

## Synthesis, characterization and thermal study of the interacted polymolybdate

Subrata Chatterjee\*, Dr.P.P.Jha

Dept. of Chemistry, Ranchi College, RU PIN-834008, (RANCHI)

E-mail : Subrata.ch88@yahoo.com

### ABSTRACT

One new heteropoly complex is prepared containing  $\text{Co}^{2+}$  and  $\text{V}^{5+}$  in dilute acetic acid medium at pH 4.7 after cooling the refluxed mixture white coloured solid residue was recovered. After three days the residue was washed with moderately concentrated ethanol and dried. The elemental analysis of the residue was performed as suggested by the text book of quantitative chemical Analysis by 'Vogel'. The percentage analysis of the constituent elements of triheteropoly complex synthesized was determined chemically. The IR spectrum studies and the thermal analysis based on TGA and DTA curves of the polymolybdate complex confirm its chemical composition as  $(\text{NH}_4^+)_5 [\text{Co V Mo}_{12} \text{O}_{42}] 29\text{H}_2\text{O}$ . The stability of the isolated triheteropoly molybdate complex was determined by applying thermogravimetric and differential thermal analysis. The results of the both types of thermal stability of the complex in air. The composition of the residue product on the basis of elemental analysis is assigned as  $(\text{NH}_4^+)_5 [\text{Co V Mo}_{12} \text{O}_{42}] 29\text{H}_2\text{O}$  © 2015 Trade Science Inc. - INDIA

### KEYWORDS

Triheteropoly molybdate;  
Cryoscopy;  
IR spectral analysis;  
Thermal analysis.

### INTRODUCTION

A new heteropoly complex  $(\text{NH}_4^+)_5 [\text{Co V Mo}_{12} \text{O}_{42}] 29\text{H}_2\text{O}$  has been synthesized and characterised by chemical and instrumental methods. The synthesis of complexes having isopoly anions along with heteropoly anions of Vanadium, Molybdenum and Tungsten were started much earlier by Tsigdimos and Co-Workers<sup>[1]</sup> in the weak acidic medium created by addition of proper quantities of acetic acid into the aqueous solution of Sodium meta Vanadate Cobalt Carbonate and Ammonium Molybdate aqueous solution taken together. The first heteropoly com-

plex was prepared by Berzelus<sup>[2]</sup>. Most of the workers in this field have prepared the triheteropoly complex having Vanadium, Molybdenum and other metal or non-metal atom<sup>[3]</sup>. The Vanadium with Molybdenum along with one heteroatom have not been taken into consideration. Quantitatively the anions of such triheteropoly complex was extensively analyzed by Keggin<sup>[4]</sup> and the structure analysis of such triheteropoly complexes indicate more stability as compared to the simple oxide of the corresponding individual metals. The heteropoly complexes are now suggested as heteropoly oxometalates according to Pope<sup>[5]</sup>. The preparation of triheteropoly molybdate

complex was based on the condensation process<sup>[6-10]</sup>. Which leads to the formation of oxobridges by the elimination of large number of water molecules. In general the heteropoly complex has been prepared by mixing the theoretical quantity of the required reactants in proper acidic medium followed by heating and crystallization<sup>[11-18]</sup>. The DTA and TGA thermal study of the synthesized triheteropoly complex is important for the analysis of their thermal stability because the product isolated is associated with large number of water molecules. The thermal studies also help to fix the position of water molecules. Which may be between the intersectices or at the peripheral of the crystals. The thermal stability of the complex is determined by dehydration method which chiefly involved differential thermal analysis<sup>[19,20]</sup> and thermogravimetric analysis the higher thermal stability<sup>[21]</sup> is evident due to the substitution of hetero cation in the complex compound. It may also be either determined by direct heat treatment or by isothermal measurement. The characterization of the isolated molybdate containing two hetero atom  $\text{Co}^{2+}$  and  $\text{V}^{5+}$  is based on elemental analysis, cryoscopic measurement IR spectral studies and thermal analysis which include TGA and DTA studies of the product obtained. The molecular weight of the observed triheteropoly complex is 2540.

### EXPERIMENT

$(\text{NH}_4^+)_5 [\text{Co V Mo}_{12} \text{O}_{42}] 29\text{H}_2\text{O}$  was freshly prepared. All other segments used were of A.R. grade. The solutions were prepared in distilled water. The metals were estimated using an A.R. L3410 (Switzerland) atomic emission photometer and C, H and N by Coleman Analyzer. The IR spectra (KBr)

were recorded on a Perkin-Elmer 577 spectrophotometry DTA and TGA experiments were carried out on a STA 409 (West Germany) analyzer.

### MOLECULAR WEIGHT DETERMINATION

The molecular weight of the heteropoly complex was successfully determined by the method used by Alexander<sup>[22]</sup> and by Thilo and Krieger<sup>[23]</sup> for the molecular weight determinations of certain inorganic polyacids and polyphosphates etc in water and molten sodium sulphate decahydrate. The determination showed to be 2538 which is in the range of fair agreement for  $(\text{NH}_4^+)_5 [\text{Co V Mo}_{12} \text{O}_{42}] 29\text{H}_2\text{O}$  whose calculated molecular weight is 2540.

### PREPARATION

Preparation of the triheteropoly molybdate complex involves the mixing of Ammonium Molybdate, Sodium meta Vanadate in the ratio 1:1:12 in aqueous solution separately with 10 ml of glacial acetic acid. The pH of the mixture was further adjusted to 4.7 pH by adding about 5 ml of glacial acetic acid. The solution mixed together was refluxed for two hours and thirty minutes. It was cooled and left for crystallisation. After three days, the white coloured solid residue was obtained.

### ELEMENTAL ANALYSIS

The elemental analysis was performed on the basis of prescribed method (Vogel)<sup>[24]</sup>. As per the percentage composition of the synthesized triheteropoly molybdate. The proposal of composition of the complex may be given as 1:1:12. The

TABLE 1 : Elemental analysis of  $(\text{NH}_4^+)_5 [\text{Co V Mo}_{12} \text{O}_{42}] 29\text{H}_2\text{O}$

Elements	Percentage found				Mean	Percentage Calculated
	Exp-1	Exp-2	Exp-3			
Nitrogen	2.78	2.72	2.70	2.82	2.75	
Cobalt	2.35	2.30	2.31	2.32	2.28	
Vanadium	2.12	2.09	2.03	2.08	2.00	
Molybdenum	45.38	45.40	45.60	45.46	45.35	
Hydrogen	2.95	2.84	2.67	2.92	2.86	
Oxygen By Difference				44.40	44.76	

## Full Paper

apparent molecular weight of the prepared triheteropoly molybdate complex determined by cryoscopic method was found to be  $(\text{NH}_4^+)_5 [\text{Co V Mo}_{12} \text{O}_{42}] \cdot 29\text{H}_2\text{O}$ .

### RESULT

#### IR result analysis

The compound shows sharp IR band at  $655 \text{ cm}^{-1}$  to  $700 \text{ cm}^{-1}$  (Mo-O-Mo bridging) and strong bands at  $883 \text{ cm}^{-1}$  to  $910 \text{ cm}^{-1}$  due to independent Mo-O stretching vibrations. The bands of Mo-O and Mo-O-Mo are distinguishable although observed nearly at the same region.<sup>25</sup> The medium bands in the range of  $1019 \text{ cm}^{-1}$  to  $1052 \text{ cm}^{-1}$  may be assigned to V-O stretching vibrations in octahedral co-ordination<sup>23</sup> and those in the range of  $463 \text{ cm}^{-1}$  to  $490 \text{ cm}^{-1}$  correspond to central Co-O linkage. The peaks at  $3457 \text{ cm}^{-1}$  (asymmetric, symmetric O-H stretching) correspond to those of peripheral water molecules. The peaks at  $1644 \text{ cm}^{-1}$  to  $1566 \text{ cm}^{-1}$  correspond to H-O-H bridging mode of water. Whereas those in the lower frequency region  $655 \text{ cm}^{-1}$  are due to O-H liberation of lattice water. The N-H band<sup>26</sup> in guanidinium salt was found at  $1414 \text{ cm}^{-1}$  to  $1345 \text{ cm}^{-1}$  and  $1345 \text{ cm}^{-1}$  to  $1285 \text{ cm}^{-1}$ .

#### TGA and DTA analysis

The Thermal studies of triheteropoly molybdate prepared were based on the experimental thermogravimetric and differential thermal curves of the product which exhibit multistep elimination and decomposition of the residue obtained. However the TGA describes some exactness of the stoichiometry, involved in chemical changes, which are indicated during DTA by an exothermal and endothermal departure from the base line<sup>27</sup>. The merit of the DTA curve is that all energy changes occurring in the sample during heating are clearly observed sensitivity is adequate, and that the peak area reflects the energy involved. Some materials of course indicate no change over a wide range of temperature except melting boiling or volatilization. Each substances gives a characteristics<sup>[28]</sup> DTA curve, which is specific to that substance. Both the shape and size of the peak can give a large number of in-

formations about the nature of test sample. Thus sharp endothermic peaks often signify changes in crystallinity or fusion process where as broad endotherms arising from dehydration reactions, particularly those of an oxidative nature, are predominantly exothermic. The thermogravimetric analysis<sup>29</sup> was performed by taking 4.948 mg of the compound at constant rate of  $10^\circ\text{C}/\text{min}$ , Keoline was taken as reference material for these experiment which have been carried out in air using alumina crucible. The synthesized product started losing its weight from  $25^\circ\text{C}$  to  $250^\circ\text{C}$  temperature then  $250^\circ\text{C}$  to  $450^\circ\text{C}$ . The residue product after  $450^\circ\text{C}$  heating upto  $600^\circ\text{C}$  involve no further weight loss. Which is accompanied by DTA graph. The composition of the residue product after  $450^\circ\text{C}$  to  $600^\circ\text{C}$  temperature may be attributed as  $[\text{Co V Mo}_{12} \text{O}_{42}]$ .

### DISCUSSION

The thermal stability of the complex was studied by TGA and DTA analysis. The measured weight loss of the product at  $25^\circ\text{C}$  to  $250^\circ\text{C}$  is about 20.1% according to TGA graph. This loss of the product is assigned due to loss of twenty nine moles of water of hydration. According to the DTA curve, after losing twenty nine moles of water of hydration, the energy content of the remaining sample increased considerably suggesting the unstable state of the residue sample. The measure weight loss of the product is accompanied by DTA graph suggesting the first exothermic peak maxima at  $74.68^\circ\text{C}$  temperature having area  $1643.357 \text{ V } \mu\text{V} \times \text{second}$  and peak height (8.021). However when the heating rate is increased from  $250^\circ\text{C}$  to  $450^\circ\text{C}$  temperature again the residue sample losses its weight as per the TGA graph was 3.61%. In second thermal decomposition indicating small exothermic peak involves of  $5(\text{NH}_4^+)$  molecules at temperature  $316.97^\circ\text{C}$  having area  $26.355 \times \text{second}$  with peak height (-0.936). The residue product after  $450^\circ\text{C}$  heating upto  $600^\circ\text{C}$  involve no further weight loss the composition of the residue after  $450^\circ\text{C}$  to  $600^\circ\text{C}$  temperature may be attributed as  $[\text{Co V Mo}_{12} \text{O}_{42}]$ . The third broad large endothermic peak at temperature  $377.36^\circ\text{C}$  having area (  $1039.729 \times \text{second}$ ) with peak height 5.620

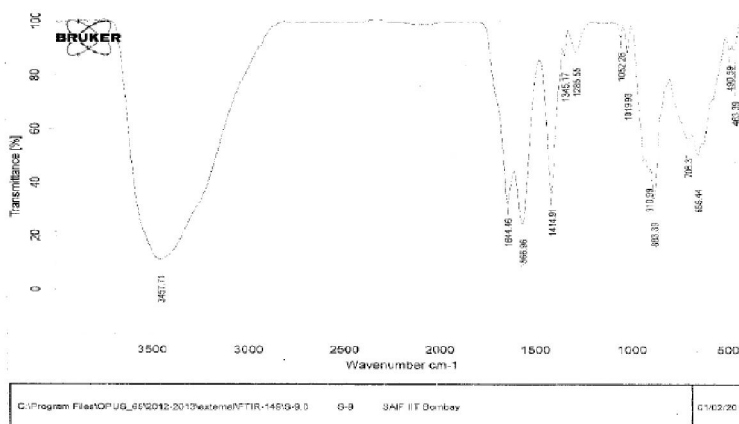


Figure 1 : FTIR graph of polymolybdate

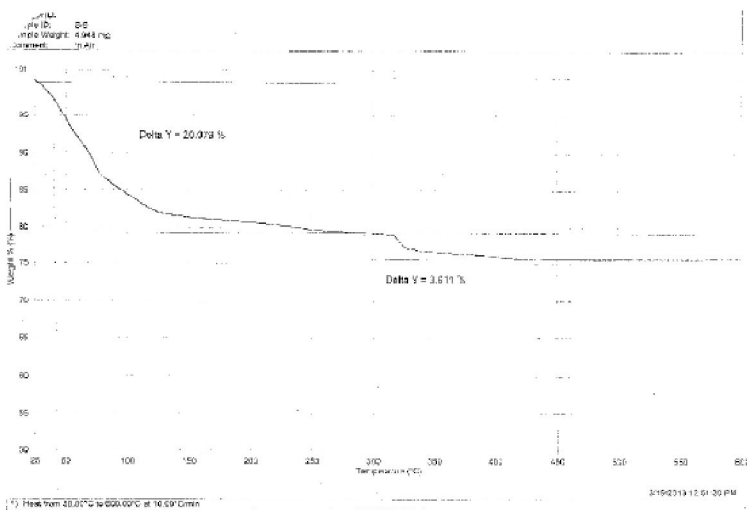


Figure 2 : TGA graph of polymolybdate

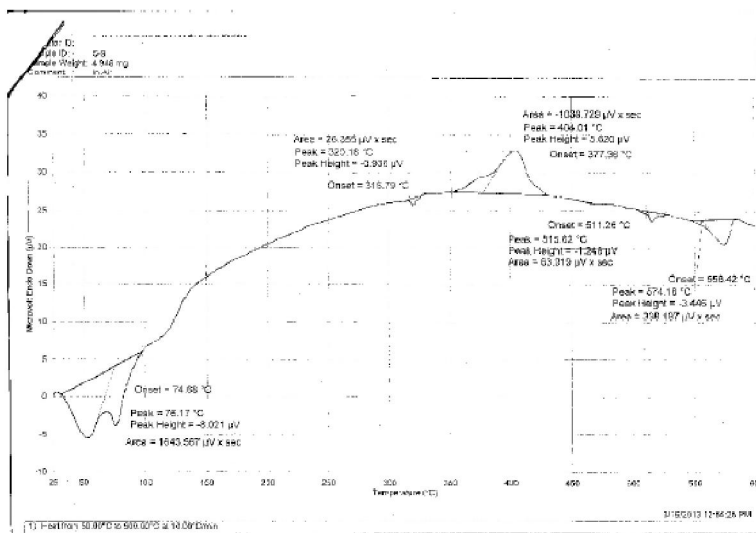


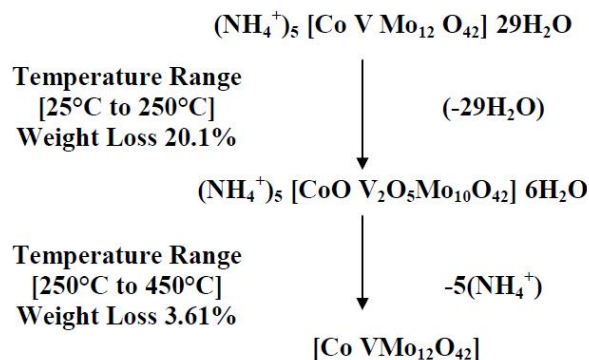
Figure 3 : DTA graph of polymolybdate

signifys dehydration reactions. The fourth small exothermic peak at 511°C temperature having area 63.919 × second with peak height (-1.246 ) indi-

cate phase transfer and the fifth small sharp exothermic peak at 556.42°C temperature having area (-338.187 × second) with peak height (-3.446) indi-

## Full Paper

cate particularly those of an oxidative nature of the complex compound.



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