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Synthesis and Characterisation of Some Heteropoly Oxomolybdates

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In present studies, some new heteropoly oxomolybdates have been prepared. Rigid physico-chemical condition for the preparation of each hetero poly complexes have been established separately by studying pH measurement. Chemical method for analysis of the compounds have been corroborated by colorimetric and flame photometric analysis. Weissenberg's X-ray crystal diffraction technique has been successfully applied to determine the actual molecular weights of some crystalline compounds. Nature of bonds and water molecules was characterized by TG, DTA and IR analysis.

Key Words: Synthesis, Characterisation, Heteropoly oxomolybdates.

INTRODUCTION

An important class of mixed 12-heteropoly anion involving the replacement of a hetero atom (vanadium) in molybdo phosphoric acid have been prepared by the Tsigdinos *et al.*[1]. The solution phase studies have been extensively studied by Spitsyn *et al.*[2]. A molybdovanadoselenious acid $H_6[SeV_2Mo_{10}O_{40}]\cdot 18H_2O$ has been prepared and characterized[3]. Catalytic and industrial application of some organo derivatives of heteropoly molybdates have recently been reported in the literature[4,5]. The present communication reports the preparation of sodium and ammonium salt of the anion of the type $[XYMo_{11}O_{40}]^{9-}$ and $[WZMo_{11}O_{40}]^{10-}$, where X = La, Y = Ni or Co, W = Cu, Z = Zn or Co.

EXPERIMENTAL

The concentration and pH of the reactant mixture are two important factors on which synthesis of heteropoly compounds depend. Here some new trihetropoly molybdates 1:12 series were synthesized[6,7] at 3.3-3.8 pH. The chemicals used were of AR grade. The solutions were prepared in distilled water. The metals were estimated by ARL 3410 atomic absorption spectrophotometer.

C, H, N, using Coleman analyzer. The IR spectra were recorded on a perkin-Elmer 577 spectrophotometer. Thermal analyzer by NETZSCH STA-

409 analyzer. X-ray diffraction by unicam weissenberg instrument as well as by X-ray diffractometer.

Ammonium molybdo-nickelo-lanthanate(III): 48 g (38 mmol) of ammonium molybdate was dissolved in 200 mL water. To this 25 mL nickel nitrate (1.025 g, 3.5 mmol) and 25 mL of lanthanum nitrate (1.51 g, 3.5 mmol) was added one by one with constant stirring. Finally, pH 3.3 to be maintained constant by adding 48 mL of acetic acid to the reaction mixture. The reaction mixture was refluxed at a control temperature for 2 h in a round bottom flask fitted with an air condenser. The mixture was reduced to two third of its original volume on a water bath and left for crystallization. Light green crystal were collected after 4 to 5 d from the mother liquor and washed with ethanol and dried.

Yield (28.25 g) (Found : La, 5.25; Ni, 2.70; Mo, 42.77; H, 3.46; N, 5.07 $(NH_4)_9$ $[LaNi Mo_{11}O_{40}]\cdot 22H_2O$ calculated for: La, 5.66; Ni, 2.40, Mo, 43.00; H, 3.26, N, 5.13 %)

Sodium molybdo-cobalto-lanthanate(III): An aquous solution 30 cm^3 containing lanthanum(III) nitrate (1.58 g, 3.67 mmol) was added with constant stirring to cobalt nitrate (1 g, 3.67 mmol) solution 25 mL. The mixture was warmed on a water bath for 0.5 h. This solution was added in small installments (2 mL) to ammonium molybdate (50 g, 40 mmol) dissolved in water (200 mL) with stirring. The mixture was again heated on a water bath for 3 h. The content was reduced about 100 mL the resulting crystal appeared after 3 d were air-dried and washed with ethanol.

(Found: Na, 7.98; La, 5.23; Co, 2.26, Mo, 42.89; H, 1.58 % $Na_9[LaCoMo_{11}O_{40}]\cdot 22H_2O$ calculated for: Na, 8.28; La, 5.56; Co, 2.36; Mo, 42.29; H, 1.76 %)

Ammonium molybdo-zinco-cuprate (II): 25 mL of copper sulphate solution (1.25 g, 5 mmol) was added slowly with constant stirring with 25 mL of zinc sulphate solution (1.435 g, 5 mmol). This reaction mixture was added in small instalments to 200 mL of ammonium molybdate (65 g 52 mmol) kept in a round bottom flask. Finally, pH maintained by adding 40 mL of acetic acid to the remaining mixture. The reaction mixture was refluxed at a controlled temperature for 2 h. Then it is reduced to about 75 mL on a water bath and left for crystallization. Light blue colour crystals were collected after 3 d from the mother liquor and washed with ethanol dried. (Yield 29.89 g).

Found: N, 5.82; Cu, 2.49; Zn, 2.61; Mo, 43.22, H, 3.66; $(NH_4)_{10}[CuZnMo_{11}O_{40}]\cdot 24H_2O$, calculated for N, 5.74; Cu, 2.6 Zn, 2.66; Mo, 43,34; H, 3.61 %).

Sodium molybdo-cobalto cuprate(II): Copper sulphate (1.25 g, 5 mmol) in 25 mL aqueous solution was added slowly to 25 mL of cobalt chloride (1.2 g, 5 mmol) solution. The mixture was warmed on a water bath for 0.5 h. To this solution of 200 mL ammonium molybdate solution (53.9 g, 4.4 mmol) was added slowly with constant staring. 40 mL of acetic acid was added to the reaction mixture to maintain pH 3.33. The mixture was refluxed on a water bath for 4 h and reduced the volume one fourth of its original volume. After 3-4 d light blue crystals are separated from the mother liquor and washed with ethanol. Yield (27.25 g) (Found: Na, 9.02; Cu, 2.66; Co, 2.47, Mo, 42.05; H, 2.13, calculated for : Na, 9.27; Cu, 2.55; Co, 2.37, Mo, 42.5, H, 1.93 %.

RESULTS AND DISCUSSION

The formation of $(NH_4)_9[LaNiMo_{11}O_{40}]\cdot 22H_2O$, $Na_9[LaCoMo_{11}O_{40}]\cdot 22H_2O$, $(NH_4)_{10}[CuZnMo_{11}O_{40}]\cdot 24H_2O$ and $Na_{10}[CuCoMo_{11}O_{40}]\cdot 24H_2O$ were corroborated by thermometric titrimetry[8] as discussed earlier[9]. The molar proportion of reactant Mo:X:Y (11:1:1) were required for the formation of these compounds at which the pH remain constant (3.5-3.8).

Analytical methods depending on chemical (volumetric and gravimetric) and spectrophotometric methods have been applied to determine the percentage compositions of each individual compounds to determine molecular formula.

Infrared spectra of all these samples pressed in KBr Pellets have been recorded in 4000-400 cm^{-1} region Pye-unicam sp 2000 model double beam infrared spectrophotometer using gratings giving a resolution of 0.6 to 1.5 cm^{-1}. The results of IR spectra are listed in the Table-1. The assignment of key IR bands and various modes of water molecules[10] are listed in Table-1.

TABLE-1
KEY IR ASSIGNMENT (cm^{-1}) OF SOME HETEROPOLYOXOMOLYBDATES

Compd.	$\nu(H_2O)$	$\delta(H_2O/NH_3)$	M´-O	$\pi(H_2O)$	M-O-M	M-O	X-O
1. $(NH_4)_9[LaNiMo_{11}O_{40}]\cdot 22H_2O$	3540m 3468b	1660s 1420s	-	690s	940s	-	420m
2. $Na_9[LaCoMo_{11}O_{40}]\cdot 22H_2O$	3500b 3280m	1660s	1580s	660m	945s 915s	800m	-
3. $(NH_4)_{10}[CuZnMo_{11}O_{40}]\cdot 24H_2O$	3260s	1575m	-	495m	910m 905s	635s	370s
4. $Na_{10}[CuCoMo_{11}O_{40}]\cdot 24H_2O$	3530m	1625s	435m	625b	925s	890s 885s	360s

For comp. 1 and 2, M' = La, Co and Ni; For comp. 3 and 4 M' = Cu, Zn and Co.

The thermal decomposition temperature of $(NH_4)_{10}[CuZn\ Mo_{11}O_{40}]\cdot 24H_2O$ and $Na_{10}[CuCoMo_{11}O_{40}]\cdot 24H_2O$ (where Cu^{2+} or Zn^{2+} and Co^{2+} were acts as hetero atom), found to be 375 ± 10ºC. Thermal stability of the

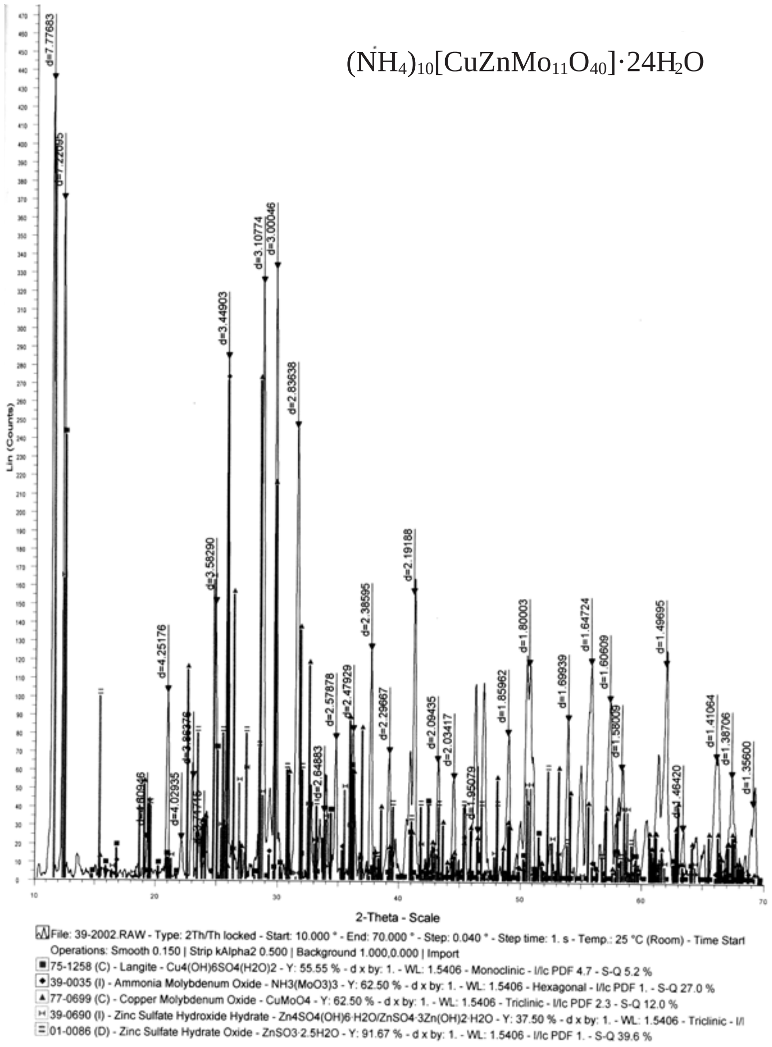

Fig. 1.

compounds ascertained by endothermic peaks DTA curves and insolubility of the compounds in water was increased from 375 ± 10ºC to 450 ± 10ºC. The first large endothermic peaks were observed in DTA within the range of 140 ± 20ºC for all the compounds which indicated the loss of peripherial water molecules, which were confirmed by the corresponding loss of weight of the compounds in TGA. At 450 ± 50ºC, sharp endothermic peaks were recorded followed by loss in weight complete decomposition of the compound to the corresponding oxides. The exothermic peaks at high temperature indicate the total loss of water of constitution of the compounds followed by the decomposition of the heteropoly oxometallic anionic cage. These were confirmed by observing the physical change in colour of the compounds and total insolubility of the last residual products in water.

The methods which are used for X-ray analysis[11,12] of compounds are crystal diffraction and powder diffraction studies. The X-ray powder diffraction using. CuKα radiation (λ = 1.5412 Å) of $Na_9[LaCoMo_{11}O_{40}]\cdot 22H_2O$ showed I/I' - d value 28 corresponding to the inter planer distance 15.2 Å. The 100 point I/I' corresponds to the d-value 12.4 Å. For $Na_{10}[CuCoMo_{11}O_{40}]\cdot 24H_2O$ using CuKα radiation (λ = 1.541 Å) showed I/I' 32 corresponding to the inter planner distance 14.3 Å. The 100 point I/I' corresponds to the d value 11.7 Å. The d-value can be calculated by using ($\eta\lambda = 2d \sin\theta$) from X-ray diffraction (Fig. 1).

The density of the compound was determined by floation method using carbon tetrachoride-bromoform mixture (D_m = 1.66 M Z / V) salt cryoscopy technique for molecular weight determination of sodium and ammonium salt of oxomolybdates ($Na_2SO_4\cdot 10H_2O$-$Na_2SO_4\cdot H_2O$) gave approximate result. The value obtained tally with the calculated anionic formulae weights. (1894 amu, 1889 amu, 1824 amu, 1818 amu).

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