



## Preparation and Characterization of Series of Triheteropolymolybdate Complexes

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Three new polymolybdate heteropoly complexes were synthesized in the laboratory having  $\text{Al}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  hetero cations. The synthesis of the three polymolybdate heteropoly complexes were prepared in acid medium at reflux temperature. The products were isolated separately, washed in ethanol and dried. The dried residues obtained possess light and dark brown colour. All the three residues of polymolybdate are paramagnetic at room temperature having magnetic moment varying from 3.02 to 3.78 BM. The magnetic moment values of triheteropoly molybdate complexes suggest the six co-ordinated octahedral around  $\text{Co(II)}$  and  $\text{Ni(II)}$  environment in the weak field. The IR spectra of all the three residues exhibit strong absorption band of hydrogen bonded  $\text{H}_2\text{O}$  group in the complexes along with metal-oxygen-metal and metal-oxygen, where metal may be Mo, Ni, Co or Al. The DTA and TGA curves of polymolybdate residues show decomposition of product in general two steps. The first step of residue involves mass loss in weight due to loss of water molecules and sodium oxide molecules, while the second step loss of weight due to loss of water of constitution. The analysis of all the product based on IR spectrum thermogravimetric studies, elemental estimation and molecular weight determination by cryoscopy method the molecular formula may be suggested as:  $\text{Na}_4[\text{NiAl}_2\text{Mo}_{12}\text{O}_{42}]\cdot 28\text{H}_2\text{O}$ ,  $\text{Na}_4[\text{CuCoMo}_{12}\text{O}_{40}]\cdot 60\text{H}_2\text{O}$  and  $\text{Na}_8[\text{CoAl}_2\text{Mo}_{12}\text{O}_{44}]\cdot 94\text{H}_2\text{O}$ .

**Keywords:** Triheteropolymolybdate, IR studies, Thermal studies.

### INTRODUCTION

This work mainly focused on the stability of isolated complexes, which is evident from the thermal analysis and evaluating TGA studies. The polyoxometalate complexes of transition metals like vanadium, niobium, tantalum, molybdenum and tungsten had been important catalyst for many organic as well as inorganic compounds synthesis and diversity of the heteropoly complexes are also suggested as oxometalates by Michael T. Pope [1,2] and Barnett Krabs [3]. The synthesis of isopoly complex is mainly performed by the condensation process [4-6] in which the oxobridges are formed from the molecules of weak acetic acid by elimination of water molecules. This type of condensation reaction takes place freely and reversibly in acidic medium, which may be compared with the condensation of chromate ion to form its corresponding isopoly di chromate ion. This condensation of chromate ion is pH dependent involving the association in acidic medium and dissociation in basic medium. The condensation behaviour of molybdate anion is similar to above condensation. One oxometalate complex with heteropoly anion is named as per IUPAC system [7]. Generally, heteropoly complexes are prepared [8-10] by mixing stoichiometric quantities of the

required reactant in proper acidic medium and then heating strongly up to 3 h. The acidic medium must be maintained up to the recovery of the solid residue. The stability of the solid residue obtained is studied on the basis of thermal process with reference to DTA and TGA analysis [9,11,12]. The cryoscopy of individual product is also performed to obtain their molecular masses which are useful for the elemental estimation of the solid heteropoly complex.

### EXPERIMENTAL

Synthesis of sodium-12-molybdo-1-aluminate nickelato hydrate  $[\text{Na}_4(\text{NiAl}_2\text{Mo}_{12}\text{O}_{42})\cdot 2\text{H}_2\text{O}]$  was performed by mixing of 50 mL of 0.95 M aqueous solution of  $\text{Na}_2\text{MoO}_4$ , 70 mL of 0.1 M  $\text{Al}_2(\text{CO}_3)_3$  and 40 mL of 0.1 M  $\text{NiCO}_3$ . The homogeneous solution was refluxed for 3 h continuously. The pH 4.6 was maintained by adding required quantity of glacial acetic acid till the solid residue was recovered. The dark brown solid crystalline residue was obtained after 2 days. The solid product was filtered off and washed. Similarly, the other two triheteropoly complexes *i.e.*,  $\text{Na}_4[\text{CuCoMo}_{12}\text{O}_{40}]\cdot 60\text{H}_2\text{O}$  and  $\text{Na}_8[\text{CoAl}_2\text{Mo}_{12}\text{O}_{44}]\cdot 94\text{H}_2\text{O}$  were prepared by taking proper required mixtures and pH of resultant mixtures.

## RESULTS AND DISCUSSION

The conversion of mono into heteropoly molybdate which is typical characteristic of group six transition metal oxide is widely examined with their structure and catalytic application. It is observed that in presence of hetero cations  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  the isopolymolybdate in acidic medium posses definite composition after the mixture were refluxed at pH 4.5. These heteropoly products are obtained at room temperature after 3 to 4 days. The interaction of sodium molybdate with hetero cation in acidic medium at pH 4.5 having ratio 12:1:1 give light and dark brown products. The same products were obtained in more than two repetition of the processes in same ratio of constituent components. All the heteropoly molybdate products are stable in air and show poor solubility in water in cold condition. However, when the products are separately dissolved in boiling water give light coloured solutions. The aqueous solution of polymolybdate complexes prepared exhibit the presence of sodium cation supporting the partial ionic character of heteropoly complexes.

**$\text{Na}_4[\text{NiAl}_2\text{Mo}_{12}\text{O}_{42}]\cdot 28\text{H}_2\text{O}$ :** The IR spectrum of the product  $\text{Na}_4[\text{NiAl}_2\text{Mo}_{12}\text{O}_{41}]\cdot 28\text{H}_2\text{O}$  show strong IR band between  $1566.20$  to  $3278.99\text{ cm}^{-1}$  due to hydrogen bonded water molecule. The prominent and strong band is also observed at  $1415.75\text{ cm}^{-1}$  which may be attributed to  $\text{Mo}=\text{O}$  stretching band. The sharp band at  $918.12\text{ cm}^{-1}$  may be assigned to  $\text{Al}-\text{O}-\text{Al}$  while the strong rocking band at  $659.66\text{ cm}^{-1}$  may be suggested for  $\text{Ni}-\text{O}$  vibration.

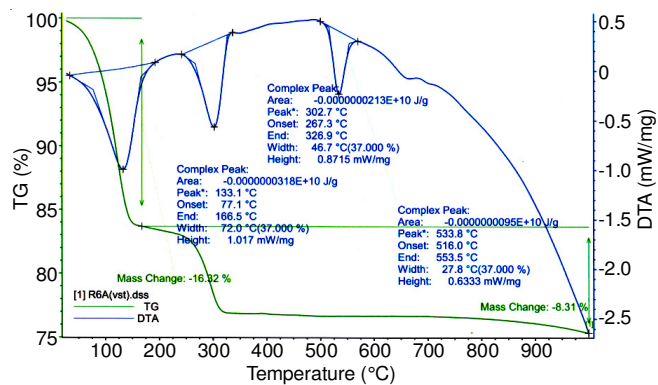
**$\text{Na}_4[\text{CuCoMo}_{12}\text{O}_{40}]\cdot 60\text{H}_2\text{O}$ :** The strong IR band between  $1562.34$  to  $3441.01\text{ cm}^{-1}$  may be assigned to the strong hydrogen bonded  $\text{H}_2\text{O}$ . The IR absorption band at  $1475.75\text{ cm}^{-1}$  is due to the presence of  $\text{Mo}=\text{O}$  stretching band while another weak band present at  $1130.29\text{ cm}^{-1}$  may be assigned to the presence of the  $\text{Mo}=\text{O}=\text{Mo}$  stretching vibration. Another prominent band at  $891.11\text{ cm}^{-1}$  due to stretching vibration of  $\text{Cu}-\text{O}$ .

**$\text{Na}_8[\text{CoAl}_2\text{Mo}_{12}\text{O}_{44}]\cdot 94\text{H}_2\text{O}$ :** Polymolybdate product suggests the strong hydrogen bonded water molecules as per the IR band absorption between  $1415.75$  to  $3340.71\text{ cm}^{-1}$ . The small sharp band at  $1288.45\text{ cm}^{-1}$  may be attributed to  $\text{Mo}=\text{O}$  oxide. The sharp IR absorption band at  $921.77\text{ cm}^{-1}$  may be assigned to  $\text{Al}-\text{O}-\text{Al}$  group. The small but sharp IR absorption stretching vibration at  $798.53\text{ cm}^{-1}$  may be suggested for the  $\text{Mo}-\text{Al}$  group. The last  $663.57\text{ cm}^{-1}$  IR band may be due to the presence of  $\text{Co}-\text{O}$  stretching vibration.

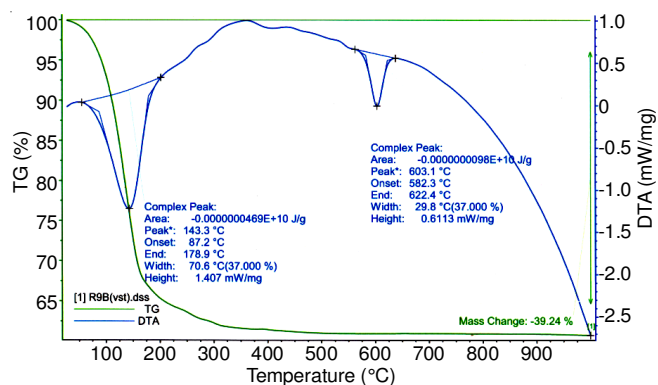
## Thermal studies

The DTA and TGA curves of polymolybdate residues exhibit the elimination as well as decomposition of the product at higher temperature. The TGA was done at heating rate  $10^\circ\text{C}$  per min in static air. The product  $\text{Na}_4(\text{NiAl}_2\text{Mo}_{12}\text{O}_{42})\cdot 28\text{H}_2\text{O}$  exhibits  $16.32\%$  loss in the first step having temperature range between  $20$  to  $170^\circ\text{C}$  (Fig. 1). The loss in mass of the product is supplemented by a DTA peak at  $133.1^\circ\text{C}$  which on set at  $77.1^\circ\text{C}$  and ends at  $166.5^\circ\text{C}$  in this range of temperature the water molecules as well as sodium oxide were lost. The same TGA and DTA curves involve  $8.31\%$  loss by weight, which is due to the loss of remaining water molecules in between the temperature  $170$  to  $310^\circ\text{C}$ . The another DTA peak was also

observed at  $302.7^\circ\text{C}$  which ends at  $326.9^\circ\text{C}$ . Another DTA peak also observed at  $533.8^\circ\text{C}$  which end set at  $553.5^\circ\text{C}$ . The DTA peak may be attributed to the internal physical transformation of the product to obtain its maximum stability as TGA analysis exhibit another loss of mass of product up to  $1000^\circ\text{C}$  temperature.

Fig. 1. TG and DTA graph of  $\text{Na}_4[\text{NiAl}_2\text{Mo}_{12}\text{O}_{42}]\cdot 28\text{H}_2\text{O}$ 

The  $\text{Na}_4[\text{CuCoMo}_{12}\text{O}_{40}]\cdot 60\text{H}_2\text{O}$  exhibits the loss of  $39.24\%$  of the total mass of isolated product in a single step, in range of temperature between  $25^\circ\text{C}$  to nearby  $500^\circ\text{C}$  (Fig. 2). This single step decomposition of isolated product may be due to loss of entire water molecule associated with the complex along with  $\text{Na}_2\text{O}$ . This loss of entire mass was  $39.24\%$  is well supported by exothermic DTA peak at  $143^\circ\text{C}$  temperature. The peak on set at  $87.2^\circ\text{C}$  and end set at  $178.9^\circ\text{C}$ . A small exothermic peak is also observed at  $603.1^\circ\text{C}$ . Which on set at  $582.3^\circ\text{C}$  and end at  $622.4^\circ\text{C}$  may be assigned to the physical transformation of the complex to attend maximum stable condition.

Fig. 2. TG and DTA graph of  $\text{Na}_4[\text{CuCoMo}_{12}\text{O}_{40}]\cdot 60\text{H}_2\text{O}$ 

The third heteropoly complex isolated is  $\text{Na}_8(\text{CoAl}_2\text{Mo}_{12}\text{O}_{44})\cdot 97\text{H}_2\text{O}$ . The TGA curve exhibits two step decomposition to loss more than  $50\%$  in between  $20$  to  $330^\circ\text{C}$  (Fig. 3). The major loss of water which is about  $47\%$  by weight involve majority of water molecules and all sodium oxide molecules, however in between  $180$  to  $320^\circ\text{C}$  the minor loss  $3.5\%$  by weight which only due to the loss of rest of water molecules. The total loss of weight, which is  $50.64\%$  of the mass is supported by the exothermic DTA peak at  $145.7^\circ\text{C}$  which on set at  $88.7^\circ\text{C}$  and end at  $180.7^\circ\text{C}$ . The DTA curve

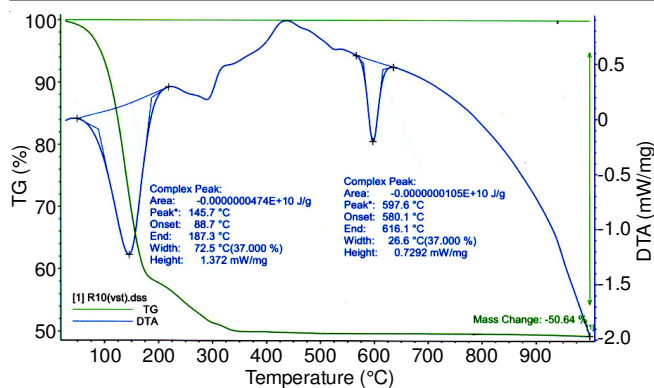


Fig. 3. TG and DTA graph of  $\text{Na}_8[\text{Co Al}_2\text{Mo}_{12}\text{O}_{44}] \cdot 94\text{H}_2\text{O}$

also exhibit another DTA peak at 597.6 °C, which on set at 580.1 °C and end at 616.1 °C. This exothermic DTA peak may suggest the physical transformation of the dehydrated product to attain more stable state.

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