

Development of Polyoxometalate-Based Ionic Liquids with Nitrogen Coordination

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ABSTRACT

Novel polyoxometalate (POM)-based ionic liquids, including a nitrogen-containing Keggin-type POM-ionic liquid, are the subject of this study's synthesis and characterisation. The POM-ionic liquid is produced by reacting a complex containing nitrogen with tetra-n-butylammonium bromide (TBAB). The process begins with the preparation of sodium nona-phosphomolybdate and continues with the formation of $K_5[(N(H_2O))PMo_{11}O_{39}] \cdot 7H_2O$. A variety of spectroscopic methods were used to characterize the synthesized compounds. The structural integrity and characteristics of the POM-ionic liquid were validated by FTIR, UV-Vis, and XRD characterization, which revealed crystalline phase purity, typical Keggin-type vibrations, and ligand-to-metal charge transfer transitions. A very viscous, well-defined ionic liquid with possible uses in catalysis and materials science is produced by combining nitrogen with TBAB.

Keywords: Polyoxometalate, Nitrogen, Ligand, Octahedra, Crystalline.

I. INTRODUCTION

With its unique qualities that combine the adaptable characteristics of polyoxometalates (POMs) with the ionic liquid (IL) structure, polyoxometalate-based ionic liquids (POM-ILs) have become an intriguing class of materials in the area of chemistry. Because of their unique characteristics, which include a large electrochemical stability window, low volatility, strong ionic conductivity, and adjustable solubility in polar and non-polar solvents, these hybrid materials have garnered a lot of interest. Catalysis, energy storage, materials science, and environmental protection are just a few of the many industrial and scientific fields that could benefit from a new class of compounds created by combining polyoxometalates—metal-oxide clusters with clearly defined structures and considerable redox versatility—with ionic liquids.

Anionic metal-oxide clusters known as polyoxometalates (POMs) usually have oxygen atoms coordinated to transition metal atoms in a highly structured, polyhedral framework. These metals include tungsten, molybdenum, and vanadium. Redox activity, acidity, and the capacity to function as Lewis acids—essential in catalysis and other chemical reactions—are among the intriguing chemical features imparted by POMs' unusual electronic structure. In addition, POMs are beneficial in harsh environments because to their great thermal stability. Their oxidation, hydrogenation, and polymerization catalytic roles are well-established, and their potential applications in renewable energy and environmental cleanup are beginning to attract interest.

In contrast, ionic liquids are salts that are liquid at or near room temperature and usually include different anions combined with large organic cations. Their distinctive properties include a large electrochemical window, low vapor pressure, inflammability, and excellent thermal stability. Ionic liquids are being investigated in several areas because of their extraordinary characteristics; they include electrochemistry, solvent extraction, catalysis, and environmental remediation, among many others. Despite their useful properties, however, it has been difficult to create ionic liquids with improved functioning and tailored uses.

By fusing POMs with ionic liquids, a new class of materials called POM-based ionic liquids (POM-ILs) is born, exhibiting the best features of both parent substances. The polyoxometalate is stabilized and becomes soluble in both water and non-water conditions thanks to the ionic liquid matrix, which also helps to avoid aggregation. Incorporating polyoxometalates into ionic liquids further improves the material's catalytic activity and chemical reactivity. More efficient, sturdy, and versatile materials with a broad variety of potential uses may be designed with the help of this combination.

Rechargeable batteries, supercapacitors, and other energy devices have investigated POM-ILs as electrolytes. Thanks to polyoxometalates' intrinsic electrochemical characteristics, strong ionic conductivity, and great thermal stability, POM-ILs have emerged as a superior alternative to traditional electrolytes. To illustrate the importance of POM-ILs for energy storage device performance over the long term, it has been shown that they display remarkable electrochemical stability. They can also be fine-tuned for use in energy storage devices, thanks to their adjustable electrochemical characteristics, which boosts both efficiency and capacity.

POM-ILs have a lot of potential for use in green technologies. Their redox activity, metal-ion solubility, and stability make them promising candidates for treating wastewater contaminated with hazardous metal ions or industrial effluents including organic contaminants. In addition, there is a rising interest in creating environmentally acceptable substitutes for conventional solvents and reagents, which is in line with the use of POM-ILs in sustainable processes and green solvents. As there is a growing interest in green chemistry and environmental protection on a worldwide scale, their contribution to creating eco-friendly technology is anticipated to intensify.

Also, there have been major developments in the synthesis of POM-ILs. To create POM-ILs with a broad variety of tunability and customisation options, many synthetic techniques have been established for various metal centers, anion types, and cation architectures. How the polyoxometalate is synthesized affects not only its size and form but also its electrical characteristics and how it interacts with the ionic liquid. This opens up a world of possibilities for researchers looking to tailor POM-ILs to specific needs by creating them with tailored features.

II. REVIEW OF LITERATURE

Silva, Dinis et al., (2022) For the refinery industry to thrive, there must be a long-term solution that can desulfurize and denitrogenate fuels in tandem. An active and recoverable catalyst is required to carry out the parallel oxidation of sulfur and nitrogen molecules found in fuels, which is crucial for accomplishing this goal. The effective synthesis of a novel heterogeneous catalyst ([BMIM]P_{Mo}12@ZIF-8) was achieved by encapsulating an imidazolium-based polyoxometalate (POM) inside a ZIF-8 framework. In order to continue the oxidative desulfurization and denitrogenation of a multicomponent model fuel that contains varied sulfur and nitrogen components, this composite material showed exceptional catalytic performance. All of these chemicals were entirely eliminated in under one hour, and the catalyst system could be reused for 10 consecutive cycles without degrading in performance. Actually, ZIF-8 was the first composite molecule to include an ionic liquid POM; this catalyst was used for the first time to perform oxidative desulfurization and denitrogenation processes simultaneously.

Martinetto, Yohan et al., (2021) This article describes four new ionic liquids that were created by pairing the cation trihexyltetradecylphosphonium with various polyoxotungstates or polyoxomolybdates. Physical factors assessed using different approaches show that the nature of the POM, especially its charge, has a significant impact on the rheological behaviors and viscosity of POM-based ionic liquids (POM-ILs). It is possible to produce viscous polymers with resin or pseudo-plastic characteristics, as well

as Newtonian liquids, by modifying the POM's characteristics. In the second phase of the research, the viability of employing these materials as solvents and catalysts for the oxidation of many alcohols is shown. Here we see how the POM-IL used has a profound effect on selectivity and strength. An easy way to recycle the catalyst is also included in the presentation.

Wang, Mei-Yan et al., (2016) The distinctive acid/base and redox properties of polyoxometalates (POMs), a family of molecular metal oxides, have led to their extensive use in a wide range of chemical reactions. Many POM-based ionic liquids (POM-based ILs) have been synthesized for applications in catalysis, structural chemistry, and materials science by manipulating the adjustable molecular structures of the anions and counter cations. Due to the effective activation of CO₂ by POM anions, POM-based ILs have shown benefits in the new area of CO₂ use, including CO₂ collection, cycloaddition to epoxides, and reduction of CO₂. Focusing on developments pertinent to CO₂ conversion, this study compiles the most up-to-date information on the catalysis of POM-based ILs.

Abia, Jude et al., (2013) A novel method was developed to dissolve and convert biomass in a single step using ionic liquids based on polyoxometalates (POM-IL). Two anionic POMs, phosphotungstate and tungstosilicate, and two cationic organic groups, 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium, were used to create a library of four functional POM-IL compounds. There are two functions performed by the POM-IL chemical. At 200 °C for 2 hours, it dissolves around 30 weight percent of cellulosic biomass. Secondly, HPLC analysis verified that POM-ILs facilitate the transformation of biomass into commercially valuable monosaccharides like xylose and glucose. Dynamic thermal stabilities over 300 °C were observed in all of the produced POM-IL compounds that underwent IR and thermogravimetric examination.

Zhu, Wenshuai et al., (2011) Environmental catalysis research has recently focused on deep desulfurization of diesel oil as a means to produce ultra low-sulfur diesel. A very promising desulfurization method is the extraction and catalytic oxidation desulfurization (ECODS) technology. A class of materials known as MIMPS that combine ionic liquids with Keggin-type polyorganic compounds. Similar to [Bmim]1-butyl 3-methyl imidazolium phosphotungstate, the chemical formula 3PW12O40•2H2O is also similar to [Bmim]3PW12O40. Ionic liquid (IL) served as a solvent, 3-butyl-3-methyl imidazolium phosphomolybdate (3PMo12O40) and 1-butyl-3-methyl imidazolium silicotungstate [Bmim]4SiW12O40] were synthesized in this study using POM-ILs materials as catalysts and hydrogen peroxide as an oxidant. The most effective catalyst, according to experimental tests, was [MIMPS]3PW12O40•2H2O, which removed all S ions after one hour at 30°C. A thorough investigation was conducted into the primary process variables, which included temperature, catalyst dose, and the O/S (H₂O₂/DBT) molar ratio. Dibenzothiophene (DBT) and 4,6-DMDBT (4,6-dimethyl-dibenzothiophene) are capable of achieving excellent desulfurization efficiencies when given the right circumstances. Additionally, real diesel oil showed strong activity in the reaction system, allowing a reduction from 1113 ppm to 198 ppm. There would be a little drop in activity throughout the reaction system's eight recycling cycles.

Ortiz-Acosta, Denisse et al., (2008) Ionic liquids have several potential uses due to their low melting point, low vapor pressure, excellent solubility, and high thermal and chemical stability. A wide range of sizes and heterometals may be used to manufacture polyoxometalates, which are oxygen clusters of early transition metals. The most appealing aspect of POMs is their ability to have their physical characteristics, including their electrical, magnetic, and optical properties, changed by following established protocols. Superconductivity and energy transfer are two cooperative qualities that POMs have shown. Choosing the right cation allows one to create POM ionic liquids. Novel POM ionic liquids are being developed by

researchers to make light-emitting materials by mixing different alkyl ammonium and alkyl phosphonium salts with organic or inorganic luminescent centers. Activated polymerizable groups on ammonium and phosphonium cations are used to further polymerize the ionic liquid into solid, transparent materials with a high metal density.

III. MATERIALS AND METHODS

It was unnecessary to purify the chemicals before using them as they were easily accessible from commercial sources. The reagent grade Na_2MoO_4 and TBAB were used in their original form. As a solvent, deionized water was used.

Physical Measurements

A Perkin Elmer Spectrum Version 10.4.1 FTIR spectrophotometer was used to record the infrared (IR) spectrum ($400\text{--}4000\text{ cm}^{-1}$) of the solid sample in KBr pellets. Bruker Tensor II FTIR spectroscopy was used to characterize the POM-ILs sample. Separate KBr pellets were used to distribute the material for infrared examination. The OPUS Bruker program was used to capture the spectra, which have a resolution of 4 cm^{-1} and range from 4000 to 400 cm^{-1} .

A Japanese Shimadzu UV-1800 spectrometer equipped with the specialized spectroscopy software UV Probe version 2.34 was used to measure the UV-Vis spectra over the 200 to 800 nm wavelength range. The sample was collected using a quartz cuvette with an optical path length of 1.0 cm in isopropanol as the solvent.

Bruker D8 Advance diffractometers equipped with LynxEye XE T discriminating $\text{CuK}\alpha$ radiation were used to measure X-ray powder diffraction patterns. A plastic specimen container that was flat had samples stacked on top of it.

Synthesis of Sodium Nona Phosphomolybdate $\text{Na}_9[\text{PMo}_9\text{O}_{34}]$ (1)

To reach a pH of 8, dissolve 24 gm of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in 30 ml of water. Gradually add 15 ml of $85\%\text{ H}_3\text{PO}_4$ while stirring. In order to get a final pH of about 7, 8 milliliters of glacial acetic acid are added dropwise while swirling vigorously. A substantial amount of white precipitate is produced when AcOH is added. The precipitate is collected and dried by suction filtration after being agitated in the solution for 1 hour .

Synthesis of $\text{K}_5[(\text{NH}_2(\text{H}_2\text{O}))\text{PMo}_{11}\text{O}_{39}] \cdot 7\text{H}_2\text{O}$ (2)

The solution was prepared by gently boiling and stirring 10 g (3 mmol) of $\text{Na}_9[\text{PMo}_9\text{O}_{34}]$ (1) into 20 ml of water. A dark crimson solution was produced by adding 0.61 gm (3 mmol) of nitrogen-containing reagent. Two grams of solid KCl (27 millimoles) was added to the reaction mixture after it had been agitated for three hours at room temperature. A precipitate of pale yellow color was produced and collected during the filtering process. After a thorough washing in ethanol and diethyl ether, it was let to air dry.

Synthesis of Keggin Polyoxometalate Ionic Liquid $[(\text{n-C}_4\text{H}_9)_4\text{N}]_5[\text{PMo}_{11}\text{O}_{39}\text{N}(\text{H}_2\text{O})] \cdot 7\text{H}_2\text{O}$ (3)

$\text{K}_5[(\text{N}(\text{H}_2\text{O}))\text{PMo}_{11}\text{O}_{39}] \cdot 7\text{H}_2\text{O}$ (2). Twenty milliliters of hot water was used to dissolve $7\text{H}_2\text{O}$ (2). A distinct beaker was used to dissolve 0.972 g (3 mmol) of TBAB (Tetra butyl ammonium bromide) in 30 ml of toluene, with slow stirring. Subsequently, TBAB in toluene solution was added to the POM (2) solution drop by drop. After 10 minutes of vigorous stirring, the organic layer was extracted. After $30\text{ more milliliters}$ of toluene were added to the reaction mixture in the separation funnel, it began to separate into two layers. Under vacuum, the organic layer and solvent were separated. The exceedingly viscous, light yellow liquid was washed extensively with an additional 50 ml of toluene after the solvent had been removed under decreased pressure. The POM-IL, which had just created a new liquid phase, was the very viscous liquid.

IV. RESULTS AND DISCUSSION

FTIR Spectrophotometer

Figure 1 shows that (1) has the IR spectra that are typical of a Keggin-type structure. The values of ν (P-O), ν (Mo=O), and ν (Mo-O-Mo) at 1219.81, 1073.28, 973.47, 903.66, and 772.40 cm^{-1} are confirmed to be five distinct vibration bands. In addition to these bands, the IR spectra of the compound in question displays distinct polyoxoanion bands at 502.14, 594.44, and 772 cm^{-1} , respectively, which are attributable to ν (Mo=Ot terminal), ν (Mo-Ob-Mo octahedral edge sharing), and ν (Mo-Oc-Mo octahedral corner sharing). The existence of lattice water is confirmed by the ν (-OH) absorption and the hydrogen bonds, which are shown by a large peak at 3532.39 cm^{-1} .

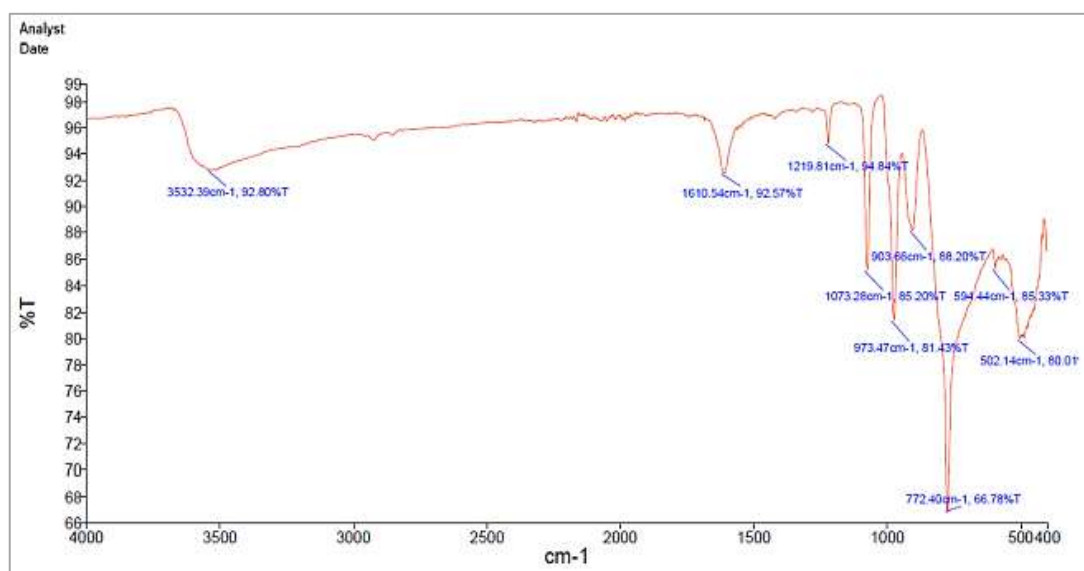


Figure 1: FTIR Spectrum of Complex 1 Analyzed in KBr Pellet Form

A trilacunary Keggin-type structure is suggested by the infrared spectra of complex 2, as seen in Figure 1. As a result, PMo9 exhibits its characteristic five strong symmetric and asymmetric stretching frequencies between 1070 and 1150 cm^{-1} , with a shoulder peak between 860 and 900 cm^{-1} , and a value of $\nu_{\text{as}}(\text{P-Oi})$ between 1060 and 1150 cm^{-1} , representing the value of $\nu_{\text{as}}(\text{Mo=Ot})$ with terminal oxygen., $\nu_{\text{s}}(\text{Mo-Oc-Mo})$ octahedral corner sharing), 760-800 cm^{-1} , and 550-600 cm^{-1} , all of which are related to octahedra that share edges, corners, and other structural features.

Both PMo9 (1) and NIPMo9 (2) have very comparable FT-IR spectra, suggesting that the polyoxomolybdate structure is the primary source of the vibration bands. The antisymmetric stretching vibrations $\nu_{\text{as}}(\text{P-Oi})$, the primary band of the ligand, are moving from the 1200-700 cm^{-1} region to higher frequencies, as can be shown by comparing the infrared spectra of the PMo9 ligand (1) with the NIPMo9 (2) complex. Because of the coordination of the nitrogen ions, the trilacunary structure seems to be more cohesive. A larger shift of the $\nu(\text{Mo-Oc,e-Mo})$ stretching vibrations for the bonds from the belt and cap regions suggests that oxygen atoms from corner-sharing and edge-sharing octahedra coordinate N ions. The presence of a notable absorption band at 524 cm^{-1} , which may be explained by the N-O stretching mode, serves as evidence of the presence of an N-O bond. Aside from these, a new band with the abbreviation $\nu_{\text{s}}(\text{Mo-Ob-Mo})$ emerges in the 1000-700 cm^{-1} range, which stands for the two PMo9O34 units connected by bridging Ob atoms in the complex. In addition, a big and strong peak at 3502 cm^{-1} , which is explained by ν (-OH) absorption together with the hydrogen bonds, confirms the presence of lattice water.

Figure 2's peaks make the use of the tetra butyl ammonium ion as a counter cation quite evident. C-H, -CH₂-, and -CH₃ stretching vibrations, both symmetric and asymmetric, produced peaks between 2850 and 3250 cm⁻¹. The C-N bonding may be seen by observing the peaks about 1000-1350 cm⁻¹. In this case, the region between 1400 and 1600 cm⁻¹ is determined by C-C and C-N bonding.

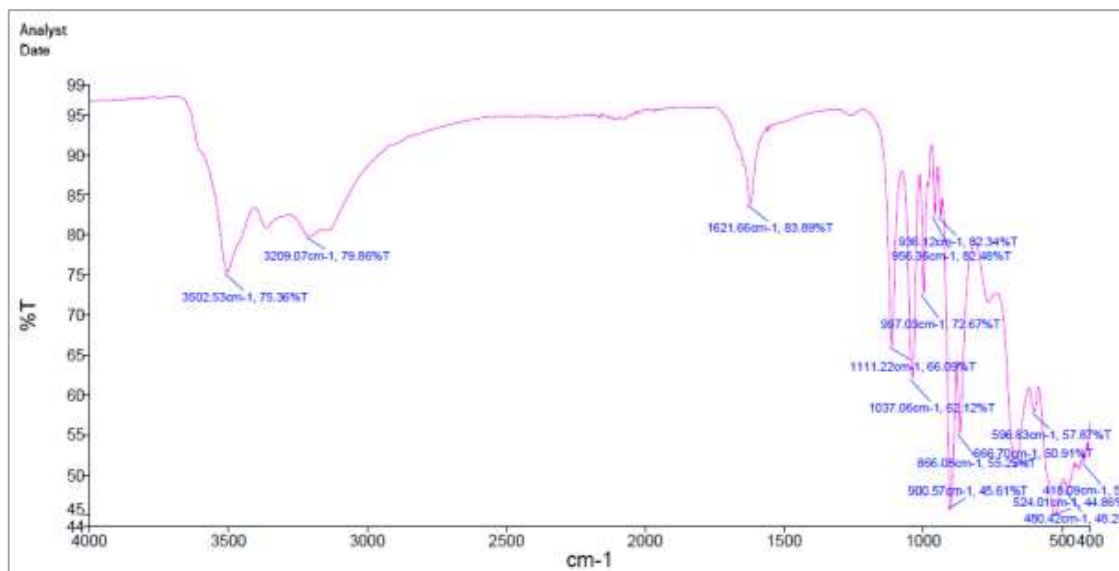


Figure 2: FTIR Analysis of Complex 3 in KBr Pellet Form

UV-Vis spectroscopy

When exposed to ultraviolet light, polymers derived from transition metals in their highest oxidation states (POM) show substantial absorption characteristics in the UV region below 400 nm. You may attribute these absorptions to the oxygen-to-metal (O → M) charge transfer bands of LMCT (Ligand to Metal Charge Transfer). Polyoxoanions have electrons moved from their low-energy occupied 2p orbitals to their high-energy unoccupied d orbitals. Both the 240 and 300 nm absorption peaks are shown by the phosphorus mono nitrogen molybdic Keggin cluster [PMo₁₁O₃₉N(H₂O)]⁵⁻. These characteristics are blamed on the intramolecular ligand to the charge transfer of metal transitions (LMCT), specifically on the Ot → W and Ob,c → W transitions. A small absorption peak at around 780 nm is also observed in the spectra. The d-d transition of the nitrogen hetero d-element is responsible for this absorption. The hybrid compound's yellow hue is explained by its absorption in the visible spectral region, which occurs at around 800 nm.

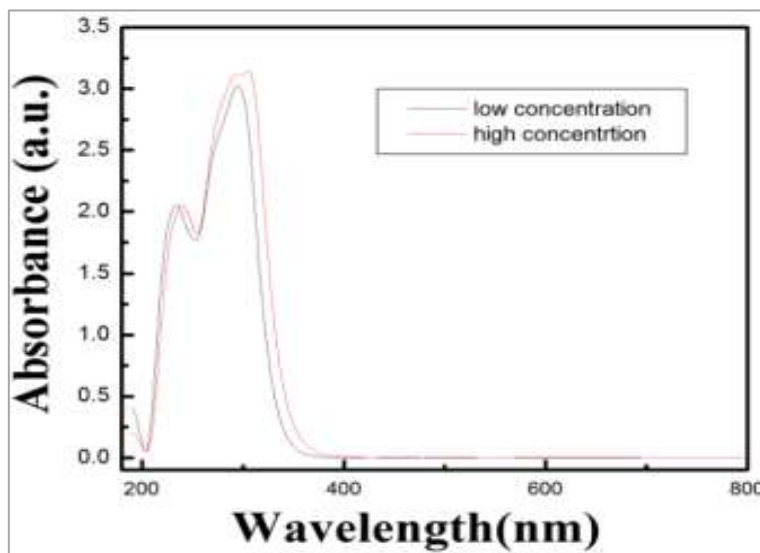


Figure 3: UV-Vis Spectral Analysis of Complex 3

X-ray Diffraction

Additionally, the X-ray diffractometry method validated the structure of the synthesized N-POM. The chemical mentioned before was subjected to a powder XRD experiment to determine the purity of its crystalline phase. Consistent with the existence of a single crystalline phase corresponding to the chemical, the sample patterns were determined. The X-ray diffractogram of the prepared N-POM structure is shown in Figure 4. The four fundamental peaks in the X-ray diffractogram are located at 7.5, 8.9, 11.3 and 20.1 Å. This structure is definitely a POM structure, as these peaks prove.

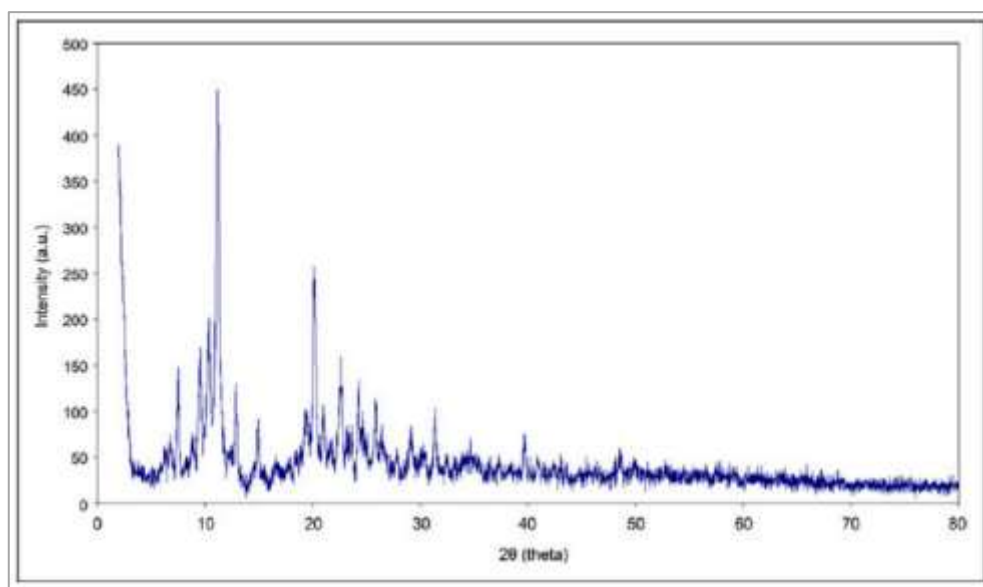


Figure 4: X-ray Diffractogram of Complex 3

V. CONCLUSION

The promise of the nitrogen-containing Keggin-type polyoxometalate (POM)-ionic liquid as a novel material with unusual chemical and structural properties has been shown by its effective production. Extensive analysis by FTIR, UV-Vis, and XRD methods validated the predicted structural characteristics, such as the existence of metal-to-ligand charge transfer and the compound's pure crystalline phase. A highly viscous ionic liquid with possible uses in catalysis, materials science, and other cutting-edge domains was produced by incorporating nitrogen into the POM framework, with tetra-n-butylammonium bromide serving as the counter cation. Future technical developments may benefit greatly from this work's insights into the design and synthesis of functional ionic liquids based on nitrogen-containing polyoxometalates.

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