

Mono Manganese (IV) Substituted Anderson Type POMs: Synthesis, Characterization And Their Catalytic Behavior

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ABSTRACT

Two novel Anderson type POMs, $K_2[Mn(OH)_6Mo_6O_{18}].4H_2O$ (1) and $K_2[Cu(MnO_4)Mo_6O_{18}]$ (2) have been prepared in hydrothermal condition and characterized by Energy Dispersive X-Ray Analysis (EDX), Infra-red(IR) spectroscopy and thermo gravimetric analysis (TGA). Molecular weight of both the compounds was determined by cryoscopy method and it is observed that the experimental value of molecular masses of these compounds is quite lower than their respective theoretical molar mass. This shows their dissociative nature ($i>1$). Both the compounds (1 and 2) have been used as low cost, user friendly green catalysts for the acetylation of benzene-1,2-diamine and its derivative using acetyl chloride as acetylating agent.

Keywords: Anderson, polyoxometalates, hydrothermal, green catalyst.

INTRODUCTION

POMs constitute an exceptionally fascinating class of inorganic compounds having oxygen rich surface. They are oligomeric coordination clusters of some transition metal oxides with metal ion configuration d^0 or d^1 . They are represented as $[X_aM_bO_x]^{n-}$ where M is called addenda atom (most probably Mo, W, Ta, Nb or/and V), X is heteroatom and O represents oxide ligands. POMs have a history of more than two hundred years however; an accelerated rate of research and discoveries has been observed in past few years only, due to the development of various cutting edge multifarious characterization techniques.

POMs have a great ability to incorporate with both organic and inorganic ligands which provides them a versatile topology and diversity in properties. Hence, they have been showing their presence in various fields

[1-5] such as medicines, biology, catalysis, material science, magnetism etc.

On the basis of the atomicity of heteroatom POMs are divided into two main groups isopolyoxometalates (where $b = 0$) and heteropolyoxometalates (where $a \geq b > 1$). Remolding of POM cluster with respect to size, shape, composition and properties is possible by changing reaction conditions such as conc. of heteroatom, pH, temp. etc. This gives rise to ten basic structural archetypes [6] of POMs namely Keggin, Dawson, Waugh, Anderson, Silverton, Lindqvist, Weakley, Standberg, Finke and Preyssler structure. However, further modification in these parent structures is possible by incorporation of transition metal or inner transition metal in corresponding lacunary (defective) structure. Depending on the nature of incorporated atom, POMs may further be subdivided into two categories- transition metal substituted polyoxometalates (TMSPs) and lanthanide substituted polyoxometalates (LSPs). Stability of these clusters depends on ionic interaction, M-O d_{π} - π bonding, H-bonding and Vander Waal forces etc.

2. EXPERIMENTAL

Both the compounds (1 and 2) were synthesized by hydrothermal method which is highly convenient and economic. All chemicals were collected from commercial sources and used without further purification.

2.1 SYNTHESIS OF $K_2[Mn(OH)_6Mo_6O_{18}].4H_2O$ (1)

Compound 1 was synthesized by dissolving 0.01mol of ammonium molybdate in 120 ml distilled water followed by addition of 1.94 mmol of potassium

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aluminum sulphate. 20 ml of saturated solution of potassium permanganate was prepared and added to the previous solution with constant stirring. The mixture was boiled for 10 minutes and left at room temperature for 3 days. Shining orange crystals thus obtained were collected, washed and preserved for analysis.

2.2 SYNTHESIS OF $K_2[Cu(MnO_4)Mo_6O_{18}]$ (2)

An aqueous solution of ammonium molybdate was prepared by adding 0.01mol of ammonium molybdate in 100 ml of hot distilled water. 4 mmol of hydrated copper sulphate was added to it with constant stirring. A saturated solution of potassium permanganate was prepared by dissolving excess of potassium permanganate in 10 ml of distilled water. Both the solutions were mixed together and pH was maintained to 1.8 by drop wise addition of 10% (v/v) sulphuric acid solution. Finally, the mixture was boiled for 3 minutes and left in dark at room temperature. Big orange crystals were obtained after ten days. Washed with distilled water and preserved for analysis.

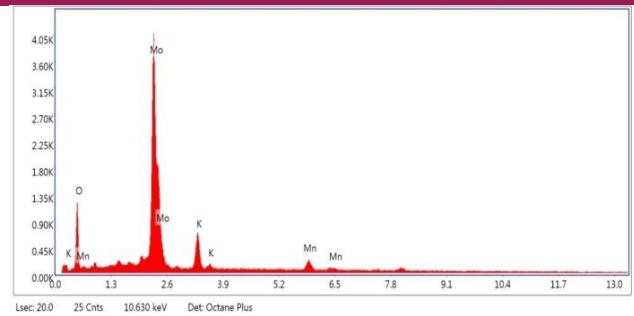
3. RESULTS AND DISCUSSION

Two manganese based Anderson type POMs (1 and 2) were prepared by one pot synthesis and characterized by various instrumental techniques such as EDX, FTIR, TGA and SEM.

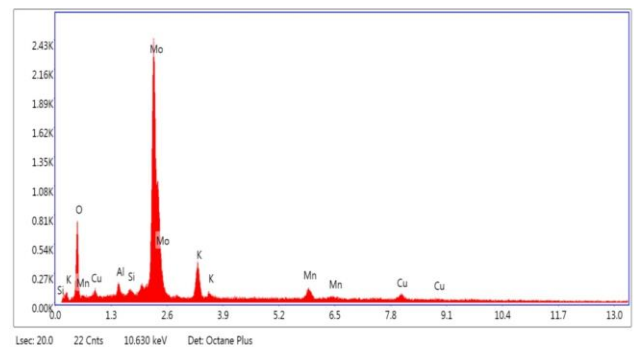
3.1 ELEMENTAL ANALYSIS

Elemental composition of compound **1** as estimated gravimetrically is K, 7.5%; Mn, 4.7%; Mo, 49.92% ; and O, 37.88%. This composition was further confirmed by EDAX {Fig -1(a)} which shows K, 7.53%; Mn, 4.39%; Mo, 52.26% ; and O, 35.82%.

Percentage composition of compound **2** as estimated gravimetrically is K, 5.84%; Mn, 5.0%; Mo, 48.83%; Cu, 6.2%; and O, 33.13%. This composition was further confirmed by EDX {Fig-1(b)} which showed K, 5.75%; Mn, 4.96%; Mo, 48.62%; Cu, 7.4% and O, 32.14%. The result shows that the elemental percentage is in good agreement.



(a)



(b)

Fig.-1 EDX of (a) $K_2[Mn(OH)_6Mo_6O_{18}].4H_2O$ and (b) $K_2[Cu(MnO_4)Mo_6O_{18}]$

3.2 THERMO GRAVIMETRIC ANALYSIS (TGA)

Thermo gravimetric analysis of compound **1** showed an overall weight loss of nearly 5.8 % around 120°C which corresponds to four water molecules in the compound.

TGA thermograph of compound **2** showed weight loss around 110°C which is negligible. This weight loss may be due to moisture content in the POM cluster.

3.3 IR SPECTROSCOPY

IR spectra of compounds **1** and **2** were recorded on Shimadzu Corpn, Japan; IR-Prestige 21 in the region 7500-350 cm^{-1} . Values in the spectra correspond to those found in the literature [7].

IR spectrum of compound **1** {Fig-2(a)} shows characteristic absorption peaks near 3433 – 3213 cm^{-1} and 1643 cm^{-1} due to O-H stretching and bending frequency of H₂O molecules respectively. Absorption at 764, 617, 559 and 945 cm^{-1} are due to Mo-O_b-Mo, Mo-O_c-Mo, Mn-O vibration and Mo=O_d stretching respectively.

IR spectrum of compound **2** {Fig-2(b)} exhibited a broad peak near 3541-3124 cm^{-1} due to stretching of free O-H while absorption at 1608 cm^{-1} is assigned to O-H bending vibration of water molecules respectively. Shifting in absorption frequency is observed due to extensive H-bonding. Peaks at 540 cm^{-1} and 497 cm^{-1} are assigned to Mn-O and Cu-O stretching respectively. The bands at 694 cm^{-1} and 594 cm^{-1} are assigned to vibration of Mo-O_b-Mo and Mo-O_c-Mo respectively. A peak at 934 cm^{-1} is due to Mo=O_d stretching frequency. This confirms the presence of corner sharing bridging O-atom (O_c), edge sharing bridging O-atom (O_e) and terminal O-atom (O_d) in the cluster.

Similar nature of spectra of both the reported compounds indicates the presence of similar type of Anderson unit and similar type of bonds in both the clusters. However, difference in intensity of peaks is due to the presence of Cu in compound **2**.

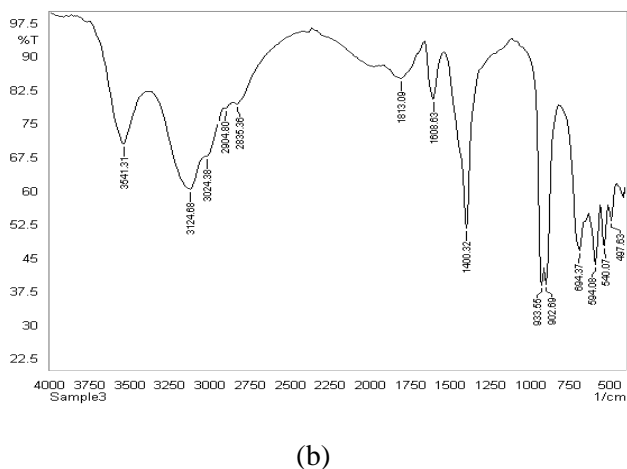
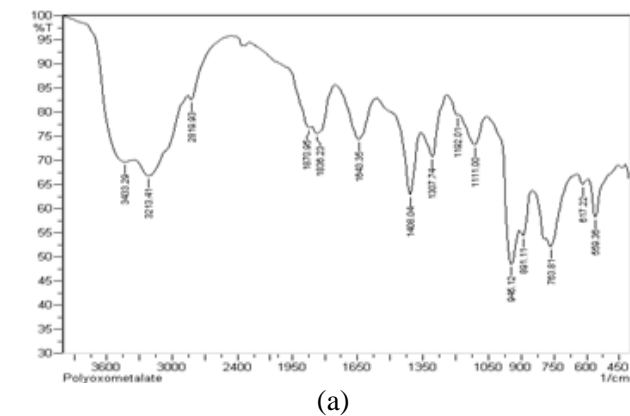


Fig – 2 FTIR spectra of
 (a) $\text{K}_2[\text{Cu}(\text{MnO})_4\text{Mo}_6\text{O}_{18}].4\text{H}_2\text{O}$ and
 (b) $\text{K}_2[\text{Cu}(\text{MnO})_4\text{Mo}_6\text{O}_{18}]$

3.4 MOLECULAR WEIGHT DETERMINATION

Cryoscopy [8] method was applied to determine the molecular weight of the compounds. It is observed that the experimental value of molecular mass of compound **1** (620) and compound **2** (744) is quite lower than their theoretical molar mass (1170 and 1124 respectively). This confirms their dissociative nature ($i > 1$).

3.5 SURFACE ANALYSIS

Surface nature and texture of POM clusters are studied from SEM micrographs {Fig 3(a) and (b)}; recorded on a JEOL/EO, JSM-6390 LV Mag. 2500-5000. General view of the surfaces show that these compounds are formed by chemical reactions. SEM micrograph of compound **1** shows some 1D crystal like whiskers {Fig 3(a)}. Some terraces are observed on the surface and from the corner. It is clear that these terraces are formed by a stack of crystals.

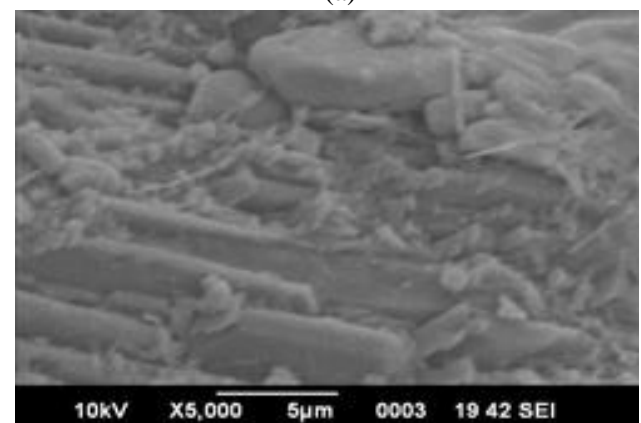
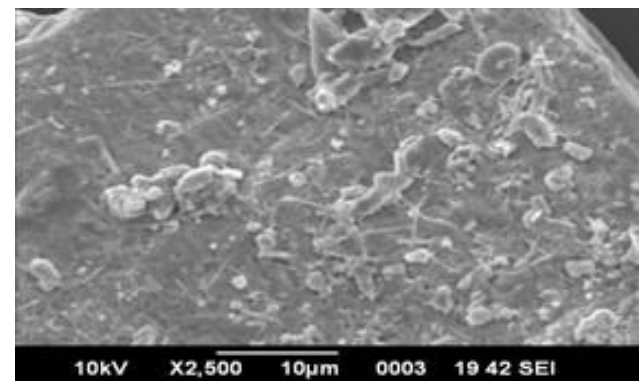


Fig-3 SEM micrographs of
 (a) $\text{K}_2[\text{Mn}(\text{OH})_6\text{Mo}_6\text{O}_{18}].4\text{H}_2\text{O}$
 (b) $\text{K}_2[\text{CuMn}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$

4. APPLICATION

Among various applications of POMs; catalysis [9-10] is so far the most important and most applied field of POMs and POM based materials. Their catalytic behavior is a direct consequence of acidic property and reversible redox behavior. POMs offer a strong candidature as acid catalysts for acetylation of benzene-1,2-diamines. The advantage of using POMs over other catalysts is due to reaction simplicity, low cost and their eco -friendly nature. We have tried to convert benzene-1,2-diamine [11] into substituted benzimidazole by using POM **1** and **2** as acid catalyst (scheme 1).

Scheme-1



Benzene-1,2-diamine Acetyl chloride

2-Methyl benzimidazole

Table 1
**Catalytic activity of synthesized POMs in
acetylation of benzene-1,2-diamine**

Sl. No.	Catalyst used	Time (Hrs)	Yield (%)
1	$K_2[Mn(OH)_6Mo_6O_{18}] \cdot 4H_2O$	4	68
2	$K_2[Cu(MnO_4)Mo_6O_{18}]$	4	67

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