

A New Avenue in Hybrid Polyoxometalate Chemistry: Synthesis and Characterization of Mn (II) Functionalized POM Based Ionic Liquids

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Abstract

The synthesis of novel hybrid materials, combining the properties of organic and inorganic components in one compound, results in materials with unique physical and chemical properties. The organic-functionalization of POMs with covalently or non-covalently linked organic species opens a large spectrum of possibilities and research challenges. The development of such novel systems for metal-organic architectures is an attractive research field. Lacunary polyoxometalates (POMs) offer structurally well-defined coordination sites with various coordination directions; thus, lacunary POMs are ideal building blocks for inorganic-organic architectures. Here, we report the successful self-assembly of transition metal substituted anionic POM along with a new generation POM based ionic liquid. We know that the counter-cations in polyoxometalate chemistry play immense role beyond charge balance. That is why the resultant structure is furthermore utilized as a stable and reactive building block to synthesize POM based ionic liquid (POM-IL), an inorganic-organic architecture comprising 3d-metal substituted mono-lacunary POM and tetrabutyl ammonium (TBA) ligands.

Keywords: Organic-inorganic hybrid, Polyoxometalate based ionic liquid (POM-IL)

Introduction

Metal-organic architectures have received increasing research interest owing to their outstanding properties for application in many fields of science, including molecular recognition, separation, catalysis, and energy conversion [1–2]. The properties of metal–organic architectures are highly dependent on their constituent metals, organic ligands, and structure (i.e., shape and size), and, therefore, the development of novel systems will lead to unexplored functions and applications for these fascinating materials. In this sense, may be the field of polyoxometalates (POMs) lies between the organic and the inorganic world. Hybrid organic-inorganic materials are pulling major attention due to their potential to generate unusual structures and properties by combining the features of the organic and inorganic components. Among them, hybrid materials containing polyoxometalates (POMs) have shown fascinating electronic, optical, magnetic and catalytic properties. Literally, every day a new combination of polyoxometalate anion and organic cation could be originated, thus opening a large spectrum of possibilities and research challenges. In this context this paper pretends to give an insight in a small but

rapidly developing recent area dedicated to the production, structure elucidation of a hybrid polyoxometalates based ionic liquids. POMs are clusters of anionic metal oxides where the metals are high oxidation states (e.g., Mo^{6+} , W^{6+} , V^{5+}), and their chemical and physical properties can be readily modulated by appropriate selection of the structures and metal atoms, resulting in a wide range of applications, such as catalysis, photocatalysis, sensors, batteries, energy conversion, and magnetism [3–6]. Lacunary POMs, where one or more $\{\text{MO}_x\}$ units are removed, possess structurally well defined and highly reactive vacant sites for organic ligands and metal species. [7–8] To date, several fully occupied POMs, such as vanadate, [9–11] Ni-substituted POMs, [12] $\{\text{Mo}_6\}$ [13] and $\{\text{XM}_6\}$ ($\text{M} = \text{Mo}$ or W), [14] have been utilized for the construction of inorganic–organic architectures upon connection with organic ligands (e.g., carboxylate and phosphate ligands). However, multivacant lacunary POMs are metastable and frequently suffer from unexpected isomerization or decomposition reactions, and the construction of transition metal substituted POM–TBA architectures has no precedent. Here, we have reported the successful self-assembly of anionic POM–organic architectures comprising mono-vacant lacunary POMs and tetra butyl ammonium ions. By introducing Mn (II) ions to its vacant sites, the tri-vacant lacunary phosphomolybdate $[\text{A}-\alpha\text{-PMo}_9\text{O}_{34}]^{9-}$ is significantly stabilized in organic solvents in the form of $[(\text{Mn}^{\text{II}}(\text{H}_2\text{O}))\text{PMo}_{11}\text{O}_{39}]^{5-}$ ion. Not only that, monolacunary Mn-incorporated Keggin POM $\text{K}_5[(\text{Mn}^{\text{II}}(\text{H}_2\text{O}))\text{PMo}_{11}\text{O}_{39}]\cdot 7\text{H}_2\text{O}$ is further rendered to POM based ionic liquid $[(\text{n-C}_4\text{H}_9)_4\text{N}]_5[\text{PMo}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})]$ in presence of tetra butyl ammonium ion. POM-Ionic Liquids (POM-IL) are salts in the liquid state with a melting point below 100°C and are typically formed by an organic bulky cation and an inorganic polyoxometalate anion [15]. Electrostatic interactions are the dominant interactions between ions and some intermolecular interactions help the supramolecular organization of the ionic liquids (ILs). For most applications, room-temperature ILs are the most desirable. The field of ILs and their application is growing in number and diversity in both the academic research and industrial development [16]. A variety of IL-related materials have been developed as ILs can be easily incorporated in different supports such as silica, activated carbons, metal-organic frameworks (MOFs) or in a polymer matrix. Thus ionic liquids have found a plethora of direct or indirect applications in catalysis [17], biocatalysis [18] electrochemical devices [19] or engineering fluids amongst several others. The use of POM as corrosion inhibitors for Al, Zn, steel and other metals were investigated by many studies. The most common cations for ILs are imidazolium, ammonium and guanidinium cations [20]. The use of anionic polyoxometalates (POMs) molecular cluster gave rise to a new family of interesting, polyoxometalate-ionic liquids (POM-ILs) [21]. But our reported tert-butyl cation, counterbalanced by transition metal functionalized POM can be marked as a novel POM based ionic liquid. The aim of this article is to demonstrate that cations are not simple spectator ions, but are key players in 21st century POM science.

Experimental

Materials and methods

Chemicals were readily available from commercial sources and were used as received without further purification. Na_2MoO_4 , tetra butyl ammonium bromide (TBAB) (AR Loba, India) were of reagent grade and were used as received. Deionized water was used as the solvent.

Physical measurements

IR ($400\text{--}4000\text{ cm}^{-1}$) of solid sample was recorded in KBr pellets on a Perkin Elmer Spectrum Version 10.4.1 FTIR spectrophotometer. POM-ILs sample was characterized by FTIR spectroscopy using Bruker Tensor II spectrometer. The sample was spread between KBr pellets for IR analysis. The obtained spectrum was recorded from $4000\text{ to }400\text{ cm}^{-1}$ with resolution of spectra is 4 cm^{-1} using OPUS Bruker software.

The UV-Vis spectrum was measured over the wavelength ranges from 200 to 800 nm using a Shimadzu UV-1800 spectrometer (Japan), with special spectroscopy software UV Probe version 2.34. Sample was recorded in isopropanol as solvent with cuvette of quartz (optical path length equal 1.0 cm).

Thermo gravimetric analysis (TGA) was performed using TA instrument TGA Q500. Temperature was ramped up from room temperature to $100\text{ }^{\circ}\text{C}$ at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$, held isothermally at $100\text{ }^{\circ}\text{C}$ for 15 mins, ramped up to $200\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. It is then finally and ramped up to $500\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$.

X-ray powder diffraction patterns were measured on a Bruker D8 Advance diffractometer using LynxEye XE T discriminated $\text{CuK}\alpha$ radiation. Samples were layered on a flat plastic specimen holder.

Synthesis of sodium nona phosphomolybdate $\text{Na}_9[\text{PMo}_9\text{O}_{34}]$ (1)

24 gm $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ is dissolved in 30ml of water and then 15 ml of 85% H_3PO_4 is added drop wise with stirring to achieve pH at 8. Later on 8 ml of glacial AcOH is added drop wise with vigorous stirring to achieve the final pH of ~ 7 . During addition of AcOH, large quantities of white precipitate is formed. The solution is then stirred for 1hr and the precipitate is collected & dried by suction filtration. The same synthetic procedure was followed as reported by Knoth et al [22].

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

10 g (3mmol) of $\text{Na}_9[\text{PMo}_9\text{O}_{34}]$ (1) was dissolved in 20ml of water by gentle heating and stirring. Solid 0.61 gm (3mmol) of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ was added resulting in to a dark red solution. The reaction mixture was stirred for 3 h at room temperature, and 2g solid KCl (27 mmol) was added on the resulting mixture. Pale yellow precipitate was formed which was isolated during filtration. It was washed with ethanol, diethyl ether; and air dried.

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

15 g (3mmol) of $\text{K}_5[(\text{Mn}^{\text{II}}(\text{H}_2\text{O}))\text{PMo}_{11}\text{O}_{39}]\cdot 7\text{H}_2\text{O}$ (2) was dissolved in 20 ml of hot water. 0.972 g (3mmol) of TBAB (Tetra butyl ammonium bromide) was dissolved in 30ml of toluene in a separate beaker by gentle stirring. Afterwards TBAB in toluene solution was added drop wise to the POM (2) solution. The mixture was vigorously stirred for 10 minutes and the organic layer was separated. In the separation funnel, the reaction mixture was started to separate into two layers after addition of another 30 mL of toluene. The organic layer was separated, and the solvent was separated under vacuum. After removal of the solvent under reduced pressure, the pale yellow highly viscous liquid was thoroughly washed with another 50 ml portion of toluene. The heavily viscous liquid was the POM-IL which formed a new liquid phase.

Results and discussion

Vibrational Spectra of $\text{Na}_9[\text{PMo}_9\text{O}_{34}]\cdot x\text{H}_2\text{O}$ (1)

The IR spectra of (1) display the characteristic features of a Keggin-type structure as shown in Fig-1. Five strong vibration bands are indeed observed for $\nu(\text{P}-\text{O})$, $\nu(\text{Mo}=\text{O})$, and $\nu(\text{Mo}-\text{O}-\text{Mo})$ at 1219.81, 1073.28, 973.47, 903.66, and 772.40 cm^{-1} . Apart from these, the IR spectrum of the title compound has some characteristic bands for the polyoxoanion at 502.14, 594.44 and 772 cm^{-1} which are attributed to $\nu(\text{Mo}=\text{O}_t \text{ terminal})$, $\nu(\text{Mo}-\text{O}_b-\text{Mo}$ octahedral edge sharing), and $\nu(\text{Mo}-\text{O}_c-\text{Mo}$ octahedral corner sharing) respectively. In addition, a strong broad peak observed at 3532.39 cm^{-1} is assigned to $\nu(-\text{OH})$ absorption along with the hydrogen bonds which proves the presence of lattice water.

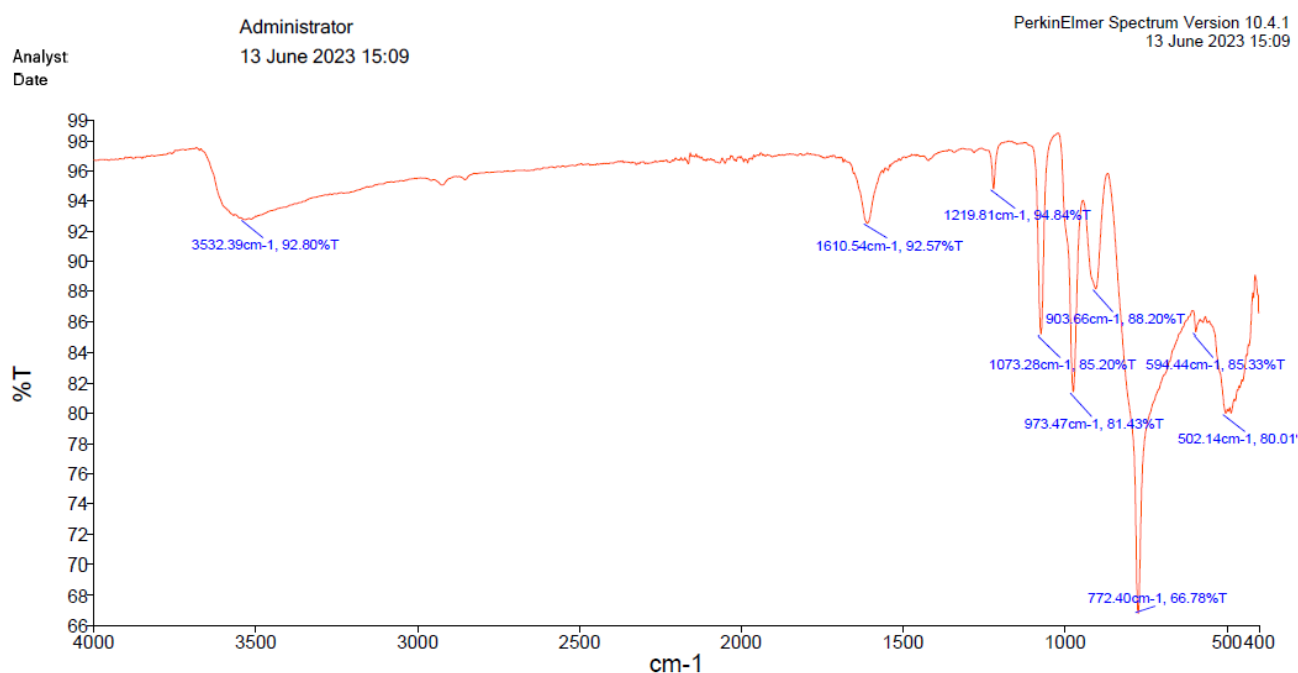


Fig-1: FTIR spectrum of complex 1, taken as KBr pellet

Vibrational Spectroscopy of POM-ionic liquid $[(n-\text{C}_4\text{H}_9)_4\text{N}]_5[\text{PMo}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})]$ (3)

The IR spectra of (2) in Fig-1 display the characteristic features of a typical trilacunary Keggin-type structure. That is why PMo_9 shows usual five strong symmetric and asymmetric stretching frequencies in the range of 1070–1150 cm^{-1} [$\nu_{\text{as}}(\text{Mo}=\text{O}_t$ with terminal oxygen O_t)], shoulder peak in between 860–900 cm^{-1} [$\nu_{\text{as}}(\text{P}-\text{O}_i$ with internal oxygen atom which links P and Mo)], 970–1000 cm^{-1} [$\nu_{\text{s}}(\text{Mo}-\text{O}_e-\text{Mo}$ where O_e connects edge-sharing octahedra,)], 760–800 cm^{-1} [$\nu_{\text{s}}(\text{Mo}-\text{O}_c-\text{Mo}$ octahedral corner sharing)] and 550–600 cm^{-1} [$\nu_{\text{s}}(\text{Mo}-\text{O}_{c,e}-\text{Mo}$ where $\text{O}_{c,e}$ connects corner and edge-sharing octahedra,)]. Similarity of FT-IR spectra for PMo_9 (1) and for $\text{Co}^{\text{II}}\text{PMo}_9$ (2) shows that vibration bands are mainly due to the polyoxomolybdate structure. When comparing the IR spectra of $\text{Mn}^{\text{II}}\text{PMo}_9$ (2) complex with that of the PMo_9 ligand (1), a shift of the antisymmetric stretching vibrations $\nu_{\text{as}}(\text{P}-\text{O}_i)$, the main band of the ligand, appearing in the 1200–700 cm^{-1} range towards higher frequencies indicates that the coordination of the transition metal ions increases the cohesion of the trilacunary structure [23]. On the other hand, the larger shift of the $\nu(\text{Mo}-\text{O}_{c,e}-\text{Mo})$ stretching vibrations for the bonds from the belt and cap areas indicates the coordination of $\text{Mn}(\text{II})$ ions by O_c and O_e oxygen atoms from corner-sharing and edge-sharing octahedra. The strong absorption band at 524 cm^{-1} can be allotted to the $\text{Mn}-\text{O}$ stretching mode, demonstrating the existence of $\text{Mn}-\text{O}$ bond. Apart from these, in the range 1000–700 cm^{-1} , the

complex exhibits a new band, due to the asymmetric stretching vibrations of the bridges $\nu_s(\text{Mo-O}_b\text{-Mo})$, proving the presence of two $\text{PMo}_9\text{O}_{34}$ units connected by bridging O_b atoms. In addition, a strong broad peak observed at 3502 cm^{-1} is assigned to $\nu(-\text{OH})$ absorption along with the hydrogen bonds which proves the presence of lattice water.

The incorporation of tetra butyl ammonium ion as counter cation can be well understood by the peaks depicted in the Fig-2. The peaks from 2850 to 3250 cm^{-1} originated from the asymmetric/symmetric stretching vibration of the C-H, $-\text{CH}_2-$, and $-\text{CH}_3$ groups. The C-N bonding is revealed by the peaks at approximately 1000 – 1350 cm^{-1} . The region between 1400 to 1600 cm^{-1} is dominated by the C-C and C-N bonding in this case.

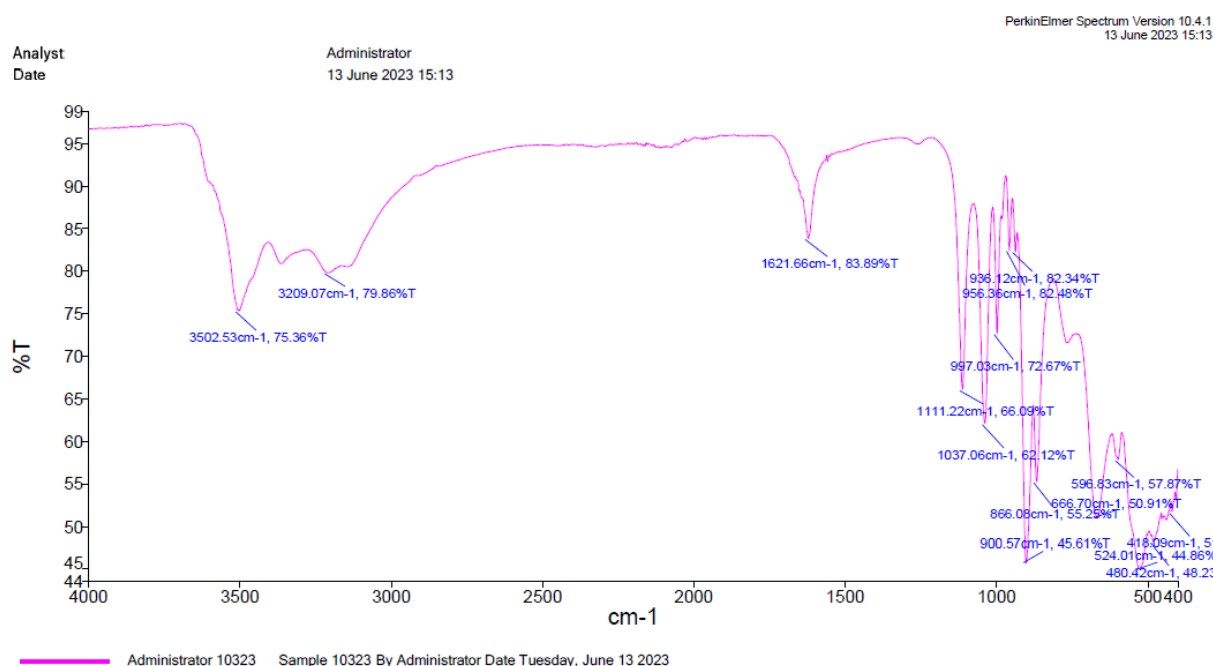


Fig-2: FTIR spectrum of complex 3, taken as KBr pellet

UV-Vis spectroscopy

It is known that when POM, based on transition metal in their highest oxidation states, are irradiated with UV light, they exhibit strong absorption features in the UV area below 400 nm . These absorptions can be assigned to oxygen-to-metal ($\text{O} \rightarrow \text{M}$) bands of charge transfer LMCT (Ligand to Metal Charge Transfer). Electrons are transferred from the occupied electronic states of low energy (oxygen $2p$ orbitals in polyoxoanions) to the vacant states of high-energy (metal d orbitals). The phosphorus mono manganese molybdc Keggin cluster $[\text{PMo}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})]^{5-}$ exhibits absorption top peaks at 240 and 300 nm . These features are attributed to the intra molecular ($\text{O}_t \rightarrow \text{W}$ and $\text{O}_{b,c} \rightarrow \text{W}$) ligand to the charge transfer of metal transitions (LMCT). In addition, the spectrum presents a weak absorption peak in the visible spectrum at around 780 nm . This absorption is due to $d-d$ transition of the manganese hetero d-element. A comparison with the UV-Vis spectrum of the well-known manganese hexaqua complex shows an interesting similarity about the absorption in the visible spectral range occurring at around 800 nm and explains the yellow color of the hybrid compound. This comparison indicates that the manganese retains its octahedral coordination environment in the organic phase with a sixth coordination position bounded to a water ligand (5 oxygen bonding from the Keggin cluster and the sixth oxygen bonding through aqua ligand) [24].

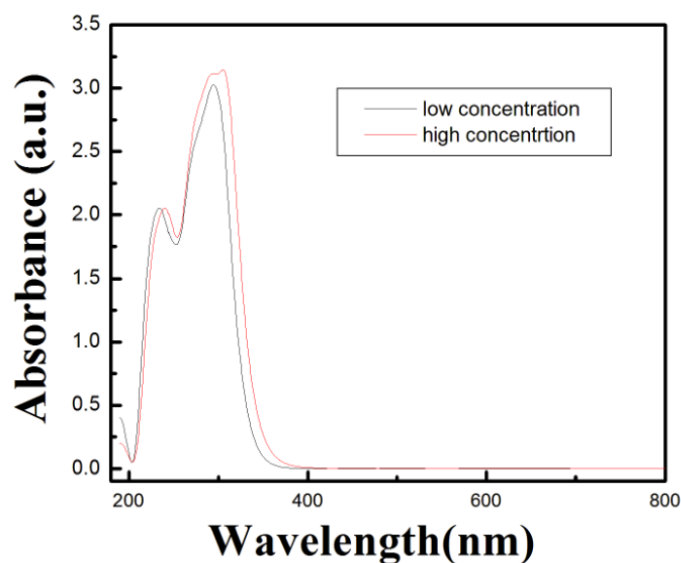


Fig-3: UV-vis spectrum of complex 3

The synthesized Mn-POM structure was also confirmed by X-ray diffractometry technique. The powder XRD experiment was carried out on the aforesaid compound in order to observe its crystalline phase purity. The obtained patterns of the samples were consistent as it indicated the presence of one crystalline phase which corresponded to the compound. Fig-4 shows the X-ray diffractogram of the prepared Mn- POM structure. In the X-ray diffractogram, there are four basic peaks at 7.5, 8.9, 11.3 and 20.1 Å. These peaks confirm that the structure is POM structure [25].

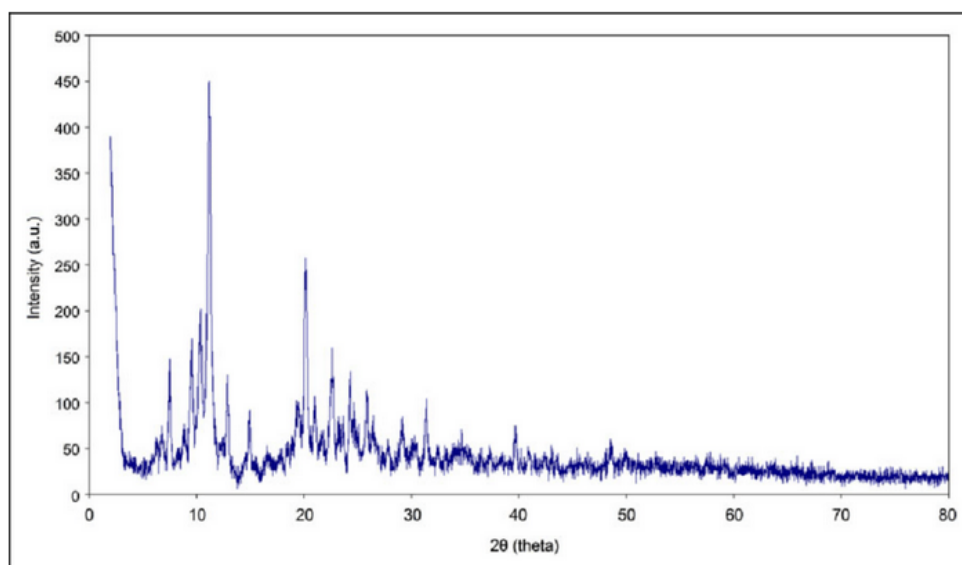


Fig-4: X-ray diffractogram of POM-ionic liquid [(n-C₄H₉)₄N]₅ [PMo₁₁O₃₉Mn(H₂O)]

Thermo gravimetric analysis (TGA)

TGA of the product derived is given in the figure below. The viscous ionic liquid has a mass loss of 40% by weight in the temperature change of 30 to 220 °C. Thus we have observed an average loss of 8 water molecules between room temperature and 220 °C corresponding to crystallization and coordinated water molecules. The thermogravimetric analysis experiment of POM-IL was performed under nitrogen gas atmosphere with a heating rate of 10°C min⁻¹ in the temperature range from room temperature to 800

°C. As shown in figure 3, the TGA curves have two main steps of the weight loss for both the organic moieties and the POM cluster. With increasing temperature there was the first sudden weight loss step from 100 to 120°C with the weight loss of 12% is corresponding to the removal of TBA moiety. The second weight loss steps of 28% in the range of 200–220°C can be ascribed to the loss of all the remaining oxo–manganese parts and complete decomposition of the Keggin cluster $[PMo_{11}O_{39}]$ residues in the compound. The two step weight losses of the whole decomposition of POM-IL are in consistence with the calculated values. This also supports the chemical composition of the successful synthesis of the compound.

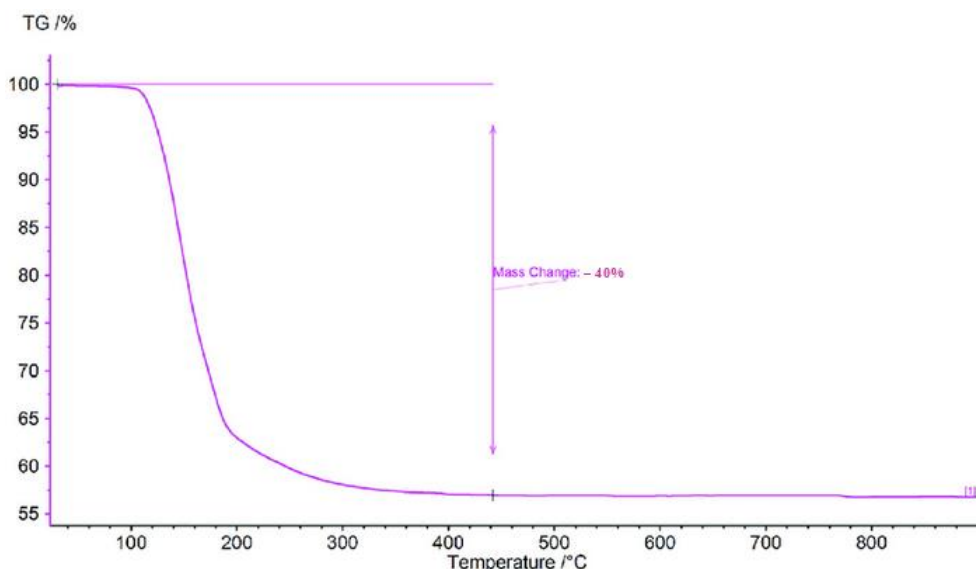


Fig-5: Thermo gravimetric analysis weight loss profile of complex 3

Rheological experiments

Rheological experiments were performed using a modular rotating rheometer (MCR501, Co. Anton-Paar). The EC motor (electronically commutated) equipped with a high-precision air bearing system for minimal friction losses. Rheological tests were conducted in the rotational and oscillatory mode. The rheological measurements were performed to analyze the relationship between the friction coefficient and rheological properties of POM based ionic liquid. The evolution of the shear stress (τ) as a function of the shear rate ($\dot{\gamma}$) at various temperatures is given in the figure below. From the observed straight line flow curves, it appears that the compound is a Newtonian fluid ($\tau = \eta \times \dot{\gamma}$ where η is the viscosity) in the 20–100°C temperature range and that the viscosity (i.e., the slope of the curves) gradually decreases with the increase of the temperature. Our POM based ionic liquid is a Newtonian liquid at room temperature which is confirmed by the linear dependence observed between the shear stress and the shear rate.

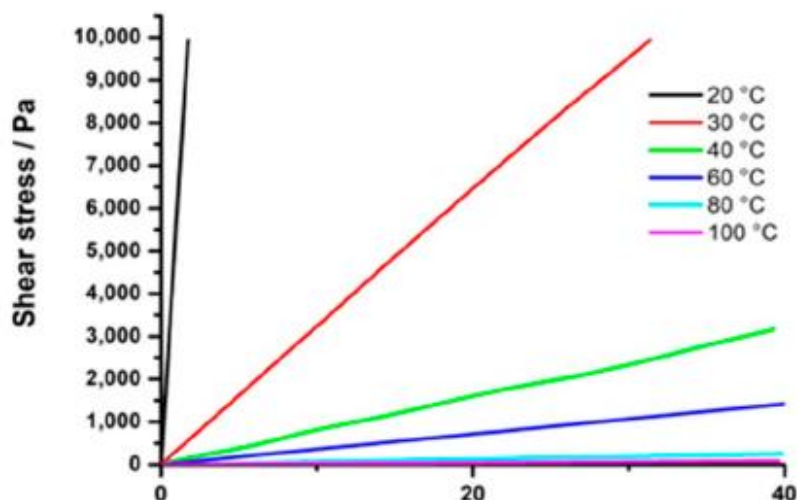


Fig-6: Flow curves $\tau = f(\gamma)$ measured between 20 and 100 °C for complex 3

Conclusion

In this work we have prepared and characterized Keggin polyoxometalate ionic liquid (POM-IL) [(n-C₄H₉)₄N]₅[PMo₁₁O₃₉Mn(H₂O)]. This is a transition metal substituted lacunary POM where phosphorus acts as the central atom and the reproducibility of this giant complex is praiseworthy with a good precision value of percentage elemental composition. The resulting organic–inorganic hybrid POM has been fully characterized by various techniques such as XRD, FTIR, UV-Vis, TGA and rheological measurements. As a conclusion of this work, we also characterized the nature of ionic liquid produced. Rheological investigation which is one of the very significant tests for ionic liquids helped us to demonstrate the true ionic liquid nature of this compound.

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