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COMPARATIVE ANALYSIS OF ANTIBACTERIAL POTENTIALS OF POLYOXOMETALATES BASED RUTHENIUM AND COPPER COMPLEXES

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Abstract

Polyoxometalates (POMs) are versatile metal–oxygen clusters known for their structural diversity, strong Brønsted acidity, and broad catalytic and biological activities. In this study, two metal-substituted POM complexes, POM-1 and POM-2, were synthesised and thoroughly characterised using UV–visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The FTIR spectra displayed the characteristic vibration bands associated with metal–oxygen frameworks, confirming the successful formation of the POM-based complexes and clearly revealing the fingerprint regions typical of these structures. XRD analysis showed that the crystalline sizes of the synthesised complexes fall within the nanoscale range of 40–80 nm. The antibacterial performance of the complexes was evaluated against both Gram-positive and Gram-negative bacteria, where the copper-doped POM complex demonstrated notably enhanced activity, producing inhibition zones of approximately 18 ± 2 mm and 30 ± 3 mm, respectively. These results highlight the potential of metal-substituted POMs, particularly Cu-modified systems, as promising candidates for future antimicrobial applications.

Keywords: Polyoxometalates, Copper, Ruthenium, Antibacterial.

1. Introduction

Polyoxometalates (POMs) are polyatomic metal–oxygen cluster anions composed of three or more transition-metal centers—commonly molybdenum, tungsten, or vanadium—linked through shared oxygen atoms to form stable three-dimensional frameworks [1-3]. These anions display diverse structures, colors, and magnetic properties, and they serve as an important class of coordination compounds with wide applications in catalysis, materials science, and medicine. Depending on their composition, POMs are categorized as isopoly anions, which contain only metal–oxygen units, or heteropoly anions, which incorporate a central heteroatom such as phosphorus, silicon, or boron [4-7].

Among their structural families, the Keggin, Dawson, Anderson, and Preyssler types are the most widely studied. The Keggin ion, with the general formula [XM12O40]n–, consists of a tetrahedral heteroatom surrounded by 12

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distorted MO6 octahedra linked by 24 bridging oxygens, giving a compact and thermally stable cluster. These anions also exist as several isomers (α, β, γ, δ, ε). The Dawson ion ([P2W18O62]6−) features two heteroatoms encapsulated within an elongated metal–oxygen framework, while the Anderson ion is formed by six edge-sharing octahedra arranged around a central octahedral heteroatom in a planar conFiguration. The Preyssler anion is a larger doughnut-shaped structure composed of thirty WO6 octahedra surrounding five PO4 units and a central Na+ ion. Its exceptional stability, acidity, and oxidation ability make it particularly attractive for green catalysis[7-13].

POMs can be synthesized and modified using chemical methods such as the sol–gel process or general wet-chemical routes, both of which allow control over particle size, composition, and dispersion. Their structural tunability has enabled the development of numerous functional materials, including efficient catalysts, redox-active components in supercapacitors, and biologically active complexes [13-16]. In particular, several POMs exhibit antiviral and antibacterial properties, with some showing activity against HIV proteases and multidrug-resistant bacterial strains. Hybrid structures formed by coupling POMs with organic ligands or metal complexes often enhance stability, reactivity, and sensing performance.

In organic synthesis, molecules such as imidazole-4-carboxaldehyde play a role as precursors for constructing heterocyclic compounds and functional materials. In the present work, the synthesis and characterization of copper- and ruthenium-substituted polyoxometalates are explored, aiming to expand the functional versatility of POM-based systems [16-20].

2. Experimental

2.1 Chemicals used:

All the chemicals Ammonium molybdate tetrahydrate pure, Copper chloride, Ruthenium chloride, imidazole-4-carboxaldehyde and Di-sodium hydrogen phosphate were purchased from Merck. All the chemicals were used without any further purification.

2.2 Preparation of polyoxometalate (POM) based hybrid material:

2.2.1 Preparation of Copper-based POM:

The hybrid material of Cu-POM is prepared by dissolving ammonium molybdate (1.30 g; 2 mmol) and copper chloride (0.102 g; 1.5 mmol) in 30 ml of distilled water. The solution was mixed at 50°C with constant stirring. To the hot solution, di-sodium hydrogen phosphate solution was added. Then the content was transferred to the solution with continuous stirring for 10-15 minutes [21]. After that, imidazole-4-carboxaldehyde(I4C) (0.16 g; 0.5 mmol) was added to the above solution and stirred for 15-30 minutes. After adding the solution, the pH was adjusted by adding few drops of con.H2SO4. Then the solution was transferred into 100 ml of stainless Teflon autoclave at 100 °C for 3-6 hours. Then the solution was kept for cooling down for room temperature. The green precipitate was obtained, filtered and dried at room temperature through slow evaporation.

2.2.2. Preparation of Ruthenium based POM:

The hybrid material of Ru-POM is prepared by dissolving ammonium molybdate (1.30 g;2 mmol) and Ruthenium chloride (0.102 g; 1.5 mmol) in 30 ml of distilled water. The solution was mixed at 50°C with constant stirring. To the hot solution, di-sodium hydrogen phosphate solution was added. Then the content was transferred to the above solution with continuous stirring for 10-15 minutes [21]. After that, imidazole-4-carboxaldehyde (I4C) (0.16 g; 0.5 mmol) was added to the solution and stirred for 15-30 minutes. After adding the solution, the pH was adjusted by adding few drops of con.H2SO4. Then the solution was transferred into 100 ml of stainless Teflon autoclave at 100 °C for 3-6 hours. Then the solution was kept for cooling down for room temperature. The violet precipitate was obtained, filtered and dried at room temperature through slow evaporation.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The XRD pattern of POM-1 and POM-2 are shown in Fig-1.1 The grain size of the prepared compound is given in table.1.1. The characteristics peaks also revealed that the metal is incorporated with the I4C. The crystalline size is estimated according to the Debey- Scherer equation,

$D = k\lambda / \beta\cos\theta$

The crystalline size of the prepared I4C is around 40-80 nm approximately [25]. The peak of POM-1 is at 9.7°,16.22°,21.93°,25.85°,28.34°,33.93°,44.72°,57.32° are corresponds to the POM-1 confirms the prepared material is shown in Fig 1.1.The peak of POM-2 is at 9.79°,10.85°,17.73°,19.60°,25.94°,26.25°,27.41°,36.59 are corresponds to the POM-2 confirms the prepared material is shown in Fig 3.6. The particle size varies between POM-1 and POM-2 with slight difference of about approximately 2.5 nm. The particle sizes of the POM-1 and POM-2 are about 60 nm and 65 nm, respectively.

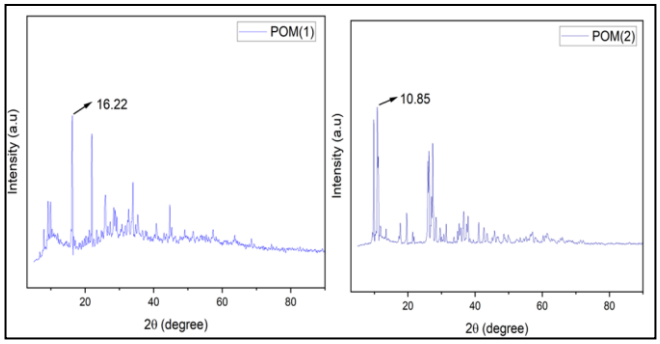

Fig 1.1 XRD pattern of POM-1 & POM-2

Table.1.1 XRD pattern of POM-1 and POM-2:

S.NO	Complex	Theta (2θ)	Grain Size (nm)
1	POM-1	9.17	50
		16.22	55
		21.93	59
		28.34	65
		33.93	67
		44.72	69
		57.32	75
2	POM-2	9.79	52
		10.85	55
		19.60	60
		25.94	64
		26.25	70
		27.41	71
		36.59	75

3.2 FTIR Analysis

FT-IR spectrum of metal-doped POM-1 & POM-2 is shown in Fig. 1.2. The peaks belong to Ru, Cu-POM, imidazole-4-carboxaldehyde (I4C), and metal bond stretching frequency appears at 450-1300 cm^{-1}. The bands in the

region 3200-1300 cm^{-1} belong to the imidazole-4-carboxaldehyde (I4C). The peak belongs to N-H stretching appears at 3142 cm^{-1}. The peak appears at 1666 cm^{-1} showing the presence C=N ring [23] in POM-1. The peak belongs to N-H stretching appears at 3144 cm^{-1}. The peak appears at 1606 and 1680 cm^{-1} showing the presence C=N ring in POM-2. The peak at 2831 cm^{-1} indicates the C-H of aromatic ring. The peak at 2947 cm^{-1} indicates the C-H of aromatic ring. The M-Ot appears at 1057 cm^{-1}, 1093 cm^{-1}. The peaks at 868, 895 and 937,953 cm-1 correspond to vibration stretching bands of M-Ob. One peak at 612, 615 cm^{-1} is attributed to vibration (M-O-M). The peaks at 458 cm^{-1} , 511 cm^{-1} are attributed to the M-O bond. The observed peaks correspond to the fingerprint region of the prepared POM complex [24]. The functional groups of POM-1 & POM-2 complex are tabulated in Table 1.2.

Table.1.2 FT-IR spectral data of POM-1& POM-2:

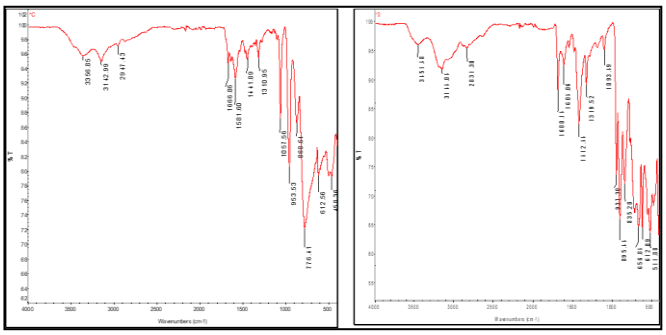

Fig 1.2 FT-IR spectrum of POM-1 & POM-2

3.3 UV-Visible Spectroscopy

The UV-Visible spectroscopy is recorded in the range of 200-800 nm. A green solution of POM-1 shows a band at 207 nm and band gap is calculated about 5.99 eV is given in table.1.3. A violet solution of POM-2 has been absorbed

Complex	Enterococcus (mm)	Salmonella (mm)
POM-1	18±2	30±3
POM-2	10±1	10±2

band at 204 nm. The absorption bands appear at 207 and 204 for POM-1 and POM-2 respectively. These absorption bands are appeared due to the Inter-Valence Charge Transfer (IVCT) [22].

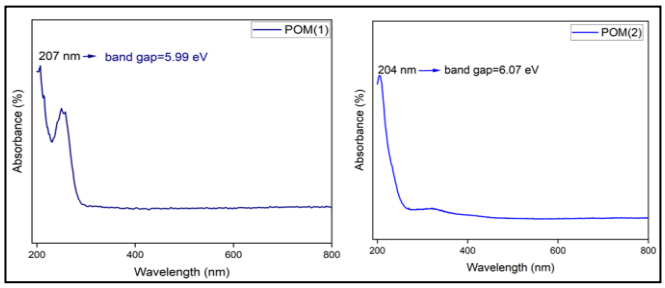

Fig. 1.3 UV-Vis spectrum of POM-1 & POM-2

Table.1.3 UV-Visible data of POM-1 and POM-2:

Complex	Cu-POM (cm^{-1})					Imidazole-4-carboxaldehyde (I4C) (cm^{-1})		
	$M\text{-}O_t$	M-O_b	M-O-M	M-O	N-H bond	N-H stretching/ bending	C=N ring	C-H aromatic
POM-1	1057	868, 953.	612	458	3142	1581	1666	2947
POM-2	1093	895, 937.	612, 615	511	3144	1412	1606, 1680	2831

The Antimicrobial studies of the metal doped POM-1 and POM-2 are tested in vitro by the well distributed method. The bacteria of Enterococcus and Salmonella has been used to finding antimicrobial property of different POM's. The zone inhibition values of the POM-1 and POM-2 and control values shows increased in activity of the a I4C

doped metals. The Antimicrobial studies of the compound acts on gram-positive and gram-negative cell activity. The result for POM-1 shows gram positive (Enterococcus)18±2, and 30±3 gram negative (Salmonella). POM-2 shows gram positive (Enterococcus) 10±1 and 10±2 gram negative (Salmonella).

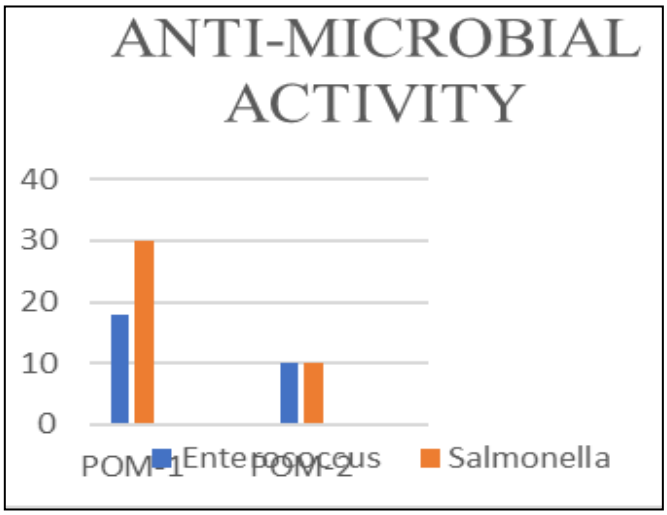

Fig.1.5 Bar diagram of anti-microbial activity of various complexes

Fig 1.6 The anti-microbial activity of the Gram positive (Enterococcus) and Gram negative (Salmonella) of POM-1

Table.1.4 Anti-microbial activity of POM-1 and POM-2:

Complexes	Absorption band (nm)	Band gap (eV)
POM-1	207	5.99
POM-2	204	6.07

Fig 1.7 The anti-microbial activity of the Gram positive (Enterococcus) and Gram negative (Salmonella) of POM-2

The cell wall of the bacterial has been well interact along with prepared complexes to make the bacterial efficient and effective activity.

4.CONCLUSION

The complexes of POM-1 & POM-2 have been synthesised and characterised using spectral techniques such as UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The IR spectral data shows that the characteristic peaks, which confirm the formation of POM based complexes. The fingerprint region for the POMs have been observed. The crystalline size of the synthesised complexes have been calculated which lies in the range of 40-80 nm. The Cu doped POM complexes, show enhanced bacterial activity of gram positive and gram negative of about 18±2 and 30±3 mm.

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