



## Preparation and Characterization of Isolated Polyvanadate Containing Mn<sup>2+</sup> and W<sup>6+</sup> Hetero Ions

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One new triheteropoly complex was synthesized containing two hetero cations Mn<sup>2+</sup> and V<sup>6+</sup> substituted in the polyvanadate anion having composition [V<sub>9</sub>O<sub>27</sub>]<sup>9-</sup>. The product obtained was dull yellow in appearance. Infrared spectral analysis of the product suggest the presence of Na<sup>+</sup>, W=O, V=O, V-O, Mn-O, W-O-W and W-Mn along with hydrogen bonded H<sub>2</sub>O group in the complex. The flame photometric experiment also indicates the association of sodium with the complex as a golden yellow flame was obtained on heating the product in flame photometer. The molecular weight determination of the triheteropoly complex by cryoscopic method was almost in accordance with the calculated result of the isolated product. The stability of the isolated triheteropoly vanadate complex was determined by applying thermogravimetric and differential thermal analysis. The results of the both types of thermal analysis suggest the thermal stability of the complex in the air at room temperature. The composition of the residue product on the basis of elemental analysis is assigned as Na[MnWV<sub>9</sub>O<sub>27</sub>]9H<sub>2</sub>O.

**Key Words:** Triheteropoly vanadate preparation, Cryoscopy, Thermal analysis.

### INTRODUCTION

The first heteropoly complex was prepared by Berzelius<sup>1</sup>. The most of the workers in this field have prepared the triheteropoly complex having vanadium, molybdenum and other metal or non-metal atom<sup>2</sup>. The vanadium with tungsten along with one heteroatom are not taken into consideration. Quantitatively the anions of such triheteropoly complex was extensively analyzed by Keggin<sup>3</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>4</sup>. The preparation of triheteropoly vanadate complex was based on the condensation process<sup>5-8</sup>, which lead to the formation of oxobridges by the elimination of large water molecules. This type of condensation reaction usually occurs freely and reversibly in the moderate to weak acidic medium. The mechanism of such condensation reaction may be compared with the path way of the formation of dichromate ion from chromate ion in the acidic medium which may be regarded as pH dependent system. The pH for the specific acidic medium is studied, which suggest the formation of heteropoly anion. Mostly the heteropoly complexes have been prepared<sup>9-15</sup> by mixing the calculated quantity of the required reactants in specific acidic medium and subsequently refluxing the mixture and then subject to crystallization. The DTA and TGA<sup>16,17</sup> thermal studies of the

synthesize triheteropoly complex are important for the studies of their thermal stability because the product isolated is associated with large number of water molecules mainly as water of hydration. The thermal studies of the complex also help to fix the position of water molecule which may be between the interstices or at peripheral region of the crystal. The thermal stability of the complex may be either determined by direct heat treatment or by isothermal measurement. The emphasis in this paper is given on the synthesis and characterization of the isolated triheteropoly vanadate containing two hetero atoms manganese and tungsten based on the elemental analysis, cryoscopic measurement, infrared spectral studies and TGA and DTA studies.

### EXPERIMENTAL

Synthesis of triheteropoly vanadate complex was performed by mixing of an aqueous solution of 60 mL of 0.35 (M) of sodium vanadate 20 mL of 0.84 (M) of manganese sulphate aqueous solution and 50 mL. of 0.25 (M) aqueous solution of sodium metavanadate with 15 mL of glacial acetic acid to maintain pH 4.5 of the mixture solution and refluxed for 2.5 h. The solution was cooled and left for crystallization. After almost three days at room temperature, dull yellow coloured residue was obtained which was filtered and washed with moderate concentrated ethanol aqueous solution. Finally the residue was dried and collected as solid isolated product.

The elemental analysis of the synthesized triheteropoly vanadate was performed as per the chemical method and flame photometric method (for sodium estimation) suggested by Vogel<sup>18</sup>. The following chart on the basis of element estimation gives the percentage composition of each constituent elements of the triheteropoly vanadate complex.

Elements	Percentage found			Calculated (%)
	Exp.-1	Exp.-2	Mean	
Vanadium	34.32	34.68	34.5	34.90
Tungsten	13.89	13.97	13.93	14.02
Manganese	4.23	4.49	4.36	4.18
Sodium	1.79	1.82	1.80	1.75
Hydrogen	1.44	1.46	1.45	1.37

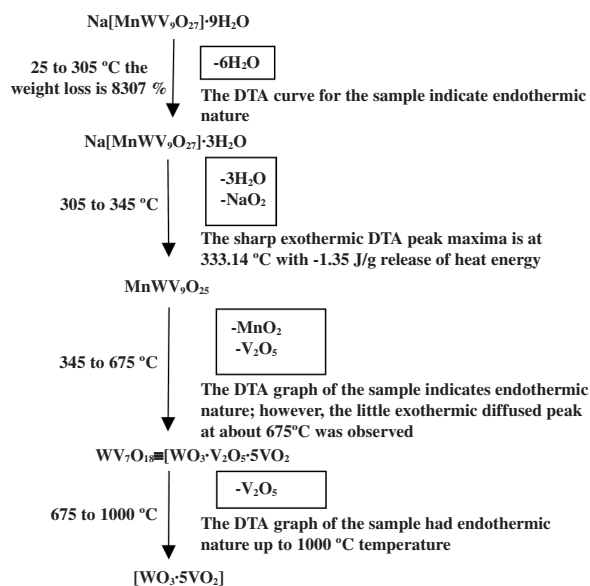
Cryoscopic measurement of the product obtained suggest the apparent molecular weight equal to 1310 which is close to the calculated molecular weight 1315 for the composition of the Na[MnWV<sub>9</sub>O<sub>27</sub>].9H<sub>2</sub>O.

## RESULTS AND DISCUSSION

The infrared spectra of trihetero polyvanadate exhibit sharp absorption peaks at 3213, 2825 and 2420 cm<sup>-1</sup> due to presence of water of hydration bonded strongly to the peripheral complex. Further δ(H<sub>2</sub>O) band are also associated with the trihetero poly oxometalate evident from the sharp absorption peaks at 1938, 1678, 1608, 1517 and 1404 cm<sup>-1</sup> suggesting the different modes of water of hydration associated with the synthesized sample. Further the broad absorption peak at 1159 cm<sup>-1</sup> may be assigned to W = O group frequency. Again the sharp absorption peak at 1002 cm<sup>-1</sup> suggest the association of V = O group frequency. The sharp absorption peak at 968 cm<sup>-1</sup> may be assigned to the sodium associated with the trihetero poly complex as Na<sup>+</sup> ion<sup>19</sup>. The sharp absorption peak at 736 cm<sup>-1</sup> assigned to V-O-V group frequency. The medium broader peak at 669 cm<sup>-1</sup> is assigned to manganese oxygen (Mn-O) group frequency. Another prominent sharp peak at 530 cm<sup>-1</sup> is suggested for W-O-W group frequency and finally the peak at 463 cm<sup>-1</sup> may be due to the presence of W-Mn group frequency.

The thermal studies of triheteropolyvanadate prepared were based on the experimental thermogravimetric and differential thermal curves of the product which exhibit multistep eliminations and decompositions of the residue obtained. The TG analysis was performed with heating rate 10 °C per min in static air. The synthesized product start losing its weight from 25 °C and in first phase continues up to 305 °C temperature. During this range of temperature, the complex loses its weight 8.07 % according to the TGA graph. This loss of the product is assigned due to the loss of six moles of water of hydration. According to the DTA curve, after losing six moles of water of hydration from the sample, the energy content of the remaining sample increased considerably suggesting the unstable state of the residue sample. However when the heating rate is increased from the 305 to 345 °C temperature again the residue sample loses its weight which as per the TGA graph was 8.25 %. This weight loss supposed to be loss of remaining 3 mol of water of hydration molecules may associated in different mode as compared to the 6 mol of water of hydration loss earlier. The sample also loses 1 mol of sodium dioxide which

is substantiated further by the formation of sharp exothermic DTA peak maxima at 333.14 °C releasing 1.53 J/g heat energy. This decomposition step may form meta stable state of the remaining residue sample. The third step of the weight loss from the residue sample was 21.2 % when the rate of heating was again increased from 345 to 675 °C as per the TGA graph. This 21.2 % of weight loss may be due to the loss of 1 mol of each MnO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> components from the sample. The DTA peak suggests the sharp increase in the heat content followed by a little exothermic diffused peak at about 675 °C, which is unmarked in the DTA curve. Finally when the temperature is raised upto 1000 °C, the 16.32 % weight loss was depicted in the TGA graph This weight loss may be attributed to the loss of 1 more mol of V<sub>2</sub>O<sub>5</sub> molecules. The DTA curve of the sample 25 to 1000 °C, indicate sharp increase in heat content from about 500 upto 1000 °C suggesting the highly energetic and unstable state of the remaining residue. The sequence of the thermal decomposition reaction of the isolated product can be summarized in the following steps:



The isopoly and heteropoly complex of vanadium(V), molybdenum(VI) and tungsten(VI) transition metals form an important and exceedingly diverse classes of compounds referred as isopoly and heteropoly complexes of oxometalates as suggested by Michael T. Pope and latter by Bernet Krabs<sup>20</sup>. It has been found that in the presence of Mn<sup>2+</sup> and W<sup>6+</sup> the sodium metavanadate in acidic medium at 4.5 pH form triheteropoly oxovanadate having composition Na[MnWV<sub>9</sub>O<sub>27</sub>].9H<sub>2</sub>O at reflux temperature after standing its concentrated solution for almost three days at room temperature. The interaction of Sodium vanadate anion with Mn<sup>2+</sup> and W<sup>6+</sup> cation in acidic medium has the ratio Mn:W:V::1:1:9. The colour of the isolated residue is dull yellow. The similar product was obtained is more than five consecutive repetition of the process with appropriate ratio of constituent components. The residue obtained is quite stable in air as well as in cold water. However the product in boiling water is completely dissolved parting the light coloured solution. The aqueous solution of poly complex is ionic in nature containing Na<sup>+</sup> cation which is evident from

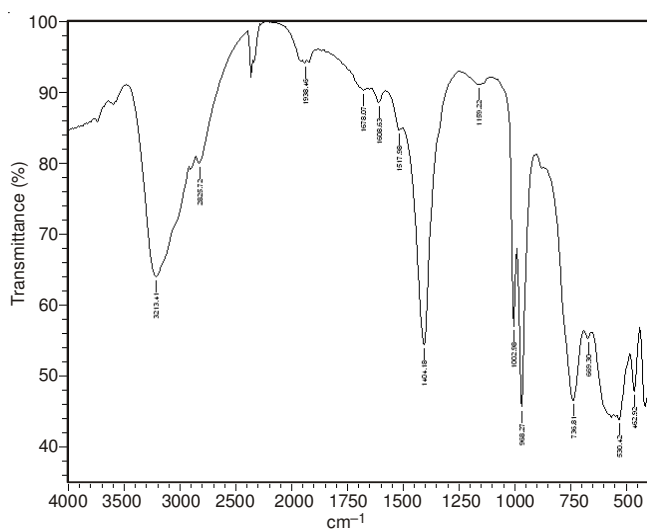


Fig. 1. I.R. graph of the sample

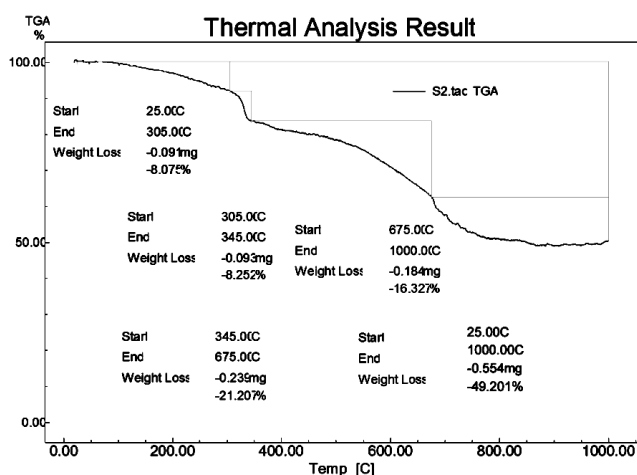


Fig. 2. TGA Graph of the sample

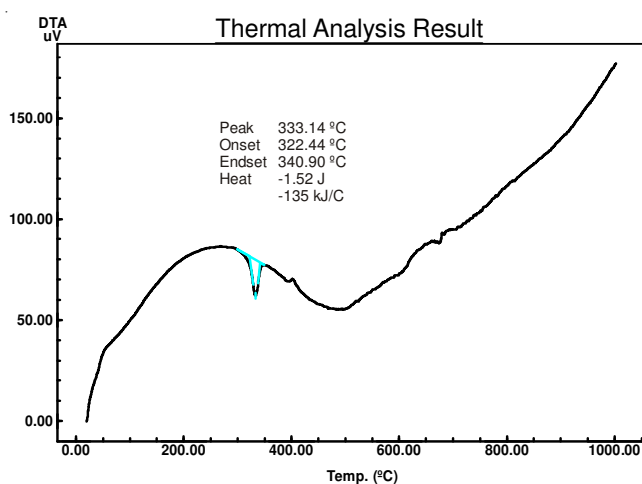


Fig. 3. DTA Graph of the sample

infrared spectral study. The higher thermal stability<sup>21</sup> is evident due to the substitution of hetero cations  $Mn^{2+}$  and  $W^{6+}$  into vanadate anion  $[V_9O_{27}]^{9-}$ . The following graphs are supporting the result and discussion of the synthesized sample.

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