ANDERSON-TYPE POLYOXOMOLYBDATE: SYNTHESIS, STRUCTURE AND APPLICATIONS

A literature review submitted in partial fulfilment of the requirements for the degree of **Master of Science in Chemistry (Analytical Chemistry).**

BY

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DECLARATION

I declare that the literature review titled “**Anderson type Polyoxomolybdate: Synthesis, structure and applications**’’ has been carried out by me in the Chemistry Department, School of Chemical Sciences, Goa University. The information derived from the literature has been duly acknowledged in the text and a list of references is provided.

ABHISHEK ANIL NAIK

CERTIFICATE

This is to certify that the literature review entitled: “**Anderson type Polyoxomolybdate: Synthesis, structure and applications**” submitted by the student is the record of research work carried out by the candidate during the academic year 2021-2022 under my supervision in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

Dr. Savita Kundaikar	Dr. Vidhyadatta Verenkar
(Project Guide)	(Dean of SCS, Goa,University)

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Introduction

The structure of polyoxometalates (POM) can be generally defined as molecular metal oxide clusters which are formed by condensation reaction of early transition metal-oxygen anions.[1]

Berzelius in 1826 discovered the first polyoxometalate compound,[2] now known as $(NH_4)_3[PMo_{12}O_{40}]$, which was produced as yellow coloured precipitate by acidification of ammonium molybdate solution with phosphoric acid. However, the analytical compositions of polyoxometalate compound like these were not accurately determined until Marignac invented tungstosilicate salt in 1862. By the beginning of the 20th century many heteropolyacids of the form $H_3PW_{12}O_{40}$ and large number of their salts had been discovered. Only the theoretical aspects and possible structural compositions of heteropolyanions were presented before the invention of X-ray diffraction method by Laue[3] in 1912 which was then developed by W. L.Bragg and W.H.Bragg.[4]

There is rapid growth in research in field of polyoxometalate chemistry worldwide which is due to the great structural and electronic diversity of POM systems and their potential uses in many other fields of scientific work, POMs are regarded as fragments of nonmolecular metal oxide lattices giving a wide distribution from insulator to superconductor in their electronic properties, the principal units that make up most of polyoxometalates are MO_6 octahedra or MO_4 tetrahedra. Generally, MO_6 octahedra can be linked together by a single oxygen atom (termed corner-sharing) and two oxygen atoms (termed edge-sharing).[5]The two types of the MO_6 unit linkage afford a great variety for the anion structure. In addition, the variety of metal atoms constituting the lattice offers an interesting chance of physiochemical properties such as redox properties, photochemical activities, ionic charge, conductivity and oxidation catalyst[6]–[8]. , energy transfer, and biological activity. Polyoxometalates may be characterized by six features: (1) electrochemical or photochemical reversible multi-electron redox reaction, (2) high solubility in water and occasionally in polar organic solvents such as acetonitrile, dimethilformamide and dioxane, (3) co-ordination of large amounts of water molecules, (4) easiness of the modifications of anion size, structure, anion charge and replacement of metal atoms by other metal atoms, (5) co-ordination of a great variety of heteroatoms up to 75% of elements in the periodic table at well-defined geometric sites in the lattice, and (6) capsulation of neutral molecule (acetonitrile) or ion (carbonate and halide).[9] Due to these properties POMs can be seen as molecular device systems, Figure 1 shows research fields towards this direction.[10]

. Some applications of POM include medicine e.g., targeting of antiviral chemotherapy, coating e.g. corrosion-resistant coating, sensors, sorbents of gases[11], electrooptics, electrochemistry/ electrodes[11], [12], dyes/pigments, nuclear waste processing[11].

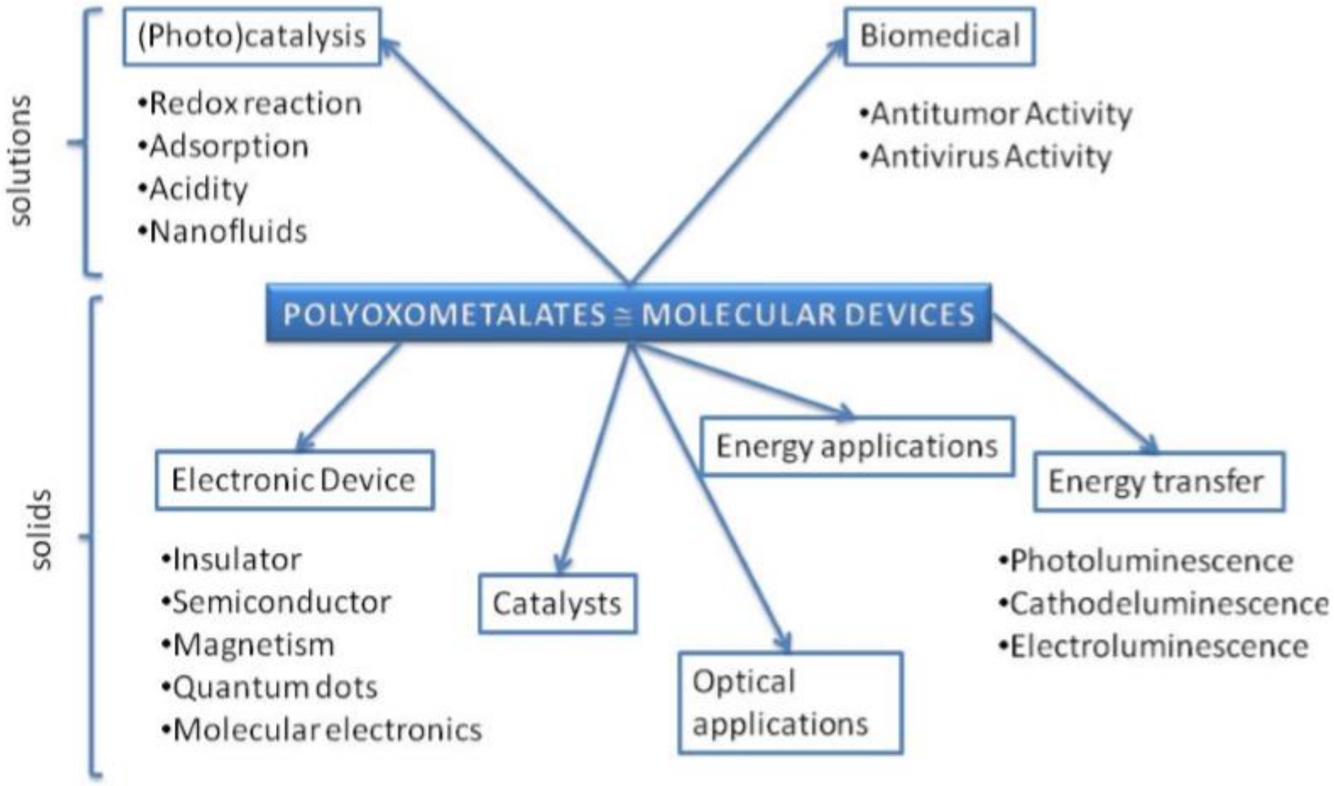


Figure1: Conceptual panel summarizing applications of polyoxometalate-based molecular device systems.

Structural Aspect of polyoxometalates

Polyoxometalates (POMs) are the clusters of the early transition metal-oxygen anions where the transition metals (V, Nb, Ta, Mo, W) are generally in their highest oxidation state where in metal cations exists as d^0 species.[13]

These soluble metal-oxide clusters can be considered as aggregates of {MOx}-type building-block units where the metal, M, (also known as the addenda atom) was best visually placed at the centre of polyhedron with coordinated oxygen ligands (X=4-7) defining the vertices. The overall structure of a POM can be represented by aggregated sets of such polyhedra with corner or edge sharing modes as shown in Figure 2. Face sharing of polyhedra is also possible, but is rarely seen.

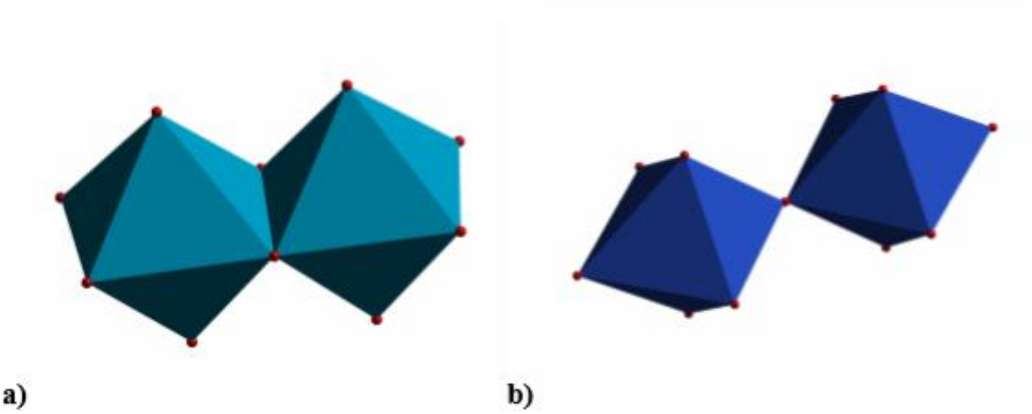
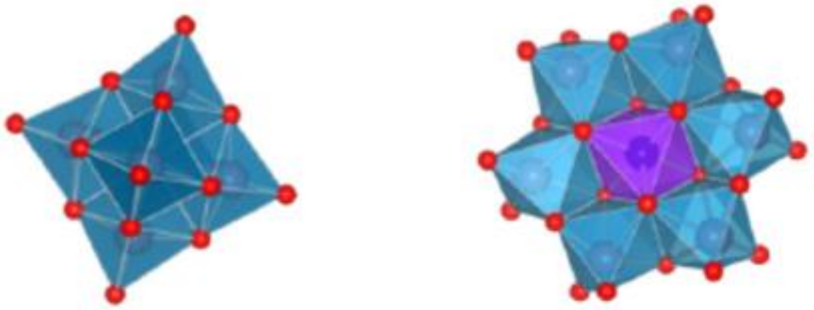


Figure 2: Example of {MOx} polyhedra where M = group 5 or 6 transition metal such as Mo or W, linked through a) edge-sharing, and b) corner-sharing modes.

Classification of polyoxometalate structures

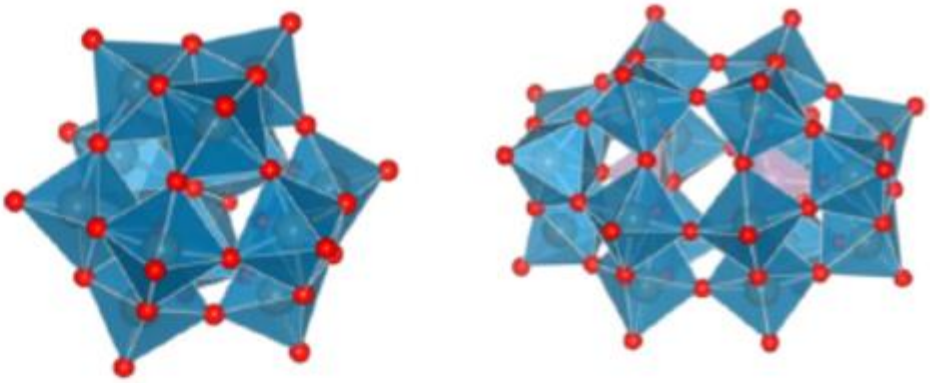
Polyoxometalate structures can be classified into two main families, i.e. the isopolyoxometalates, and the heteropolyoxometalates. Isopolyoxometalate anions consist only of the metal cation and oxide anion framework structure, e.g. $[Mo_7O_{24}]_6^{-}$, therefore, are often much more unstable, and are fewer in number, than their heteropolyanion counterparts. On the other side heteropolyoxometalate anions consist of one or more p, d or f block 'heteroatoms' coordinated with the metal-oxide cluster. e.g. the central P^{V} heteroatom within the $[PW_{12}O_{40}]_3^{-}$, they may be referred to as ‘primary’ or ‘central’ heteroatoms; whereas those coordinated within the outer metal-oxide framework, e.g. the Cr^{III} in $[CrSiW_{11}(H_2O)O_{39}]_5^{-}$,[1] may be referred to as ‘secondary’ or ‘peripheral’ heteroatoms. It is due to the wide variety of heteroatoms which may be incorporated into these heteropolyoxometalate structures that there are many more of these structures known than for the isopolyoxometalates.

From a structural point of view, the polyoxometalates can be considered as aggregates, usually anionic, formed by oxo species of transition metals with one or more bridging oxygen atoms. These clusters contain at least three metal atoms, in most cases from Groups 5 or 6 of the periodic table, usually in their highest oxidation state, with (heteropolyoxometalates) or without (isopolyoxometalates) heteroatoms (such as B, Al, Ge, Si, P, and many more). A lot of structures have been described, the most ubiquitous being the Lindqvist $[M_6O_{19}]^{n-}$. Anderson $[XM_6O_{24}]^{n-}$, Keggin $[XM_{12}O_{40}]^{n-}$, and Wells-Dawson $[X_2M_{18}O_{62}]^{n-}$ ones (where X=heteroatom, M=metal, n=overall cluster charge) Figure 3.[14]



Lindqvist

Anderson-Evans



α-Keggin

Wells-Dawson

Figure 3: Various structural types of polyoxometalates. Mo or W (V, Nb, Ta)=blue polyhedra, heteroatoms=violet polyhedra, O=red balls

The Anderson polyoxoanion $[Hx(XO_6)M_6O_{18}]^{n-}$

The structure of Anderson polyoxoanion can be assigned to the standard formula $[Hx(XO_6)M_6O_{18}]^{n-}$ where x = 0-6, n = 2-6 and 8, M = Mo or W, and X = central heteroatom.[15] This polyoxometalate anion is composed of six edge-sharing $\{MoO_6\}$ or $\{WO_6\}$ octahedra surrounding a central, edge-sharing heteroatom octahedron i.e. $\{XO_6\}$, leading to the planar arrangement shown in Figure 4. The overall structure, therefore, has approximate D_{3d} symmetry.

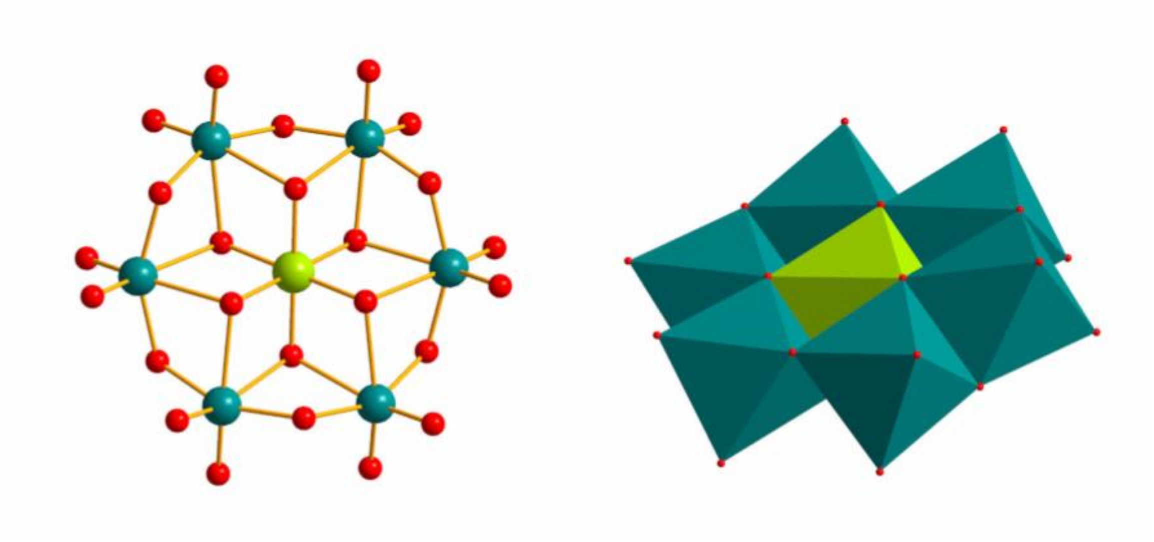


Figure 4: Representation of the molybdenum Anderson [TeVIMo$_8$O$_{24}$]$^{6-}$ anion. Left: Ball-and-stick representation showing the octahedral coordination environment of the central heteroatom. Right: Polyhedral representation showing the seven edge-sharing octahedra forming a planar arrangement. Colour scheme: Mo, teal (polyhedra); Te, light green (central polyhedron); O, red.

Anderson-type POMs are regarded as ideal inorganic building blocks for constructing multifunctional hybrid materials because of their easy access to covalent modification. For example, Anderson-type hybrids with D$_{10}$ metal heteroatoms and aromatic ligands show attractive fluorescence properties and can be used as luminescent materials.[16] By attaching to organic photosensitizers. Anderson-type POMs exhibit a wider light absorption range and show excellent catalytic efficiency in the hydrogen evolution reaction, which promotes their application in green energy technologies.[17] Anderson-type POM nanoclusters functionalized with fatty acids can deliver remarkable proteinbinding properties with enhanced bioavailability and antitumor selectivity. [18]

In recent years, the synthesis and structural research on Anderson-type POMs have experienced rapid development and their applications have spread to numerous fields including nanoelectronic materials, photosensitive devices, green energy, etc. Figure 5.[19]

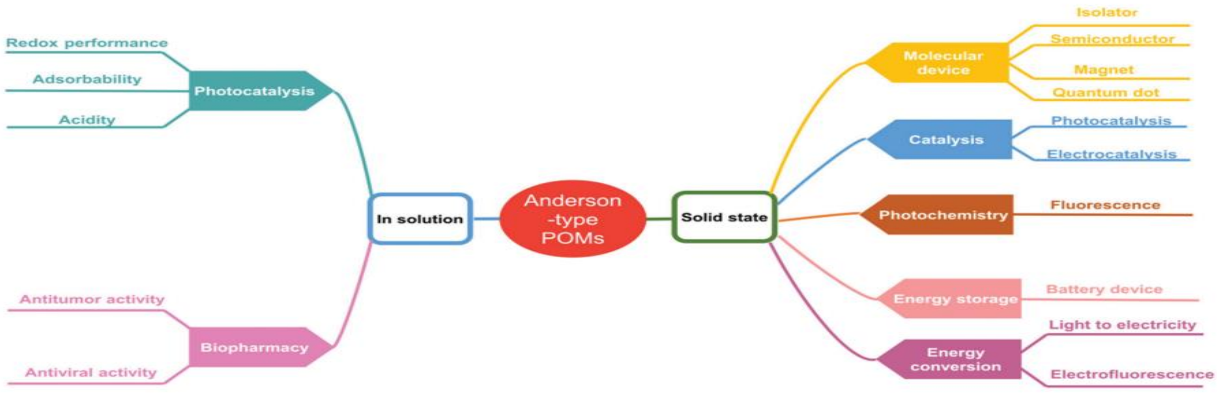


Figure 5: Applications of Anderson type POMs

The structure of Anderson-type POMs was proposed by J. S. Anderson in 1937 and confirmed by H. T. Evans in1948[20] by determining the single crystal structure of $[Te^{VI}Mo_6O_{24}]^{6-}$,[19] which was the first identified Anderson structure,[21] however since that time many other examples of Anderson structure containing heteroatom in a range of oxidation states from +2 to +7 has been identified. Some molybdate examples include: $[Mn^{II}(OH)_6Mo_6O_{18}]^{4-}$, $[Co^{II}(OH)_6Mo_6O_{18}]^{4-}$, $[Cr^{III}(OH)_6Mo_6O_{18}]^{3-}$ $[Al^{III}(OH)_6Mo_6O_{18}]^{3-}$, $[Mn^{IV}(OH)_6Mo_6O_{18}]^{2-}$, $[Te^{VI}O_6Mo_6O_{18}]^{6-}$, and $[I^{VII}O_6Mo_6O_{18}]^{5-}$. While the more limited range of tungsten examples includes: $[Ni^{II}(OH)_6W_6O_{18}]^{4-}$, $[Mn^{IV}O_6W_6O_{18}]^{8-}$, $[Ni^{IV}O_6W_6O_{18}]^{8-}$, $[Te^{VI}O_6W_6O_{18}]^{6-}$, $[I^{VII}O_6W_6O_{18}]^{5-}$.

The anions which have higher oxidation state heteroatoms such as Te^{VI} and I^{VII} can be seen to have unprotonated structures and are sometimes referred to as A-type Anderson structures. The anions of lower oxidation state that is +2 or +3 are sometimes referred to as B-type Anderson structures, and these anions generally have a non-acidic proton bonded to the oxygen ligands of the central $\{XO_6\}$ octahedron.[21]The lower oxidation state examples, e.g., oxidation state of +2 or +3, are sometimes referred to as B-type Anderson structures, and these anions usually have non-acidic protons bound to the oxygen ligands of the central $\{XO_6\}$ octahedron. However, there is one reported B-type structure, $[H_6Pt\ (IV)Mo_6O_{24}]^{2-}$, where four of the central μ_3-bridging oxo ligands and two of the μ_2-bridging oxo ligands are protonated.[22]

In general, the Anderson polyoxometalates structures can be isolated from the aqueous solutions of molybdate or tungsten followed by acidification to pH 3-4., however, the $\{X(II)Mo_6\}$ salts where X = Mn and Cu, have been found to be unstable and cannot be recrystallized.[15][23]

There are examples of both molybdenum Anderson and tungsten Anderson clusters undergoing further coordination with transition metal complexes e.g. Cu and Ag and lanthanide cations, e.g. La, Ce and Pr. However, prominent examples of further functionalization of B-type molybdenum Anderson structures involve their ability to coordinate a wide variety of tris(alkoxo) ligands, i.e. $RC(CH_2OH)_3$ where R = a chosen substituent group, e.g. alkyl, aryl, nitro etc. This has led to the isolation of many organic-inorganic hybrid compounds through the use of an indirect method of synthesis. This method involves the rearrangement of $[\alpha\text{-}Mo_8O_{26}]^{4-}$ cluster anions, in the presence of the heteroatom acetate salt, e.g. $Mn^{III}(CH_3CO_2)_3$, and the tris(alkoxo) ligand of choice, e.g. $CH_3C(CH_2OH)_3$, in order to isolate the derivatized Anderson cluster.

Table 1. List of structurally characterized Anderson type POMs

Sr.No.	Compound Name	Synthetic Details	Space group	Characterisation Technique	Application	Ref.
1	$Na_{12}[NiVMo_5O_{24}].11H_2O$	Hydrothermal/ $NiCl_2$ /$NaVO_4$ /CH_3COOH /$NaMoO_4$	--	TG-DTA, IR Spectroscopy, SEM	--	[24]
2	$Na_3[CrMo_6O_{24}H_6]$. $8H_2O$	$Na2MoO_4.2H_20$/ pH=4.5 (HNO_3)/ $Cr(NO_3)_3.9H_20$	$P\bar{1}$	X ray powder pattern and Single- crystal	catalytic studies	[6], [21]
3	$(NH_4)_3[CoMo_6O_{24}H_6]\cdot 7H_2O$	$CoSO_4.7H_2O/H_2O_2$ /$(NH_4)_6Mo_7O_{24}.4H_2O$	--	IR spectra and UV absorption	catalytic studies	[7], [15]
4	$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)3CNH_2\}_2]$	$[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ /$Mn(CH_3COO)_3\cdot 2H_2O$ /$(HOCH_2)_3CNH_2$ / acetonitrile / reflux / ether vapors / vacuum.	P c m n	IR spectra, ^1H NMR and ^{13}C NMR	Metal binding sites	[25]
5	$[N(C_4H_9)_4]_3[FeMo_6O_{18}\{(OCH_2)3CNH_2\}_2]$	[N(C4H9)4]4[α-Mo_8O_{26}]/$Fe(acac)_3$ /$(HOCH_2)3CNH_2$ /acetonitrile/reflux/ /ether vapours/ DMF.	C 2/m	IR spectra, ^1H NMR and ^{13}C NMR	Metal binding sites	[25]
6	$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)3CN=C(2\text{-}C_5H_4N)\}_2]$	2-pyridinecarbaldehyde /acetic acid /$[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)3CNH_2\}_2]$ /methanol/ reflux /	P 21/c	IR spectra, ^1H NMR and ^{13}C NMR	Metal binding sites	[25]

		$[N(C_4H_9)_4](OH)$ /vacuum.				
7	$[\{Ni(H_2O)_4\}_2\{Ni(OH)_6Mo_6O_{18}\}]\cdot4H_2O$	$Ni(CH_3COO)_2\cdot4H_2O$ / $H_3PMo_{12}O_{40}$ /r.t	P12 1/c 1	SEM, IR Spectrometry, TGA, DSC, XRTD	--	[26]
8	$[Ni(H_2O)_6][Ag_2\{Ni(OH)_6Mo_6O_{18}\}]\cdot8H_2O$	$Ni(CH_3COO)_2\cdot4H_2O$ /$H_3PMo_{12}O_{40}$ /Ag_2CO_3 /35°C	$P\bar{1}$	SEM, IR Spectrometry, TGA, DSC, XRTD	--	[26]
9	$K_{0.75}Na_{30.75}[PdMo_6O_{24}H_{3.5}]\cdot17H_2O$	$Na_2MoO_4\cdot2H_2O$ /$K_2[PdCl_4]$,/ pH=4.50 (H2SO4)/ KNO_3/,$(NH_4)_2SO_4$	$P\bar{1}$	XRD, IR Spectrometry, UV Spectrometry, TGA	--	[27]
10	(C6H10N3O2)2Na(H20)2[Al(OH)6Mo6O18].6H_2O	$Al(NO_3)_9.9H_2O$ /glacial acetic acid /$Na_2MoO_4.2H_2O$/ pH=3.4 (HCl)	$\bar{P}$ (2)/1	XRD, IR Spectrometry, UV Spectrometry, TGA	--	[28]
11	$Na_4[Ni(OH)_6Mo_6O_{18}]\cdot16H_2O$	$Na_2MoO_4\cdot2H_2O$ / pH=1.00.(HNO_3.) /$Ni(NO_3)_2$ /thermostated at T = 65°C/ d/w	$P\bar{1}$	TG, DTA, XRD, IR Spectrometry	--	[29]
12	$Na_2[NH_3C(CH_2OH)_3][Ni(OH)_3Mo_6O_{18}(OCH_2)_3CNH_3]\cdot11.75\ H_2O$	$Na_4[Ni(OH)_6Mo_6O_{18}]\cdot16H_2O$ / reflux/ $NH_2C(CH_2OH)_3$ /tetrabutylammonium bromide	$P\bar{1}$	IR Spectroscopy, ESI-MS, TGA and X-ray crystallography	--	[29]
13	$TMA_4H_8[Na_5Sb_3(Sb_2Mo_{12}O_{57})]\cdot17H_2O$	$(NH_4)_6Mo_7O_{24}\cdot4H_2O$ /H2O /,Sb_2O_3/ HCl / Sb_2O_5 /TMAOH/ pH =5.44 /NaOH /FeSO4	Cmcm	IR Spectroscopy, UV Absorption Spectroscopy, TGA , X-ray powder diffraction (XPRD), X-ray photoelectron spectra (XPS)	--	[30]
14	$[(C_4H_9)_4N]_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$	$[(C_4H_9)_4N]_4[Mo_8O_{26}]$/ Mn (III) acetate dehydrate/ $(CH_3CO_2)_3Mn.2H_2O$/		IR Spectroscopy, UV-Visible Spectroscopy,	biological activities	[31]

		acetonitrile/vacuum /diethyl ether.		HPLC, ESI-MS, spectropolarimeter, ^{1}H-NMR, Transmission electron microscopy		
15	$[(C_4H_9)_4N]_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_2)_2COOH\}_2]$ui	$[(C_4H_9)_4N]_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ /succinic anhydride /DMF /ether /CH_3CN.		IR Spectroscopy, UV-Visible Spectroscopy, HPLC, ESI-MS, spectropolarimeter, ^{1}H-NMR, Transmission electron microscopy	biological activities	[31]
16	$[(C_4H_9)_4N]_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_2)_2CO(C_4H_4NO_3)\}_2]$	DCC /NHS /DMF. /(dicyclohexylurea/ diethyl /CH_3CN		IR Spectroscopy, UV-Visible Spectroscopy, HPLC, ESI-MS, spectropolarimeter, ^{1}H-NMR, Transmission electron microscopy	biological activities	[31]
17	$(NH_4)_4[CuMo_6O_{24}H_6]•5H_2O$	$(NH_4)_6[Mo_7O_{24}]•6H_2O$ / $Cu(NO_3)_2•6H_2O$ / pH=5.5.		ICP, FTIR, UV-Vis spectroscopy	Photocatalytic Degradation of indicator	[8]
18	$(NH_4)_4[ZnMo_6O_{24}H_6]•5H_2O$	$(NH_4)_6[Mo_7O_{24}]•6H_2O$ / $Zn(NO_3)_2•6H_2O$/ pH=5.5.		ICP, FTIR, UV-Visible spectroscopy	Photocatalytic Degradation of indicator	[8]
19	$Na_3[AlMo_6O_{24}H_6]$	$Na_2MoO_4·2H_2O$ /$AlCl_3$ /pH =1.8 /HCl / acetone/distilled water	P-1	XRD, FT-IR, Laser Raman Spectrometry, SEM,	Cathode Material of Lithium Ion Battery	[12]
20	$[Cu(2\text{-}pzc)(H_2O)_2\}_2\{H_7AlMo_6O_{24}\}]·17H_2O$	$Na_2MoO_4·2H_2O$ /$AlCl_3$ /glacial acetic acid. /2 pyrazine carboxylic acid	P2(1)/c	Single crystal X-ray diffraction, SEM, TGA,	dye absorption properties	[32]

		$/CuCl_2 \cdot 2H_2O$ /methanol/H_2O		UV-Vis spectrometry, IR Spectrometry		
21	$[Co^{III}(bpy)3][Cr(OH)5Mo6(OCH3)O18].12H2O$	2,2-Bipyridine /methanol/ oxalic acid $/CoCl_2.6H_2O$ $/Na_3[Cr(OH)_6Mo_6O_{18}].8H_2O$ The pH =1.85	P 2(1)/c	IR spectroscopy, XRD and TGA	magnetic properties	[33]
22	$[Co^{III}(bpy)_3][Cr(OH)_6Mo_6O_{18}].15H_2O$	Methanol /2,2-bipyridine /oxalic acid/$CoCl_2.6H_2O$ $/Na_3[Cr(OH)_6Mo_6O_{18}].8H_2O/\ H_2O$ pH =2.5	$P\bar{1}$	IR spectroscopy, XRD and TGA	magnetic properties	[33]
23	$[La(H_2O)_7Cr(OH)_6Mo_6O_{18}] \cdot 4nH_2O$	$La(NO_3)_3 \cdot 6H_2O$ / H_2O /glacial acetic acid $/Na_2MoO_4 \cdot 2H_2O$ /CrCl3 /pH =2.60 $/HNO_3$	Pca21	IR spectroscopy, UV-visible spectroscopy, EPR spectroscopy, TGA, Powder X-ray diffraction		[34]
24	$[Gd(H_2O)_7Cr(OH)_6Mo_6O_{18}] \cdot 4nH_2O$	$Gd(NO_3)_3 \cdot 6H_2O$ $/H_2O/$ glacial acetic acid $/Na_2MoO_4 \cdot 6H_2O$ $/CrCl_3$ /pH=2.60 / HNO_3	Pca21	IR spectroscopy, UV-visible spectroscopy, EPR spectroscopy, TGA, Powder X-ray diffraction	--	[34]
25	$[Gd(H_2O)_7Al(OH)_6Mo_6O_{18}] \cdot 4nH_2O$	$Gd(NO_3)_3 \cdot 6H_2O$ $/H_2O$ / glacial acetic acid $/Na_2MoO_4 \cdot 2H_2O$ $/AlCl_3 \cdot 6H_2O$ /pH =2.60 $/HNO_3$ /r.t	Pca21	IR spectroscopy, UV-visible spectroscopy, EPR spectroscopy, TGA, Powder X-ray diffraction	--	[34]
26	$[Eu(H_2O)_7Al(OH)_6Mo_6O_{18}] \cdot 4nH_2O$	$Eu(NO_3)_3 \cdot 6H_2O$ $/H_2O$ / glacial acetic acid $/Na_2MoO_4 \cdot 2H_2O$ $/AlCl_3 \cdot 6H_2O$ /pH =2.60 $/HNO_3$ /r.t	Pca21	IR spectroscopy, UV-visible spectroscopy, EPR spectroscopy, TGA, Powder X-ray diffraction	--	[34]

27	(H3O)[(3-C5H7N2)2(Cr(OH)6Mo6O18)] . 3H2O	Hydrothermal synthesis/ CrCl$_3$6H$_2$O /Na$_2$MoO$_4$.2H$_2$O MoO$_3$ /3-aminopyridine /H$_2$SO$_4$/H$_2$O/ Teflon-lined bomb	P$\bar{1}$	X-ray crystallography, TG-DTA, UV-Vis Spectroscopy	catalytic studies	[35]

(acac = acetylacetonate), DMF=Dimethylformamide, TGA=Thermal Gravimetric Analysis, DTA=Differential thermal analysis, XRD= X-ray Diffraction, r.t=room temp.

Synthetic Aspect and Characterisation

1) The compound Na_{12} [$NiVMo_5O_{24}$].11H_2O from the ref.[24] was hydrothermally synthesis by mixing $NiCl_2$ and $NaVO_4$ in CH_3COOH, this solution was then added to $NaMoO_4$ (Mo Source) till constant pH.

The above compound was characterised using TG-DTA, IR Spectroscopy, SEM techniques.

2)The compound $Na_3[CrMo_6O_{24}H_6]$. 8H_2O from the ref.[6], [21] was synthesized by dissolving Na_2MoO_4.2$H_2$0 (Mo source) in d/w and pH was adjusted to 4.5 using HNO_3, other solution of $Cr(NO_3)_3$.9$H_2$0 was prepared in d/w and was mixed with the first solution and boiled followed by hot filtration.

The above compound was characterised using X ray powder pattern and Single- crystal techniques.

3)The compound $(NH_4)_3[CoMo_6O_{24}H_6]\cdot 7H_2O$ from the ref.[7], [15] was synthesized by preparing aqueous solution of $CoSO_4$.7H_2O and H_2O_2 which was then added to the boiling solution of $(NH_4)_6Mo_7O_{24}$.4H_2O (Mo source).

The above compound was characterised using IR spectroscopy and UV absorption techniques.

4)The compound $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)3CNH_2\}_2]$ from the ref.[25] was synthesized by mixing $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$(Mo source), $Mn(CH_3COO)_3\cdot 2H_2O$ and $(HOCH_2)_3CNH_2$ in acetonitrile which was then refluxed, after refluxing the solution was filtered, cooled and exposed to ether vapours. Which gives a large orange crystal which were washed with acetonitrile and ether and dried under vacuum.

The above compound was characterised using IR spectra, ^{1}H NMR and ^{13}C NMR techniques

5) The compound $[N(C_4H_9)_4]_3[FeMo_6O_{18}\{(OCH_2)3CNH_2\}_2]$ from the ref.[25] was synthesized by mixing $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$(Mo source) with $Fe(acac)_3$ and $(HOCH_2)3CNH_2$ in Acetonitrile which was refluxed that gives red coloured was then cooled in r.t and the solid was removed by filtration and the filtrate was exposed to ether vapour to give microcrystalline solid which is isolated by filtration and compound was later recrystallized from DMF.

The above compound was characterised using IR spectra, ^1H NMR and ^{13}C NMR techniques.

6)The compound $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)3CN{=}C(2\text{-}C_5H_4N)\}_2]$ from the ref.[25] was synthesized by adding 2-pyridinecarbaldehyde and acetic acid to the boiling solution of $[N(C_4H_9)_4]_3[MnMo_6O_{18}\{(OCH_2)3CNH_2\}_2]$ (Mo source) in methanol, this solution was then refluxed cooled at r.t and methanolic solution of $[N(C_4H_9)_4](OH)$ was added, the precipitate was filtered washed with methanol and dried under vacuum.

The above compound was characterised using IR spectra, ^1H NMR and ^{13}C NMR techniques

7) The compound $[\{Ni(H_2O)_4\}_2\{Ni(OH)_6Mo_6O_{18}\}]\cdot4H_2O$ from the ref.[26] was synthesized by adding $Ni(CH_3COO)_2\cdot4H_2O$ to the solution of $H_3PMo_{12}O_{40}$ (Mo source) to obtain a light blue crystals at r.t.

The above compound was characterised using SEM, IR Spectrometry, TGA, DSC, XRTD techniques.

8)The compound $[Ni(H_2O)_6][Ag_2\{Ni(OH)_6Mo_6O_{18}\}]\cdot8H_2O$ from the ref.[26] was synthesized by adding $Ni(CH_3COO)_2\cdot4H_2O$ to $H_3PMo_{12}O_{40}$ (Mo source), to solution Ag_2CO_3 was added and heated at 35°C for 2h, the solid obtained was eliminated and the filtrate was kept at r.t to obtain thin needle-shaped green crystals.

The above compound was characterised using SEM, IR Spectrometry, TGA, DSC, XRTD techniques.

9) The compound $K_{0.75}Na_{3.75}[PdMo_6O_{24}H_{3.5}]\cdot17H_2O$ from the ref. [27] was synthesized by adding $Na_2MoO_4\cdot2H_2O$ (Mo source), to the solution of $K_2[PdCl_4]$, pH of solution was adjusted to 4.5 and was allowed to stand for at r.t. , a colourless precipitate was form which was eliminated and filtrate remaining was divided in three fractions to which KNO_3, $(NH_4)_2SO_4$ and no solution were added to produce crystals of the complex.

The above compound was characterised using XRD, IR Spectrometry, UV Spectrometry, TGA techniques.

10)The compound $(C_6H_{10}N_3O_2)2Na(H_20)2[Al(OH)_6Mo_6O_{18}].6H_2O$ From the ref.[28] was synthesized by prepared by mixing aqueous solution of $Al(NO_3)_9.9H_2O$, glacial acetic acid and $Na_2MoO_4.2H_2O$ (Mo source). Other solution of $C_6H_9N_3O_2$ was dissolved in d/w was added dropwise to the first solution, pH of mixture was adjusted to 3.4.

The above compound was characterised using XRD, IR Spectrometry, UV Spectrometry, TGA techniques.

11)The compound $Na_4[Ni(OH)_6Mo_6O_{18}]\cdot16H_2O$ from the ref.[29] was synthesized by dissolving $Na_2MoO_4\cdot2H_2O$(Mo source) in d/w ,HNO_3 was added to adjusted to pH =1.0 and to this $Ni(NO_3)_2$ was added. This solution was thermostated at T=65°C after 15 days crystals were form which was filtered, washed with d/w and air dried.

The above compound was characterised using TG, DTA, XRD, IR Spectrometry techniques.

12)The compound $Na_2[NH_3C(CH_2OH)_3][Ni(OH)_3Mo_6O_{18}(OCH_2)3CNH_3]\cdot11.75\ H_2O$ from the ref. [29]was synthesized by dissolving $Na_4[Ni(OH)_6Mo_6O_{18}]\cdot16H_2O$ (Mo source) in water, this solution was refluxed and $NH_2C(CH_2OH)_3$ was added, after refluxing tetrabutylammonium bromide was added and cooled at r.t.

The above compound was characterised using IR Spectroscopy, ESI-MS, TGA and X-ray crystallography techniques.

13)The compound $TMA_4H_8[Na_5Sb_3(Sb_2Mo_{12}O_{57})]\cdot17H_2O$ from the ref.[30] was synthesized by dissolving $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (Mo source) in water at 50 °C ,other solution of Sb_2O_3 was dissolved in HCl , and this solution was then added to previously prepared solution dropwise. After the solution was cooled, TMAOH was added, pH of solution was adjusted to 5.44, again the solution was heated at 60 °C followed by addition of $FeSO_4$. The solution was allowed to cool at r,t to obtain crystals of compound.

The above compound was characterised using IR Spectroscopy, UV Absorption Spectroscopy, TGA , X-ray powder diffraction (XPRD), X-ray photoelectron spectra (XPS) techniques.

14) The compound $[(C_4H_9)_4N]_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ from the ref.[31] was synthesized by dissolving $[(C_4H_9)_4N]_4[Mo_8O_{26}]$ (Mo source), Mn (III) acetate dehydrate, $(CH_3CO_2)_3Mn.2H_2O$, TRIS with acetonitrile and heated at 80^{o}C for 24 h, the precipitate was removed by filtration and filtrate was heated under vacuum to give

white precipitate which was also removed by filtration and the filtrate was crystallized under diethyl ether atmosphere to obtain orange crystals of the compound.

The above compound was characterised using IR Spectroscopy, UV-Visible Spectroscopy, HPLC, ESI-MS, spectropolarimeter, ^{1}H-NMR, Transmission electron microscopy techniques.

15) The compound $[(C_4H_9)_4N]_3[MnMo_6O_{18}\{(OCH_2)_3\,CNHCO(CH_2)_2COOH\}_2]$ from the ref.[31] was synthesized by dissolving $[(C_4H_9)_4N]_3[MnMo_6O_{18}((OCH_2)_3CNH_2)_2]$ (Mo source), succinic anhydride in DMF. The solution was heated at 50ºC for 24h, Orange crystals were obtained under ether atmosphere which filtered and washed with ether and the crystallization was repeated after dissolving the crystals in CH_3CN.

The above compound was characterised using IR Spectroscopy, UV-Visible Spectroscopy, HPLC, ESI-MS, spectropolarimeter, ^{1}H-NMR, Transmission electron microscopy techniques.

16) The compound $[(C_4H_9)_4N]_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_2)_2CO(C_4H_4NO_3)\}_2]$ from the ref.[31] was synthesized by dissolving DCC, NHS in DMF, the solution was stirred for 2h at r.t then the precipitate obtained was removed and the orange solution was placed under diethyl ether atmosphere for a first crystallization. The product was then recrystallized from CH_3CN and washed with diethyl ether.

The above compound was characterised using IR Spectroscopy, UV-Visible Spectroscopy, HPLC, ESI-MS, spectropolarimeter, ^{1}H-NMR, Transmission electron microscopy techniques.

17) The compounds $(NH_4)_4[CuMo_6O_{24}H_6]\bullet 5H_2O$ and $(NH_4)_4[ZnMo_6O_{24}H_6]\bullet 5H_2O$ from the ref.[8] were synthesized on the similar lines to synthesise these compounds aqueous solution of $(NH_4)_6[Mo_7O_{24}]\bullet 6H_2O$ (Mo source) and $Cu(NO_3)_2\bullet 6H_2O$/ $Zn(NO_3)_2\bullet 6H_2O$ were prepared in stoichiometric proportions, pH=5.5 was maintain in the solution, After precipitation, the solution was filtered and dried at room temperature.

The above compound was characterised using ICP, FTIR, UV-Vis spectroscopy techniques.

18) The compound $Na_3[AlMo_6O_{24}H_6]$ from the ref.[12] was synthesized by adding $Na_2MoO_4{\cdot}2H_2O$ (Mo source), $AlCl_3$ in d/w, the pH of the solution adjusted to 1.8, the solution was evaporated at 40°C to obtain precipitate which was then wasted with acetone/water mixture followed with acetone and dried at 80 °C.

The above compound was characterised using XRD, FT-IR, Laser Raman Spectrometry, SEM techniques.

19) The compound [Cu(2-pzc) $(H_2O)_2\}_2\{H_7AlMo_6O_{24}\}]\cdot17H_2O$ from the ref.[32] was synthesized by adding $Na_2MoO_4\cdot2H_2O$ (Mo source) to solution of $AlCl_3$ in water which was then acidified by adding glacial acetic acid. Another solution was prepared by mixing 2 pyrazine carboxylic acid to solution of $CuCl_2\cdot2H_2O$ in water and methanol. This solution was then added to the previously prepared solution which gave a blue block crystal of the compound.

The above compound was characterised using Single crystal X-ray diffraction, SEM, TGA, UV-Vis spectrometry, IR Spectrometry techniques.

20)The compound $[Co^{III}(bpy)_3][Cr(OH)_5Mo_6(OCH_3)O_{18}].12H_2O$ from the ref.[33] was synthesized by dissolving 2,2-bipyridine in methanol followed by aqueous solution of oxalic acid, $CoCl_2.6H_2O$ and $Na_3[Cr(OH)_6Mo_6O_{18}].8H_2O$ (Mo source), the pH was adjusted to 1.85 . The mixture was heated to 50ºC, and then the solution cooled to room temperature and was filtered. The crystals obtain from filtrate after 2 weeks.

The above compound was characterised using IR spectroscopy, XRD and TGA techniques.

21)The compound $[Co^{III}(bpy)_3][Cr(OH)_6Mo_6O_{18}].15H_2O$ from the ref.[33] was prepared from Methanol containing 2,2-bipyridine, CoCl2.6H2O, $CoCl_2.6H_2O$ and $Na_3[Cr(OH)_6Mo_6O_{18}].8H_2O$ (Mo source), the pH was adjusted to 2.5, The mixture was heated to 50ºC, and then the solution cooled to room temperature and was filtered. The crystals obtain from filtrate after 2 weeks.

The above compound was characterised using IR spectroscopy, XRD and TGA techniques.

22)The compounds $[La(H_2O)_7Cr(OH)_6Mo_6O_{18}]\cdot$ $4nH_2O$ and $[Gd(H_2O)_7Cr(OH)_6Mo_6O_{18}]\cdot$ $4nH_2O$ from the ref.[34] were synthesized on the similar lines to synthesize these compounds $La(NO_3)_3\cdot$ $6H_2O$/ $Gd(NO_3)_3\cdot$ $6H_2O$ were dissolved in water followed by addition of glacial acetic acid, $Na_2MoO_4\cdot$ $6H_2O$ (Mo source) and $CrCl_3$. The pH was adjusted to 2.6 and this mixture was boiled at 80–85◦C and then filtered to obtain a pinkish crystal.

The above compound was characterised using IR spectroscopy, UV-visible spectroscopy, EPR spectroscopy, TGA, Powder X-ray diffraction techniques.

23)The compounds $[Gd(H_2O)_7Al(OH)_6Mo_6O_{18}]\cdot 4nH_2O$ and $[Eu(H_2O)_7Al(OH)_6Mo_6O_{18}]\cdot 4nH_2O$ from the ref.[34] were synthesized on the similar lines, to synthesize these compounds $Gd(NO_3)_3\cdot 6H_2O$/ $Eu(NO_3)_3\cdot 6H_2O$ were dissolved in water followed by addition of glacial acetic acid, $Na_2MoO_4\cdot 2H_2O$ (Mo source), $AlCl_3\cdot 6H_2O$. The pH of the solution was adjusted to 2.60 and the filtered solution (filtrate) was kept in an open flask at room temperature for five days, during which time the solution afforded white block-shaped crystals of the compound was obtained.

The above compound was characterised using IR spectroscopy, UV-visible spectroscopy, EPR spectroscopy, TGA, Powder X-ray diffraction techniques.

24) The compound $(H_3O)[(3\text{-}C_5H_7N_2)_2(Cr(OH)_6Mo_6O_{18})].3H_2O$ from the ref.[35] was hydrothermally synthesized by mixing $CrCl_36H_2O$, $Na_2MoO_4.2H_2O$ (Mo source), $MoO_{3,}$ 3-aminopyridine, 1:1 sulfuric acid and water, which was sealed in a 25-mL Teflon-lined bomb and heated at 170ºC and then cooled to r.t by filtrating, washing with distilled water, and air-drying to purple block-like crystals.

The above compound was characterised using X-ray crystallography, TG-DTA, UV-Vis Spectroscopy techniques.

General Aspects

From the scrutiny of the above collected data it has been seen that $Na_2MoO_4.2H_2O$ is the most widely use molybdenum source for synthesis of Anderson type polyoxomolybdate.

It can be also seen that most of the synthesis are carried out in refluxed conditions and at the acidic pH.

Scenes most of the Anderson type poluoxomolybdate forms coloured complexes their absorbance can be easily found out using UV-Vis spectroscopy and being crystalline its crystal data can also be found out.

It requires almost 2-3 weeks' time for Anderson type polyoxomolybdate to form crystals with good yield.

The Anderson type polyoxomatales shows a wide range of applications like Catalytical activity , provides binding sites for metals, used to study biological activity, Cathode Material of Lithium Ion Battery, magnetic properties and many more.

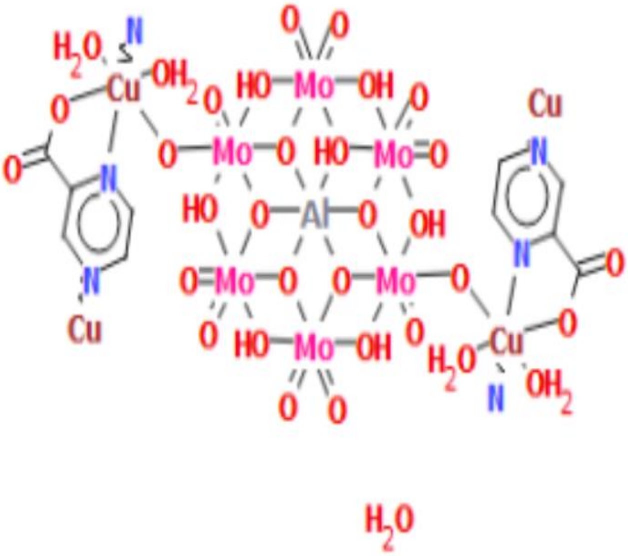
Structures of Anderson type Polyoxomolybdates

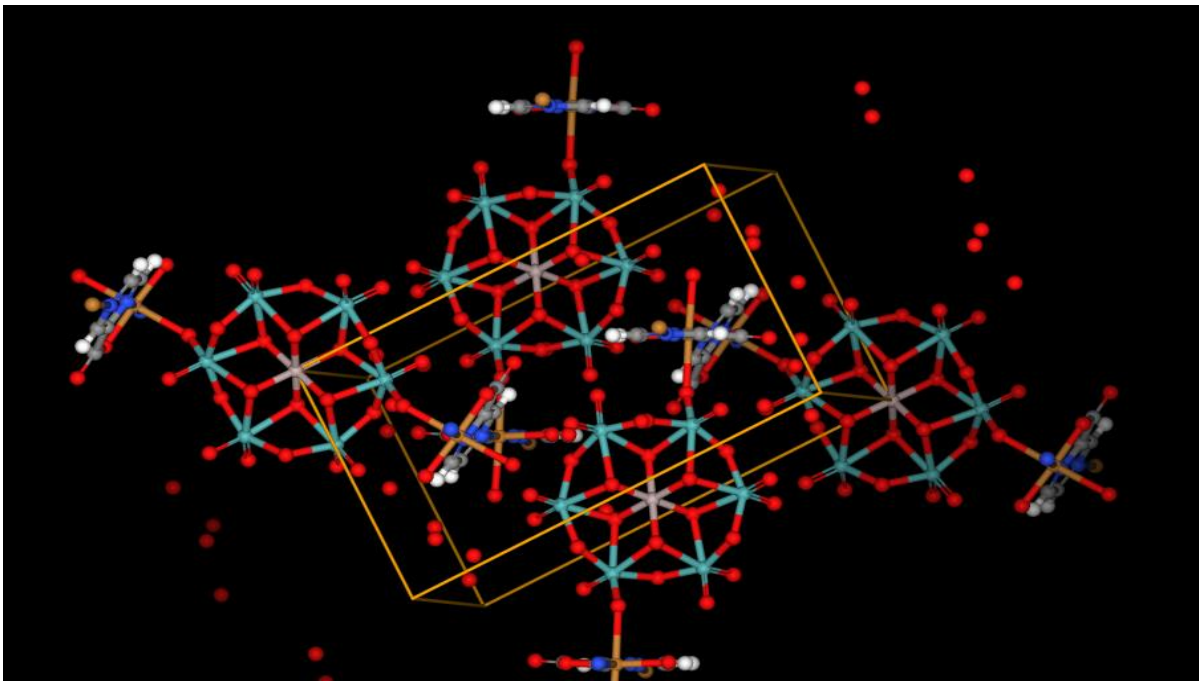
1) $[Cu(2\text{-}pzc)\ (H_2O)_2\}_2\{H_7AlMo_6O_{24}\}]\cdot 17H_2O$ [32]

Space Group:P 2 1/c

Cell: a= 10.880Å,b=17.031Å,c= 13.617Å, α=90.00º,β=107.73º,γ=90.00º

Chemical Diagram



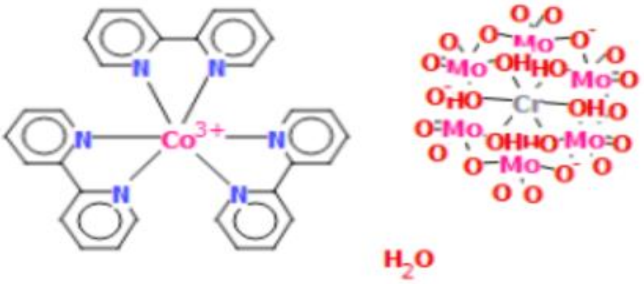


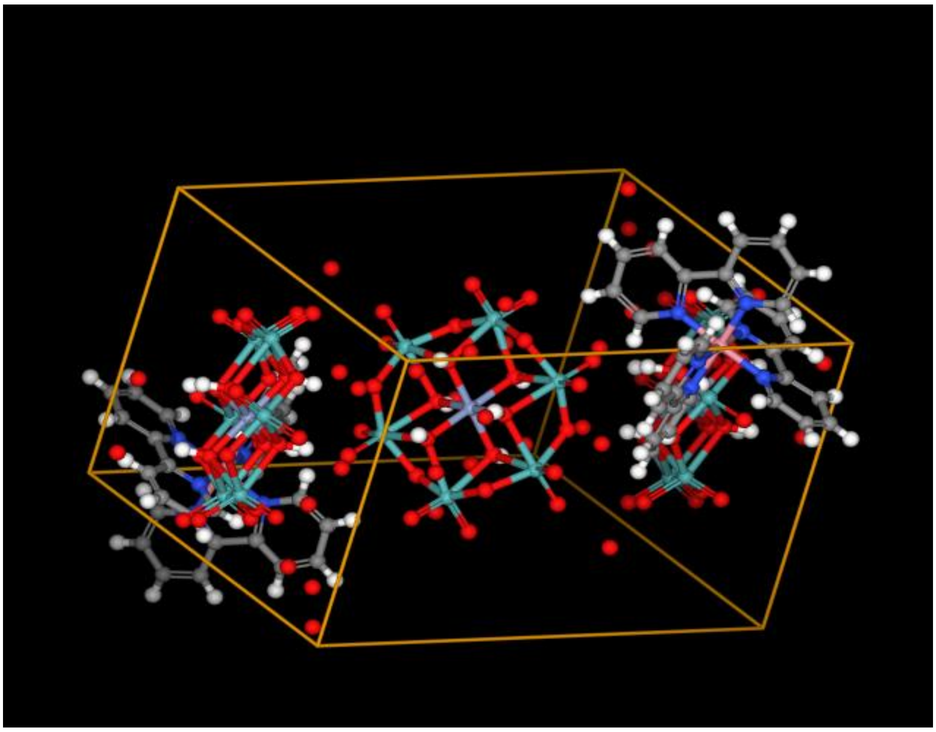
2) $[Co^{III}(bpy)_3][Cr(OH)_6Mo_6O_{18}].15H_2O$ [33]

Space Group: $P\bar{1}$

Cell: a= 12,196Å, b=12.231Å, c= 19.752Å, α=84.078º, β=85.675º, γ=89.030º

Chemical Diagram





Conclusion

From the gathered data it seen that most of the Anderson type polyoxomolybdate are synthesized by using $Na_2MoO_4.2H_2O$ as a Molybdenum source for the synthesis, most of the reactions are carried out by reflux condition or are synthesized at room temperature. Most of the compounds shows a space group of P-1. The Anderson type polyoxomolybdate exhibits different magnetic and catalytical properties and are used in different applications.

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