

One pot hydrothermal synthesis and characterization of self organized novel Anderson type mixed heteropolyoxomolybdate complex $\text{Na}_{14} [\text{CuNiMo}_5\text{O}_{24}] \cdot 20\text{H}_2\text{O}$ applicable as catalyst

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Abstract

Harmful chemicals become a serious threat to the environment. To protect the environment from harmful effects of hazardous organic/inorganic chemicals, researchers are trying to introduce green chemistry. Polyoxometalate is one of the pioneers in this field. An eco-friendly sodium salt of molybdenum containing mixed heteropoly complex $\text{Na}_{14} [\text{CuNiMo}_5] \cdot 20\text{H}_2\text{O}$ has been synthesized hydrothermally which is analogous to Anderson type anion $[\text{XM}_6\text{O}_{24}]^{n-}$. The compound is prepared from aqueous solution of copper chloride, nickel chloride and sodium molybdate at a pH 4.0. The elemental analysis has been done by inductively coupled plasma optical emission spectroscopy (ICP-OES) which predicts 1:6 atomic ratio of the heteroatom to the addenda atom.

FTIR spectra show nature of bonding of Ni-O, Cu-O and Mo-O bonds. The morphology and texture of as synthesized compound have been examined by Scanning electron microscopy (SEM with EDS) followed by study of thermal stability by thermogravimetric analysis (TG-SDTA). The average molecular weight of the compound has been obtained by employing cryoscopy method. The synthesized compound has been applied in the acetylation of O-PDA and 4 - methylphenylenediamine.

Keywords: Heteropoly anderson type, hydrothermal, molybdate, cryoscopy.

Introduction

Metal-oxygen anion clusters (polyoxometalates or POMs) are large and rapidly growing class of inorganic chemistry. POMs are non-toxic (eco- friendly) negatively-charged clusters of early-transition metals. POMs provide a wide range of versatile structure.¹ Due to diverse and discrete molecular structures, their applications range from catalysis to functional materials. POMs have been noted for their catalytic²⁻⁵ magnetic⁶, biological⁷⁻¹⁰, supramolecular¹¹⁻¹², efficient adsorbants¹³ and electrochemical applications¹⁴.

POMs are cluster compounds having M-O and M-O-M linkages with large number of lattice water in the interstitial position³ where M comprises of early transition elements in

their d^0 and d^1 electronic configuration state for example V (V), Mo (V) and Mo (VI), or W (VI).

POMs are categorized as isopolyanions for example $[\text{W}_6\text{O}_{19}]^{2-}$, heteropoly anions such as $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and partially reduced "wheel like" oxomolybdate clusters. Scientists and researchers showed great interest towards polyoxometalate chemistry due to their fast growing applications in different fields of science and technology.

Anderson type $[\text{XM}_6\text{O}_{24}]^{n-}$ of polyoxometalate is composed of a central hetero atom in a regular octahedral coordination mode XO_6 surrounded by six octahedra of addenda atoms more commonly MoO_6 or WO_6 by edge sharing. Anderson type POMs have planar arrangement with idealized D_3 point symmetry. Anderson types of POMs are more efficient as catalyst than the Keggin and Dawson forms of polyoxometalate.

Molybdenum (Mo) based polyoxometalates show excellent catalytic activity in various inorganic and organic transformations. Addenda atoms [in this case molybdenum (Mo)] in Anderson type of POMs have two terminal oxygen atoms which make them highly reactive and allow them to attach with other transition elements¹⁵⁻¹⁸. POM complexes exhibit fast reversible redox transformations in mild conditions.

Conventional hydrothermal method has been applied for the preparation of the compound. This method is very simple, cost effective and energy efficient. It is very popular method for the formation of crystal compounds. Single crystal is crystallized at high temperature under high pressure. In the present study, a new molybdenum based Anderson type polyoxometalate compound synthesized by hydrothermal method has been reported. Further the compound has been characterized by analyzing the data obtained from different chemical and modern instrumental techniques.

Material and Methods

Analytical grades of copper chloride, nickel chloride and sodium molybdate were used for preparation of the compound. Solutions of these reagents were prepared in distilled water in a 250 ml beaker over a magnetic stirrer in a controlled temperature. The pH measurement was carried out by EI digital pH meter.

Solutions were prepared fresh and used for the experiment. The solutions were prepared by dissolving stoichiometrically required amount of the reagents in distilled water. The elemental analysis of copper (Cu), nickel (Ni), molybdenum (Mo) and sodium (Na) present in the synthesized compound was carried out by using inductively coupled plasma optical emission spectroscopy (ICP-OES) from CSIR-NML, Jamshedpur followed by FTIR spectra recorded by Perkin Elmer spectrophotometer in the region 4000-400 cm^{-1} from IISC, Bangalore.

The morphology and percentage of the elements were analyzed by SEM with EDS model ULTRA 55 from IISC, Bangalore. The thermal stability of the heteropoly compound was carried out by using thermal gravimetric analyzer and differential scanning calorimeter model TGA-SDTA 851e and DSC 823e from IISC, Bangalore. The average molecular weight of the synthesized compound was determined cryoscopically by using Beckmann's thermometer.

Synthesis: The mixture of 15ml copper chloride solution prepared by dissolving 1gm (5.86mmol) of the solute, 15 ml of nickel chloride solution prepared by dissolving 1.394gm (5.09mmol) of the solute and 10 ml glacial acetic acid was added drop-wise to 40 ml of sodium molybdate solution prepared by dissolving 7.09 gm (29.29mmol) with continuous stirring till constant pH. After addition of 40 ml of the mixed solution to sodium molybdate solution, the pH of the final mixture became 4.0. The mixture was refluxed for 5 hrs after putting a buffer tablet into it. It was filtered and the filtrate was left for crystallization at 5°C. Blue shiny crystals were separated out which were washed with n-hexane and preserved for analysis.

Results and Discussion

Physico-chemical method has been applied for the preparation of the metal oxide complex. The mixture of the reagents was refluxed under a pH 4.0. The compound was synthesized by taking stoichiometric ratio of the reagents on the basis of probable Anderson formula $[\text{XM}_6\text{O}_{24}]^{-n}$.

Role of pH in the synthesis of compound: The pH of the reactant solution plays a key role in the assembly process which occurs during the synthesis of polyoxometalate complexes. It has been observed from the exhaustive literature survey that the perfect POMs are formed in acidic medium at a constant pH and is always less than 7. The mixture of acidified copper chloride and nickel chloride solution was added drop-wise to sodium molybdate solution to get final acidic solution. When a graph was plotted between the volumes of heteroatom solution added and the pH of the resulting solution, initially gradual fall in the pH was observed, but after some addition, the pH became constant. This constant pH of the graph indicated the formation of some polymeric species.

ICP: The percentage of the elements in the as synthesized compound observed from ICP-OES model (thermo scientific iCAP 7600 ICP-OES Duo semi- demountable EMT torch) are tabulated below:

Table 1
Percentage (%) of elements from ICP-OES

S.N.	Elements	Percentage(%)
1.	Copper(Cu)	3.61
2.	Nickel (Ni)	3.43
3.	Molybdenum (Mo)	28.21
4.	Sodium (Na)	19.72

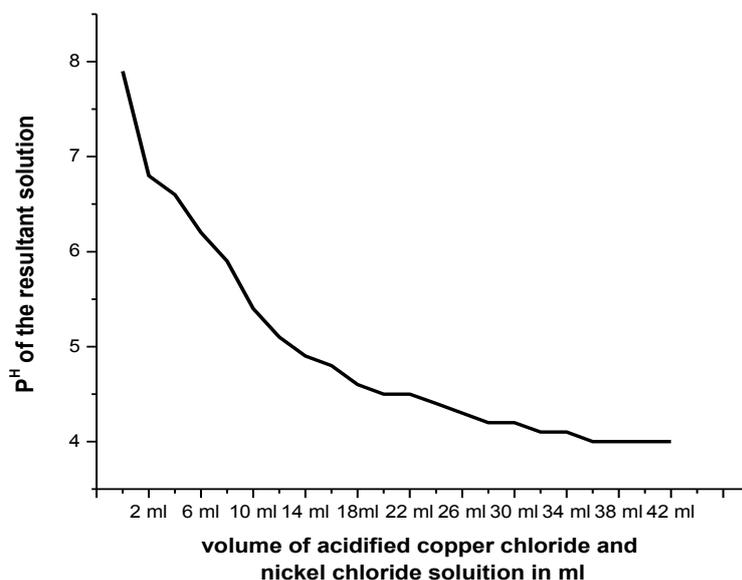


Figure 1: Variation of pH with addition of heteroatom to the addenda atom solution.

FTIR: The bands in the region $769\text{--}1145\text{ cm}^{-1}$ are due to Mo-O bonds. The sharp peaks at 1145 cm^{-1} and 1086 cm^{-1} are attributed to the Mo-O stretching vibrations; moving towards the lower frequency the sharp absorption peaks at 864 cm^{-1} and 834 cm^{-1} correspond to the doubly bridged (Mo-O-Mo) bond which results from corner shared oxygen found more commonly in two MoO_6 octahedra. The bands at 574 cm^{-1} and 460 cm^{-1} are assigned to Ni-O bonding vibrations but the band at 601 cm^{-1} is associated with Ni-O-H stretching vibration.

The presence of band at 506 cm^{-1} 658 cm^{-1} correspond to the bending vibrations of Cu-O bond and the appearance of a sharp peak at 1638 indicates the stretching vibration of Cu-

O bond. The bands at 3515 cm^{-1} and 3463 cm^{-1} belong to asymmetric and symmetric stretching vibrations of O-H bond of adsorbed water respectively. Also, the presence of a sharp peak at 1592 cm^{-1} is due to the bending vibration of O-H bond.

SEM: The SEM micrograph show almost uniform particle sizes with few large aggregate particles. The large particles are possibly due to the polyoxometalates present in the salt of metal oxide mainly responsible for Anderson structure. The image also depicts the microporous nature of the compound. EDS spectrum reveals the presence of the corresponding elements in the as synthesized compound.

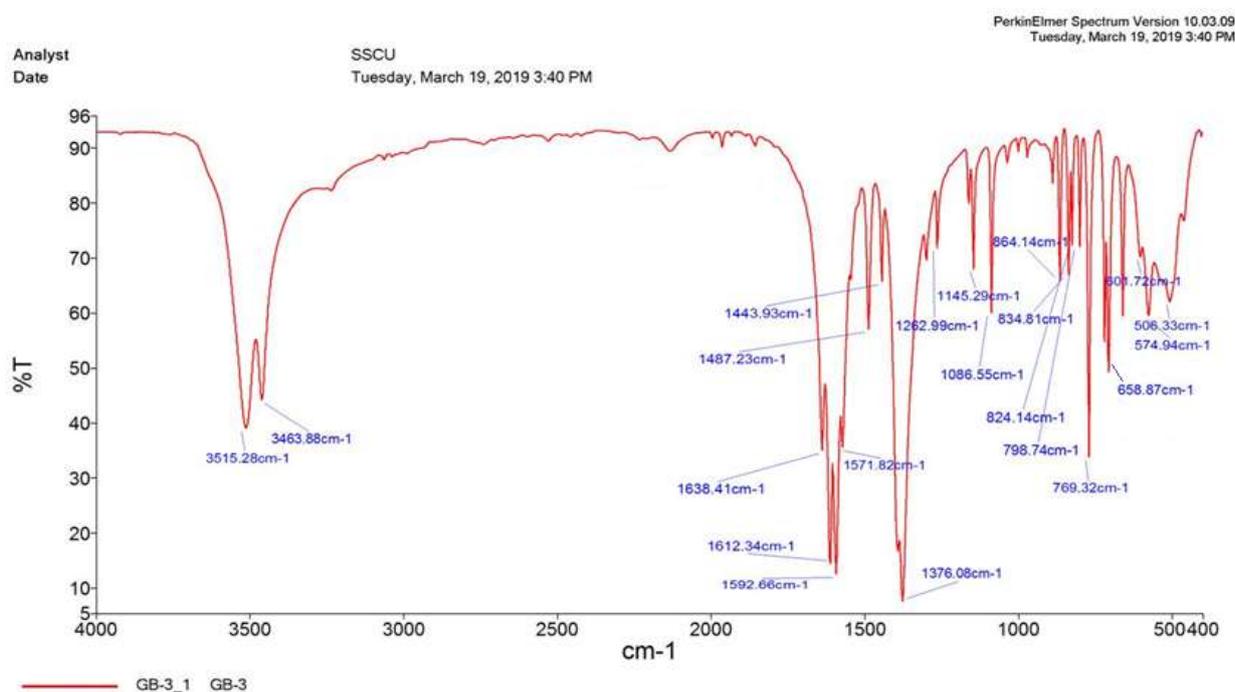


Figure 2: FTIR spectra

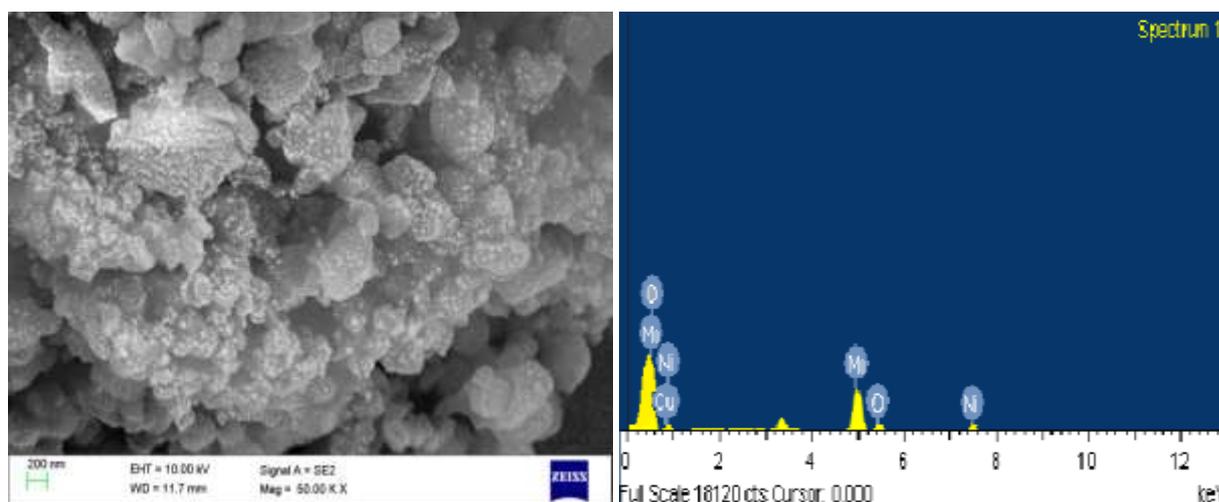


Figure 3: SEM image with EDS

TG-DTA: Figure 4 shows TG/SDTA result of the molybdenum based heteropoly compound. The TG curve shows two stages of mass loss (i) 130 - 160 °C, (ii) 160-260 °C. The corresponding weight losses in these two stages are 6.6% and 15.4%. The weight loss in the first stage may be due to dehydration of lattice water and the second stage is release of the co-ordinated water molecules present in the compound. The numbers of water molecules lost in the two stages are 6 and 14 respectively. After 260 °C, the compound converts into its oxide form and around 400 °C, it completely degrades.

Molecular weight determination: The apparent molecular weight of as synthesized compound has been determined by

using cryoscopic method. The average molecular weight has been calculated by putting depression in freezing point (ΔT) obtained by graphical method by using Beckmann's thermometer in the formula:¹⁹

$$M = \frac{1000kf X}{W \cdot \Delta T}$$

where M= Molecular weight of the solute, X= Weight of solute in gm 0.4gm, W= Weight of solvent in gm 22 gm and ΔT =Depression in freezing point 0.02 (obtained from graph). The average molecular weight of the synthesized compound observed cryoscopically (M_{observed}) is 1603.23 (Cal 1665.01).

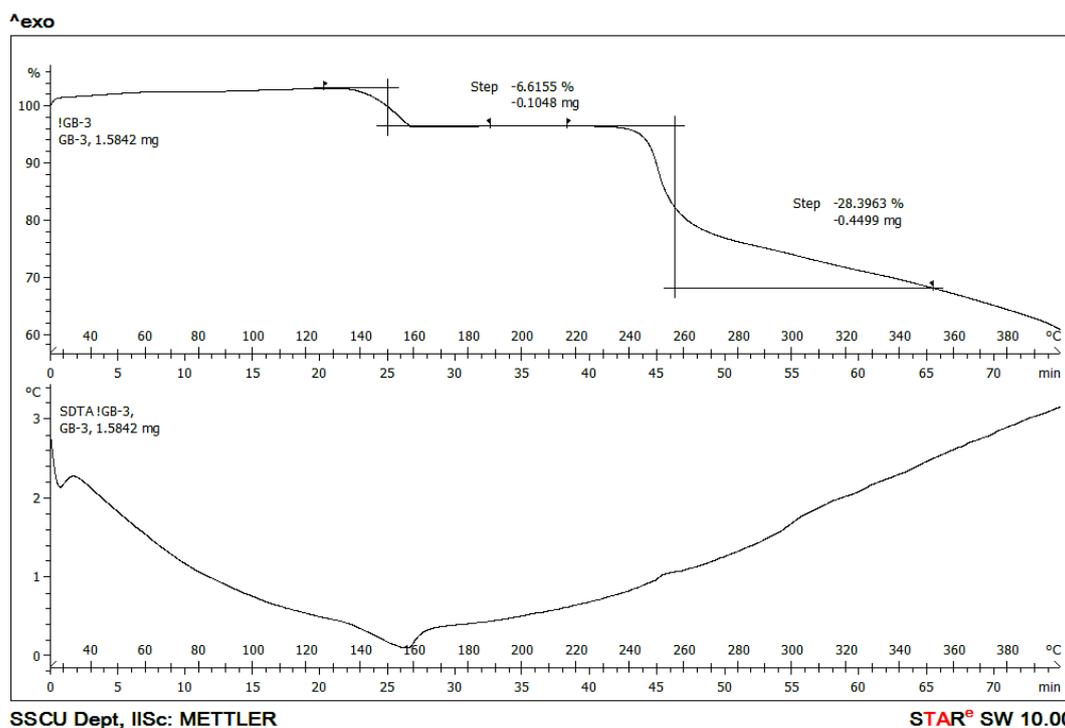


Figure 4: TGA/SDTA graph

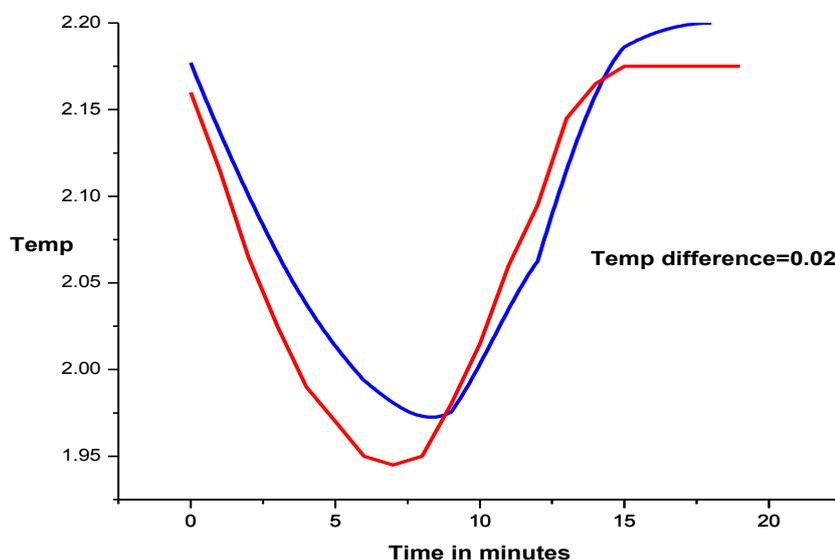


Figure 5: Difference in the temperatures of solute (blue) and solvent (red)

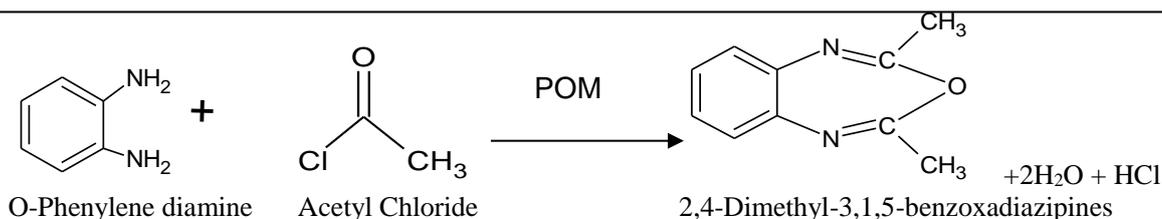
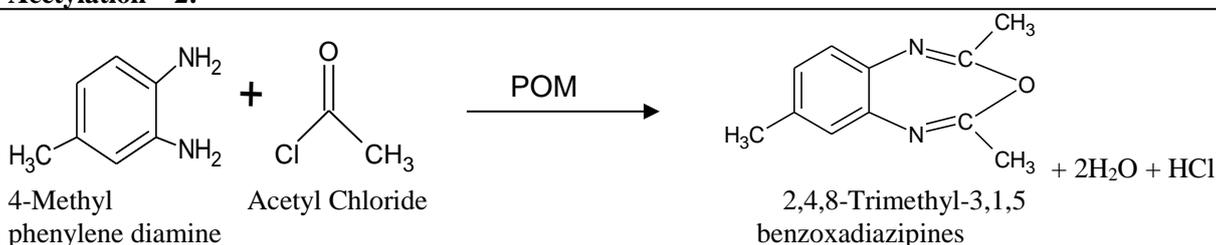
Acetylation – 1:**Acetylation – 2:**

Table 2
Application of Na₁₄[CuNiMo₅O₂₄] 20H₂O as Catalyst in Acetylation reaction

S.N.	Reactions	Type of catalysts	Time(h)	Product Yield%
1.	Acetylation (1) Acetylation of O-Phenylene diamine	Anderson	3	67
2.	Acetylation (2) Acetylation of 4-Methyl Phenylene diamine	Anderson	3	71

Application: The application of Anderson type heteropoly compounds as catalytic materials is growing continuously in the catalytic field. The wide range of properties of Anderson type compounds make them multipurpose catalysts. Substitution of harmful liquid acids by the solid reusable polyoxometalates as catalysts in organic synthesis is the most promising application of Anderson type POMs. In the present piece of work, we studied the application of as synthesized sodium salts Anderson type anion Na₁₄[CuNiMo₅O₂₄] 20H₂O in the acetylation of O-PDA and 4-methylphenylenediamine.

Conclusion

Sodium salt of mixed heteropoly molybdate has been synthesized successfully by an established procedure. The as synthesized complex Na₁₄[Cu(II)Ni(II)Mo₅(VI)O₂₄] 20H₂O has typical Anderson type structure corroborated from elemental and thermal analysis. The elemental analysis (ICP-OES) reveals 1:1:5 atomic ratio of Cu:Ni:Mo. EDS spectra also confirm the presence and percentage of the corresponding elements in the synthesized compound. IR spectra show different M-O and M-O-M linkages of Cu-O, Ni-O and Mo-O bonds.

The apparent molecular weight observed from cryoscopy method is in good agreement with the calculated molecular weight of the compound. The present work confirms that the hydrothermal process is a simple, powerful and low cost technique for the synthesis of new structural eco friendly

polyoxometalate complexes. The synthesized compound gives good yield % of the product. It can be utilized as efficient and eco-friendly heterogeneous catalyst for different organic and inorganic transformations and also can be applied in different fields of science.

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