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COMPARATIVE STUDIES OF KEGGIN TYPE POLYOXOMETALATE BASED 3-API & RUTHENIUM COMPLEXES & THEIR ANTIMICROBIAL ACTIVITIES

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Abstract

Two novel polyoxometalate (POM) complexes, POM-1 and POM-2, were synthesized and their structures confirmed through UV-visible and FTIR spectroscopy, along with X-ray diffraction (XRD). In biological evaluations, POM-1 demonstrated moderate antibacterial activity, with similar inhibition zones against Gram-positive and Gram-negative bacteria. In contrast, POM-2 showed a marked increase in efficacy, generating significantly larger zones of inhibition. The superior performance of POM-2 is likely due to its distinct structural features, positioning it as a promising candidate for development into a nanoscale antibacterial agent.

Keywords: polyoxometalate, 3-(aminopropyl)-imidazole, Metals, Antimicrobial.

1. Introduction

The term polyoxometalate (abbreviated POM) is applied to an extremely large group of generally anionic clusters with frameworks built from transition metal oxo anions linked by shared oxide ions. The term is usually applied to clusters of 3 or more transition metal atoms from group 5 and group 6 in their high oxidation states (d^0 and d^1 configuration), e.g., (Mo (VI) and W(VI). Historically, the first example, the ammonium phosphomolybdate containing the $[PMo_{12}O_{40}]^{3-}$ ion, was discovered in 1826. POMs have a variety of applications in fields such as catalysis, energy storage, and materials science. For example, POMs have been used as heterogeneous catalysts in organic reactions, as electrode materials in batteries and supercapacitors, and as building blocks for designing functional materials with tailored properties. In addition, POMs have been investigated for their potential as antimicrobial agents and in biomedical imaging [1-5].

Polyoxometalates (POMs) are a diverse class of inorganic compounds that consist of clusters of metal oxides connected by oxygen atoms. They exhibit a wide range of structural and chemical properties, making them useful in a variety of applications, such as catalysis, energy storage, and materials science [6,7]. The structural principles of POMs are key to understanding their properties and potential applications. Iso-polyacids are a class of inorganic compounds that contain multiple metal atoms linked to-

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gether by bridging ligands. These compounds can be thought of as metal analogues of organic polymers, where the repeating units are metal atoms instead of organic groups. Iso-polyacids can have a wide range of structures and properties, depending on the metal ions and ligands involved. Keggin structures are a type of polyoxometalate (POM) consisting of a central tetrahedral or octahedral metal ion (usually molybdenum or tungsten) surrounded by 12 or 6 oxide ions, respectively, forming a cage-like structure [8-13]. The Dawson structure is a type of polyoxometalate (POM) that is a variation of the Keggin structure. It is named after the chemist Edwin E. Dawson, who first synthesized it in 1927. The Dawson structure has the general formula $[X_2M_{18}O_{62}]^{n-}$. The planar topological structure of Anderson-type POMs was proposed by J. S. Anderson36 in 1937 and confirmed by H. T. Evans37 through determining the single crystal structure of $[TeMo_6O_{24}]^{6-}$. The nanoparticles can be made from a variety of materials, including metals, ceramics, and polymers. Nano composites are often used in applications such as coatings, structural materials, and electronic devices [14-17]. Hybrid materials, on the other hand, are materials that consist of two or more distinct components that are combined to create a new material with unique properties. The components can be of different chemical compositions or phases, and they can be mixed together or arranged in a layered structure. Hybrid materials can exhibit a wide range of properties depending on the specific combination of components and can be used in a variety of applications, including sensors, catalysts, and energy storage devices.

The main difference between nanocomposites and hybrid materials is that nanocomposites involve the addition of nano-scale particles to a matrix material, while hybrid materials involve the combination of two or more distinct components to create a new material. Sol-gel reactions are generally followed by a thermal treatment (450–600°C) to remove the organic part and to crystallize either anatase or rutile TiO_2. Wet chemistry is a form of analytical chemistry that uses classical methods, such as observation, to analyze materials. It is called wet chemistry since most analyzing is done in the liquid phase. Hydrothermal synthesis is a process of creating materials or compounds under high-temperature, and high-pressure conditions using a water-based solution as a reaction medium. The stages of hydrothermal synthesis typically include [18]. Polyoxometalates (POMs) have been studied for their potential applications in medicine, including drug delivery, imaging, and cancer therapy. Some of the notable applications of POMs in medicine [19]. 3-(aminopropyl)-imidazole is an organic compound with the chemical formula $C_7H_{12}N_2$. It is a derivative of imidazole, a five-membered heterocyclic compound that contains two nitrogen atoms in the ring.

2. Experimental

2.1 Chemicals used

All the chemicals and reagents were purchased from Merck [3-(aminopropyl)-imidazole, Ammonium molybdate, di-sodium hydrogen phosphate (Na_2HPO_4), Sulfuric acid (H_2SO_4)]. All the chemicals were used without further purification.

2.2 Preparation of polyoxometalate (POM-1) based complexes

Preparation of 3-API-Based Polyoxometalate

The kegging-type polyoxometalate is prepared by dissolving ammonium di-molybdate (1.30 g; 2 mmol) and disodium hydrogen phosphate (1.0 g; 1.0 millimole) in 30 ml of double-distilled water, then mixing under constant stirring for 10-15 min at 63°C. After that, (3-aminopropyl)-imidazole (3-API) (1g; 0.5 millimole) was dissolved in 10 ml of double-distilled water. Then the content was transferred to the above solution, the sulfuric acid (H_2SO_4) was added drop by drop with continuous stirring for 20-40 mins. The solution was transferred into a 100ml of stainless Teflon autoclave at 100 °C for 2-4 hours. Then the solution was kept for cooling down to room temperature. The precipitate was obtained in a yellow color. The precipitate was filtered and dried at 32 °C (room temperature) through slow evaporation [20].

Preparation of Ruthenium-based polyoxometalate (POM-2)

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 a few drops of con.H_2SO_4. Then the solution was transferred into a 100 ml stainless-steel Teflon autoclave at 100 °C for 3-6 hours. Then the solution was kept to cool down to room temperature. The violet precipitate was obtained, filtered and dried at room temperature. The violet precipitate was obtained, filtered and dried at room temperature through slow evaporation.

3. RESULTS AND DISCUSSION

3.1. UV-Visible Spectroscopy

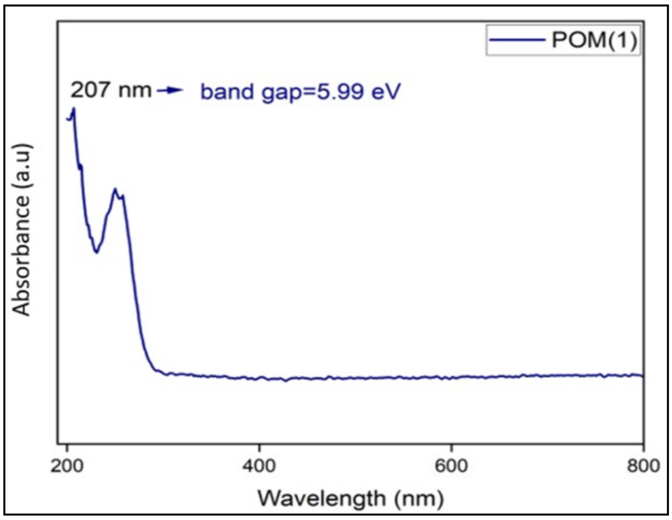


Fig. 1 UV-Vis spectrum of POM -1

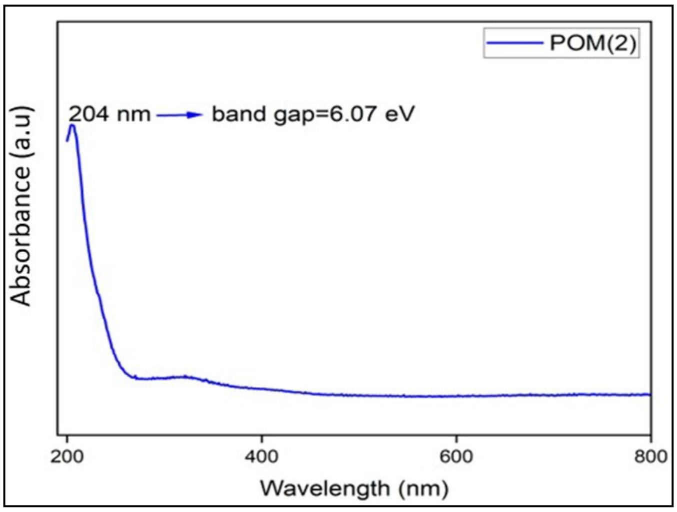


Fig. 2 UV-Vis spectrum of POM-2

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 the band gap is calculated to be about 5.99 eV, as given in Table 1. POM-2 has been absorption band at 204 nm. The band gap is calculated to be about 6.07 eV and is given in Table 1. The absorption bands appear at 207 and 204 for POM-1 and POM-2, respectively [22].

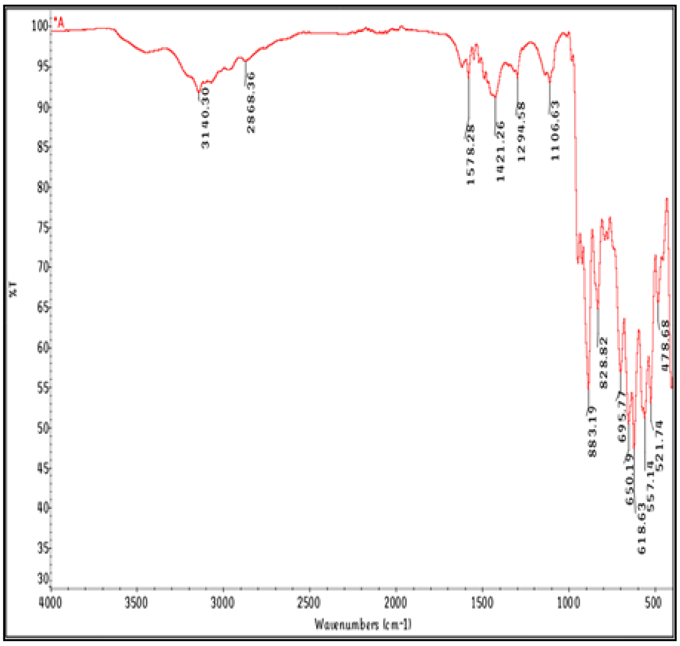
Table 1. FT-IR spectral data of POM -1 & POM-2

Complexes	Absorption band (nm)	Band gap (eV)
POM -1	210	5.87
POM-2	204	6.07

3.2. FT-IR Analysis

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

FT-IR spectra of POM-1 are shown in the figure. The POM-1 peaks of 1200-600 cm^{-1}.The POM peak at 1106 cm^{-1} shows that vibration (M-O t) stretching band. A peak at 883 cm^{-1} to 1106 cm^{-1} corresponds to vibration (M-Ob) stretching bands. The POM-1 peak at 618 cm^{-1} is attributed to vibration (M-O-M). The absorption of the organic molecule API, the 3140 cm^{-1} peaks belong to the N-H stretching bond. The POM 1421 cm^{-1} peak vibration corresponds to the (N-H) group. At 1597 cm^{-1} indicates aromatic C-H functional group. At 1578 cm^{-1} peak exhibits the presence (C=N) ring & peak 478 cm^{-1} is assigned to the (M-O) bond. The POM-1 absorbed peaks correspond to the fingerprint region of the prepared POM-1 complex. Fig 3. The peaks POM-2 Ru-POM, imidazole-4-carboxaldehyde (I4C) and metal bond stretching frequency appear at 500-1300cm^{-1}. The bands in the region 3200-1300 cm^{-1} belong to the imidazole-4-carboxaldehyde (I4C). The peak belonging to N-H stretching appears at 3144 cm^{-1}. The peak appears at 1606 and 1680 cm^{-1}, showing the presence C=N ring [23] in POM-2. The peak at 2831 cm^{-1} indicates the C-H of aromatic ring. The M-Ot appears at 1093 cm^{-1}. The peaks at 895 and 937 cm^{-1} correspond to



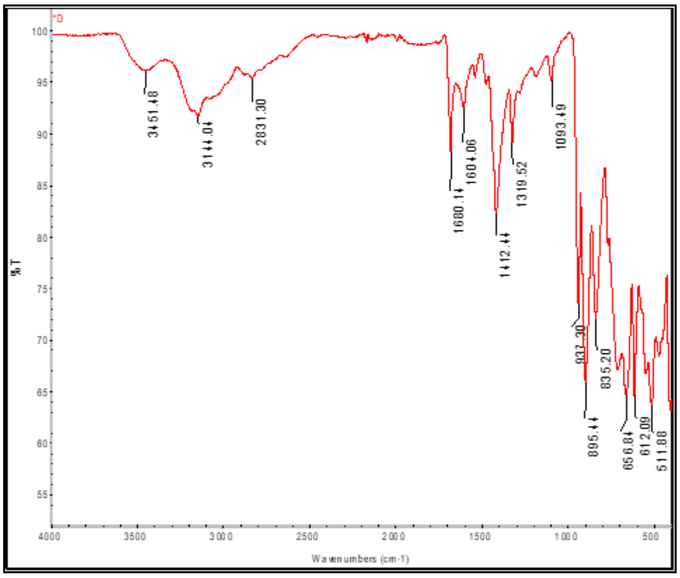


Fig. 3 FT-IR spectrum of POM -1 & POM-2

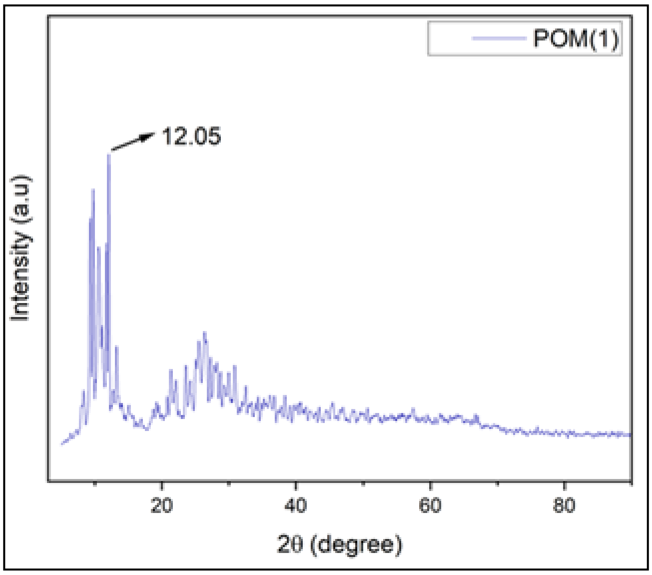
vibration stretching bands of M-Ob. The peaks at 612 and 615 cm^{-1} is attributed to vibration (M-O-M).

The peak at 511 cm^{-1} is attributed to M-O bond. The observed peaks are corresponding to the fingerprint region of the prepared POM complex [24]. The functional groups of POM-2 complex is tabulated in Table 2.

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

Complex	Ru-POM (cm^{-1})					Imidazole-4- carboxaldehyde (I4C) (cm^{-1})		
	$M\text{-}O_t$	$M\text{-}O_b$	M-O-M	M-O	N-H bond	N-H stretching/ bending	C=N ring	C-H aromatic
POM -1	1106	883-953	618	478	3140	1421	1578	1597
POM-2	1093	895, 937.	612, 615	511	3144	1412	1606, 1680	2831

3.3 XRD Analysis



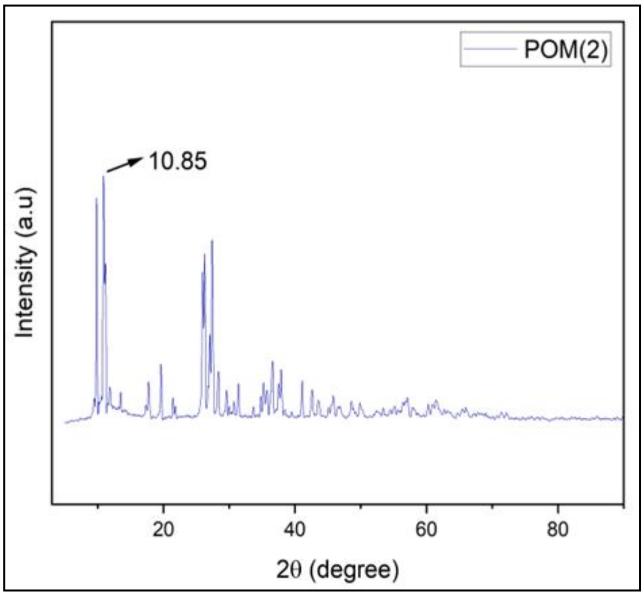


Fig. 4 XRD patterns of POM -1 and POM-2

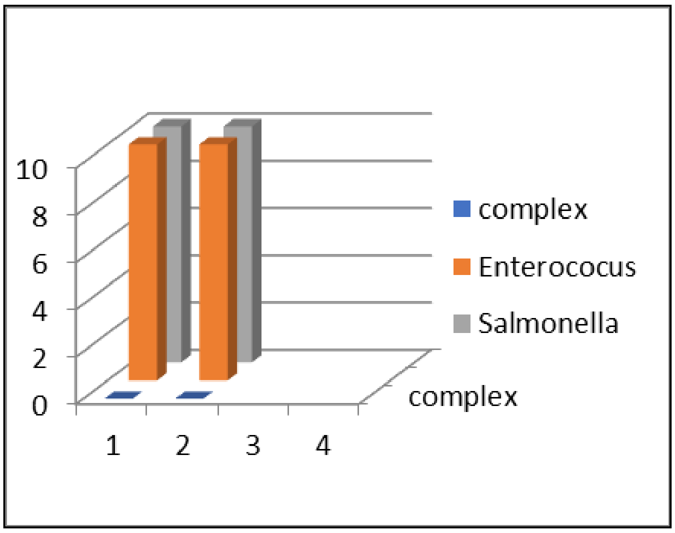
4. Anti-microbial activity

The Antimicrobial studies of the POM-1 and POM-2 are tested in vitro by the well-distributed method. The bacteria of Enterococcus and Salmonella have been used to find antimicrobial properties of different POM's. The zone inhibition values for POM -1, POM -2, and control values show increase in activity. The Antimicrobial studies of the compound act on gram positive and Gram-negative cell activity. The result for POM-1 shows gram-positive (Enterococcus) 10±1, and 10±2 gram-negative (Salmonella). POM-2 shows gram-positive (Enterococcus) 18±2and 20±2 gram-negative (Salmonella) [25].

The cell wall of bacteria has been well studied along with prepared complexes, to make the bacteria efficient and effective.

Table 3. Anti-microbial activity of POM-1, POM-2.

S.no	Complex	Theta (2Θ)	Grain Size (nm)
1	POM-1	9.74	58
		10.59	40
		12.10	48
		13.21	63
		25.59	52
		26.39	65
2	POM-2	9.79	52
		10.85	55
		17.73	58
		25.94	64
		26.25	70
		27.41	71



Bar diagram of Antimicrobial activity of POM-1 and POM-2.

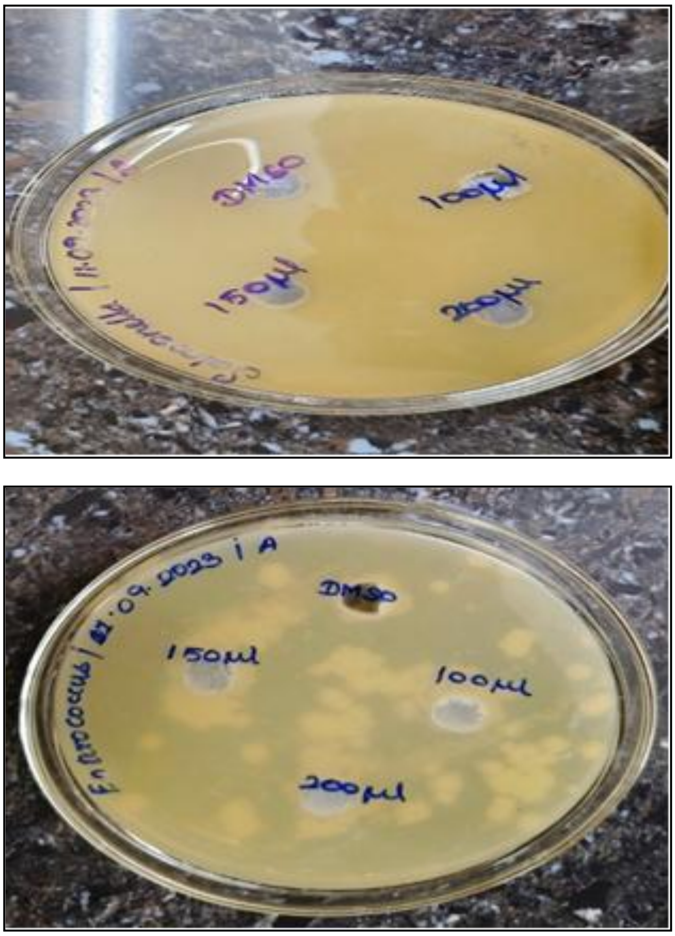


Fig .5 The (Gram +ve) Enterococus & (Gram -ve)Salmonella anti-microbial activity for POM-1.

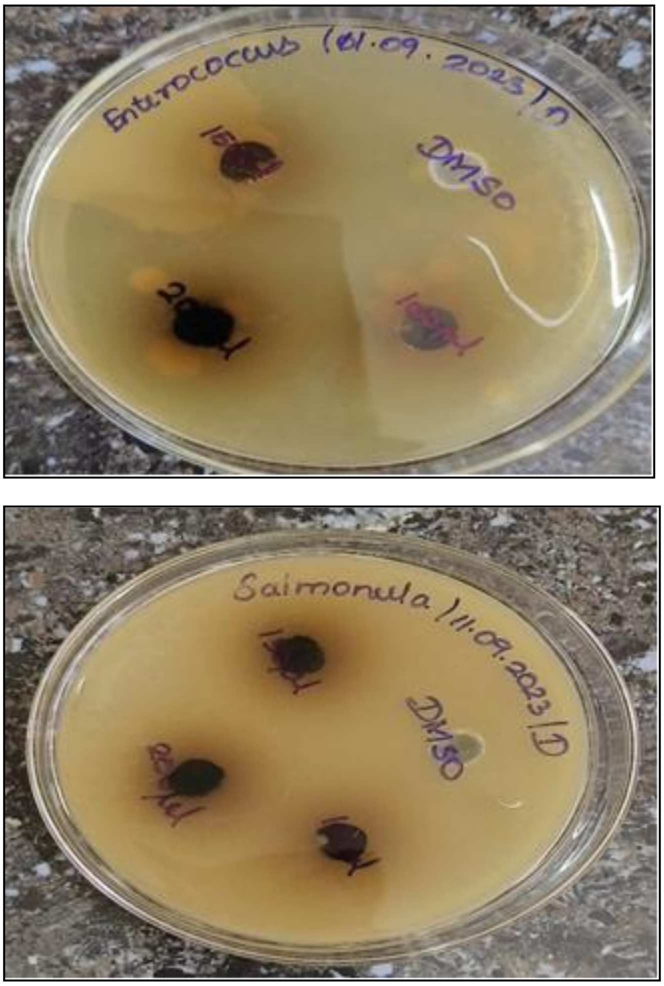


Fig 5. The anti-microbial activity of the Gram-positive (Enterococcus) and Gram-negative (Salmonella) of POM-2.

Table 4. Anti-microbial activity of POM-1, POM-2.

Complex	Enterococus (mm)	Salmonella (mm)
POM-1	10±1	10±2
POM-2	18±2	20±3

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 show that the characteristic peaks, which confirm the formation of POM-based complexes. The fingerprint region for the POMs has been observed. The crystalline size of the synthesised complexes has been calculated, which lies in the range of 40-80 nm. The POM-1 complexes show enhanced bacterial activity of Gram-positive and Gram-negative bacteria of about 10±1mmand 10±2mm for the POM complexes. The POM-2 complexes show high enhanced bacterial activity of gram-positive and gram-negative bacteria of about 18±2 and 20±3 mm.

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