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ISOLATION OF A 2D HETEROMETALLIC VANADIUM(V)-COPPER(II) POLYOXOMETALATE: CHARACTERIZATION AND CATALYTIC ACTIVITIES

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ABSTRACT

A new hetero-metallic polyoxovanadate ($\{Na(H_2O)_3\}_2(\mu_2\text{-}H_2O)_4\{Cu(H_2O)_4\}_2[V_{10}O_{28}])\cdot 2H_2O$ (1) has been isolated by refluxing a mixture containing an aqueous solution of $CuCl_2$ and sodium meta-vanadate at acidic condition (pH ~3.4). The Infra-Red spectroscopies along with TGA and SEM analysis have been performed in order to characterize the isolated complex. Besides, the single crystal X-Ray analysis has been carried out to determine the crystal structure of 1. The crystal structure determination from the X-ray analysis reveals that the resulting POM has a 2D layer network which is produced from the interconnection of one-dimensional chains through the sodium salt of Cu(II) associated decavanadate *via* O atom of decavanadate with in crystallographic '*ab*' plane. The complex shows good catalytic activity towards the acetylation of ortho phenylenediamine (O-PDA) and its derivatives at usual reaction conditions.

Keywords: Synthesis, Crystal Structure, Polyoxometalate, Hetero-Metallic, Catalysis.

RASĀYAN *J. Chem.*, Vol. 16, No. 3, 2023

INTRODUCTION

Polyoxometalates (POMs) are oxygen-enriched negatively charge species and they can be regarded as a typical class of metal–oxo clusters.[1] Polyoxometalate (POM) and related solid-state materials have wide potential in different research fields like conductivity, electrical, catalysis, medicinal chemistry, and materials science.[2,3] They can catalyze several organic as well as inorganic reactions such as azide–alkyne cycloaddition, peptide bond hydrolysis, Cleavage of C−C and M−C Bonds, photoreduction of CO_2, alkene polymerization, oxidation of a wide range of substrates such as sulfides, N- and S- containing compounds, alkene, arene, phenols, carbonyls, etc.[4,5] Depending upon the types of metal ions, polyoxometalates are categorized into two classes; homo- or hetero- polyoxometalates. A large number of TM or RE-substituted POMs can be isolated by the introduction of various transition-metal (TM) or rare-earth (RE) cations.[6] One-, two- and three-dimensions extended structures are constructed using anionic POM clusters as molecular building blocks, and the resulting network structures are regarded as new metal-oxide-based materials.[7] These polyoxoanion clusters have well-defined structures such as Anderson, Keggin, Anderson-Evans, Lindqvist and Well-Dawson.[8] The final structure of the hetero-polyoxometalates can be controlled by various conditions like the type of POM, quality of the hetero-metal, temperature, solvent, template, and moreover pH of the reaction mixture. Among them, the pH executes a powerful act in the synthesis of POMs.[9] The variation of pH triggers the formation of different network structures of resulting POM.[10] In this paper, we have synthesized a two-dimensional Keggin-type extended structure ($\{Na(H_2O)_3\}_2(\mu_2\text{-}H_2O)_4\{Cu(H_2O)_4\}_2[V_{10}O_{28}])\cdot 2H_2O$ (1) by the reaction of an aqueous solution of $CuCl_2$ with an aqueous solution sodium meta-vanadate in an aqueous ammonium acetate buffer. The single crystal X-ray analysis has been performed to establish the structure of 1.

EXPERIMENTAL

Material and Methods

The starting materials; i.e., Sodium meta-vanadate, cupric chloride dihydrate, and glacial acetic acid were inherited from commercial sources. Reagent-grade solvents were used. An aqueous solution of (30 mL) of $CuCl_2$ (1.398 g, 8.2 mmol) was acidified with 10 ml. of glacial acetic acid and stirred for 10 minutes. An

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aqueous solution (75 mL) of sodium meta-vanadate (5 g, 41 mmol) was allowed to react with the resulting solution dropwise. The brown-colored mixture was stirred continuously at room temperature. The pH of the mixture was noted at regular time intervals in order to get a constant pH value. Then, the pH of the mixture was fixed at 3.4 by adding a suitable buffer solution. Finally, the mixture was refluxed slowly for about 5-6 hours and then filtered. The evaporation of the resulting filtrate was carried out in an open atmosphere. After 4 days, prismatic-shaped brown (1) crystals appeared at the bottom of the vessel. The crystals were characterized by different spectroscopic techniques along with an X-ray diffraction analysis. Complex 1: Yield: 4.2 g (79%) (With respect to $CuCl_2$). IR (KBr pallet, cm^{-1}): 3290sb, 2351w, 1614m, 970sb and 841m.

Detection Method

A Perkin-Elmer 2400 series II CHN analyzer was used to analyze C, H, and N. A Perkin-Elmer RXI FT-IR spectrophotometer was utilized to record the IR spectra in KBr pellets. A Joel-Japan, JSM-6390LV, 5X-300000X was used to know the morphology of the synthesized compounds. The TGA data were recorded by thermal gravimetric analyzer using a TGA analyzer, Simazdu DTG-60, Japan. A Bruker-AXS SMART APEX II diffractometer was used to determine the crystal structure of the complex. The data collection and refinement were done using the reported method.[11] The following program was used to refine and draw the structures; SADABS[12], SHELXS 97,[13] SHELXL 97,[14] PLATON 99,[15] ORTEP-32[16] and WINGX system ver-1.64.[17,18] Crystallographic data are summarized in Tables-1 to 3.

Table-1: Crystal Structure Data of Compound 1

Crystal data	Corresponding values
Molecular formula	$Na_2(H_2O)_{14}[Cu_2V_{10}O_{28}].2H_2O$
Molecular weight	1386.48
Crystal system	Triclinic
Space group/Z	'p-1'/1
Lattice parameters (bond length(a,b,c)/ bond angles(α/β/γ)	a=8.7340(5), b=10.76(6),c=11.1228(6); α=65.023(2),β=74.875(2), γ=70.502(2)
Volume(V)	884.49(9)
Density (Calculated)in g/cm^3	2.603
Absorption Co-efficient(μ) in nanometer(nm)	3.847
F(000)	662
Size(mm^3)	0.24 x 0.12 x 0.08
Color	Brown
Intensity measurement	
Diffractometer	Enraf-Nonius_CADA
Monochromator	graphite
Wavelength, Mo K\a	0.71073Å
Temperature	296(2)
Theta range	2.362(Min), 25.410(Max)
h,k,l range	-10/10,-12/12,-13/13
Number of independent	3243
Structure determination	
Unit reflection considered	3096
Program used	SHELXT-2014/4 (SHELDRICK,2014)
Number of refined parameters	262
Goodness_of_fit_ref	2,341
R(anisotropic)	0.0732
R_w(anisotropic)	0.2735
Extinction coefficient	Δρ max/ Δp min.
Largest shift/error	0.008

Table-2: Some Selected Bond Lengths (Å) of Compound 1

M-O bond	Bond length (Å)	M-O bond	Bond length (Å)
Cu01-O00O	2.030(6)	V004-O00A	2.239(5)
Cu01-O00N	2.035(6)	V004-V003	3.0506(16)
Cu01-O00Q	2.056(6)	V004-V006	3.0819(17)
Cu01-O00L	2.056(6)	V005-O00P	1.585(6)
Cu01-O00M	2.064(6)	V005-O00H	1.832(5)
Cu01-O00E	2.073(6)	V005-O00G	1.865(5)
V002-O00B	1.680(5)	V005-O00C	1.895(5)
V002-O00D	1.697(5)	V005-O00D	2.021(5)
V002-O008	1.896(5)	V006-O00R	1.592(6)
V002-O009	1.937(5)	V006-O00F	1.844(5)
V002-O00A	2.122(5)	V006-O00H	1.844(6)
V002-O00A	2.128(5)	V006-V002	1.657(5)
V002-V006	3.0647(16)	Na07-O00T	2.740(8)
V002-V005	3.0844(16)	Na07-O00I	2.775(6)
V003-O00I	1.610(5)	Na07-O00F	2.781(6)
V003-O00J	1.817(5)	Na07-O00L	2.914(7)
V003-O00C	1.838(5)	Na07-O00E	2.994(7)
V003-O008	2.002(5)	Na07-O00R	2.998(6)
V003-O009	2.007(5)	Na07-V006	3.623(3)
V003-O00A	2.221(5)	O008-V003	2.002(5)
V003-O004	3.0506(16)	O009-V004	2.003((5)
V004-O00K	1.608(5)	O00A-V002	2.122(5)
V004-O00F	1.821(5)	O00B-V006	2.055(6)
V004-O00G	1.840(5)	O00F-Na07	2.781(6)
V004-O008	1.978(5)	O00R-Na07	2.998(6)
V004-O009	2.003(5)		

Table-3: Selected Bond Angles of Compound 1

Bond angles	Bond angles in Å	Bond angles	Bond angles in Å
O00O-Cu01-O00N	90.9(3)	O00R-V006-V002	130.7(2)
O00O-Cu01-O00Q	90.3(3)	O00F-V006-V002	79.80(16)
O00N-Cu01-O00Q	175.2(3)	O00H-V006-V002	125.60(17)
O00O-Cu01-O00L	91.7(3)	O00R-V006-V005	136.7(2)
O00N-Cu01-O00L	86.6(3)	O006-V006-V004	135.0(2)
O00Q-Cu01O00L	88.8(3)	O00R-V006-Na07	54.7(2)
O00O-Cu01-O00M	90.6(3)	O00F-V006-Na07	48.85(16)
O00N-Cu01-O00M	97.0(2)	O00H-V006-Na07	94.38(17)
O00Q-Cu01-O00M	87.6(3)	O00T-Na07-O00I	72.3(2)
O00L-Cu01-O00M	175.7(2)	O00T-Na07-O00F	123.6(2)
O00O-Cu01-O00E	176.9(3)	O00T-Na07-V006	97.29(18)
O00N-Cu01-O00E	85.9(3)	O00I-Na07-V006	168.16(15)
O00Q-Cu01-O00E	92.8(3)	V002-O008-V004	108.5(2)
O00L-Cu01-O00E	87.8(2)	V002-O003-V003	107.2(3)
O00B-V002-O00D	107.6(3)	Cu01-O00L-Na07	99.1(2)
O00B-V002-O008	99.0(2)	V006-O00R-Na07	99.7(3)
O00D-V002-O008	97.3(2)	O008-V002-O00A	81.0(2)
O00B-V002-O009	96.1(2)	O009-V002-O00A	80.3(2)
O00D-V002-O009	96.4(2)	O00B-V002-O00A	165.7(2)
O008-V002-O009	155.3(2)	O00D-V002-O00A	86.5(2)
O00B-V002-O00A	87.7(2)	O008-V002-O00A	80.6(2)
O00D-V002-O00A	164.6(2)	O009-V002-O00A	79.9(2)

RESULTS AND DISCUSSION

Syntheses

The complex was prepared by refluxing an aqueous solution of $CuCl_2$ with an aqueous solution of sodium meta-vanadate at pH ~3.4 by adding a buffered tablet. The X-ray quality brown single crystal was isolated at the bottom of the vessel after 4 days (Fig.-1).

Fig.-1: A Brown Crystalline Complex of 1 Under a Microscope

Infra-Red Spectra of the Complex

All the characteristic peaks observed in the spectrum of 1 are in good agreement with the Keggin structure. It shows broad peaks at 2351 cm^{-1} and 3500 cm^{-1} (Fig.-2) due to the stretching vibration of the Cu-O bond and peripheral H_2O molecules respectively. It also exhibits a sharp band at 1614 cm^{-1} arises corresponding to the V=O stretching vibration. The V=O bending vibration at 970 cm^{-1} and the V-O stretching vibration at 841 cm^{-1} indicate appear in the IR spectrum of complex 1.

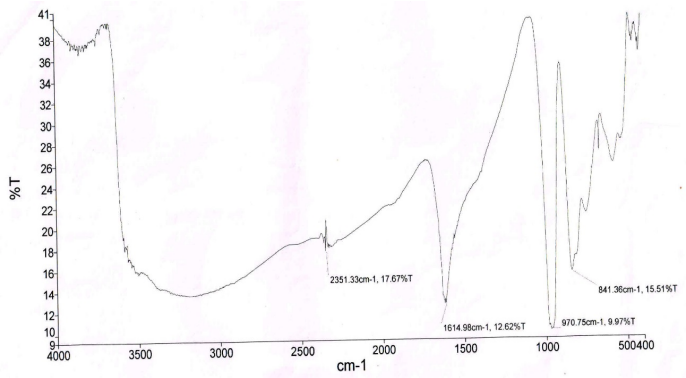


Fig.-2: The IR- Spectra of the Compound 1

TGA of the Complex

The thermogram of 1 has been shown in Fig.-3. It is clear that the compound's weight decrease occurred in three subsequent steps.

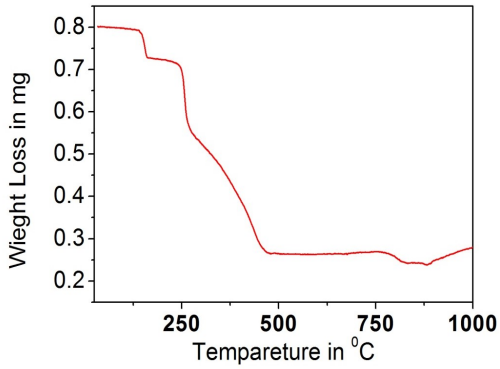
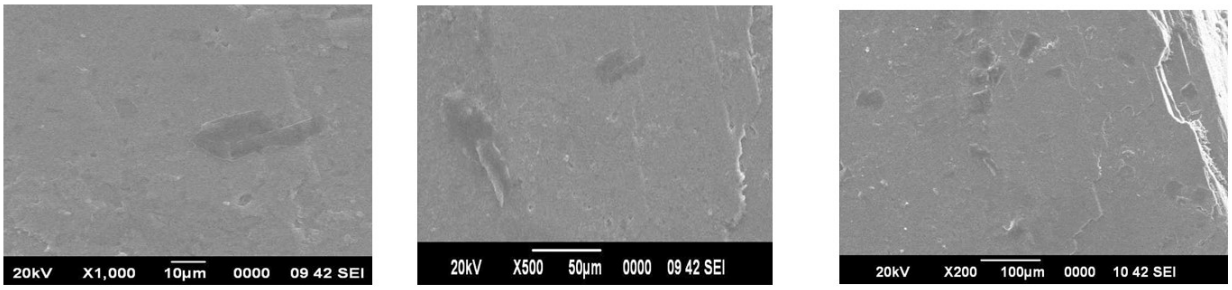


Fig.-3: TGA Curve of Compound 1

The initial loss in weight is 6.25% from 100°C up to 200°C due to the loss of uncoordinated H_2O and some loosely bound H_2O. The subsequent loss in weight is about 9.5% from 200°C to 280°C probably due to the loss of strongly bonded water molecules. After this temperature (Ti = 350°C) complex starts to decompose. The TG analysis strongly suggests that the complex consists of a large number of water molecules in its clusters.

Scanning Electron Microscopy (SEM) of the Complex

In order to investigate the morphology and elemental analysis of the synthesized compound, the SEM technique has been performed. The SEM micrograms of compound 1 have been studied in 500X, 1000XR, and 500XR magnification which are depicted in Fig.-4 (a-c) respectively.



(a) (b) (c)

Fig.-4: Different Views (a-c) of SEM Images of Compound 1

SEM image of compound 1 shows that it is a Keggin-type structure. Figures-5(a-c) show some big crystals with some small crystals. This picture indicates the embedded particles are spherical in shape of 2-4 µm. This picture shows there are some big uniform crystals. Perhaps these are produced by aggregation. These are clearly visible crystals. It is clear from the EDS analysis plot that the compound contains Cu, V, and O (Fig.-5).

Fig.-5: EDS Analysis Plot of the Compound 1

Descriptions of X-Ray Crystal Structure

The X-Ray crystal structure of 1 having moiety of formula $Na_2(H_2O)_{14}[Cu_2V_{10}O_{28}].2H_2O$ is shown in Fig.-6. Selected bond lengths and angles around metals are summarized in Table-2 and 3. A decavanadate ion $[V_{10}O_{28}]^{6-}$ ions, two sodium ions, two copper ions, and sixteen water molecules consist of an asymmetric unit. The two non-coordinated H_2O molecules are not displayed here due to clarity.

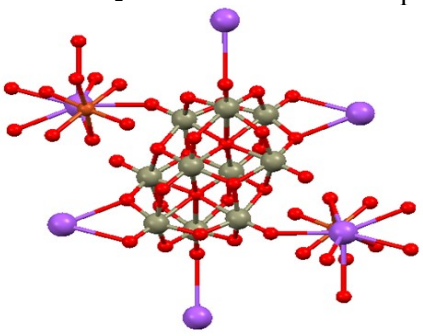


Fig.-6: Ball Stick Model of Compound 1

The structure of decavanadate ion $[V_{10}O_{28}]^{6-}$ is depicted in Fig.-7. The oxidation state of vanadium in decavanadate is +5. The decavanadate ion $[V_{10}O_{28}]^{6-}$ consists of 10 fused VO_6 octahedra and has D_{2h} symmetry. The decavanadate anions contain three sets of equivalent V atoms. These contain 2 central VO_6 octahedra and 4 each peripheral tetragonal pyramidal VO_5 units. Seven unique groups of oxygen atoms are labeled as O00A, O00K, O00M, O00N, O00F, O00L, and O00E in this structure. Two of these bridges to six V centers, four bridges to three V centers, fourteen of these span edges between pair of V centers, and eight are peripheral.

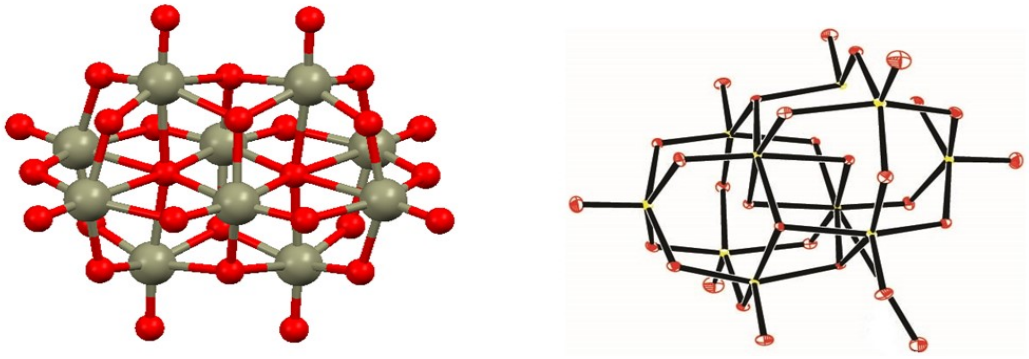


Fig.-7: The Structure of Decavanadate Anion in Compound 1

The six deprotonated oxygen atoms of decavanadate ion $[V_{10}O_{28}]^{6-}$ coordinated with the six sodium ions to form $Na_6[V_{10}O_{28}]$ salt. The coordination numbers of sodium ions in this structure are seven. It is bounded by seven oxygen atoms: four from terminal water molecules, two from bridging water molecules, and one from decavanadate ion $[V_{10}O_{28}]^{6-}$. The Na-O bond lengths are in the ranges 2.740(8)-2.998(6) Å. The resulting sodium salt, $Na_6[V_{10}O_{28}]$ bridged to copper ions through the oxygen atoms of water molecules to form rare hetero-metallic salt of decavanadate ion. The coordination numbers of copper (II) ions in this structure are six. It is bounded by the six oxygens: 4 from terminal H_2O and 2 from bridging H_2O to result in an octahedral environment around copper ions. The Cu-O bond distances are in the ranges 2.030(6)-2.073(6) Å. The hetero-metallic salts form one dimensional polymer (Fig.-8) along a crystallographic screw axis parallel to the *b* axis.

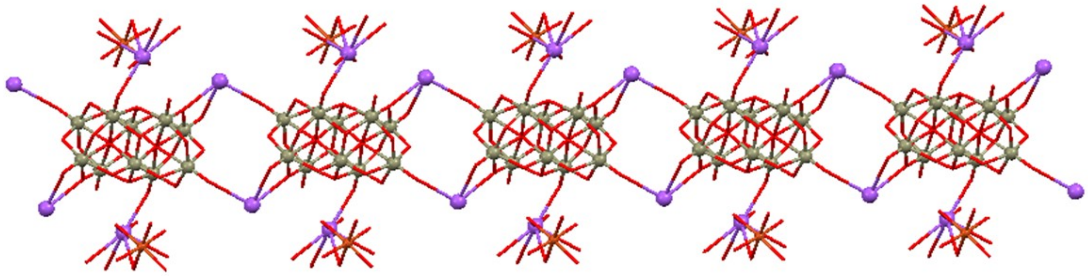


Fig.-8: The 1D Polymeric Chain of Compound 1 Along Crystallographic *b* Axis

The two-dimensional layer (Fig.-9) of 1 resulted from the in-connection of one-dimensional chains by sodium-copper salt of decavanadate via the O atom of decavanadate with in crystallographic 'ab' plane.

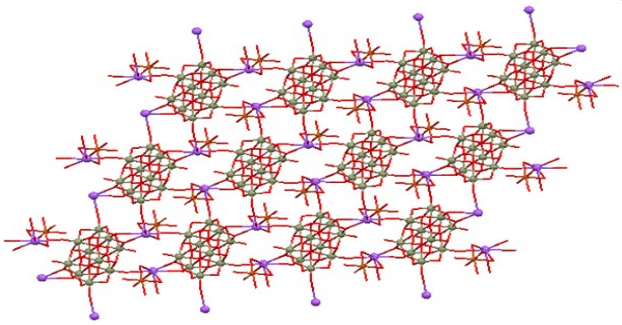
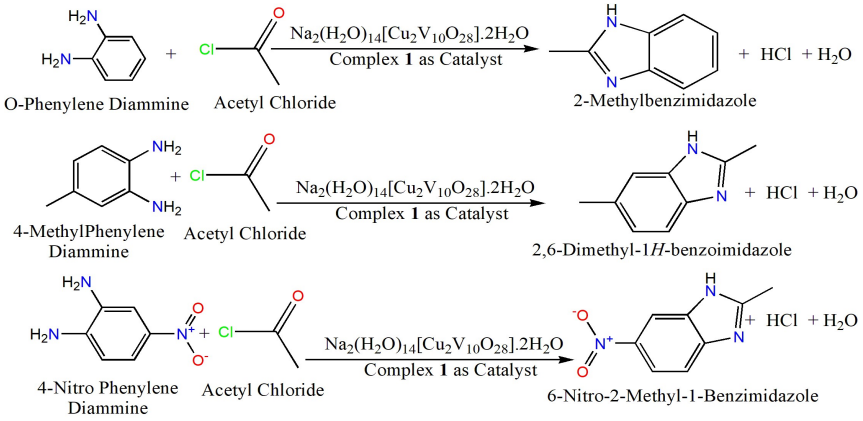


Fig.-9: The 2D Layer of Compound 1 Along Crystallographic *ab* Plane

Catalytic Properties

Complex $(\{Na(H_2O)_3\}_2(\mu_2\text{-}H_2O)_4\{Cu(H_2O)_4\}_2[V_{10}O_{28}])\cdot 2H_2O$ (1) shows excellent catalytic properties towards the acetylation of ortho-phenylenediamine (O-PDA) and its derivatives to the corresponding 2-Methylbenzimidazole. It has been observed that the reaction occurs in lesser time and produces a high yield of products in the presence of a catalyst. The names of reactants, products, and % of the yield of these acylation reactions have been tabulated in Table-4. The reaction Scheme 1 is shown below. Therefore, it can be said that the synthesized compounds are very effective catalysts, especially in acetylating benzoylation. It is also evident from the above tables that the nature of catalysts plays a significant role in the yield of the products.



Scheme-1: The Acetylation of *ortho*-phenylenediammine (O-PDA) and its Derivatives to the Corresponding 2-Methylbenzimidazole Catalyzed by the Synthesized Complex

Table-4: The Names of Reactants, Products, and % of Yield of this Acylation (Acetyl Chloride) Reactions in the Presence of Synthesized Catalyst $Na_2(H_2O)_{14}[Cu_2V_{10}O_{28}].2H_2O$ (1)

S. No.	Reactant	Product	% yield
1	*o*-Phenylene Diamine	2-Methylbenzimidazole	62
2	4-Methyl Phenylene Diamine	2,6-Dimethyl-1H-benzoimidazole	65
3	4-Nitro Phenylene Diamine	6-Nitro-2-Methyl-1-Benzimidazole	68

CONCLUSION

In summary, we have isolated an interesting hetero-metallic polyoxovanadate $(\{Na(H_2O)_3\}_2(\mu_2\text{-}H_2O)_4\{Cu(H_2O)_4\}_2[V_{10}O_{28}])\cdot 2H_2O$ (1) 2D polymer by refluxing a mixture containing an aqueous solution of $CuCl_2$ and sodium meta-vanadate at pH ~3.4. The compound was synthesized by a simple hydrothermal method. The asset of this method is to use of nonpoisonous reactants and water as solvent. The compound has been characterized by using several spectroscopic techniques. The thermal study of this complex indicates that it contains several water molecules with different types; both coordinated and non-coordinated. Finally, single crystal X-Ray diffraction analysis has been used to determine the structure. The XRD study shows that the asymmetric unit consists of a decavanadate ion $[V_{10}O_{28}]^{6-}$ ions, two sodium ions, two copper ions, and sixteen water molecules. The sodium salt, $Na_6[V_{10}O_{28}]$ bridged to copper ions through the oxygen atoms of water molecules to form rare hetero-metallic salt of decavanadate ion. It has been also observed that the polymer has the good potential to act as a catalyst towards the acylation reaction of ortho-phenylenediamine (O-PDA) and its derivatives to the corresponding 2-Methylbenzimidazole. Therefore, the present system opens up a route for the synthesis of bimetallic systems and an avenue for the synthesis of V_{10} derivatives with various other transition and inner-transition metals. Moreover, these types of hetero-metallic polyoxometalate can be utilized in future prospects of several biological applications namely medicines with antiviral, anticancer, and antimicrobial properties.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHORS CONTRIBUTION

Both authors contributed significantly to this manuscript and participated in reviewing/editing. Dr. P.S. Singha synthesized the compounds and he approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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