

Study of the Inorganic and Organic salts of the Vanadonickelocuprate(II) Heteropolyanion

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ABSTRACT: A new compound $\text{Na}_{21}[\text{CuNiV}_{11}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ has been synthesized under hydrothermal conditions. Potassium, guanidinium, tetramethylammonium salts of triheteropoly oxoanion $[\text{CuNiV}_{11}\text{O}_{40}]^{-21}$ are prepared by metathesis. They are characterized by scanning electron microscopy (SEM), Infrared spectroscopy (IR), elemental analyses, thermal analyses and molecular weight determination which confirm the existence of the heteropoly Keggin type anion in these compounds. Following four salts of the heteropoly anion $[\text{CuNiV}_{11}\text{O}_{40}]^{-21}$ have been synthesized.

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| 1. $\text{Na}_{21}[\text{CuNiV}_{11}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ | 3. $[\text{C}(\text{NH}_2)_3]_{21}[\text{CuNiV}_{11}\text{O}_{40}]\cdot 15\text{H}_2\text{O}$ |
| 2. $\text{K}_{21}[\text{CuNiV}_{11}\text{O}_{40}]\cdot 19\text{H}_2\text{O}$ | 4. $[\text{N}(\text{CH}_3)_4]_{21}[\text{CuNiV}_{11}\text{O}_{40}]\cdot 9\text{H}_2\text{O}$ |

KEY WORDS: Vanadonickelocuprate, Heteropoly salts, Vanado-anion

INTRODUCTION

In recent years, Polyoxometalates (POMs) are one of the most widely used inorganic components and have been attracting considerable interest in the solid state material chemistry due to the vast range of their topological properties, variability of composition, novel structural characteristics, electronic properties and potential applications¹⁻² in many interdisciplinary areas. Among the numerous molecular structures, the compounds with the well known Keggin structures $[\text{XM}_{12}\text{O}_{40}]^n$ receive the most attention^{3,4} where X is the heteroatom and M is addenda atom. The structures of approximately 180 polyoxometalates have been reported⁵⁻⁸ by 1995. Recently, transition metal substituted polyoxometalates have gained much interest due to their use as catalysts for the oxidation of organic substrates⁹. The vanadium substituted polyoxometalates have attracted the attention of researchers in the field of the catalytic activities¹⁰⁻¹¹. In addition, transition metal substituted polyoxometalates generally provide better selectivity as industrial catalysts i.e eco- friendly, green and simply recyclable.

To ensure the solubility in the organic solvents convenient to some catalytic studies, several tetrabutylammonium salts have been prepared either by precipitation or by phase- transfer processes¹².

Herein, we report the synthesis and characterization of two organic and two inorganic salts of vanadonickelocuprate (II) heteropoly anion.

EXPERIMENTAL:

All the reagents were purchased commercially and used without further purification.

The solutions were freshly prepared using distilled water. EI digital pH meter was used for the record of the activity of hydrogen ion in the solution. The elemental analyses of sodium, potassium, copper, nickel, vanadium were carried out by inductively coupled plasma atomic emission spectrometry (Jobin Yvon France of model JY Ultima-2) at IIT Powai. C, H, N were analysed using CHNO analyzer Thermofinigan, Italy Model flash EA 1112 series. A Jeol, Japan, JSM-6390LV, 5X-300000X Scanning Electron Microscope (SEM) was employed to observe the morphology of the compounds. The infra-red spectra were recorded on Perkin Elmer 577 FT-IR spectrometer. The samples were grounded with dry KBr and pressed into transparent disks for recording infrared spectra ($4400\text{--}450\text{cm}^{-1}$). Thermal analysis, both thermo gravimetric analyses (TGA) and derivative thermogravimetry (DTA) were estimated by Perkin-Elmer USA of model diamond TGA – DTA, under nitrogen flow with a heating rate of $10^\circ\text{C}/\text{min}$. The

molecular weights were determined by cryoscopic method using Beckmann's thermometer.

Synthesis of Sodium 11-vanadonickelocuprate (II).

Copper chloride solution, prepared by dissolving 1g, 5.87mmol of the solute in 30mL distilled water, was mixed with 30mL nickel chloride solution, prepared by dissolving 1g, 5.87mmol solute.10mL acetic acid was added to the above solution for its acidic environment.

The above mixed solution was added dropwise to the sodium vanadate solution prepared by dissolving 10.22g, 64.5mmol in 75 mL of the distilled water. After the addition of 56mL of the solution, the pH became constant at 4.1.

The above reaction mixture was refluxed for 4 hrs with acidic buffer tablet of pH 4. It was filtered and the filtrate was left over night at 5°C. 4.2 g blue crystals were separated out which were washed with n-hexane and preserved for analysis.

Synthesis of Potassium 11-vanadonickelocuprate (II).

The potassium salt of the heteropoly anion $[\text{CuNiV}_{11}\text{O}_{40}]^{21-}$ was prepared by the metathesis of sodium 11-vanadonickelocuprate (II). The sodium salt solution, prepared by dissolving 1.28g, 0.64mmol of solute in 75mL distilled water, was mixed drop-wise to the potassium chloride solution, prepared by taking 1g, 13.42mmol of the solute in 25mL distilled water. The reaction mixture was refluxed for about 3 hrs. It was ice cooled, filtered and the filtrate was left overnight for crystallization. Pale blue crystals were separated out which were kept for analysis.

Synthesis of Guanidinium 11-vanadonickelocuprate (II).

The compound reported was prepared by mixing a solution of sodium salt of the heteropoly anion $[\text{CuNiV}_{11}\text{O}_{40}]^{21-}$ (1.39g, 0.49mmol in 75 mL distilled water) dropwise

with guanidinium chloride solution (1g, 10.47mmol dissolved in 25 mL of the distilled water). The reaction mixture was digested for 4hrs and left overnight. The resulting light blue crystals were air dried and kept for analysis.

Synthesis of Tetramethylammonium 11-vanadonickelocuprate (II).

The tetramethylammonium salt of the heteropoly anion $[\text{CuNiV}_{11}\text{O}_{40}]^{21-}$ was prepared by the reaction of the sodium 11-vanadonickelocuprate (II) salt of the heteropoly anion (1.3g, 0.43mmol of the solute dissolved in 75mL distilled water) with tetramethylammonium chloride solution (1g, 9.13mmol of the solute dissolved in the 25 mL of the distilled water). The above reaction mixture was refluxed for 2 hrs. The filtrate was ice cooled as a result of which blue crystals were separated out which were analysed.

RESULT AND DISCUSSIONS

Hydrothermal synthetic techniques have been demonstrated to be an effective strategy in the preparation of the organic-inorganic hybrid material¹³.

Under hydrothermal conditions, many factors can influence the formation and crystal growth of the products, such as the type and stoichiometry of the starting materials, reaction time, pH values and temperature.

Elemental analyses of the compounds:

The molecular formula of the compounds 1, 2, 3 and 4 are derived from the result of the elemental analysis as obtained from ICPAES and chemical analysis. The percentage of the different elements present in these compounds are also calculated which are in good agreement with the analytical results. The results are depicted in Table 1.

IR study of the compounds:

The infrared spectrum of the compounds exhibit characteristics metal-oxo stretching bands¹⁴ between 1100-600 cm^{-1} .

All the compounds show distinct bands for the polyvanadates. (Table 2)

The bands in the range of 1090-1060 cm^{-1} in all the compounds may be assigned to the independent ν (V-O) stretching vibration and the broad bands in the range 810-780 cm^{-1} may be attributed to the ν (V-O-V) bridge vibrations. The small but sharp bands in the range of 572-520 cm^{-1} depict the presence of the Cu-O bond¹⁵ in all the reported Keggin complexes. The vibrations in the range of 987-940 cm^{-1} show the presence of ν (Ni-O) bond in all the Keggin structures. The broad bands in the range between 3461-3425 cm^{-1} indicate the lattice water molecules. In addition, the bending vibration¹⁶ bands of -NH₂ group in guanidinium salt and -CH₃ group in tetramethyl salt appear at 1641-1607 cm^{-1} and 1470-1434 cm^{-1} respectively.

Thermal analyses of the compounds:

The thermal robustness of Keggin-type anions varies considerably, being dependent upon the type of transition metal in the structure and the nature of the counter cation, among other factors.¹⁷. The thermal decompositions are characterized by the loss of the water of crystallization and constitution.

All the compounds show the loss of crystallization water at a temperature around 150°C. On further increase in the temperature upto 300°C, two more endotherms are observed which indicate the further loss of water molecules at different temperatures.

For all the compounds, the weight loss of 2.7%, 3.6%, 3.2% and 1.2% are observed during first step till 150°C. But on further heating upto $\approx 300^\circ\text{C}$ all the four compounds lose, a average weight of 27.7%. The whole weight loss is in agreement with the calculated weight loss.

Molecular weights of the compounds

The apparent molecular weight¹⁸ of the compound nos 1, 2, 3 and 4 have been found as 1892.5, 2381, 2763.1 and 2935.1 against calculated molecular weight of 1995.6, 2483.1, 2852.1 and 3038.1 respectively.

Ni and Cu act as heteroatoms which may occupy tetrahedral or octahedral void by replacing vanadium atom from Keggin anion.

SEM of the compounds:

The SEM micrographs of these compounds are studied in different magnification as shown in the fig 1, 2, 3 and 4 respectively. The SEM micrographs ¹⁹ of the compounds

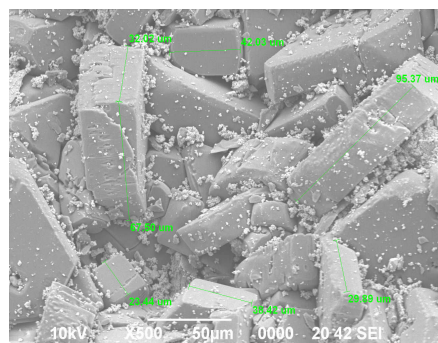
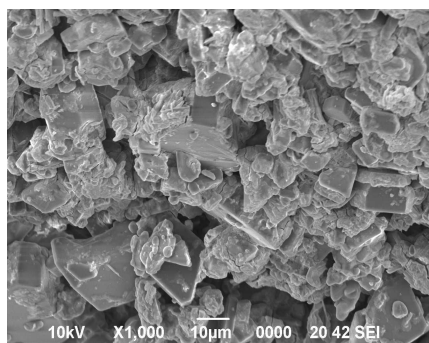
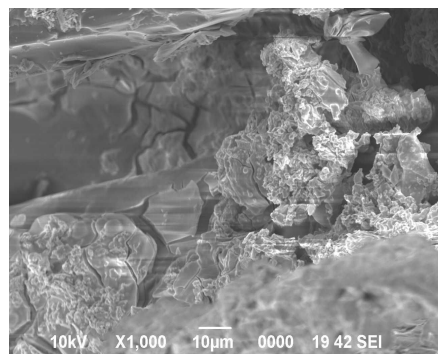
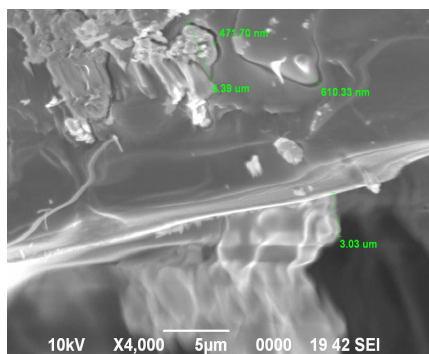
featured as mixture of small crystals with few big crystals. The large particles are observed possibly due to the polyoxometalates present in the metal oxide. The embedded particles are spherical in shape having a size of 2-4µm but the average particle size in the compound 3 is 1-1.5 µm ,although some big cluster like areas are also seen. This may be due to heteropoly anion in these salts

Table 1 :Result of elemental analysis (%)

Compound	Results	Na/K	Cu	Ni	V	O (by diff)	C	N	H
1.Na ₂₁ [CuNiV ₁₁ O ₄₀]. 10H ₂ O	Anal	24.5	3.4	3.3	28.2	31.9	-	-	-
	Calc	24.7	3.2	3.0	28.1	32.0	-	-	-
2.K ₂₁ [CuNiV ₁₁ O ₄₀].1 9H ₂ O	Anal	32.8	2.8	2.9	22.4	25.6	-	-	-
	Calc	32.9	2.6	2.4	22.5	25.8	-	-	-
3.[C(NH ₂) ₃] ₂₁ [CuNi V ₁₁ O ₄₀].15H ₂ O	Anal	-	2.4	1.9	19.3	22.1	7.94	31.93	4.42
	Calc	-	2.2	2.1	19.6	22.4	8.84	30.92	4.42
4.[N(CH ₃) ₄] ₂₁ [CuNi V ₁₁ O ₄₀].9H ₂ O	Anal	-	1.96	2.2	18.5	20.24	32.18	9.98	8.59
	Calc	-	2.1	2.0	18.4	21.1	33.18	9.68	8.29

Table 2 : Infrared spectra of the heteropoly compounds IR assignments (cm⁻¹)

M ₂₁ [Cu ^{II} Ni ^{II} V ^V ₁₁ O ₄₀].nH ₂ O	ν (HOH)	ν (V-O)	ν (Cu-O)	ν (Ni-O)	ν (V-O-V)	ν (NH ₂)	ν (CH ₃)
M=							
Na	3461	1090m	572	987	810	-	-
		1089	530	985	802		
K	3453	1085	574	990	815	-	-
		1075	561	987	811		
[C(NH ₂) ₃]	3447	1080	563	960	798	1641	-
		1065	555	954	795	1607	
[N(CH ₃) ₄]	3425	1070	530	955	790	-	1470
		1060	520	940	780		1434

SEM photographs**1. $\text{Na}_{21}[\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}\text{V}^{\text{V}}_{11}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$** **Fig 1****3. $[\text{C}(\text{NH}_2)_3]_{21}[\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}\text{V}^{\text{V}}_{11}\text{O}_{40}]\cdot 15\text{H}_2\text{O}$** **Fig 3****2. $\text{K}_{21}[\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}\text{V}^{\text{V}}_{11}\text{O}_{40}]\cdot 19\text{H}_2\text{O}$** **Fig 2****4. $[\text{N}(\text{CH}_3)_4]_{21}[\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}\text{V}^{\text{V}}_{11}\text{O}_{40}]\cdot 9\text{H}_2\text{O}$** **Fig 4****REFERENCES**

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