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Studies on the interacted polytungstate preparation and characterization

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ABSTRACT

The interacted polytungstate complex was prepared containing Mn2+ and V5+ hetero cations associated with polytungstateanion [W10O39]-18 by conventional method. The medium for the preparation of the triheteropolycomplex is kept at pH 4.5 by mixing appropriate quantities of glacialacetic acid and refluxed for two and half hours. By cooling the refluxed mixture bright brown coloured solid residue after three days was recovered. The residue was washed with moderate 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 triheteropolycomplex synthesized, the I.R. spectrum studies and the thermal analysis based on TGA and DTA curves of the polytungstate complex confirm its chemical composition as Na6[MnV2W10O39]14H2O. Further the thermal analysis of the triheteropolytungstate indicate the measure weight losses in between 250C to 1200C and then further heating up to 3330C with DTA exothermic peaks maxima at 74.47 and 107.990C and also a sharp DTA exothermic peak maxima at 325.310C. The magnetic moment measurement at room temperature suggests the para-magnetic properties of the triheteropolycomplex residue.

KEYWORDS

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

INTRODUCTION

The synthesis of complexes having isopoly anions along withheteropoly anions of vanadium, molybdenum and tungstenwere started much earlier by Tsigdimos and co-wokers,[1] in the weak acidic medium created by addition of proper quantities of acetic acid into the aqueous solution of sodium tungstate, sodiummetavanadate and manganese sulphate aqueous solution taken together. After heating at reflux temperature for two and half hours, the bright brown coloured residue was formed in its solid state. The role of weak acidic medium is to form poly tungstate anion since 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 mediumis created then the simultaneous elimination of water molecules enable to form 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 $[M_{12}O_{40}]^{n-}$ composition. Further if the composition of the poly anion changed to $[M_{18}O_{62}]^{n-}$ then the structure of the oxometallatesdiffers.[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, since the dilute acidic medium is provided for the synthesis of the complex compound. Hence the thermal studies of the isolated complex is important to 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 cataions 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 prepared complex compound. The presence of Mn,V,W,Na,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.

EXPERIMENTAL

Preparation

Preparation of the triheteropolytungustate 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) manganese sulphate. In this mixture the step addition of 50ml aqueous solution of 0.25(M) sodiummetavanadate was performed with continuous stirring. After complete mixing of sodium metavanadate 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 two hours and thirty minutes. The solution was cooled and left for crystallization. After 3 days, the bright brown coloured solid residue was obtained, which was washed with moderate concentrated alcohol and dried.

Elemental analysis

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

As per the percentage composition of the synthesized triheteropoly tungstate constituent elements,the proposed composition of the complex may be given as $Na_6[MnV_2W_{10}O_{39}]14H_2O$. The apparent molecular weight of the prepared triheteropoly tungstate complex was determined by the cryoscopic method, the apparent molecular weight found to be 3008 which is almost in accordance with the calculated molecular weight of the product 3011.

Elements	Percentage found			Percentage Calculated
	Exp.-	Exp.-	Mean	
Tungsten	61.2	61.4	61.3	61.01
Vanadium	3.74	3.79	3.76	3.38
Manganese	1.91	1.95	1.93	1.83
Sodium	4.4	4.35	4.38	4.58
Hydrogen	1.20	1.02	1.11	0.92
Oxygen	(By difference)		27.52	28.28

RESULT AND DISCUSSION

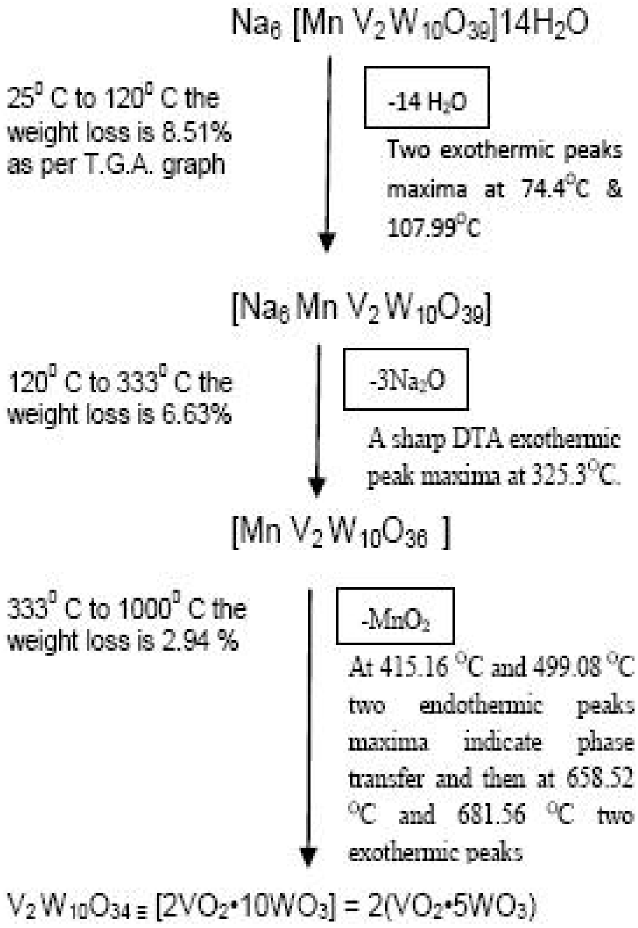
IR spectrum results of polytungstate residue

The I.R. spectrum of the residue exhibitthe broad band at 2094.69 cm^{-1} and 3415.93 cm^{-1} [17] can be suggested to strong hydrogen bounded water molecules. The I.R. bands from nearly 1300to 1650cm^{-1} may be assigned to ä(H_2O) in the polytungstate anion. The prominent and strong band observed at 1132.21cm^{-1} may be assigned to Na$^+$ion[18] and another strong band at 1018.41 cm^{-1}

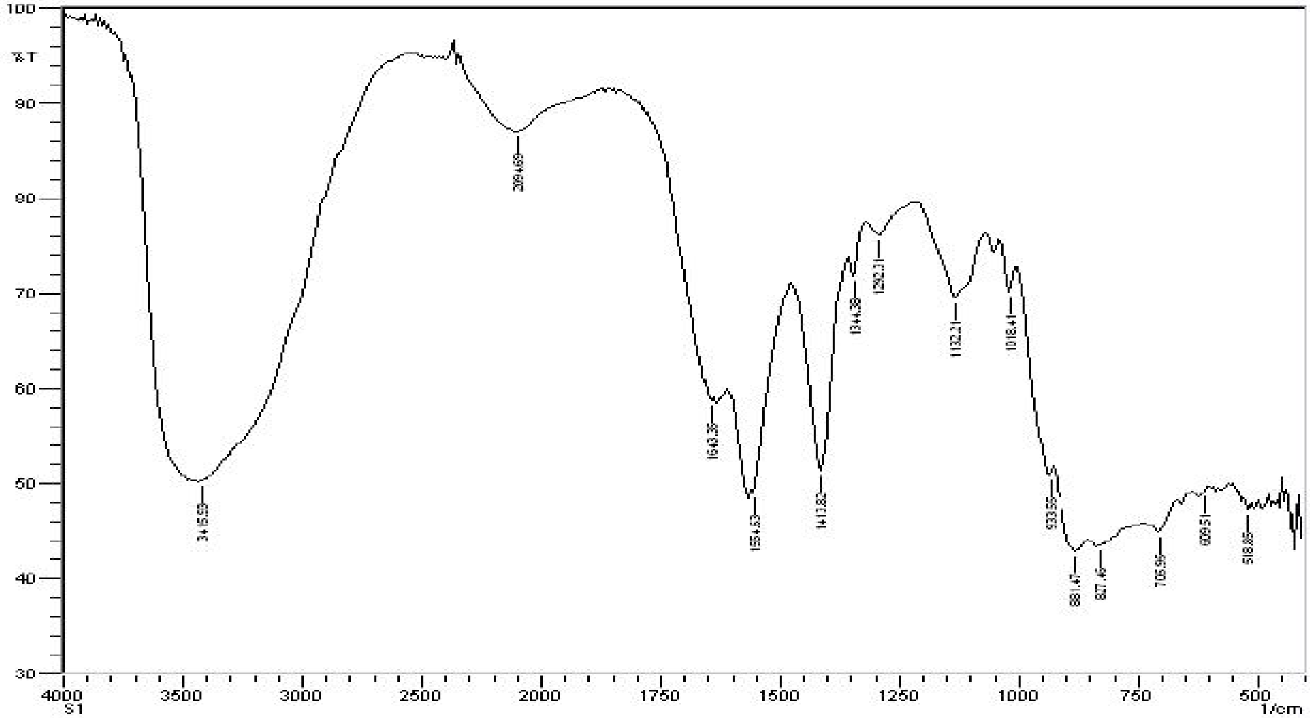
due to the presence of õ(W-O) starching band. The sharp band at 933.55cm^{-1}may be due to presence of í (W-V) of the residue. The broad band at 881.47cm^{-1} assigned to õ (V=O) bond. The band at 827.46 cm^{-1}assigned to õ (V-Mn) bond. Further the I.R. spectral band at 705.95,609.51 and 518.85 cm^{-1}may be assigned to stretching frequency bands õ (W-O-W), õ (Mn-O) and õ (V-O-V) respectively. 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 polytungstate complex indicate the three steps of thermal dissociation process in between 25^{0}Cto120^{0}C, 120 ^{0}C to 333^{0}C and finally from 333^{0}C to 1000^{0}C. The first thermal decomposition step involves elimination of entire water molecules which are 14 moles of H_2O between 25^{0}C to 120^{0}C temperature compairsing about 8.51%of weight loss of the isolated product. However from DTA exothermic peaks maxima it seems that these weight loss due to 14 H_2O moles not carried in single step but may involve two steps which is indicated by the two prominent DTA exothermic peaks maxima at 74.4^{0}C and 107.9^{0}C. On further heating from120 ^{0}C to 333^{0}C temperature, as per the TGA graph the weight loss is about 6.63 % of the total weight of the isolated product. This weight loss may be assigned to the loss of $3Na_2O$moles from the residue sample. The DTA curve for this weight loss suggested initial endothermic nature indicating unstable state of the residue,however, almost immediate after 315^{0}C heating the DTA curve accompany by sharp exothermic peak at 325.3^{0}C temperature forming meta stable product. Finally heating from 333^{0}C to1000^{0}C of the remaining residue product produce 2.94% of weight loss is recorded according to TGA graph. This loss from the product may be due to loss of one mole of MnO_2. This loss of one mole MnO_2 from the residue product indicates the unstable state of the remaining residue upto 1000^{0}C temperature,which also evident from the endothermic DTA peaks maxima at 415.16^{0}C and 499.08^{0}C supporting the phase transfer of the residue sample. Again at 658.52^{0}C and 681.56^{0}C two closely associated exothermic peaks maxima of the sample indicate the formation of expected components VO_2 and WO_3 associated together. The following flow sheet diagram of the thermal decomposition of the isolated product may be summarized as:

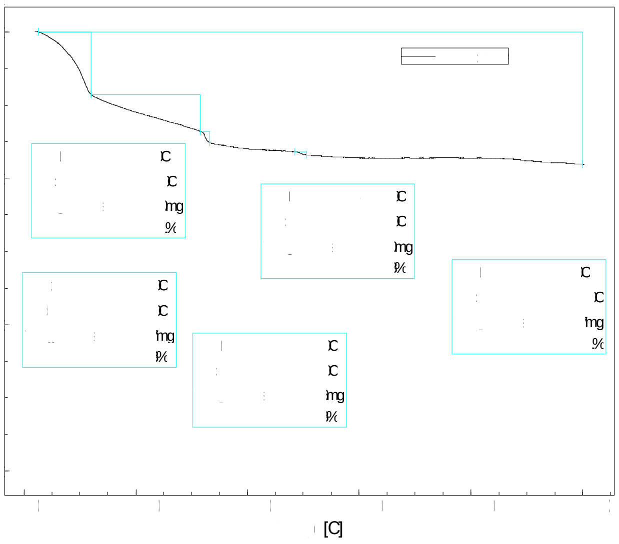


The formation of triheteropoly complex of tungsten involve metal oxy cations and their structural aspects dependon the specific polytungstate anions formed. The formation of polytungstate complex with composition $Na_6 [MnV_2W_{10}O_{39}]14 H_2O$ at required pH 4.5 and refluxed for two and half hours. After standing the concentrated refluxed solution for three days at room temperature, the product was isolated. The formation of product involves interactions of sodium tungstate anions with Mn^{+2} and V^{+5}cations in the acetic acid medium. The ratio of the three metal ions is Mn:V:W:: 1:2:10 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

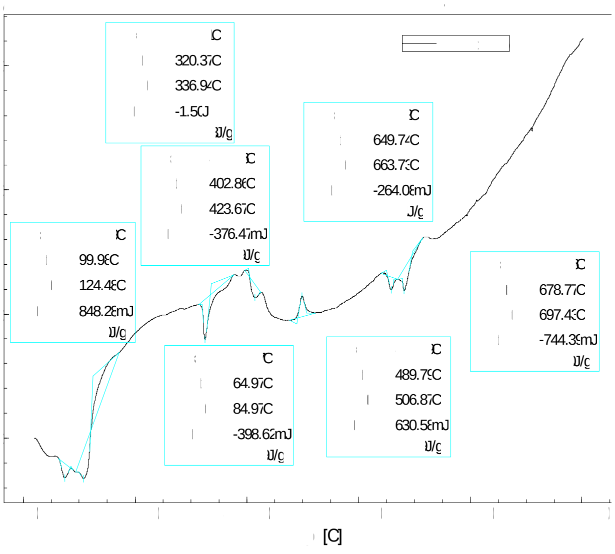


Graph 1 : IR of poly tungstate residue

in boiling water. The aqueous solution of the poly complex is ionic in nature containing sodium cations Na^+. The presence of Na^+cationconfirmed by the I.R. spectral analysis of the sample and also from the flame photometric experiment which form golden yellow flame of the sodium. The magnetic moment determination at room temperature indicates strong paramagnetic nature of the product. 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[20] The thermal analysis indicates that the thermolysis of the metaloxide complex proceeds by loosing first the water of crystallization and then subsequently the water of constitution[21] which are important components in building up the structure of heteropoly complex compounds.



Graph 2 : TGA of poly tungstate residue



Graph 3 : DTA of poly tungstate residue

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