

Synthesis and characterisation of two mixed polyoxomolybdates

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Abstract: The synthetic conditions of formation, preparation and analysis of two new mixed triheteropoly compounds have been carried out by pH measurement, thermometric titrations, chemical and atomic emission spectral methods. The compounds were finally characterised by UV-Visible, IR, DTA, TGA, DTG and X-ray diffraction methods.

Keywords: Oxometallates, polyoxoanion

Introduction

The synthetic methodology and techniques for the polynuclear heteropoly oxometallates are too different from other branches of coordination chemistry of metal clusters. A large potential field have been provided by the extensive class of polyoxoanion formed by transition metal of group V and VI. As heteropoly and isopoly acids with polyanions have been known and investigated for more than a century in aqueous solution, vanadium, molybdates, tungstates and to smaller extent niobates, tantalates and chromates undergo complex hydrolysis polymerisation reactions upon acidification. The major solute species generated by such reactions are the so called isopolyanions of which heteromolybdate $\text{Mo}_7\text{O}_{24}^{6-}$ are well characterised examples. The metal atoms in all these compounds can be considered to be occupying interstices in close packed arrays of oxide ions. [1]

In polyoxomolybdates, vanadates and tungstates, anions in which the metal atoms occupy sites of approximately C_{4v} symmetry with one terminal oxygen each are reducible in reversible one or two electron step to mixed valence polyanions (heteropoly blues).

Heteropoly blues are class of mixed valence complexes, which are obtained by reduction of isopoly and heteropoly vanadates and Molybdates. [2] The redox chemistry of these anions has been elucidated as discrete anions with general formula [3-7], $\text{X}_a\text{Z}_b\text{O}_c\text{H}_d^{n-}$ and $\text{Z}_b\text{O}_c\text{H}_d^{n-}$ respectively.

The polyoxomolybdates of sodium metal with niobium and tantalum as heteroatom and with terminal oxygen atom are reducible by one or two electron steps to mixed valence polyanions [8,9] called heteropoly blues. It has been established that in heteropoly blues, the valence electrons are trapped on a single metal atom. In literature [10,11] there are direct evidence for the intervalence charge transfer upon optical and ESR spectra. As a part of our investigation of polyoxomolybdates, the present work deals with the preparation and characterisation of sodium salt of two mixed triheteropoly molybdovanadoniobate and molybdovanadotantalate.

Experimental

All the reagents used were of AR grade and BDH mark. The solution of sodium hexaniobate ($\text{Na}_7\text{HNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$) and sodium hexatantalate ($\text{Na}_7\text{HTa}_6\text{O}_{19}\cdot 16\text{H}_2\text{O}$) were freshly prepared [10] in distilled water. The metals were estimated using an A.R.L 3410 (Switzerland), atomic emission photometer and C, H by coleman analyser. The IR spectra (KBr) were recorded on a Perkin-Elmer 577 spectrophotometer. The X-ray data were recorded on a D- 500/501 (Siemen) instrument. DTA, DTG and TGA experiments were carried on STA 409 (West Germany) analyser.

Synthesis of Sodium 10-molybdo 2-vanadoniobate $\text{Na}_5[\text{NbV}_2\text{Mo}_{11}\text{O}_{40}] 18\text{H}_2\text{O}$

The studies or the condition of formation of this compound has revealed that on addition of 45 mL of 0.008 M aqueous solution of sodium metavanadate with aqueous solution of 45 mL of 0.007 M Sodium orthoniobate and added 10 mL of glacial acetic acid. The mixture of these solution was gradually added each turn 2mL to the 80 mL of 0.025 M Sodium molybdate aqueous solution. The pH value of the solution gradually decreased which became constant at 2.80 by the addition of 64 mL of the mixture solution and remained constant upto addition of 74 mL of mixture solution. The molar concentration of reactant molecule in plateau range is 1:2:10 = Nb: V: Mo.

For higher yield of product, the multiplied number of reactants would be taken in same ratio.

0.3 g, 2.459 mmol sodium metavanadate dissolved in 30 mL water was added to 30 mL aqueous solution containing 0.3 g, 0.225 mmol sodium orthoniobate. This mixture solution was added with 70 mL aqueous solution containing 3.64 g 20.22 mmol molybdic acid with constant stirring. Acetic acid was added in regular intervals to maintain the pH 2.70 to 2.85. The mixture was taken in a high-necked round bottom flask and refluxed about 4 hours fitted with air condenser. After the reflux, the volume of mixture solution was reduced one third of its original volume by heating on a water bath. Then cooled and left for crystallisation in a small beaker. After 36 hours it started to precipitate which was filtered after complete crystallisation. The pale-yellow powder compound formed was filtered from its mother liquor, washed with ethanol and recrystallisation by hot water to get fine shining crystal. (Yield 2.20 g), dried and kept in weighted tube in a dessicator for the analysis of the elements present in the complex.

Sodium 10-molybdo 2-vanadotantalate $\text{Na}_5[\text{TaV}_2\text{Mo}_{10}\text{O}_{40}] 24 \text{H}_2\text{O}$

For the preparation of the compound sodium metavanadate, sodium orthotantalate and molybdic acid were used as starting materials. On the basis of the studies for previous compound, 45 mL 0.008 M solution of sodium metavanadate, 45 mL 0.006 M aqueous solution of sodium orthotantalate and 10 mL of glacial acetic acid was taken in a burette. The mixture solution was gradually added each turn 2 mL to 80 mL 0,025 M aqueous solution of molybdic acid. The pH value of this solution was gradually decreased and after the addition of 68 mL of mixture solution it was constant at pH 3.15 which remained constant upto the addition of 78 mL mixture solution. The multiplied amount of the reactant was taken for the higher yield of the product.

0.24 g, 1.96 mmol sodium metavanadate dissolved in 30 mL water, mixed with 30 mL aqueous solution containing 0.24 g, 0.13 mmol sodium orthotantalate. The mixture solution was then added in 80 mL aqueous solution of molybdic acid containing 2.88 g, 16 mmol in the same process of the previous compound.

The bright orange crystal obtained, were washed with ethanol and dried (yield 2.15 g). The compound was preserved for further analysis.

Results and discussion

The conditions of formation of the sodium salt of heteropolyoxomolybdates containing niobium, vanadium and tantalum as a heteroatom of general chemical formula $\text{Na}_5[\text{ZV}_2\text{Mo}_{10}\text{O}_{40}] \cdot x\text{H}_2\text{O}$ (where Z= Nb or Ta) have been carried out by pH measurement and thermometric titration as discussed in our earlier communications [14]. The approximate range of pH at which the compound could be isolated was found to be 2.80 to 3.15. The metal contents of the compound were determined by standard chemical methods and the results of such observations were corroborated by ICP atomic emission spectra. The aqueous solution of the compound $\text{Na}_5[\text{NbV}_2\text{Mo}_{10}\text{O}_{40}]18\text{H}_2\text{O}$ and $\text{Na}_5[\text{TaV}_2\text{Mo}_{10}\text{O}_{40}]24\text{H}_2\text{O}$ were examined spectrophotometrically in various buffer solution to investigate their stability. The distinct characteristic absorption maxima at 320 nm and minima at 305 nm are observed for $\text{Na}_5[\text{NbV}_2\text{Mo}_{10}\text{O}_{40}]18\text{H}_2\text{O}$ in 0.01 M K_2SO_4 -0.02 M KHSO_4 buffer solution (pH = 2.8). When the absorption spectrum of the compound was taken in 0.1 M CH_3COOK -0.1 M CH_3COOH buffer (pH = 3.1) and the absorption maxima remain almost unchanged. Thus, from these observations it is clear that the complex anion which is stable at pH 2.5 (K_2SO_4 - KHSO_4) buffer obeyed Beer's law to 5% in the concentration range of 10^{-2} to 10^{-4} M.

In these compounds, Mo-O-Mo bridging shows sharp IR bands at $780\text{-}840\text{ cm}^{-1}$ (Fig 1) and due to independent Mo-O stretching vibrations shows strong bands at $830\text{-}910\text{ cm}^{-1}$ (Fig. 1). The bands of Mo-O and Mo-O-Mo are distinguishable although observed nearly at the same region. [11] The medium bands in the range $920\text{-}980\text{ cm}^{-1}$ (Fig 2) may be assigned to Nb-O stretching vibration. In octahedral coordination [12] and those in the range of $480\text{-}452\text{ cm}^{-1}$ corresponds to the central Nb-O linkage. The peaks at $3420\text{-}3310\text{ cm}^{-1}$ and $3180\text{-}3100\text{ cm}^{-1}$ region (asymmetric, symmetric O-H stretching) corresponds to those of peripheral water molecules. The peaks at $1640\text{-}1600\text{ cm}^{-1}$ corresponds to H-O-H bridging mode of water. Whereas those in the lower frequency region $645\text{-}580\text{ cm}^{-1}$ are due to O-H vibration of lattice water.

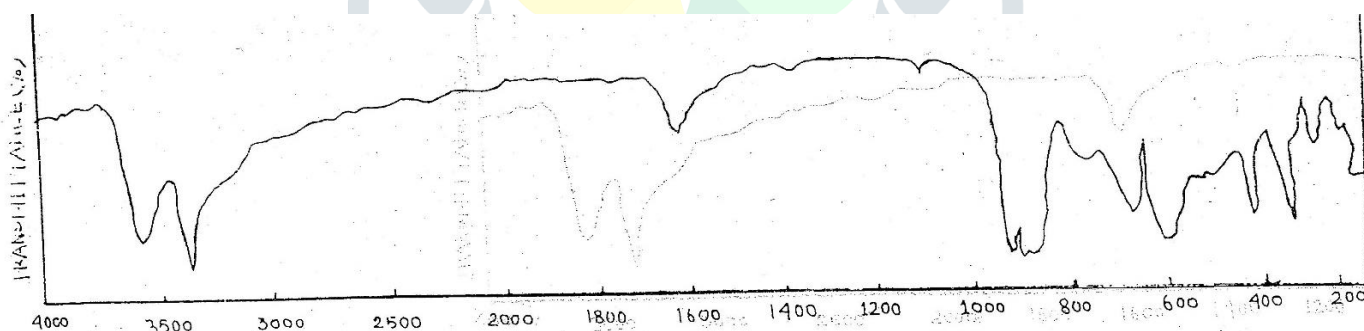


Fig. 1: FTIR spectrum of $\text{Na}_5[\text{NbV}_2\text{Mo}_{10}\text{O}_{40}]18\text{H}_2\text{O}$

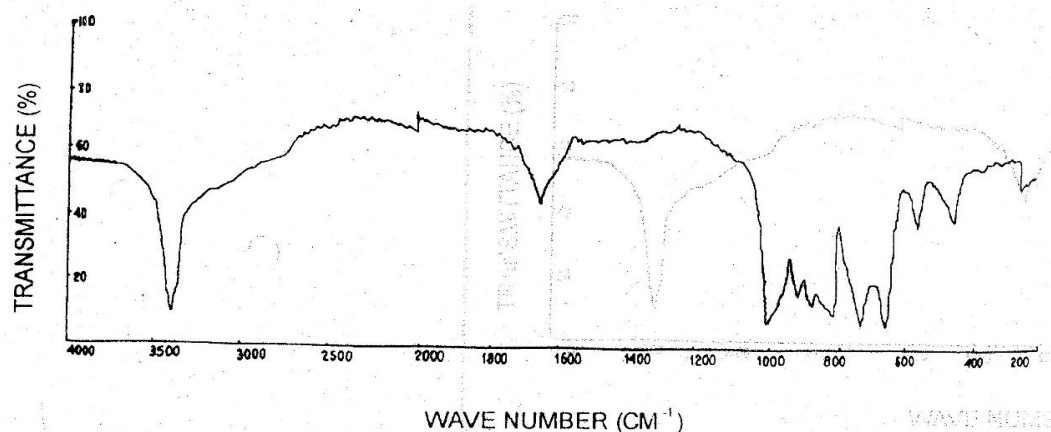


Fig. 2: FTIR spectrum of $\text{Na}_5[\text{TaV}_2\text{Mo}_{10}\text{O}_{40}]24\text{H}_2\text{O}$

The preliminary X-ray data of these crystalline sample were recorded by rotation and Weissenberg photographs. The densities were determined by floatation method by using carbon tetrachloride-bromoform mixture. The crystal data of the compounds are as follows:

For $\text{Na}_5[\text{NbV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 18\text{H}_2\text{O}$:

Crystal structure -Orthorhombic

$a = 1.4102 \times 10^1 \text{ \AA}$, $b = 1.25 \times 10^1 \text{ \AA}$, $c = 1.3525 \times 10^1 \text{ \AA}$

$\alpha = \beta = \gamma = 90^\circ$

$V = 2.32005 \times 10^3 \text{ \AA}^3$ Space group- $D_{2h}^{27}\text{Pnnn}$; $Z = 2$; $\rho_{\text{obs}} = 3.26 \text{ gdm}^{-3}$; $\rho_{\text{calc}} = 3.30 \text{ gdm}^{-3}$;

$M_{\text{obs}} = 2.252 \times 10^3 \text{ gmol}^{-1}$ against $M_{\text{calc}} = 2.3528 \times 10^3 \text{ gmol}^{-1}$

For $\text{Na}_5[\text{TaV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 24\text{H}_2\text{O}$:

Crystal structure - Hexagonal

$a = 1.1750 \times 10^1 \text{ \AA}$, $b = 1.1760 \times 10^1 \text{ \AA}$, $c = 1.4850 \times 10^1 \text{ \AA}$

$\alpha = \beta = \gamma = 90^\circ$

$V = 2.21080 \times 10^3 \text{ \AA}^3$, $Z = 2$, $\rho_{\text{obs}} = 4.02 \text{ gdm}^{-3}$, $\rho_{\text{calc}} = 4.37 \text{ gdm}^{-3}$,

$M_{\text{obs}} = 2.758 \times 10^3 \text{ gmol}^{-1}$ against $M_{\text{calc}} = 2.81703 \times 10^3 \text{ gmol}^{-1}$

The thermogravimetric analysis [14] was performed by taking 25 mg of the sample compound at constant heating rate of 10K min^{-1} , which have been carried out in air using alumina crucible by taking keoline as reference material and the TG data is given in Fig. 3 and Fig.4.

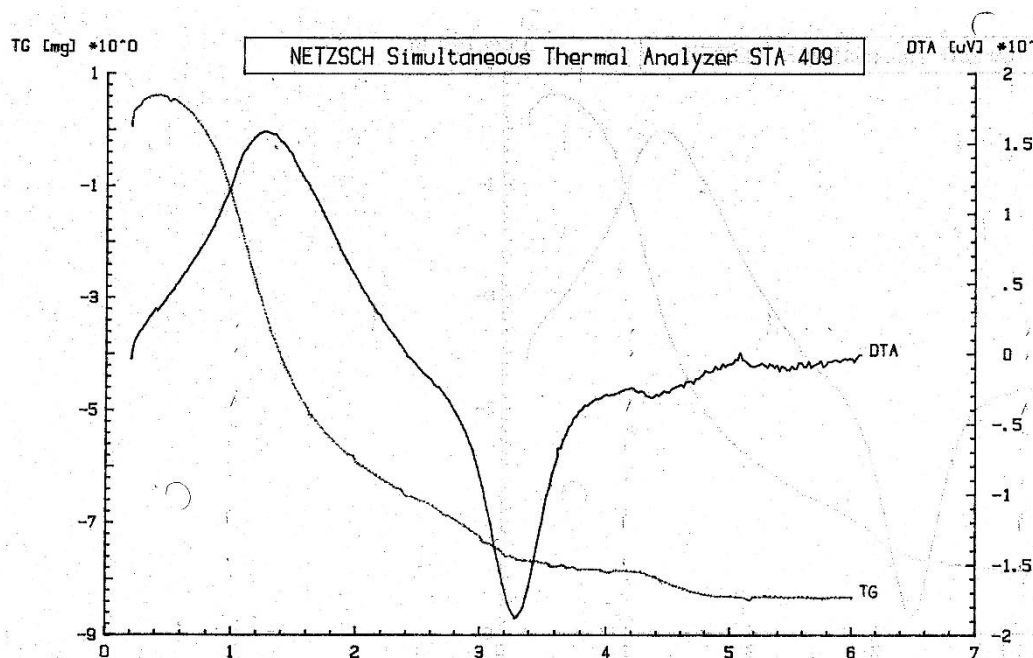


Fig. 3: TG curve of $\text{Na}_5[\text{NbV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 18\text{H}_2\text{O}$

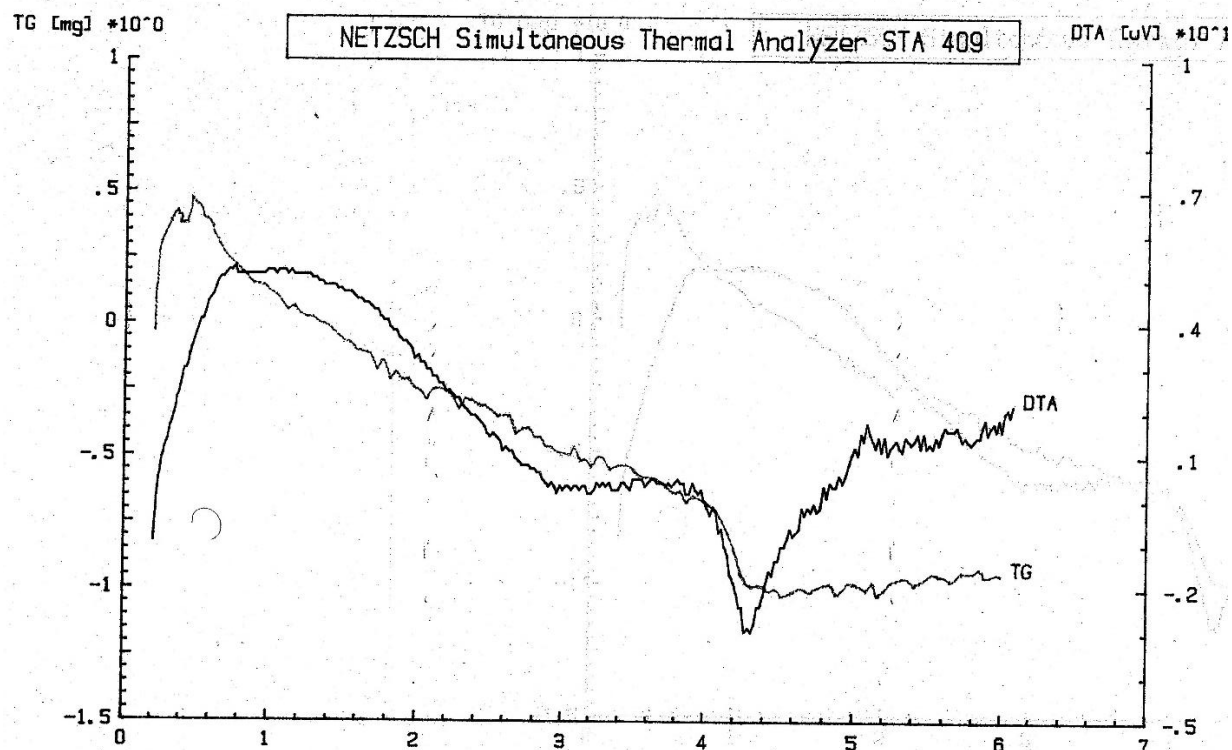


Fig. 4: TG curve of $\text{Na}_5[\text{TaV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 24\text{H}_2\text{O}$

From the analysis of TGA graph, (Fig. 3 and Fig. 4) the percentage loss in weight of the compound at different range of temperature showing the corresponding loss of number of water molecules recorded in the following table. The characteristic endothermic peak upto the range 573K corresponds to the loss of water of crystallisation and peak at 573-705 K indicate the number of loss of water of constitution. A plateau followed by a number of weak exothermic peak above 650-750 K and due to the decomposition of heteropoly anionic cage to lower oxides of the constituent metal atom, which were confirmed by the total insolubilities of the ignited sample at this temperature.

The IR spectra of the ignited samples further confirmed the complete decomposition of the heteropolyoxometallic cage.

Table 1: TGA data of the samples

Compound	273-373		373-473		473-573		573K-705K	
	% weight loss	No. of water molecules lost	% weight loss	No. of water molecules lost	% weight loss	No. of water molecules lost	% weight loss	No. of water molecules lost
$\text{Na}_5[\text{NbV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 18\text{H}_2\text{O}$	3.75	4	3.00	5	3.73	5	3.60	4
$\text{Na}_5[\text{TaV}_2\text{Mo}_{10}\text{O}_{40}]\cdot 24\text{H}_2\text{O}$	5.27	7	3.40	6	4.85	7	3.10	4

References:

- [1] Weakley T.J.R, *Pruct Bonding (Berlin)*, 1974, 18, 131
- [2] Matsumoto K.Y, Kobayaski A, *Bull.Chem. Soc. Japan*, 1975, 48, 3146
- [3] Sasaki Y, *Bull.Chem. Soc. Japan*, 1975, 48, 3146
- [4] Kazanskii L.P, *Acad, Navk SSSR*, 1978, 274, 549
- [5] Kazanskii, L.P, *DOKI Akad., Navk SSSR*, 1979, 244, 372
- [6] Fedotov, M.A, *DOKI Akad., Navk SSSR*, 1979, 244, 379
- [7] Potapova, I.V, Spitsyn V.I, *DOKI Akad., Navk SSSR*, 1979, 244, 372
- [8] Zoving, W, Shaung G, Lin X, Enhong, Enbor W, *Polyhedron*, 1996, 15, 1383
- [9] Strong J. W, Ostradev R., Rheingold, Mobala E. A, *J Am. Chem.Soc*, 1994, 116, 3601
- [10] Miller, G.L, *Metallurgy of rare earth metals*, 1959, Vol-VI
- [11] Pope M.T, *Heteropoly and isopolyoxometalates*, Springer-Verlag, New York, 1983

[12] Praust A, Thauvenot R., Chaussade, M., Robert F., Gouzerh P, *Inorg. Chem Acta*, 1994, 81, 224

[13] Bruce I., Humphrey M.G., Mattisons J.G., Roy S. K, Swinger A.G., *Aust. J. Chem*, 1984, 37, 1955

[14] Kumar H.N., Roy S.K., *J. Indian Chem Soc.* 2004, 81, 233

