

Evaluation of two synthesised triheteropolytungstate

Vishnu Shankar Tiwari*, Alok Kumar Thakur, G.S.Tiwari, Rajesh Kumar
University Department of Chemistry, Ranchi University, Ranchi, Jharkhand, (INDIA)
E-mail : alok98351@gmail.com

ABSTRACT

The series of polytungstate complex was prepared containing Co^{2+} , Cu^{2+} and Ni^{2+} hetero cations inducted into the polytungstate anion $[\text{W}_{10}\text{O}_{39}]^{-18}$ by conventional method. The acidic medium was kept (pH= 4.5) by mixing appropriate quantities of glacial acetic acid and refluxed for two and half hours. After cooling the refluxed mixture produce bright brown coloured solid residue almost after four days. The residue was washed with moderate concentrated ethanol and dried. The elemental analysis of the residue was performed as mentioned in the text book of Quantitative Chemical Analysis by 'Vogel'. The percentage analysis of the constituent elements of triheteropolycomplex prepared is characterised on the basis of the I.R. spectrum studies and the thermal analysis. On the basis of above analysis the chemical composition of the two different polytungstate complexes were assigned as $\text{Na}_2[\text{CuNiW}_{12}\text{O}_{39}] \cdot 63.5\text{H}_2\text{O}$ and $\text{Na}_2[\text{NiCoW}_{12}\text{O}_{39}] \cdot 37\text{H}_2\text{O}$. The DTA and TGA curves of the two triheteropolytungstate complex it is observed that the major weight losses were in between 20°C to 700°C temperature. The magnetic moment measurement at room temperature of both polytungstates indicate the para-magnetic properties of the products.

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KEYWORDS

Tri heteropolytungstate (THPT) preparation; Cryoscopy; TGA & DTA thermal studies; I.R.spectral studies.

INTRODUCTION

The heteropoly complexes containing isopoly anions along with hetero atoms of vanadium, molybdenum and tungsten were synthesized much earlier by Tsigdimos and co-workers,^[1] in the weak acidic medium created by addition of proper amount of acetic acid into the aqueous solution of sodium tungstate, sodiummetavanadate and sodium molybdate aqueous solutions. The method of synthesis of heteropoly tungstate involve heating at reflux temperature for two and half hours of the mixture solution & as a result the bright brown coloured residue was formed in its solid state. The role of weak acidic

medium is to form poly tungstate anion because in the strong acidic medium as well as in alkaline medium the poly tungstate anions will split into simple tungstate anions. The mechanism of the formation of poly tungstate anions suggested as when the proper weak acidic medium is created then the simultaneous elimination of water molecules enable to form poly oxometallate anion of the tungsten containing metal oxygen bridge which ultimately form giantpolycomplex ion having specific ionic structure depend on the number of oxometallate bridge formed. For example the Keggin structure^[2] of poly oxometallates may be formed when the poly anions bears $[\text{M}_{12}\text{O}_{40}]^{n-}$ composition. Further if the composition of the poly

anion changed to $[M_{18}O_{62}]^n$ then the structure of the oxometallates differs^[3]. The synthesized triheteropoly complex collected in the form of solid residue may contain moderate to large number of water molecules as water of hydration as well as water of constitution, due to the fact that the dilute acidic medium is provided for the synthesis of the complex compound. Thus the thermal studies of the isolated complex product is important which suggest the stability of the compound which may be based on the position of the water of molecules at peripheral region as well as between the interstices of the crystalline solid and also the effect of the insertion of hetero cations into polytungstate anion. The occupation of hetero cations into the voids in the centre of tungstate anion increases the thermal stability much effectively^[4]. The thermal stability of the triheteropoly complex was determined by direct heat treatment^[5-14] or by dehydration methods which mainly involved differential thermal analysis and thermo gravimetric analysis^[15,16] of the synthesized complex compound. The presence of Cu, Ni, W, Na, Co, H and O elements have been confirmed by elemental analysis, IR, spectral analysis and thermal analysis based on TGA & DTA of the synthesized poly tungstate residue^[17-21].

EXPERIMENTAL

Preparation

Preparation of the triheteropolytungstate complex involves the mixing of an aqueous solution of 60ml of 0.33(M) sodiumtungstate mixed with 10ml of glacial acetic acid and 40ml aqueous solution of 0.84(M) Nickel carbonate. In this mixture the step addition of 50ml aqueous solution of 0.25(M) copper carbonate was performed with continuous stirring. After complete mixing of copper carbonate solution, the pH of the mixture was further adjusted to 4.5 by adding about 5ml of glacial acetic acid. Now the mixture solution was refluxed for three hours. The solution was cooled and left for crystallization. After 4 days, the bright brown coloured solid residue was obtained, which was washed with moderate concentrated alcohol and dried. The second triheteropoly complex was prepared by same method only cobalt carbonate was taken instead of copper carbonate. The solid residue was obtained.

Elemental analysis

The elemental analysis was performed on the basis of prescribed methods suggested by Vogel. The quantitative estimation of the constituent elements of the product is given below in the chart:

Elements	Percentage found			Percentage
	Exp.-1	Exp.-2	Mean	Calculated
Tungsten	53.3	53.29	53.3	53.3
Copper	1.52	1.53	1.52	1.52
Nickel	1.42	1.41	1.42	1.42
Sodium	1.11	1.12	1.11	1.11
Hydrogen	3.07	3.06	3.07	3.07
Oxygen	(By difference)		39.58	39.58

As per the percentage composition of the synthesized triheteropoly tungstate constituent elements, the proposed composition of the complex may be given as $Na_2[CuNiW_{12}O_{39}]63.5H_2O$. The apparent molecular weight of the prepared triheteropoly tungstate complex was determined by the cryoscopic method, the apparent molecular weight found to be 4134 which is almost in accordance with the calculated molecular weight of the product 4143.

Elemental analysis of the second complex the constituent elements of the product is given below in the chart:

Elements	Percentage found			Percentage
	Exp.-1	Exp.-2	Mean	Calculated
Tungsten	60.29	60.31	60.3	60.3
Cobalt	1.59	1.62	1.61	1.61
Nickel	1.62	1.60	1.61	1.61
Sodium	1.25	1.27	1.26	1.26
Hydrogen	2.03	2.01	2.02	2.02
Oxygen	(By difference)		33.2	33.2

As per the percentage composition of the

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synthesized triheteropoly tungstate constituent elements, the proposed composition of the complex may be given as $\text{Na}_2[\text{NiCoW}_{12}\text{O}_{39}]\cdot 37\text{H}_2\text{O}$. The apparent molecular weight of the prepared triheteropoly tungstate complex was determined by the cryoscopic method, the apparent molecular weight found to be 3660 which is almost in accordance with the calculated molecular weight of the product 3662

RESULT AND DISCUSSION

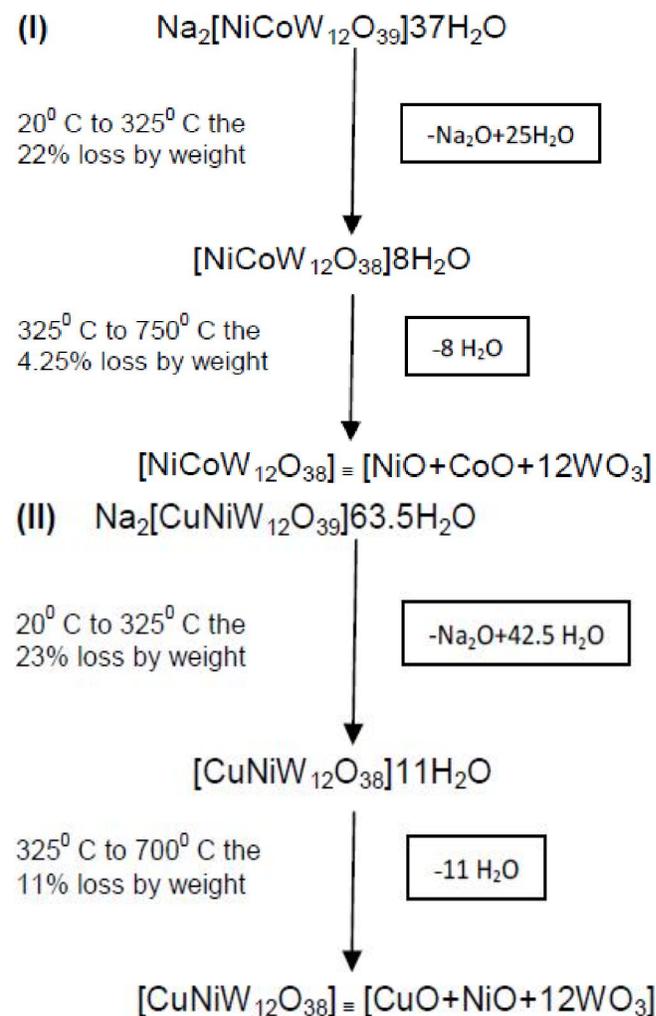
IR spectrum results of polytungstate residue

The two different triheteropolytungstate residue obtained exhibit the broad band at 3111.01 cm^{-1} and 3106.29 cm^{-1} along with other prominent band at 1566.20 cm^{-1} suggesting the strong hydrogen bonded water molecules. The band at 2118.70 cm^{-1} also assigned to the hydrogen bonded water molecules. The other band lying between 1415.7 cm^{-1} to 1288.45 cm^{-1} may be assigned to $\Delta\text{H}_2\text{O}$ in the polytungstate anions. The strong band at 1718.91 cm^{-1} due to presence of $\Delta(\text{W-O})$ stretched bond. The other band at 891.11 cm^{-1} may be assigned to Cu-O stretched bond the sharp band at 798.53 cm^{-1} is assigned to Ni-Co stretched bond which is also appeared in the other polytungstate heteropoly complex with slight shift at 775.38 cm^{-1} . This shifting of Ni-O stretching bond in this triheteropoly complex is attributed due to the change in electronic environment since the Cu^{2+} ion is replaced in the complex by Co^{2+} cation

Thermal analysis involving TGA and DTA result

The TGA curve of the two isolated polytungstate complex indicate the two steps of thermal dissociation stages. The first stage of thermal decomposition is assigned between 20°C to 325°C and then the second thermal dissociation in between 325°C to nearly 750°C temperature. The percentage weight loss up to 1000°C temperature as indicated in the TGA graph are 26.25, 34.05 percentage for $\text{Na}_2[\text{NiCoW}_{12}\text{O}_{39}]\cdot 37\text{H}_2\text{O}$ and $\text{Na}_2[\text{CuNiW}_{12}\text{O}_{39}]\cdot 63.5\text{H}_2\text{O}$ respectively. The first thermal decomposition steps involves the major loss of water molecules along with the loss of sodium oxide molecules. This loss of almost equal to 22% loss of mass if the total weight of isolated product for the both triheteropoly complexes which is also accompany with

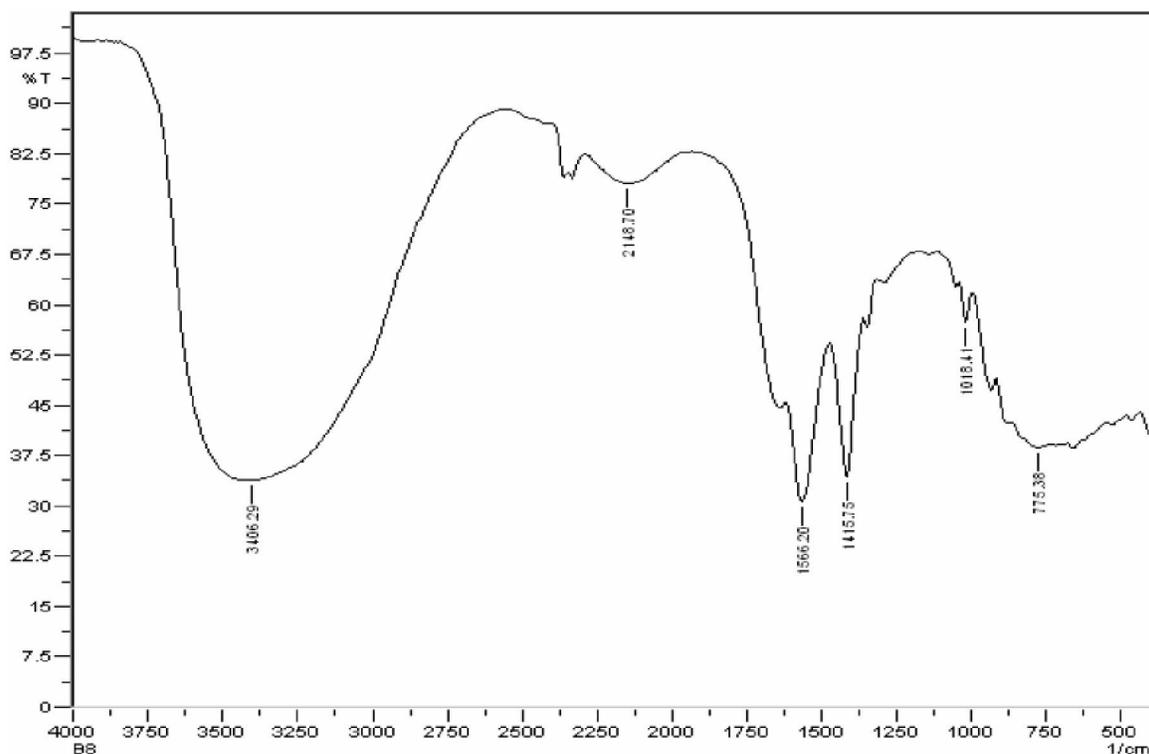
exothermic DTA curves shown at about identical temperature about 150°C further the second thermal dissociation stage of the products start from 325°C continues upto 750°C involve the loss of water of crystallization to form sent percent unhydrated product. This is also evident from the DTA curve of the products which indicate another exothermic DTA peak at about 700°C temperature. After 750°C no loss of weight for the two products are observed. Hence it may be concluded that of about 750°C temperature the metastable products are obtained. The formation of triheteropoly tungstate complexes involve metal oxocations and their structural aspects depend on the specific polytungstate anion formation finally it may be concluded that the induction of hetero cations to the isopolytungstate anions increases the thermal stability of the oxometalate complex formed. The following flow sheet diagram are representing the two steps thermal dissociation processes of the product.



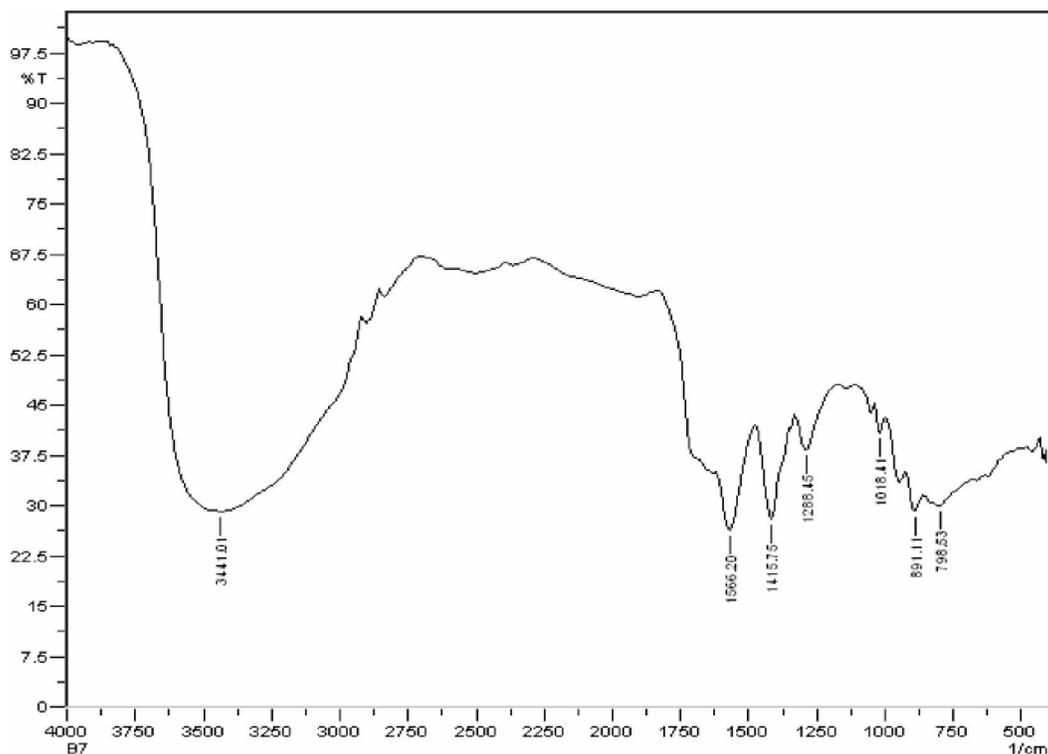
CONCLUSION

The two products of isopoly tungstate anions are prepared in the ratio of metal ions Ni:Cu:W ::1:1:12

producing bright brown coloured product which were quite stable in air and poorly soluble in water at room temperature. however the products were completely soluble in warm to boiling water. The aqueous solution

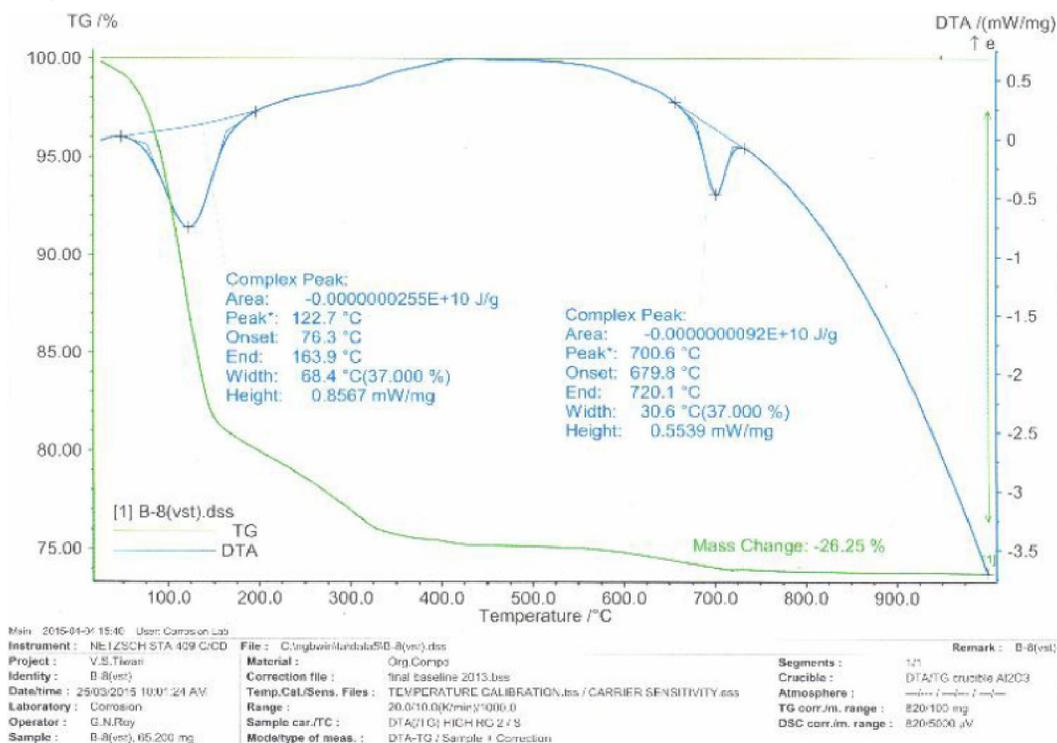


Graph 1 : IR of poly tungstate residue I

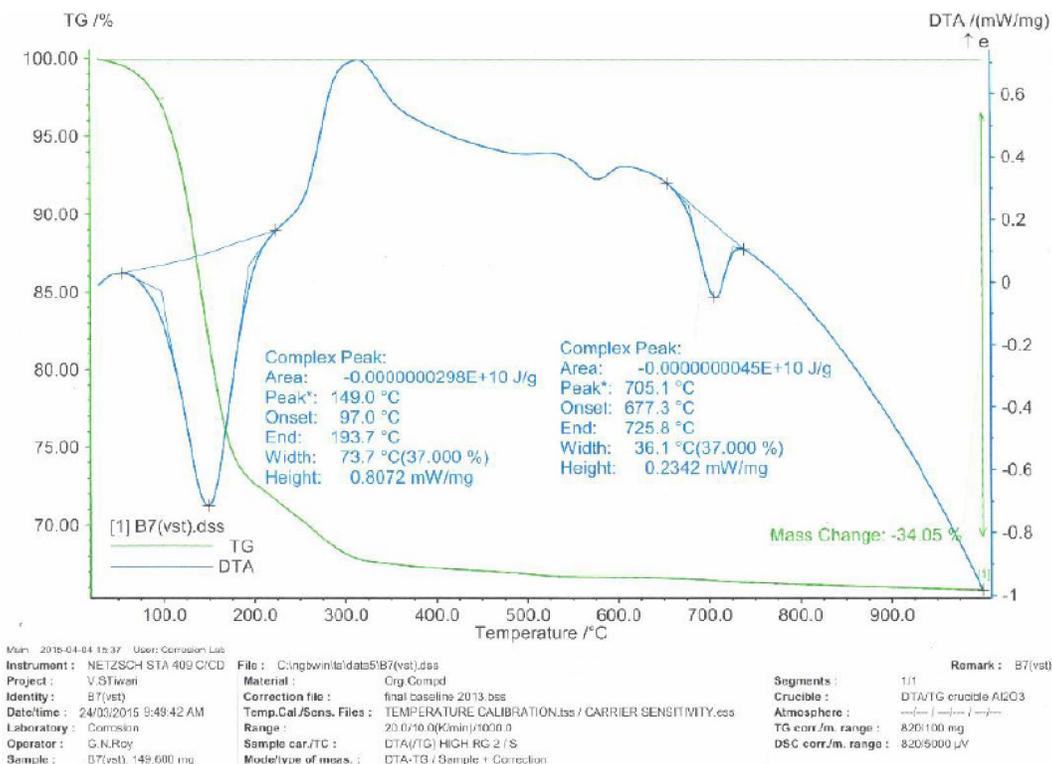


Graph 2 : IR of poly tungstate residue II

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Graph 3 : TGA/DTA Of poly tungstate residue I



Graph 4 : TGA/DTA Of poly tungstate residue II

of the heteropoly complex were ionic in nature containing Na^+ . The evidence of the presence of Na^+ cations is confirmed from their IR spectral analysis in which sodium oxide IR absorption bands were

observed. The presence of Na^+ is also confirmed from the flame photometric experiment to calculate the elemental percentage of sodium element during heating in the flame photometric experiment the golden yellow

flame is produced whichn indicate the presence of sodium. The magnetic moment determination at the room temperature suggests the strong paramagnetic nayure of the isolated products. he thermal analysis of the complexes were studied on the basis of DTA & TGA curves analysis of the products. Which indicates the presence of different modes of water molecules. However it is not possible to determine the H₂O molecules in terms of water of crystallization and water of constitution. The thermal analysis indicate that the thermolysis of oxometalates complexes produced by loss of water of crystallization and then subsequently the loss of water of constitution. Hence it may be concluded that the water constitution may involve in building up the structure of triheteropoly complex compound.

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