

## Preparation of Series of Heteropoly Complex's Containing $Ce^{4+}$ and $Al^{3+}$ Cations with Isopoly Molybdate, Vanadate, Tungstate

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### Abstract

The series of heteropoly complexes were prepared by conventional reflux method in the water bath separately by taking Isopoly anions of Mo, V, W. All the products isolated were crystalline in nature appeared as dark yellow products. The chemical as well as physical methods were applied to characterize all the three isolated products the chemical analysis suggests the ionic nature of complexes since the complexes were dissolved in warm water. The inorganic wet analysis suggests ionic nature of sodium as its cation in association with complexes. The IR analysis applied for identification of group frequencies also suggests the ionic nature of sodium for the isolated complexes in solid state. The thermal analysis involving DTA and TGA support the stability of complexes in the atmosphere due to the presence of large no of water of hydration. The magnetic susceptibility analysis supports the paramagnetic nature of all the isolated series of products containing  $Al^{3+}$  and  $Ce^{4+}$  hetero cation. The structure of the heteropoly complexes synthesised may be suggested as Anderson's structure. The study of elemental analysis and molecular weight determination as well as chemical and physical analysis of the products, the following formula based on the IUPAC system may be proposed as:

1.  $Na_2 (Al_2CeMo_7O_{27}) 150H_2O$  (sodium-7-molybdo-1-cirate-2 aluminate hydrate)
2.  $Na_2 (Al_2CeV_4O_{16}) 72H_2O$  (sodium-4 -vanado-1-cirate-2 aluminate hydrate)
3.  $Na_4 (Al_2CeW_4O_{19}) 177H_2O$  (sodium-4-tungstato-1-citrate-2-aluminate hydrate)

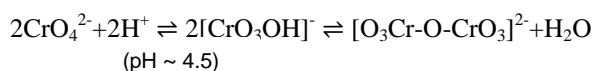
**Keywords:** Preparation; Cryoscopy; TGA and DTA thermal studies; Magnetic susceptibility; I.R. spectral studies

### Introduction

The triheteropoly complex compounds have important application in the field of absorption catalysis due to enhanced solid-state surface area. The contribution of presence of two different hetero cations further increase the surface area of the heteropoly complexes and thermal stability of the product which is evident from the thermal analysis of the entire product

synthesised [1]. The chemistry of synthesis of heteropoly complex compound was started quite earlier by Tsigdimos and co-workers [2] in the moderate acidic medium formed with the help of addition of adequate quantity of CH<sub>3</sub>COOH. As per the literature survey of preparation of triheteropoly complex compounds the preparation of the product based on mixing of proper concentration of sodium tungstate, two different hetero cations aqueous solution and the mixture solution refluxed for about two to three hours at refluxing temperature. The mixture solution after refluxing is left for two to three days and then the lustre brown coloured crystalline residue in solid state was recovered. The condition of moderate acidic medium (~ pH 4.5) is necessary since the concentrated acidic medium or even concentrated alkaline medium may decompose the poly anion of tungsten, molybdenum, or/and vanadium in their respective mono anions. The mechanism of decomposition of poly anion may be shifted through the chemistry of dichromate anion formed from chromate anion in moderate acidic medium.

Moderate acidic  
medium



The triheteropoly anion formed contains oxygen metal bridges commonly known as oxometalate bridges possessing various structures namely Anderson, Anderson-Evans, Keggin, Lindqvist, Well-Dawson, Dexter-Silverton [3] depending upon formulas of the poly hetero complex anions. The most common among the above structure is the Keggin's structure [4] having polyanion composition [M<sub>12</sub>O<sub>40</sub>]<sup>n-</sup>. The triheteropoly complex compound recovered as solid state lustre brown colour were subject to characterization for the evaluation of the components inserted including the presence of water molecules generally as water of hydration through IR studies [5-15] and the solubility of the triheteropoly complex were about examined through the TGA, DTA analysis [16-21] of the products.

## Experiment

The following experimental procedures were selected for the preparation of the three products namely sodium-7-molybdo-1-citrate-2 aluminate hydrate, sodium-4 -vanado-1-citrate-2 aluminate hydrate, sodium-4-tungstato-1-citrate-2-aluminate hydrate, the water solution 70 ml having 0.36 (M) concentration of sodium molybdate was mixed with 40 ml of aqueous solution of 0.65 molar aluminium carbonate in acidic medium formed by the addition of the 10 ml glacial acetic acid. Now the step wise 60 ml cerium sulphate solution having 0.35 M concentration was added, during addition of cerium sulphate continuous stirring was also performed. Finally, the pH of the entire mixture solution was maintained nearly 4.5 whenever the pH goes above 4.5 the glacial acetic acid were added to maintain the pH of the mixture solution. This mixture solution was refluxed for about three hours. The bright lustre yellow colour solid product was appeared in the bottom of the beaker after three days. This solid product was treated with concentrated alcohol to remove impurities associated with the solid residue and then the product was left to dry. Similarly, other two products were also synthesised by taking sodium meta vanadate and sodium tungstate all the three products now kept for characterization to assign the chemical formulas.

## Characterization

The characterization of all the three products involves the following experimental analysis such as Elemental analysis, Cryoscopic analysis, I.R. analysis, TGA and DTA analysis (TABLES 1-3).

**TABLE 1. The elemental analysis of the products gives emphasis on the elemental constituents that is the elements involve in the formation of the triheteropoly complex compound. This elemental analysis process is based on the experiments for evaluation of percentage of each element as per the Vogel's book [22].**

Elements	Percentage found			Percentage calculated
	Exp-1	Exp-2	Mean	
Sodium	1.15	1.13	1.14	1.14
Aluminium	1.33	1.35	1.34	1.34
Cerium	3.48	3.44	3.46	3.46
Molybdenum	16.6	16.64	16.62	16.62
Hydrogen	7.43	7.4	7.42	7.42
Oxygen	(By difference)		70.03	70.03

The apparent molecular weight of the product-I is 4038 as per cryoscopic method of evaluation. This 4038 is the apparent (approx) molecular weight of the complex compound. However, the formula molecular weight of the product comes to 4044 which is slightly higher than the apparent molecular weight. This higher formula weight is suggested for the synthesised product since the apparent molecular weight calculation is based on partial ionization of the complex compound.

**TABLE 2. The elemental evaluation of the second product for determination of the constituent elements of the complex compound as follows.**

Elements	Percentage found			Percentage calculated
	Exp-1	Exp-2	Mean	
Sodium	2.29	2.3	2.30	2.30
Aluminium	2.7	2.72	2.71	2.71
Cerium	7	7.02	7.01	7.01
Vanadium	10.21	10.23	10.22	10.22
Hydrogen	7.2	7.22	7.21	7.21
Oxygen	(By difference)		70.54	70.54

The molecular weight determination involving cryoscopic method suggests 1991 while formula weight of the complex comes 1996. Again, the slight higher formula weight indicates the incomplete ionization of the complex compound.

**TABLE 3. Finally, the third synthesised product elemental analysis indicates the following percentage composition of its constituent element.**

Elements	Percentage found			Percentage calculated
	Exp-1	Exp-2	Mean	
Sodium	1.04	1.02	1.03	1.03
Aluminium	1.22	1.2	1.21	1.21
Cerium	3.13	3.14	3.14	3.14
Tungsten	16.5	16.53	16.52	16.515
Hydrogen	7.7	7.73	7.72	7.72
Oxygen	(By difference)		70.38	70.38

The apparent molecular weight based on cryoscopic method evaluation was determined as 4451 which is again slightly lower than the formula weight 4456 of the product.

### Results and Discussion

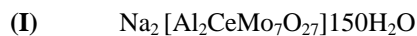
The final results for the characterization of the three products involve IR, DTA and TGA analysis. The IR graph for complex-I indicates broader peaks at  $3159\text{ cm}^{-1}$ ,  $2758.21\text{ cm}^{-1}$ ,  $2011.51\text{ cm}^{-1}$ ,  $1624.06\text{ cm}^{-1}$  and  $1408.01\text{ cm}^{-1}$  indicating the group frequencies due to the presence of water of hydration. It may be possible that some of the peaks among them may be due to the presence of water of crystallization. However, it is difficult to differentiate between the above peaks appeared due to water of hydration or/and water of crystallization. The peak appeared at  $1141.36\text{ cm}^{-1}$  may be visible due to the presence of Mo=O group frequencies again further the peaks at  $914.26\text{ cm}^{-1}$  indicated in the graph assigned to sodium cation of the complex. Another peak appeared at  $651.24\text{ cm}^{-1}$  assigned to Al-O, the  $563.21\text{ cm}^{-1}$  peak indicate the presence of Ce=O and finally the peak at  $501.49\text{ cm}^{-1}$  indicate the group frequency due to existence of Ce-Mo bond.

The IR peaks  $3443\text{ cm}^{-1}$ ,  $3282.55\text{ cm}^{-1}$ ,  $2079.26\text{ cm}^{-1}$ ,  $1631.78\text{ cm}^{-1}$  and  $1141.36\text{ cm}^{-1}$  in the IR spectral graph appeared due to the presence of water of hydration as well as water of conjugation of the dried and purified product. Again the IR peak at  $956.69\text{ cm}^{-1}$  assigned to the Na cation of the product. The shifting in sodium cation peak may be considered due to the presence of different constituent elements compared to the first product. The presence of V=O confirmed on the basis of peak appeared at  $740.67\text{ cm}^{-1}$  in the IR spectral graph. The group frequency appeared at  $617.27\text{ cm}^{-1}$  indicates the presence of Al-O bond. Finally, the  $536.21\text{ cm}^{-1}$  IR spectral peak assigned to the presence of Ce-O.

The strong broad peaks  $3456.44\text{ cm}^{-1}$ ,  $3159.40\text{ cm}^{-1}$  indicates the association of water molecules also supported by presence of two sharp peaks at  $1624.06\text{ cm}^{-1}$  and  $1400.32\text{ cm}^{-1}$  also. The appearance of  $1138.00\text{ cm}^{-1}$  may be attributed due to the presence of W=O. The peak at  $806.25\text{ cm}^{-1}$  may be due to the association of Al-O and finally the  $567.07\text{ cm}^{-1}$  small peak may be assigned for the Ce-O group frequency.

The DTA graph of the product suggest exothermal decomposition reaction for loss of water molecules and also the other minor extreme graph at  $309^{\circ}\text{C}$  and  $527.72^{\circ}\text{C}$  peak indicates the internal rearrangement of the product. The DTA peak on set at

29.29°C and peak at 68.89°C temperature range 30°C to 140°C support the loss of water of association of the product, approx 60% by weight. Another peak at 127.08°C, onset at 108.79°C supports loss of Na<sub>2</sub>O with further 1.5% loss by weight. The DTA graph supports the loss of entire water molecule associated with product by the strong exothermic peak appeared at 91.23°C which onset at 51.70°C. Loss of Na<sub>2</sub>O is supported by unnoticed small endothermic peak at about 150°C (FIG. 1-9).



32.10° C to 125°C

On set at 32.10°C

The peak maxima at

75.07°C supports loss

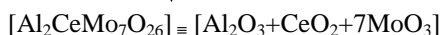
of water



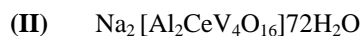
-150H<sub>2</sub>O

125°C to 525°C the

5% loss by weight



-Na<sub>2</sub>O

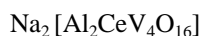


29.29°C to 140°C the

60% loss by weight

Onset at 29.29°C

Peak maxima 68.89°C



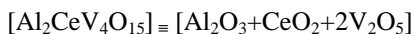
-72 H<sub>2</sub>O

125°C to 400°C the

1.5% loss by weight

Supported by DTA peak

at 127.08°C



-Na<sub>2</sub>O



22.10°C to 150°C

On set at 51.70°C

The peak maxima at

91.23°C

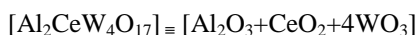


-117H<sub>2</sub>O

Loss of Na<sub>2</sub>O supported

By small endothermic

peak at about 150°C



-2Na<sub>2</sub>O

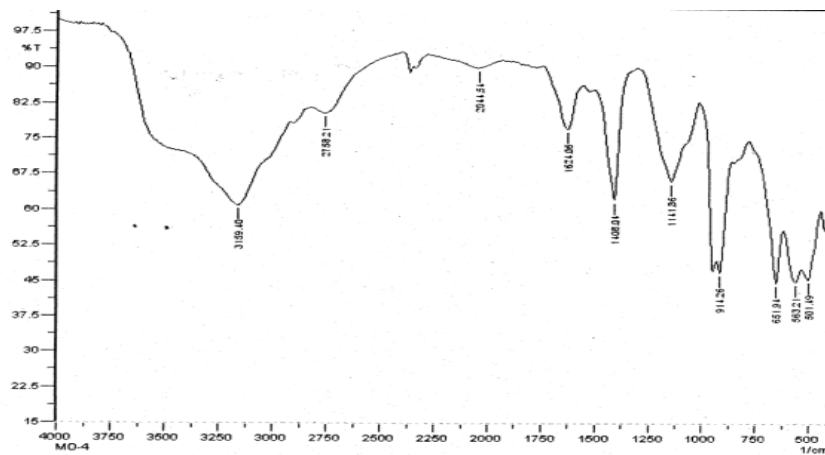


FIG. 1. IR of complex 1.

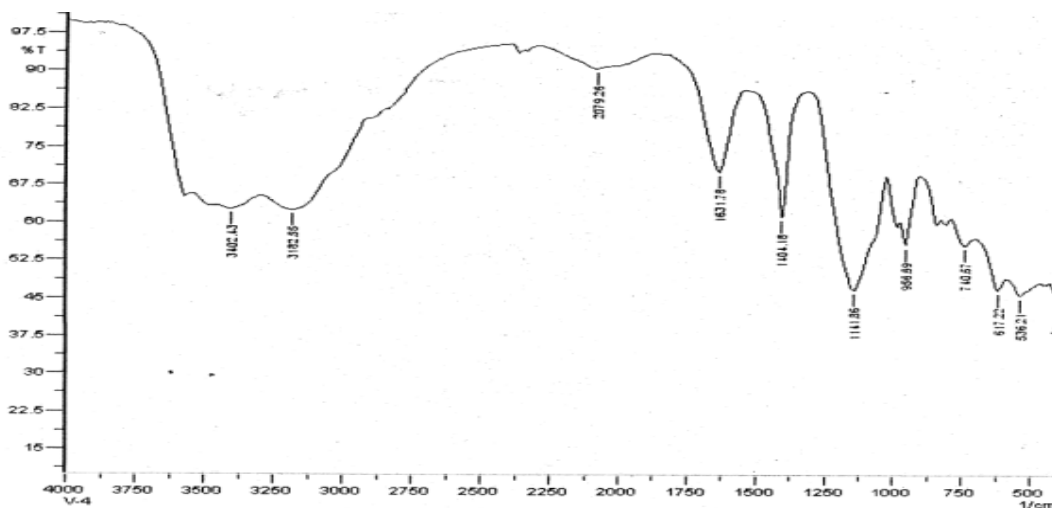


FIG. 2. IR of complex residue II.

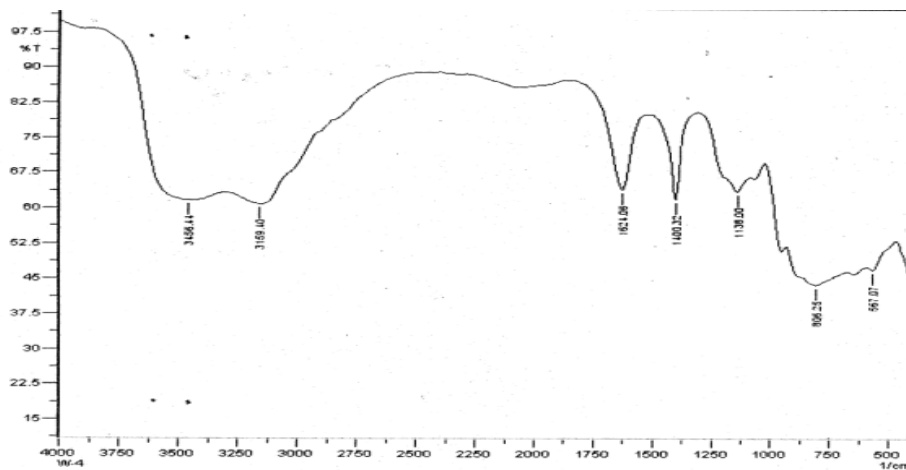


FIG. 3. IR of complex residue III.

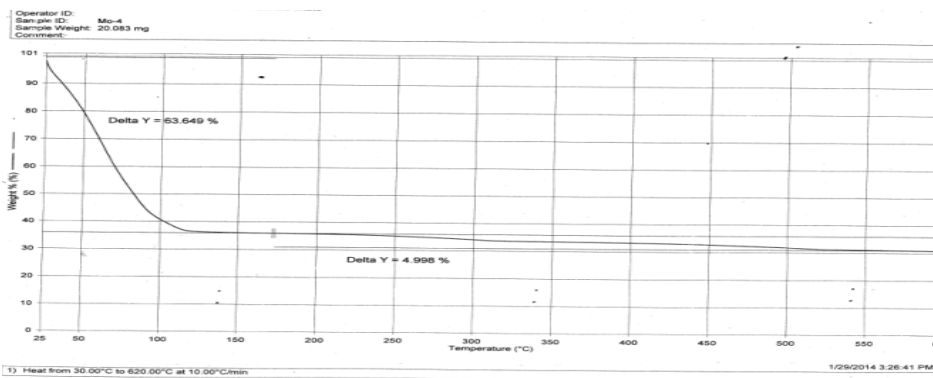


FIG. 4. TGA of complex residue I.

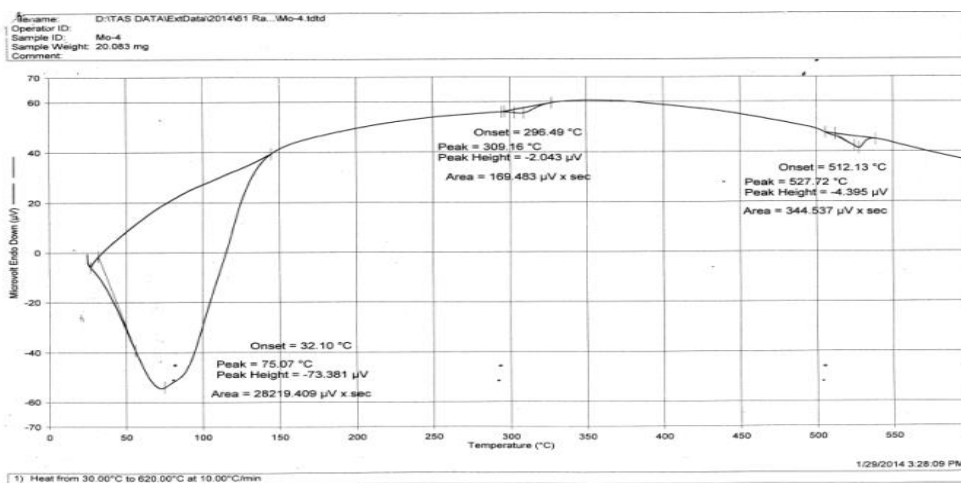


FIG. 5. DTA of complex residue I.

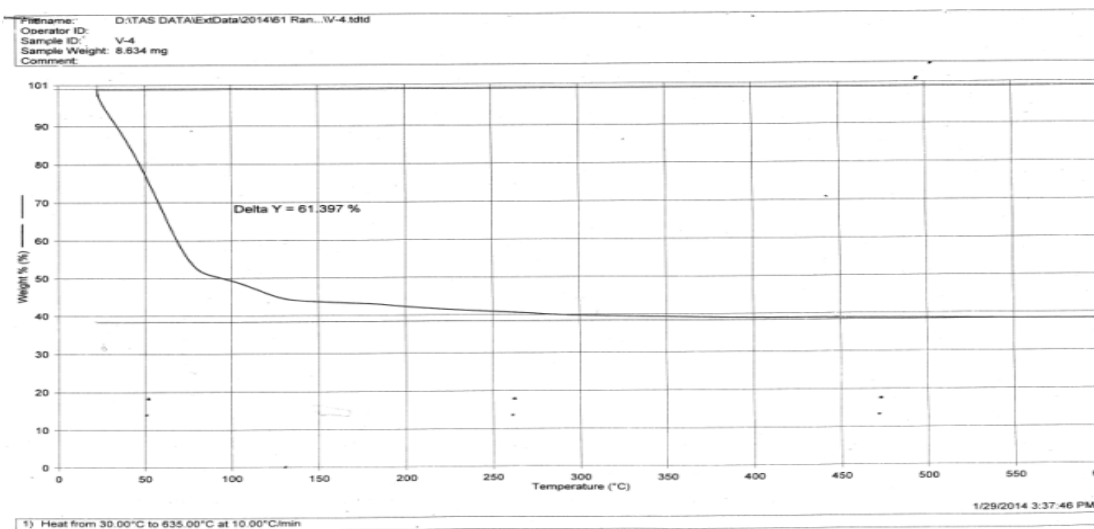


FIG. 6. TGA of complex residue II.

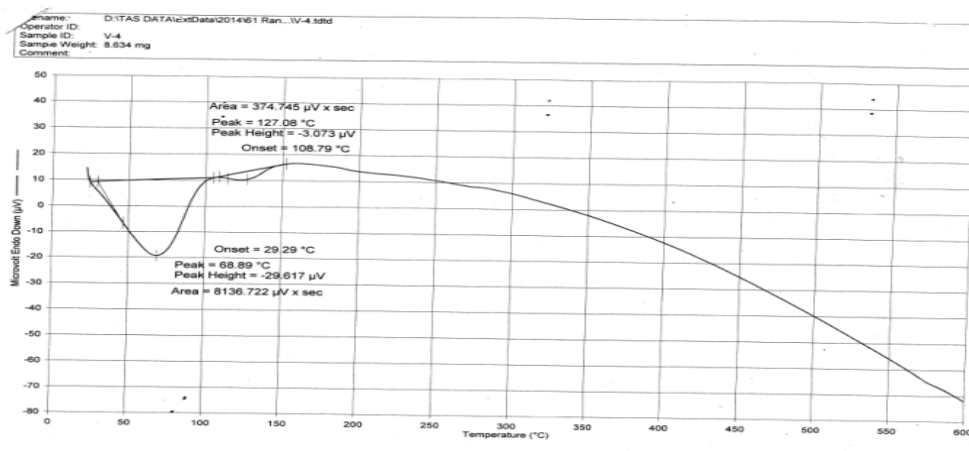


FIG. 7. DTA of complex residue II.

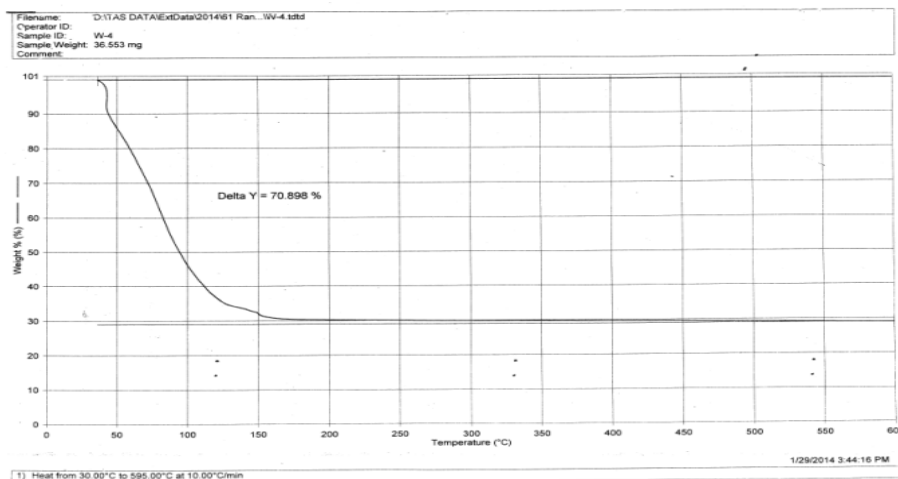


FIG. 8. TGA of complex residue III.

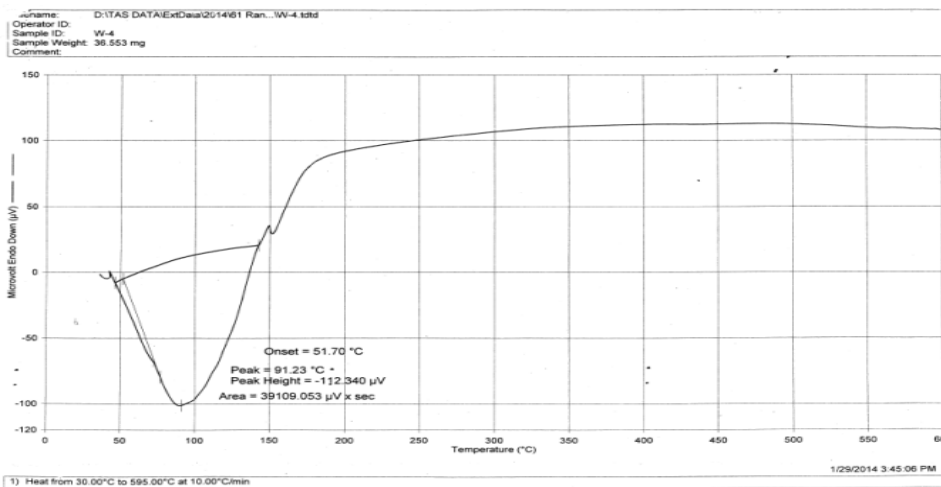


FIG. 9. DTA of complex residue III.



## Conclusion

The above analysis, results and discussion concluded on the fact that the three different triheteropoly complexes are stable in the atmospheric condition up to almost 60°C temperature. These complex compounds were recovered in the solid state in the room temperature condition. The solubility analysis of all the three different product observed as they were about insoluble in water at room temperature but completely soluble in boiling water. The association of the ionic sodium with all the three different triheteropoly complexes reveal the fact that these complex compounds are ionic in nature the association of sodium cation was confirmed on the basis of IR spectral peaks as well as also from the sodium flame photometric experiment suggesting the presence of sodium element as during the experiment he golden yellow flame is produced in the flame photometer. The magnetic moment of the three complex compounds i.e., triheteropoly complex compound by the Gouy balance method at room temperature reveal that the three different heteropoly complexes are paramagnetic in nature. The triheteropoly complexes show the curves indicating the association of water of molecules but it is not possible to evaluate the water of molecules as water of hydration or/and water of constitution however the thermal analysis curves indicate first the loss of water of crystallization and then the loss of water of constitution as the TGA graph shows the loss of water about 30°C temperature up to 150°C temperature, Finally on the basis of entire analysis involved for the characterization concluded the might be the presence of water of constitution is the basis of the building of triheteropoly compound structure.

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