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# Synthesis and Characterization of Transition Metals Derivatives of the Keggin Type Anion $[X^{n+}W_{12}O_{40}]^{-(8-n)}$

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The heteropoly compound with molecular formula $Na_9[Cu(II)Fe(III)W(VI)_{11}O_{40}]\cdot 21H_2O$ (**1**) and $Na_6[Cu(II)Mo(VI)W(VI)_{11}O_{40}]\cdot 11H_2O$ (**2**) have been synthesized from an aqueous acetate buffer solution (pH = 4) containing sodium tungstate, copper chloride, ferric chloride and (pH = 3.8) containing sodium molybdate, sodium tungstate, copper chloride, respectively by replacing $XO_4$ tetrahedron and $MO_6$ octahedron from Keggin anion $[XM_{12}O_{40}]^{-n}$. The compounds are separated as light blue crystals. Both the compounds **1** and **2** have two heteroatoms, one is central and other is peripheral, thus mixed heteropoly compounds. The substituted diheteropoly compounds are characterized by elemental analyses, IR studies, thermal analyses and molecular weight determination.

**Key Words: Synthesis, Heteropoly compounds, Transition metals, Keggin type anion.**

## INTRODUCTION

Polyoxometalates (POMs) are mostly polynuclear compounds of transitional elements containing other elements of periodic table [except, at present, the rare gases] in traces[1-3]. They are highly symmetric and water soluble compounds[4]. The chemistry of the transition elements, particularly vanadium, molybdenum and tungsten, in aqueous solution is dominated by the formation of polyoxoanion which constitute a class of metal-oxygen cluster containing compounds called heteropoly metal oxide complexes or polyoxometalates. The existence of polyoxometalates has been known for almost 200 years but the first structural details are only revealed in the last century. Metal oxide complexes with general formula $[XM_{12}O_{40}]^{n-}$, where X acts as central tetrahedral coordinated atom and M = Mo(VI), W(VI), V(V), Nb(V) or Ta(V), known as Keggin anions, constitute a unique class of polyoxometalates[5,6]. The Keggin type heteropoly anions are important materials that promises a broad range of potential applications such as catalysis, magnetism and medicine, have been quite attractive[7,8]. Transition metal substituted polyoxotungstates are interesting for their magnetic properties[9,10]. Baker[11] first reported the characterization of substituted

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heteropoly Keggin anions, $[XZ_yM_{12-y}O_{40}]^{-n}$ where X is the centrally tetrahedral coordinated atom, M is molybdenum or tungsten and Z is the second heteroatom. In recent decades, heteropoly oxometalates have found more attention because they are low in toxicity, highly stable towards humidity, recyclable and are air stable. Thus the use of heteropoly acids (HPSs) and their salts (POMs) as industrial catalysts is ecofriendly and green which reduces or eliminates the use or generation of hazardous substance throughout the entire life of chemical materials[12]. In the later part of the 20th century and beginning of 21st century, hundreds of isopoly and heteropoly acids and their salts have been reported in chemical literature[13,14]. The mechanism of formation of heteropoly metal oxide is difficult to understand because even very large structure of polyoxoanion[15] $[As_{12}Ce_{16}H_2O_{36}\ W_{148}O_{524}]^{-76}$ can be synthesized. Most of the studies so far reported has focused on the Keggin heteropolyanions with main group (X = P, As, Si, Ge, B, Al, *etc.*) as heteroatoms whereas the analogue chemistry of transition metals is not so developed[16,17], especially the reports with regard to Keggin-type polyoxoanion with the transition metals Cu(II) ion as the central atom are rather scarce[18,19]. The first copper substituted derivative of tungstoarsenate was characterized by Robert[20]. Roy and coworkers have reported a number of heteropoly oxometalates of iron(II), cobalt(II), nickel(II)[21,22]. In the present communication, we report the synthesis and characterization of copper(II) substituted tungstoferrate(III) and tungstomolybdate(VI) heteropoly salts by elemental analyses, IR studies, thermal analyses and molecular weight determination.

## EXPERIMENTAL

Following reagents were taken for the synthesis of heteropoly oxometalates: copper chloride dihydrates, sodium tungstate, sodium molybdate (all BDH), ferric chloride (E. Merck) 99.5 % purity, glacial acetic acid (AR Grade), acidic buffer tablet of pH = 4 (Qualigens).

All the above reagents were of analytical grade and used as received. The solutions were prepared freshly by dissolving the requisite amount of reagents in distilled water. The pH measurement was carried out by the EI digital pH meter model 111E. The copper, iron, tungsten,molybdenum and sodium metal present in the compound were estimated by using inductively coupled plasma atomic emission spectroscopy, (make Jobin Yvon France of model JY Ultima-2) at IIT Powai, Mumbai. The IR spectra were recorded by Perkin Elmer 577 spectrophotometer in the region 4400-450 $cm^{-1}$. The thermal studies of heteropoly compounds were carried out by thermogravimetric analysis and by heating between 42-650 ºC at 10 ºC/min using Perker-Elmer USA of model Diamond TG-DTA followed by solubility determination. The apparent molecular weight of the sodium salts were determined cryoscopically using Beckmann's thermometer.

**Synthesis of sodium-11-tungsto-1-cuproferrate(III), $Na_9[Cu(II)Fe(III)W(VI)_{11}O_{40}]\cdot 21H_2O$ (1):** The mixture of 30 mL copper chloride solution, prepared by dissloving 1.05 g (6 mmol) of the solute and 30 mL ferric chloride solution, prepared by dissolving 1 g (6 mmol) of the solute, was added drop wise to 75 mL of sodium metatungstate solution, prepared by dissolving 22.38 g (67 mmol) with continuous stirring till constant pH. 10 mL glacial acid was added to maintain the acidic conditions. After the addition of 56 mL of the above mixed solution to sodium tungstate solution, the pH of the final mixture became constant at 3.9. The mixture was refluxed for 3 h after putting buffer tablet of pH = 4. It was filtered and the filterate was left for crystallization at 5 ºC. 3.54 g of light blue small crystals were separated out which were washed with *n*-hexane and preserved for analysis.

**Synthesis of sodium-11-tungsto-1-molybdocuprate(II), $Na_6[Cu(II)Mo(VI)W(VI)_{11}O_{40}]\cdot 11H_2O$ (2):** The compound was prepared by the hydrothermal method as described for compound (**1**) by mixing aqueous solutions of copper chloride, sodium tungstate and sodium molybdate containing a molar ratio of 1:1:11. 10 mL of glacial acetic acid was added to maintain the acidic environment. The pH of the final mixture became constant at 3.5. The mixture was refluxed for 4 h and the filtrate was left overnight for crystallization. 3.2 g bluish crystals were separated out which were preserved for analysis.

## RESULTS AND DISCUSSION

Physico-chemical methods have been adopted for the preparation of metal oxide complex of tungsten on the basis of the Keggin anion $[XM_{12}O_{40}]^{-n}$ after mixing the theoretical quantities of reagents. The complex salt (**1**) is formed after refluxing the reaction mixture at a pH of 3.9. Light blue crystals are separated out whose molecular formula is established as $Na_9[Cu(II)Fe(III)W(VI)_{11}O_{40}]\cdot 21H_2O$ (**1**). Analysis [Na, 6.2; Cu, 1.9; Fe, 1.8; W, 60.29, O, 18.75 % (by diff)]. Calcd. [Na, 6.13; Cu, 1.84; Fe, 1.62; W, 60.29; O, 18.56 % (by diff)]. $Na_6[Cu(II)Mo(VI)W(VI)_{11}O_{40}]\cdot 11H_2O$ (**2**) Analysis [Na, 4.4; Cu, 2.0; Mo, 3.0; W, 64.5; O, 6.2 % (by diff)]. Calcd. [Na, 4.3; Cu, 1.96; Mo, 2.98; W, 64.4; O, 6.1 % (by diff)].

On the basis of the percentage composition of the different elements present in the compounds and the number of water molecules as calculated from the TGA data, the compounds are formulated as given above.

TABLE-1
INFRARED SPECTRA ($cm^{-1}$) OF THE REPORTED HETEROPOLY COMPOUNDS IR ASSIGNMENT

| Compounds | $\nu(H_2O)$ | $\nu$(Cu-O) | $\nu$(Fe-O) | $\nu$(Mo-O) | $\nu$(W-O) | $\nu$(W-O-W) |
|---|---|---|---|---|---|---|
| $Na_9[Cu(II)Fe(III)W(VI)_{11}O_{40}]\cdot 21H_2O$ (**1**) | 3726b | 501m<br>560m | 834s<br>932s | –<br>– | 1125s<br>1210s<br>1350m,b | 780b<br>810b |
| $Na_6[Cu(II)Mo(VI)W(VI)_{11}O_{40}]\cdot 11H_2O$ (**2**) | 3606b | 540s<br>573m | –<br>– | 950s,b<br>1000s | 1140s<br>1290m<br>1330m,b | 790b<br>820b |

The IR spectra of many heteropoly oxometalates have also been examined to ascertain M-O and M-O-M bonding and the presence of different mode of water molecules[23,24]. The compounds show sharp peaks at 1350-1125 $cm^{-1}$ which may be assigned to independent W-O stretching vibration and the broad bands at 820-780 $cm^{-1}$ reveal W-O-W[25] bridge vibration. The sharp band at 932-834 $cm^{-1}$ observed in compound (**1**) may be attributed to Fe-O and at 1000-950 $cm^{-1}$ for Mo-O linkages in the compound (**2**). The medium bands in the region of 573-501 $cm^{-1}$ show the presence of Cu-O bond in both the compounds. The broad bands at 3726 and 3606 $cm^{-1}$ show characteristic peaks for the stretching of water molecules in (**1**) and (**2**), respectively. Fe and Cu act as heteroatom in compound (**1**), on the other hand Cu and Mo serve as the heteroatom in the compound (**2**). The DTA-TGA analysis of the compound (**1**) and (**2**) shows two step dehydration processes. The first weight loss of 10 % is observed from 96 to 182 ºC and the second weight loss of 27 % is observed from 182 to 310 ºC in compound (**1**) whereas for the compound (**2**) shows the weight loss of 19 % from 90 to 200 ºC and a loss of 14 % from 200-265 ºC. Finally the insoluble oxides are given as last product. The apparent molecular weight of the compound has been found 3325.85 for (**1**) and 3113.5 for (**2**) as determined by cryoscopic method using $Na_2SO_4 \cdot 10H_2O$-water system as solvent[26] against calculated molecular weight of 3427.85 and 3217.5, respectively.

## Conclusion

Sodium salts of heteropoly tungstate have been synthesized by established procedure under reference. The anion $[Cu(II)Fe(III)W(VI)_{11}O_{40}]^{-9}$ and $[Cu(II)Mo(VI)W(VI)_{11}O_{40}]^{-6}$ have typical Keggin type structures which are corroborated from elemental and thermal analyses. Their IR spectra confirm different M-O and M-O-M linkages in the compounds. Cu(II) or Fe(III) and Cu(II) or Mo(VI) may occupy the central tetrahedral void in compound (**1**) and (**2**), respectively. The apparent molecular weights determined cryoscopically are also in good agreement with the calculated molecular weight of the compounds. This work proves that the hydrothermal technique is a powerful method for the synthesis of new structural polyoxometallic compounds.

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