_{42}]^{8-}$.

4.3 Classification on the basis of structural composition

4.3.1 Isopolyanions – The class of polyoxometalates which contains only transition metal cations interlinked through oxide ions and do not have any anionic templation are called isopolyanions. Here main group elements are absent and if present acts as ligand but never forms a part of framework. Isopolyanions (IPAs) having general formula $[M_nO_{(4n-m)}]^{(2n-2m)-}$ are formed when condensation between similar species occurs where the degree of condensation (n) must be greater than five.

Eg- $n MO_4^{2-} + 2m H^+ \rightarrow [M_nO_{(4n-m)}]^{(2n-2m)-} + mH_2O$

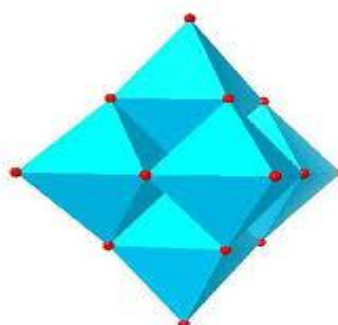


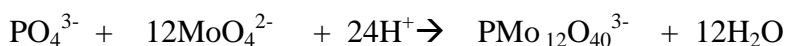
Figure-2. Lindqvist structure (An isopolyoxometalate)

The transition metals involved in isopolyanionic framework may be vanadium, niobium, tantalum, molybdenum, tungsten etc. and the number of metal centres may vary from 2 to 150. However, only a few examples are known with W because the system take more time to reach to the equilibrium (of the order of weeks). They are comparatively less stable than their counterpart^[66] heteropolyanions because their cavities are empty. This is why their availability is relatively limited and till now only a few isopolyanions are being apprehended with certainty.

Isopolyanions show many interesting physical properties like high charge and strongly basic oxygen surface etc., hence they act as an attractive building blocks^[67] of POM clusters.

The most common and most symmetrical isopolyanion structure is the Lindqvist structure. It is formed by the fusion of six octahedrons, sharing a common vertex i.e. in this structure one oxygen is linked with six metal centres. The general formula of Lindqvist ion is $[M_6O_{19}]^{n-}$, where M = Mo, W, V, Nb or Ta and the value of n depends upon the metal substitution.

4.3.2 Heteropolyanions– Heteropolyoxometalates contain one or more p-d-or f-blocks elements, called “heteroatoms”, in addition to the addenda atoms, which are involved in the formation of metal oxide clusters. They are considerably the most explored subset of POM clusters with more than 5000 papers being reported on these compounds during the last few years. Their general formula is $[X_pM_xO_m]^{n-}$. Formation of heteropolyanions (HPAs) takes place when condensation of several mononuclear oxoanions around a central hetero atom occurs in aqueous acidic medium at optimum condition of temperature and acidity, as shown below



Heteropolyanions are generally linked with certain number of water molecules which ensure the crystal cohesion of the cluster. Generally formation of HPAs are kinetically controlled. Depending on the oxidation state of the transition metal and elemental composition, the oxidised form of heteropolyanions may have various colour, however reduced forms are generally blue in colour. The reduced POM clusters are composed of localized magnetic moment that undergoes a rapid magnetic exchange (hopping) over the magnetic sites^[68] when brought within a close proximity. The O-bonds tend to be more covalent in character and can promote magnetic hopping. The unpaired electrons in the reduced clusters delocalized^[69] to give mixed valence sites^[70]. Table-II shows some common heteropolyoxometalate structures

Table-II Some Common Heteropolyacids

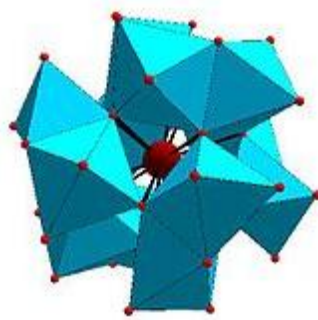
Structure type	Hetrometal ion	Formula	Charge	Building unit	Central group	Types of sharing
Keggin	P^{5+}, As^{5+}	$XM_{12}O_{40}$	8-n	M_3O_{13}	XO_4	Edge
Silverton	$Si^{4+}, Ge^{4+}, Ce^{4+}, Th^{4+}$	$XM_{12}O_{42}$	8-	M_2O_9	XO_{12}	Face
Dawson	P^{5+}, As^{5+}	$X_2M_{18}O_{62}$	6-	M_3O_{13}	XO_4	Edge
Waugh	Mn^{4+}	XM_9O_{32}	6-	M_3O_{13}	XO_6	Edge
Anderson	Te^{4+}, I^{7+}	XM_6O_{24}	12-n	M_3O_{10}	XO_6	Edge

{ where M=Mo(VI),W(VI) ,V(V or VI) }

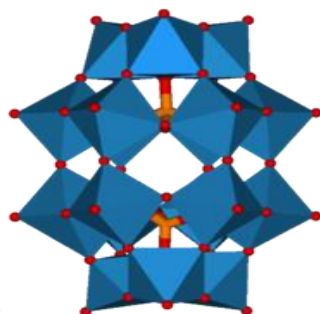
Among these structures, Keggin and Dawson structures are basic structures, while the formation of other structures occurs by the more than one Keggin or Dawson fragments.

The Keggin structure was first suggested by Pauling in 1929^[71] and confirmed by Keggin in 1933^[72], who determined the structure of $PW_{12}O_{40}^{3-}$ using X-ray diffraction. Depending on reaction temperature, different hydrated crystals of Keggin heteropolyanions can be isolated from aqueous solution. For example when temperature is very low a cubic crystal containing 29 to 39 water molecules per Keggin unit is obtained while at room temperature crystal transforms into a triclinic lattice having only 13H₂O molecules per Keggin unit and when temperature rises nearly upto 673K, anhydrous form is obtained because water molecules leave the lattice and hydrogen atoms get bound to the polyanion^[73].

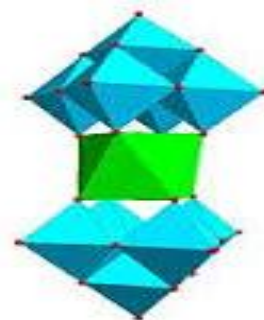
Keggin structure has a general formula of $[XM_{12}O_{40}]^{n-}$, where X is the heteroatom (most commonly P^{5+} , Si^{4+} or B^{3+}) and M is the addenda atoms. This structure consists of a centrally placed primary heteroatom surrounded by four oxygen to form a tetrahedral unit (XO_4). The heteroatom is caged by twelve octahedral MO_6 units of addenda atoms, connected by common edge to give rise four Mo_3O_{13} units.



Dexter-Silvertone Structure



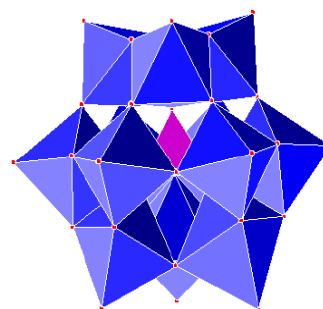
Dawson Structure



Weakley-Yamase Structure



Anderson Structure



Keggin Structure

Figure -3 Different structures of Heteropolyoxometalates

Baker and Figgis suggested that the different rotational orientation of the Mo_3O_{13} units through 60° lowers the symmetry of overall structure and gives rise to five isomeric forms represented by the prefix α , β , γ , δ , and ϵ . These isomers are sometimes named as Baker, Baker – Figgis or rotational isomers. The α isomer is the most prevalent and thermodynamically stable form, having T_d symmetry and generally the word Keggin structure is used to represent α -Keggin structure^[74] (both hydrated and dehydrated form). When one of the Mo_3O_{13} unit of α -isomer is rotated by 60° , overall symmetry changes to C_{3v} and the resulting form is called β -Keggin isomer. Similarly rotation of two, three or four Mo_3O_{13} by 60° gives rise to γ , δ , ϵ isomers respectively, which are comparatively less stable than α and β isomers.

When one of the octahedron (MO_6) is removed from the Keggin structure then it is called mono lacunary Keggin structure and is represented as $[\text{XM}_{11}\text{O}_{39}]^{n-}$. Monolacunary structure is less stable than complete keggin structure because removal of one unit results in unsaturation and causes extra ability to coordinate with metal ion. These heteropolycompounds are extensively used in industrial catalysis^[75-80] mainly in methacroleine, propylene hydration, olefin oxidation and polymerization of tetrahydrofuran^[81].

iii) Molybdenum blue and molybdenum brown reduced polyoxometalates clusters – They were first reported by Carl William Scheele, a Swedish pharmaceutical chemist in 1783. In 1995 Muller et al reported the crystallization of a very high nuclearity cluster $[\text{Mo}_{154}]$ from a solution of Mo blue. Structural characterization of this cluster showed that it has a ring topography. By changing the pH and increasing the amount of reducing agent in presence of acetate ligand gives rise to the formation of a spherical ball like cluster $[\text{Mo}_{132}]$. Development of this highly reduced POM cluster is one of the most electrifying progress in POM chemistry which has many potential takeoff application in the field of nanoscience.

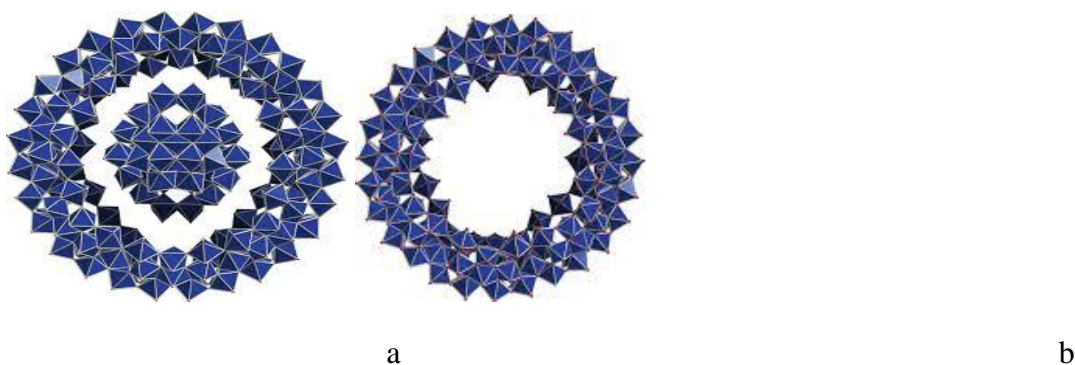


Figure-4 A polyhedral representation of (a) nanoscale $\{\text{Mo}_{36}\}$ wheel and (b) the elliptical $\{\text{Mo}_{128}\text{Eu}_4\}$ wheel

5. NON CONVENTIONAL POMS

Most of the POMs reported every year have traditional structures i.e., the metals and the structures of the newly synthesized POMs show only a little variation and alteration. Over the last

few years in the search for some new innovative applications important changes in thought have been made and hence a vast attention has been paid on designing new POM structures with novel metals (such as niobium, platinum, palladium etc.), functional groups and properties. Table -III shows some non-conventional POMs and their examples.

Table-III Some Non-Conventional Poms and Their Examples

Non-conventional POM	Examples
Polyoxoniobate	$[\text{Nb}_{24}\text{O}_{72}\text{H}_9]^{15-}$ [82], $[\text{HNb}_{27}\text{O}_{76}]^{16-}$ $[\text{H}_{10}\text{Nb}_{31}\text{O}_{93}(\text{CO}_3)]^{23-}$, $[\text{Ti}_{12}, \text{Nb}_6\text{O}_{44}]^{10-}$ [83]
Polyoxoaurate	$[\text{Au}_4\text{As}_4\text{O}_{20}]^{8-}$ [84]
Polyoxoplatinate	$[\text{Pt}_{12}\text{O}_8(\text{SO}_4)_{12}]^{4-}$, $[\text{O}=\text{Pt}(\text{H}_2\text{O})(\text{PW}_9\text{O}_{34})_2]^{16-}$
Peroxide 'end' – on POM	$[\text{M}_6(\text{O}_2)_6(\text{OH})_6(\gamma\text{-SiW}_{10}\text{O}_{36})_3]^{18-}$ (where, M=Zr, Hf)

6. SYNTHETIC STRATEGIES AND SYNTHETIC VARIABLES

Synthesis of POM clusters is very simple which requires a small no. of steps or even just one step hence often called one –pot synthesis. Generally POM formation occurs by the condensation of monomeric oxometalates (Eg- MoO_4^{2-}) in acidic aqueous solution, where protons function as oxygen abstractors and favours dehydration process [85]. Kelpert has suggested that the dehydration process accounts for a very favorable entropy change with the formation of more compact structure. [86]

The architectural design principles are empirical and based on simple calculation. Incorporation of heteroatom templates, heterometallic centre, lacunary building-units, different protonation states, cations, ligands etc. affect the overall architecture of POM and make the possibility of large number of combinatorially structure. POM can be synthesized in an aqueous acidic medium containing the relevant metal – oxide anions. However new POM clusters can be isolated by using mixture of water and organic solvent (Eg – CH_3CN) in place of aqueous solution. The geometry, composition and charge of POM clusters can be changed through synthetic variables. Important synthetic variables which affect the synthesis of POMs are concentration and type of metal oxide anion, Presence of additional ligand, ionic strength, pH, conc. & type of heteroatom, reducing agent (particularly in case of Mo), presence of additional ligands, reaction temperature, methodology (microwave / hydrothermal / refluxing / ionophore methods) etc. Variation of these parameters results in the formation of a large and versatile library of connecting units to give the desired POM structures.



Figure -5. Parameters that are often adjusted in the one-pot synthesis of new POM clusters.

Synthesis of POM is generally done in presence of simple inorganic (metal) cations such as K^+ , Na^+ , NH_4^+ etc but organic cations like tetraalkylammonium cation, protonated organic amines with hydroxyl group etc. can also be used. However use of protonated organic amine cations are restricted to vanadate system because their formation needs higher pH at which organic amines can't be protonated. Use of this type of cations (protonated organic ammonium cations) result in an inverse cation templation effect, which can be used to build new POM cluster^[66], hybrids^[87] and building framework material^[88]. Rapid aggregation can also be prevented by the use of bulky organic cation as counter ion. They also promote the ionization of self-assembled cluster in one pot reaction centre (generally called 'shrink-wrapping' process).

It should be noted that different structure appears at different pH. For example molybdate and tungstate oxoanions can be synthesized at low pH because acidification of a solution of sodium molybdate will give rise to metal oxide fragments & with decrease in pH level of the solution^[89-90] nuclearity of metal oxide fragments increases. On the other side synthesis of vanadates need neutral or higher pH^[91]. Among various methods used for the synthesis of POMs, hydrothermal method is more controllable than other methods. Hence this method is more popular & adopted, especially for the synthesis of POM based co-ordination polymers^[92]. However, it has been observed that synthesis by using microwave gives more predictable result than traditional hydrothermal method.

POMs are usually formed in aqueous medium at room temperature or at a temperature higher than the room temperature, but lower than the boiling point of solvent. However in some cases, the assembly of the oxoanions may also occur in non-aqueous medium or even in solid state

such as in minerals^[93-94]. Recently use of ionic liquids for the synthesis of POM has been reported^[95]. Due to their highly polar nature these liquids have great potential of direct assembly. Hence they can be used as solvent / cation directing species. The ability of a POM cluster to retain its structural identity without undergoing any transformation or degradation is the measure of the stability in given solvent (aqueous or non-aqueous).

7. ELEMENTAL ANALYSIS AND CHARACTERIZATION TECHNIQUES

Extensive characterization of the synthesized POM clusters is done by using multifarious sophisticated and precise techniques and instrumentations. The principle characterization techniques used to characterize the polyoxometalates includes-

(i) *Spectroscopy* (ii) *Electrophoresis* (iii) *Surface analysis*
(iv) *Thermal analysis* (v) *Crystallography*

7.1 *Mass spectroscopy (MS)*

The analytical technique which sort the ions on the basis of their mass is called mass spectroscopy. In this technique charged species (ions) are generated by ionizing the compound and then m/z ratio of ions are measured. Thus a mass spectrum shows a plot of the ion signals as a function of the m/z ratio.

Crystallographic XRD-studies^[96-98] doesn't give the exact chemical formulae and the protonation state of POM cluster anions. These difficulties can be overcome by using mass spectroscopy, which has potential to become the standard analysis techniques for complex POM clusters as it gives full information about the chemical composition of cluster down to the last proton by matching the calculated versus experimentally obtained envelopes. The availability of high resolution detector system has allowed this area to develop rapidly. High-resolution time-of flight (TOF) MS is used to investigate the structures, self-assembly or disassembly process as well as nature of high nuclearity POM clusters. Thus MS Studies have enormous potential to aid the discovery process of new POM clusters & their complex self-assembly mechanism.

7.1.1 *Electron spray ionization mass spectroscopy (ESI-MS)*

ESI-MS has been applied extensively to characterize many types of POMs including vanadate, niobate, tungstate, molybdate, chromate^[99] etc. Ma et al recently studied the fragmented species $\{[W_x O_{3x+1}]^{2-}$ and $[PW_{12-x}O_{39-3x}]^-$ where $x= 6$ to $9\}$, along with common species from protonation, loss of water and alkali metal ion association in the gas phase.

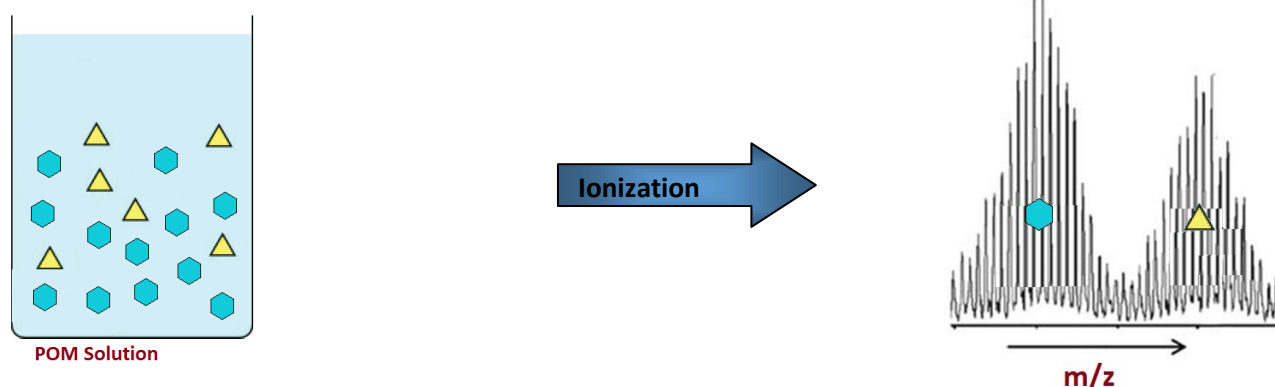


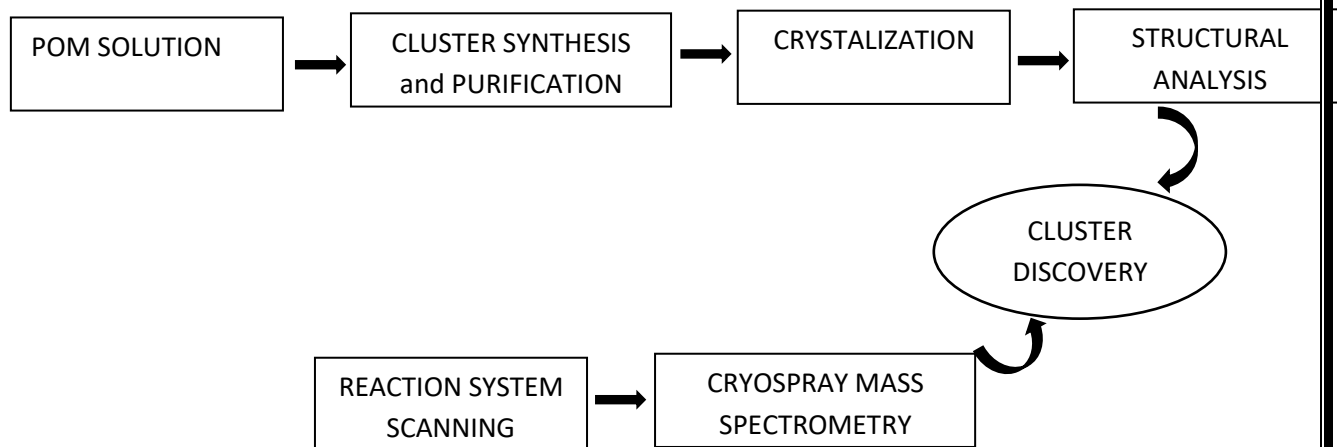
Figure -6 ESI and CSI mass spectrometry in the investigation of complex isotopic systems, such as POM-based molecules

In the characterization of complex POM clusters^[100], ESI-MS plays important role because it is used to:

- (i) establish separation methods for complex structure frameworks including synthetic intermediates and fragments^[101].
- (ii) authenticate the composition of metal & mixed –metal clusters. Eg-[Mo₁₇V₃], [W₁₉]^[102], [W₁₈I]^[103] etc.
- (iii) identify new isopolytungstates and their functionalization in solution^[104].
- (iv) explore the formation of POM-based nanostructure.
- (v) synthesize complex hybrid architectures^[105-106]. Eg- the asymmetrical Mn-Anderson POM cluster [N(C₄H₉)₄]₃ [MnMo₆O₁₈(C₄H₆O₃NO₂)(C₄H₆O₃NH₂)]
- (vi) investigate the mechanism of POM self-assembly
- (vii) investigate the reaction mechanism of polyniobates with hydrogen peroxide^[107].

7.1.2 Cryospray-ionization mass spectrometry (CSI-MS)

In order to examine the reaction mechanism and to investigate labile polyoxometalate clusters, a new technique of MS called CSI-MS has been recently employed by Cronin et al. This technique gives much faster and temperature-controlled result because it controls the temperature of infused solution and resulting electrospray. CSI-MS is useful for (a) investigation of unstable POM system, (b) investigation of weak and non-covalent interaction (where other ionization techniques, Eg- Fast Atomic Bombardment (FAB), MALDI (Matrix Laser Desorption Ionization) & ESI are not applicable because they use low resolution detectors and high temperature hence may cause bond dissociation. (c) screening of new cluster systems to show the addition of Te as heteroanion into a Dawson like cluster cage & also to monitor the reduction of Te^{VI} to Te^{IV}^[108].



Schematic representation 1 - Comparison of conventional three-step cluster characterization with the one-step cryospray mass spectrometry approach

7.1.3 Ion-mobility spectroscopy (IMS-MS)

The various building units of POM clusters differ from each other with respect to size, charge^[109], shape and conformation^[110]. A conventional mass spectroscopy allows separation of those anionic cluster which have different mass/charge ratio. But the technique is not very useful for the species having equal m/z ratio. Tungsten (W) has four stable isotopes & Mo has seven & being of transition metals both of them have tendency to show variable oxidation states. Hence conventional mass spectrum of POM clusters of these metals give complex isotopic envelops due to presence of supra molecular assemblies having equal m/z ratio. All these make POMs an ideal candidate for IMS-MS studies. Cronin et al first time performed IMS-MS studies on a Mn-Anderson cluster to deconvolute the isotopic envelops & separate the species on the basis of size. IMS-MS studies were performed on an ion-mobility mass spectrometer that combines travelling wave IMS (TWIMS) with quadrupole/Time of flight (QTOF) MS.

IMS-MS measurement opens up a crucial new dimension in the characterization field because it not only investigate supra molecular structure of clusters in the gas phase by allowing separation of the polymolecular aggregation on the basis of size but also allows a successful study of conformation change (from trans to cis) of azo bond containing photoresponsive ligands in alternate with the Mn-Anderson clusters.

7.2 IR(Infrared) spectroscopy and FTIR (Fourier-Transform Infra-red) Spectroscopy

Infrared spectroscopy is one of the most powerful analytical techniques, which indicates the possibility of chemical identification^[110]. It is based on the principle that the molecules absorb characteristic frequencies, called resonant frequencies, which corresponds to the vibration

frequency of bond or group. FTIR is done to analyze the nature of bond present between the different types of atoms (heteroatoms, addendum atom and ligand etc.) in the POM cluster. It is based on the principle that most of the molecules absorb light in IR-region of the electromagnetic spectrum. The frequency range absorbed by the cluster is measured as wave number mainly over the range $4000-600\text{ cm}^{-1}$

7.3 *Gel electrophoresis*

Electrophoresis is a process of sorting of species having different charge and size, under the influence of electric field. When a gel is used as an anticonvective and/or sieving medium then electrophoresis is called gel electrophoresis. Gel is used to suppress the thermal convection caused when electric field is applied. Thus gel electrophoresis is a method for separating and analysing macromolecules (DNA, RNA, protein etc.) and their fragments on the basis of their mobility which depends on their size and charge.

When an electric field is applied on mixture of species having different mass and charge then the species having greater charge/size ratio moves faster towards an electrode than the species having smaller charge/size ratio (this is because smaller molecules migrate more easily through the pores of gel, phenomenon is called sieving & due to more attraction of highly charged ion towards oppositely charged electrode). Hence by using gel electrophoresis it is possible to determine the surface charge density of nanoscale POM clusters and other metal-organic framework by measuring their mobility. Eg-Molybdenum brown $[\text{Mo}_{132}]$ ball moves faster than Molybdenum blue $[\text{Mo}_{154}]$ wheel^[111] due to its smaller size & higher charge.

7.4 *Surface-analysis*

Among the various devices & techniques used for the characterization, surface-related techniques have enormous potential in the analysis of POM clusters. It is generally believed that the growing number of investigations on POM clusters has been made possible due to availability of large amount of novel POM clusters but actually due credence should be given to the development of high quality, cutting edge analytical structure tools. All types of probe microscopy are together called scanning probe microscopy (SPM) and it comprises AFM^{[95], [112-113]} (atomic force microscopy) also called SFM (scanning force microscopy), SEM^[114] (Scanning electron microscopy), TEM (transmission electron microscopy) & STM^[115] (scanning tunneling microscopy), SERS (surface enhanced Raman scattering) & SNOM (scanning near-field optical microscopy) etc.

7.4.1 *Scanning electron microscope (SEM)*

A scanning electron microscope is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. It is based on scattered electron and provides a three dimensional image. The various signals are produced due to interaction of electrons with the atoms of POM clusters. These signals carry information about the surface topography and composition of the sample.

7.4.2 Transmission electron microscopy (TEM)

It is a high resolution tool which is based on transmitted electrons and illuminates the whole sample. TEM is considered as better than SEM because it has much higher resolution and hence it provides detail informations about internal composition of the POM cluster including particle size, crystallite size, etc. However, it provides only two dimensional image.

7.5 Thermal analysis

TGA (Thermal gravimetric analysis) & DSC (Differential scanning calorimetry) are methods to investigate the thermal characteristics of POMs.

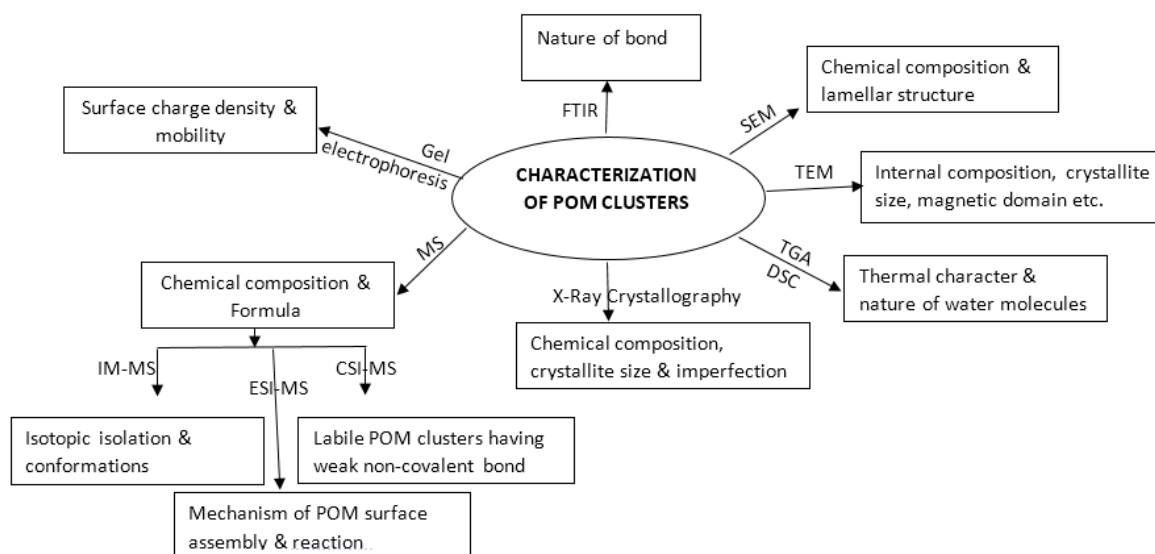
7.6. X-ray crystallography

X-ray crystallography is technique which is widely utilized in the field of structural analysis, in order to provide important structural information. Most of the POM structures are determined via this method due to its ability to provide atomic resolution structures of a wide range of POMs. It is based on the principle that when a beam of X-ray incident on the atoms of crystal they get diffracted in many specific directions. X-ray techniques include many techniques based on the scattering, emission and absorption properties of X-ray radiation. X-rays were discovered by Wilhelm Conrad Roentgen in 1895^[116]. X-ray diffraction phenomenon is governed by Bragg's law^{[117],[118]}. According to this law,

$n\lambda = 2d\sin\theta$ {where, λ is the wavelength of X-ray, θ is the scattering angle and 'n' represents the order of the diffraction peak (n= is an integer)}.

A 3-D picture of electron density is obtained by measuring the intensities & angles of the diffracted beams. However, there are a number of obstacles in macromolecular X-ray crystallography. The biggest two hurdles are (i) obtaining good single crystals diffracting to high resolution in the X-ray diffraction experiment and (ii) "phase problem" which occurs because detectors used in X-ray diffraction experiments are only able to measure the intensity of the diffracted light, but not its phase information which carries the bulk of the structural information. The unavailability of single crystal of sufficient size can be overcome by using various other X-ray techniques such as Fiber diffraction, powder diffraction, SAXS (small angle X-ray scattering) etc. Among these X-ray powder Diffraction (XRD), also called Debye-Scherrer method is the most common and suitable X-ray technique because it can analyse POM clusters even in microcrystalline form. There are three types of powder diffraction methods- (a) Debye-Scherrer method, (b) Focusing method and (c) Pinhole method.

Powder XRD is an important non-destructive technique applied for fast identification of crystalline POM clusters. XRD analysis helps in knowing crystallinity, structure imperfections, crystallite size, texture, number of atoms in the asymmetric unit cell and unit cell volume etc.



Schematic representation 2- Tools and techniques used for characterization of POM clusters

8. CONCLUSION

With the turn of century, the coming age of material science and the advent of nanotechnology, polyoxometalates are beginning to be considered as a unique chemical species that could turn from very special molecule to very useful materials. Polyoxometalates are compounds resulting from the polycondensation reaction between oxoanions of transition metals [Mo, W, V, Nb & Ta] around metal or non-metal oxoanion. A number of separate iso and heteropolyoxo clusters can be synthesized by using simple and efficient concept.

On the basis of facts collected over the period, it can be argued that discovery of novel POM building units and their self-assembly in a controlled manner are the most important things in POM chemistry. This review summarizes the structure, type, design and developments of polyoxometalates in term of building–units, architecture, synthetic variables etc. The focus is given on the fact that how the cluster templates, resulting building – units, sub-structures and overall cluster architectures need manipulations. The primary factors which influence the reaction include- molar–ratio, p^H , temp, ionic strength, nature and concentration of cations etc. By altering these factors hundreds of new compounds has been isolated easily by one–pot hydrothermal synthesis. A radical change has been taken place with respect to structure, bonding and properties of these fascinating clusters due to availability of various cutting edge characterization tools and techniques such as various types of mass spectroscopy, XRD, imaging techniques (TEM, SEM), TGA/DSC, IR-FTIR etc.

Due to their versatile properties and potential application in various fields such as catalysis, chemical sensing, medicines, material science etc., the development of POM chemistry is an interesting and creative future prospect for getting new materials with unusual features and properties.

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