

Analysis of interacted poly vanadate based on its preparation and characterization

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ABSTRACT

The triheteropoly vanadate having hetero atom Ni²⁺ and Co²⁺ cation was prepared by conventional method in the dilute acidic medium having pH-4.5 at reflux temperature. The thermal stability of the product was studied and it was observed that the product involved three step decomposition as per TGA graph producing about 20.003% weight loss which was also duly supported by DTA graph indicating one large exothermic peak maxima at 122.55°C. The product isolated is bright brown in appearance. The IR spectrum of the product indicates the presence of Na, V=O, V-Co, V-Ni, Co-O, Ni-O, V-O and Hydrogen bonded H₂O group. On the basis of analytical I.R. spectral, thermal stability its chemical composition is confirmed as Na₂ [Ni Co V₆ O₁₈] 8.5H₂O © 2014 Trade Science Inc. - INDIA

KEYWORDS

I.R.TGA & DTA;
Cryoscopic measurement.

INTRODUCTION

The credit to start synthesis of complexes containing Isopoly anions along with heteropoly anions of Vanadium, Molybdenum and tungsten goes to Trigdminos and his co-workers^[1]. The present work deals with synthesis of polyanions in weak acidic medium by adding proper quantities of acetic acid into aqueous solution of sodium metavanadate and aqueous solution together. The bright brown coloured residue in solid state was formed when triheteropoly complex was heated at reflux temperature for two and half hours. The weak acidic medium for the preparation of polyvanadate anion is necessary since the alkaline medium as well as strong acidic medium produce decomposition of polyanions. The mechanism of the formation of polyvanadate anions suggest that when the proper weak

acidic medium is created, the simultaneously elimination of water molecules enables it to form oxometallates anion of the vanadate containing metal oxygen bridge which finally form giant poly complex ion having specific ionic structure depending on the number of oxometallates bridge formed. For example the Keggin structure^[2] of poly oxometallates may be formed when the polyanions carries [M₁₂O₄₀]ⁿ⁻ composition. Further if the composition of the polyanions changed to [M₁₈O₆₂]ⁿ⁻ then the structure of the oxometallate differs^[3]. Since the dilute acidic medium is provided for the synthesis of the complex compound, the synthesised triheteropoly complex collected in the form of solid residue may contain moderate or large number of water molecule in either form of hydration or constitution. Therefore the thermal studies of the isolated complex is essential to suggest the stability of the compound which

may be based on the position of water molecules at peripheral region as well as between the interstices of the crystalline solid and also the effect the insertion of hetero cation into polyvanadate anion. The thermal stability increases because of occupation of hetero cation into the voids in the centre of vanadate anion^[4]. The thermal stability of the triheteropoly complex was determined by direct heat treatment^[5-14] or by dehydration method which chiefly involved differential thermal analysis and thermo gravimetric analysis^[15,16] of the prepared complex compound. The presence of Mo, V, W, Na, H and O were detected by elements analysis

EXPERIMENTAL

Preparation

Preparation of the triheteropoly vanadate complex involves the mixing of an aqueous solution of 50ml of 14.640 gm sodium meta vanadate mixed with 10ml of glacial acetic acid and 50ml aqueous solution of 1.26 gm nickel carbonate and 50ml aqueous solution of 1.20gm cobalt carbonate. In this mixture the step addition of 50ml aqueous solution sodium metavanadate was performed with continuous stirring. After complete mixing of sodium meta vanadate solution, the pH of the mixture was further adjusted at pH- 4.5 by adding about 50ml of glacial acetic acid. Now the mixture solution was refluxed for two hours and thirty minutes and left for crystallization. After 3 days the bright brown coloured solid residue was obtained, which was washed with moderately concentrated alcohol and dried. The triheteropolyvanadate was freshly prepared. All other reagents used were of A.R. grade. The solution were prepared in distilled water. The metal were estimated using using on A.R.L 3410 (Switzerland) atomic emission photometer and C,H and N by Coleman analysis. The IR spectra (KBr) were recorded on a Perkin-Elmer577 spectrophotometer. DTA and TGA experiments were carried out on a STA 409 (West Germany) analyser.

Elemental analysis

The elemental analysis was performed on the basis of prescribed method vogel^[17]. As per the percentage composition of the formula synthesized triheteropoly vanadate of the complex may be given as Na₂

[NiCoV₆O₁₈] 8.5 H₂O. The apparent molecular weight of the prepared triheteropolyvanadate complex determined by the cryoscopic method was found to be Na₂ [NiCoV₆O₁₈] 8.5 H₂O It molecular weight to be 908.

Determination of apparent molecular weight

The cryoscopic method as has been applied successfully by Alexander^[18] and by Thilo and Krieger^[19] for molecular weight determination of certain inorganic polyacids and polyphosphates etc, in water and molten sodium sulphate decahydrate has also been applied here for the determination of the approximate molecular weights of the compounds in the same condition i.e., in water and molten sodium sulphate decahydrate. This determination showed the molecular weight of the compound to be 908 for Na₂ [Ni Co V₆ O₁₈] 8.5 H₂O.

RESULT

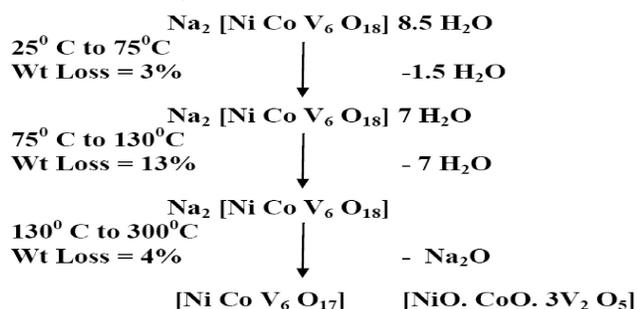
IR spectrum results of polyvanadate residue

The IR spectrum of the residue (Figure 1) exhibit the broad band at 3571.7cm⁻¹ and 2885.51cm⁻¹ can be suggested to strong hydrogen bonded water molecules^[17]. The IR bands from nearly 1300cm⁻¹ to 1650 cm⁻¹ may be assigned to a H₂O in the polyvanadate anion. The prominent and strong band observed at 956.69cm⁻¹ is (V=O) and another strong band^[18] at 844.82cm⁻¹ is (V-Co) due to the presence of stretching of (V-Ni) is 813.96cm⁻¹. The band at 742.59cm⁻¹ assigned to (Co-O) band. Further the IR spectral band at 599.15cm⁻¹ may be assigned to stretching frequency bands (Ni-O) and the band at 466.77cm⁻¹ assigned to (V-O) band. The theoretical values of some of the different stretching frequency to determine the force constants are also taken into consideration for assigning proper group frequencies.

Thermal analysis involving TGA and DTA result

The TGA curve of the isolated polyvanadate complex (Figure 2) and (Figure 3) indicate the four steps of thermal dissociation process in between 25°C to 75°C, 75°C, to 130°C, 130°C to 300°C and finally from 300°C to 600°C. The first thermal decomposition step involves elimination of 1.5 mol of H₂O molecules between 25°C to 75°C temperature comprising about 3% of weight loss of the isolated product.

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The formation of triheteropoly complex of vanadium involve metal oxy cations and their structural aspects depend on the specific polyvanadate anion formed. The formation of polyvanadate complex with composition.

DISCUSSION

$\text{Na}_2 [\text{Ni Co V}_6 \text{O}_{18}] \cdot 8.5 \text{H}_2\text{O}$ at required pH -4.5 and refluxed for two and half hours After standing the concentrated refluxed solution for three days at room temperature the product was isolated. The formation of product involves interactions of sodium meta vana-

date anions with Ni^{2+} and V^{5+} cation in the acetic acid medium. The ratio of the three metal ion is Co : Ni : V:: 1 : 1:6 producing bright brown coloured product with the suggested composition. The product isolated is quiet stable in air and has poor solubility in cold water condition. However the product is completely soluble in boiling water. The aqueous solution of the triheteropoly complex is ionic in nature containing sodium cations Na^+ . The presence of Na^+ cation was confirmed by the IR spectral analysis of the sample and also from the flame photometric experiment which form golden yellow flame of the sodium. The thermal stability of the complex was studied by TGA and DTA analysis- (19) however the modes of different type of H_2O group molecules cannot be demarcated clearly in the terms of water of crystallization and water of constitution. The thermal analysis indicates that the thermolysis of the metal oxide complex proceeds by losing first the water of crystallization and then subsequently the water of constitution which are important to the structure of heteropoly complex compound.

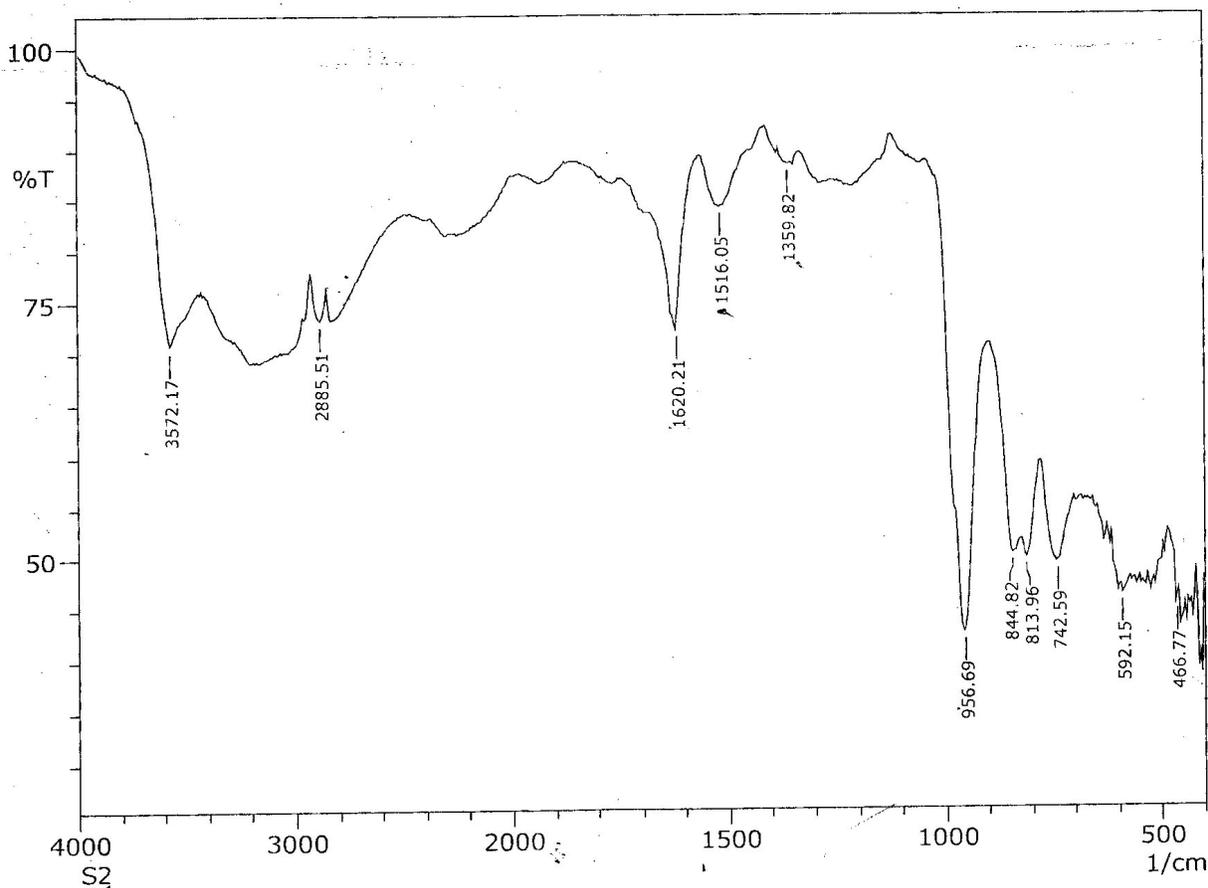


Figure 1 : FTIR graph of polyvanadate residue

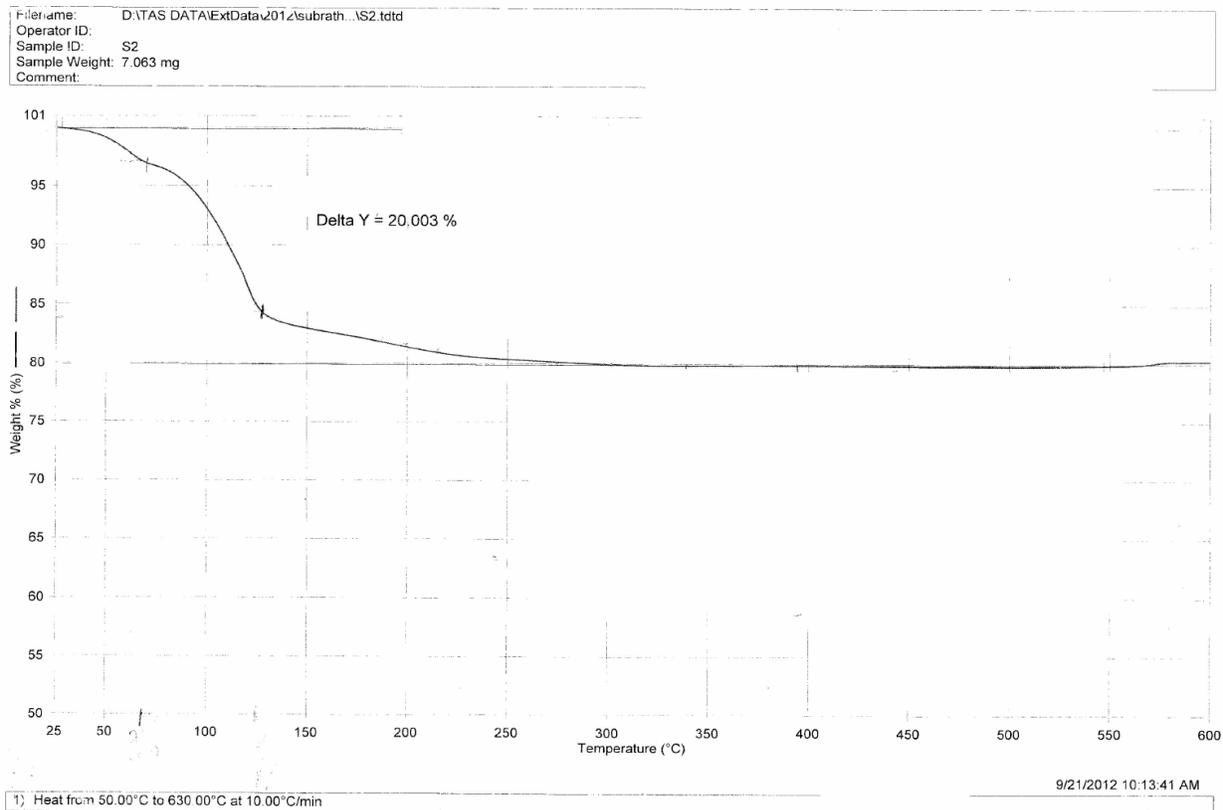


Figure 2 : TGA graph of polyvanadate residue

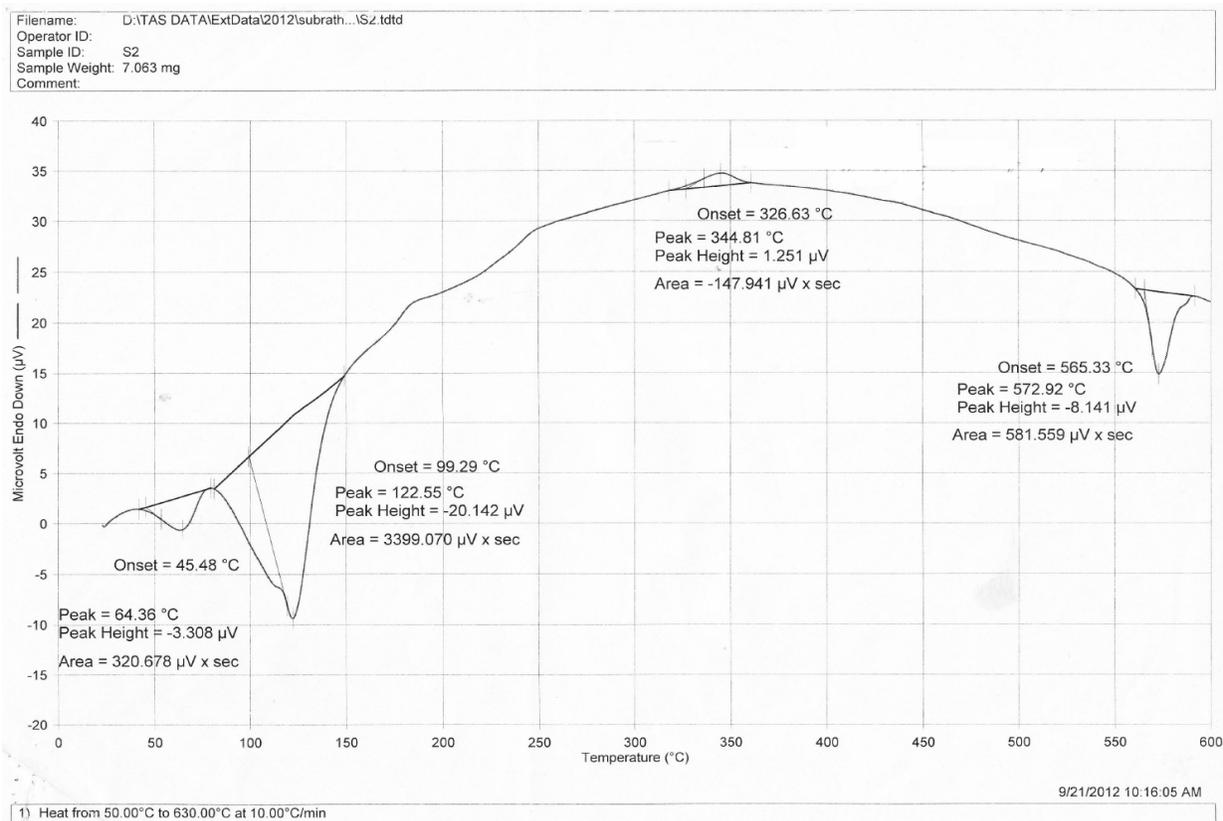


Figure 3 : DTA graph of polyvanadate residue

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