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Analysis of interacted polymolybdate based on its preparation and characterization

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ABSTRACT

One new triheteropoly complex was synthesized containing two hetero cations Ni^{2+} and Co^{2+} in the polymolybdate anion having composition $[Mo_6O_{24}]$ maintaining the pH at 4.5. Product obtained was white in apperance. The IR spectral analysis of the product suggest the presence of NH_4^+, M=0, Mo-O, Ni-Co, Mo-O-Mo along with hydrogen bonded H_20 group in the complex. The molecular weight determination of the triheteropoly complex by cryscopic method was almost in accordance with the calculated value. The thermal stability of the product was studied and it was observed that the product involved multistep decomposition as per TGA graph producing about 29.988% weight loss which was also duly supported by DTA graph indicating large exothermic peak maxima at 48.34ºC. On the basis of analytical, IR spectral and thermal stability data the composition of the product is assigned as $(NH_4^+)_8\,[NiCoMo_6O_{24}]\,19H_2O$.

KEYWORDS

Triheteropoly molybdate preparation;
Cryoscopy;
IR;
Spectral analysis;
Thermal analysis.

INTRODUCTION

Isopoly and heteropoly complexes should best be categorized as Isopoly and heteropoly oxometalates as suggested by Michael T. Pope[1,2] and latter by Bernt Krabs[3]. The synthesis in based on condensation process[4-6] which leads to the formation of oxobridges by eliminations of water molecules. Such condensation reactions generally take place freely and reversibly in acidic medium. The condensation behaviour of molybdates and vanadates are basically almost similar. The heteropoly complex are named according to IUPAC system[7]. In general the heteropoly complexes have been prepared by mixing the theoretical quantifies of the required reactants in proper acidic medium followed by heating and crystallization. The DTA and TGA thermal studies of the synthesized 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 also help to fixed the position of water molecules which may be between the intersectices or at the pheripheral of the crystal. The thermal stability of the complex may be either determined by direct heat treatment[8-18] or by isothermal measurement. The characterisation of the isolated triheteropolymolybdate containing two hetroatom Ni^{2+} and Co^{2+} is based on elemental analysis, cryoscopic measurement, IR spectral studies and thermal analysis[19-21]. Which include TGA and DTA studies of the product obtained. The Mol. Wt. of the observed triheteropoly complex $(NH_4^+)_8$ [Ni Co Mo_6 O_{24}] $19H_2O$ is 1552

EXPERIMENT

$(NH_4^+)_8$ [Ni Co Mo_6 O_{24}] $19H_2O$ was freshly prepared. All other reagents used were of A.R. grade. The solutions were prepared in distilled water. The metals were estimated using an A.R. L3410 (Switzerland) atomic emission photometer and C, H and N by coleman analyser. The IR spectra (KBr) were recorded on a Perkin-Elmer 577 spectrophotometry DTA and TGA expermients were carried out on a STA 409 (West Germany) analyser.

MOLECULAR WEIGHT DETERMINATION

The molecular weight of the heteropoly complex was successfully determined by the method as has been done by Alexander[23] and by Thilo and Kriiger[24] for the molecular weight determinations of certain inorganic polyacids and polyphosphates etc. in water and molten sodium sulphate decahydrate. The determination showed the $(NH_4^+)_8$ [Ni Co Mo_6 O_{24}] $19H_2O$ to be 1552 which is in the range of fair agreement.

PREPARATION

Preparation of the triheteropoly molybdates complex involves the mixing of ammonium molybdate, nickel carbonate and cobalt carbonate in the ratio 6:1:1 in aqucous solution with 10 ml of glacial acetic acid. After complete mixing of ammonium molybdate solution, the pH of the mixture was further adjusted to 4.5 pH by adding about 5 ml of glacial acetic acid. Now the mixture solution was refluxed for two hours and thirty minutes. The solution was cooled and left for crystallisation. After three days, the white coloured solid residue was obtained.

ELEMENTAL ANALYSIS

The elemental analysis was performed on the basis of prescribed method[22] (Vogel) As per the percentage composition of the synthesized triheteropolymolybdate. The proposal of composition of the complex may be given as 6:1:1. The apparent molecular weight of the prepared triheteropoly molybdate complex determined by cryscopic method was found to be $(NH_4^+)_8$ [Ni Co Mo_6 O_{24}] $19H_2O$. Its observed molecular weight to be 1552.

Elements	Percentage found			Mean	Percentage Calculated
	Exp-1	Exp-2	Exp-3		
Nitrogen	7.08	7.27	7.29	7.28	7.20
Nickel	3.74	3.76	3.77	3.76	3.73
Cobalt	3.70	3.78	3.78	3.78	3.73
Molybdenum	37.10	37.16	37.18	37.16	37.06
Hydrogen	4.10	4.09	4.11	4.10	3.98
Oxygen By Difference				43.92	44.30

RESULT

IR spectral result of polymolybdate products

$(NH_4^+)_8$ [Ni Co Mo_6 O_{24}] $19H_2O$

Infrared spectral of some heteropoly compounds have been examined by Tsigdinos[8], Brown[9] and Sharpless et al[10] Infrared spectra of the above mentioned heteropoly compounds in KBr pellets have been recorded from 3533.59 to 692.44 cm^{-1} on a grating IR spectrophotometer as shown in (Figure 1). Perkin-Elmer Model 577 the peaks at 3533.59 correspond to those of water12. The peaks at 2115.91 cm^{-1} assigned as H_2O. The peaks at 1546.91 cm^{-1} can be attributed to $\delta(H_2O)$. The sharp peaks at 1417.58 to 1344.38 cm^{-1} may be attributed to the presence of N-H bond[2]. Deformative frequency of the ammonium ion is also known to be active in 3533.59 – 2115.91 cm^{-1} region. So the broad band shown by these compounds in the 3533.59 to 2115.59 cm^{-1} region may be due to lattice water as well as ammonium ion. Probable assignments of peaks at 1024.20 cm^{-1} is for Mo-O stretching band. In IR spectrum assigned to (Mo=O) stretching band and sharp band at 945 cm^{-1} to NH_4^+ rocking band. The strong band at 692.44 cm^{-1} can be assigned to Mo O Mo stretching vibration.

$(NH_4^+)_8$ [Ni Co Mo_6O_{24}] 19 H_2O

Temperature Range 25ºC to 75ºC Wt. Loss 21% ↓ **$-19\ H_2O$**

$(NH_4^+)_8$ [Ni Co Mo_6O_{24}]

Temperature Range 75ºC to 300ºC Wt. Loss 8.745% ↓ **$-8\ NH_4^+$**

[Ni Co Mo_6O_{24}]

THERMAL STUDIES INVOLVING TGA AND DTA RESULT

The TGA curve of the isolated polymolybdate complex (Figure 2) and (Figure 3) indicate multisteps of thermal dissociation process in between 25ºC to 75ºC, 75ºC to 300ºC and finally from 300ºC to 600ºC. The first thermal decomposition step involves elimination of H_2O molecules. The measure weight loss of the product at 25ºC to 75ºC is about 21%. The measure weight loss of the product is accompanied by phase transfer as indicated in the DTA graph suggesting exothermic peak maxima at 48.34ºC temperature having area

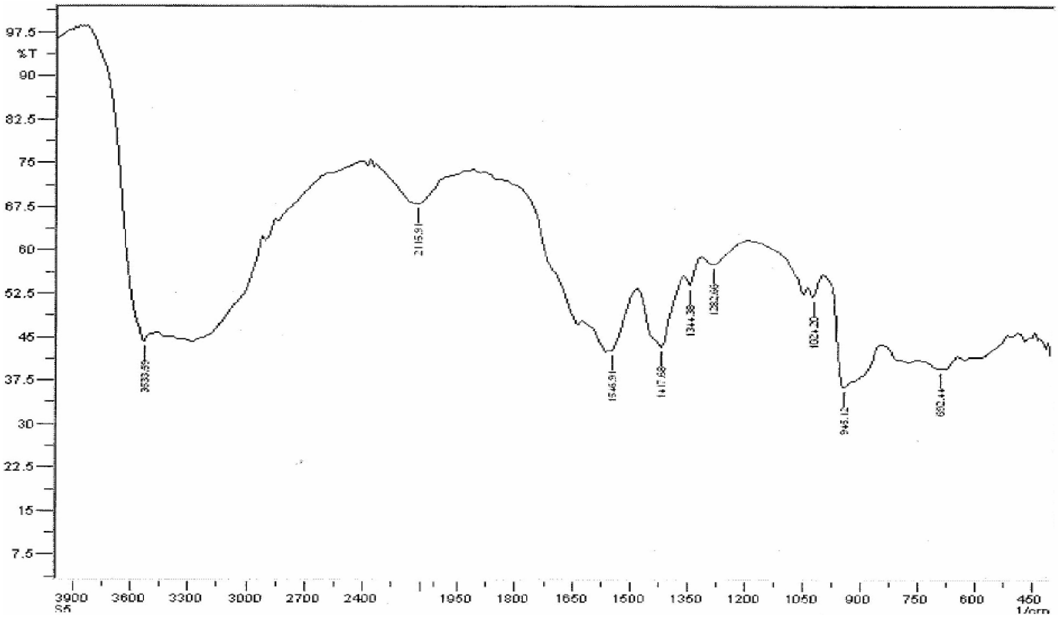
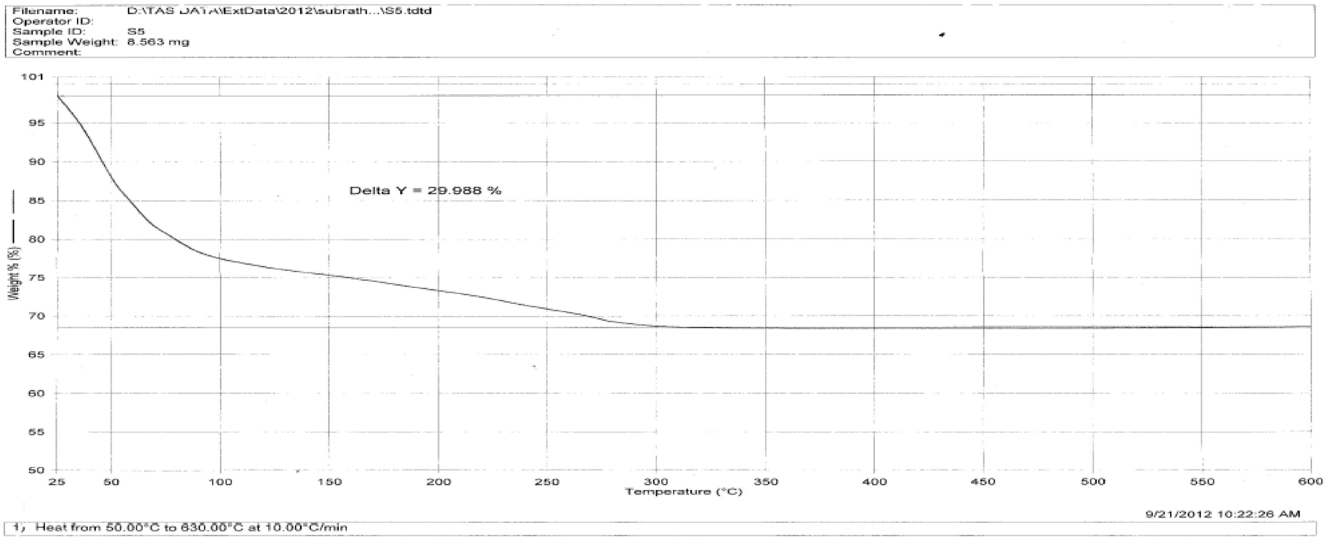


Figure 1 : FTIR graph of polymolybdate



Filename: D:\TAS DATA\ExtData\2012\subrath...\S5.tdtd
Operator ID:
Sample ID: S5
Sample Weight: 8.563 mg
Comment:

1) Heat from 50.00°C to 630.00°C at 10.00°C/min

Figure 2 : TGA graph of polymolybdate

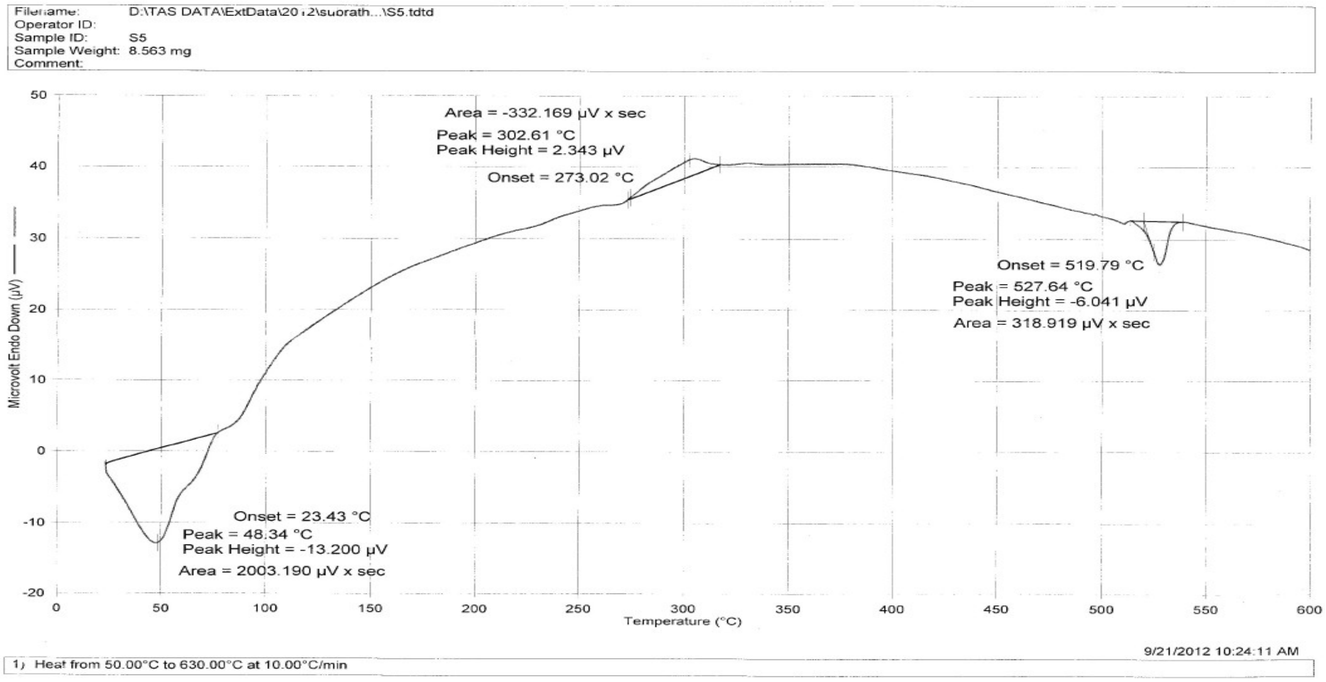


Figure 3 : DTA graph of polymolybdate

2003.190 μν × second and peak height (-13.200 μν). In second thermal decomposition involves elimination of 8 NH_4^+ molecules. The weight loss of the product between 75ºC to 300ºC is about 8.745%. The weight loss of the product is accompanied by phase transfer as indicated in the DTA graph suggesting small endothermic peak maxima at 302.61ºC temperature having area –332.169 μν × second and peak height 2.343 μν. The residue product after 300ºC heating upto 600ºC involve no further weight loss. The composition of the residue product after 300ºC to 600ºC temperature may be attributed as $[NiCoMo_6O_{24}]$. The small exothermic peak maxima is also observed at 527.64ºC which may be attributed to minor phase transfer of the residue product to settle for the long higher temperature range.

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