HYDROTHERMAL SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NOVEL TRANSITION METAL FUNCTIONALIZED HYBRID KEGGIN POLYOXOMETALATES

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Abstract

A novel copper-ethylenediamine (en) chelate based inorganic–organic hybrid complex counterbalanced by Keggin POM was synthesized hydrothermally. One-pot-synthesis procedure has been followed and the compound was completely characterized by elemental analysis, Fourier-transform infrared and UV–Vis spectroscopies, thermogravimetric analysis, powder X-ray diffraction (PXRD), and single-crystal X-ray diffraction. The structural analysis study showed that the $[SiW_{12}O_{40}]^{4-}$ ions reside in the inter space between two cationic layers as discrete counter ions and are not coordinated to the transition metal ion. The crystalline architecture showed that this hybrid inorganic-organic compound is stabilized by various non-covalent interactions such as N-H···O, C-H···O, O-H···O etc. Significantly, this hybrid material is a rare case of an inorganic–organic hybrid polyoxometalate (POM) with (en) as a chelating ligand.

Keywords: Polyoxometalates, Hydrothermal one pot synthesis, Organic-inorganic hybrid, chelates

Introduction

Polyoxometalates (POMs) are a class of anionic metal-oxygen clusters built by the connection of $[MO]_x$ polyhedra of the early transition metals in their highest oxidation states. [1] The terminal oxo-ligands are strong π-electron donors; therefore lone oxygen atoms bind very strongly to main-group transition-metal ions in high oxidation state. Today, POM chemistry is a key emerging area with the potential to develop sophisticated designer molecule-based materials and devices that bridge several length scales, exploiting the

progress made in instrumentation, nanoscale science, and material fabrication methods. [2] They are attracting increasing interest as a creative alternative for obtaining new materials with tailored structures and properties. The POM-based inorganic-organic hybrids constructed from inorganic POM building blocks and various organic ligands or transition metal- complex moieties can bring novel structural motifs and functionalities into one entity. [3] These new hybrid materials have a large variety of applications such as sensors, selective membranes, all sorts of electrochemical devices, from actuators to batteries or super capacitors, supported catalysts or photo electrochemical energy conversion cells. [4] The last decade experienced a continuous development in the field of hybrid POMs. The hybrid organic polyoxometalates can be separated in two types: [5] type I hybrids referring to compounds in which a weak nonbonding interaction between both (inorganic and organic) parts exists (e.g., electrostatic, hydrogen bonds, and van der Waals interactions) and type II where a stronger bonding interaction takes place (covalent or ionocovalent). The type II hybrids group includes all the organic ligands allowing a direct substitution of oxo group of the POMs, such as alkoxides, carboxylates, organosylil derivatives, and organoamides. Our research article is based on type I hybrid where polyoxometalate is the inorganic counter fragment of organic-inorganic hybrid POM. Derivatization of POMs with organic partners, including synthetic molecules via covalent bonding as well as electrostatic interaction is expected to result in a synergetic effect and endow novel functions to the POM hybrid. Moreover, the conjugation of an organic ligand onto the POMs offers additional advantages, such as better stability and desirable ligand orientation. [6] The most noticeable advantage of inorganic-organic hybrid POM is that they can favorably combine the often dissimilar properties of organic and inorganic components in one material. In addition, their biphasic structures lead to create multifunctional materials. For example, inorganic clusters or nanoparticles with specific optical, electronic or magnetic properties can be incorporated in organic polymer matrices. [7] The first example of organic-inorganic hybrid compounds based on POM was reported by Zorrilla *et al.* in 2003. [8] However, among rapidly increasing organic-inorganic hybrids, the hybrid compounds based on POMs and copper (II)-organic complexes are still limited. Here we have isolated a novel transition metal functionalized organic-inorganic hybrid POM where copper (II) ethylene diammine chelate cationic complex is counter balanced by POM anion. Hydrothermal synthesis of this type of compound is proved to be challenging but interesting. In this context it must be mentioned that the choice of suitable ligands is crucial for the formation of the hybrid compounds based on POMs and copper (II)-organic complexes. The ethylenediamine molecule (en) as a ligand

exhibits small steric hindrance, flexible configurations is an appropriate candidate as the primary ligand to tune the structure of the final compound. Keeping this strategy in mind, Keggin clusters and Cu^{2+} are treated as synthons, which in presence of organic ligand (en) give rise to a new hybrid compound based on POM and copper(II)-(en) complex under hydrothermal condition. Thus a new functionalized POM $[Cu(en)_2(H_2O))_2]_2[SiW_{12}O_{40}]$ was obtained. Furthermore, the complex was characterized by elemental analysis, UV-vis spectroscopy, thermogravimetric analysis, IR spectroscopy and Single crystal X-ray diffraction.

Experimental

Materials and methods

Sodium nonatungstosilicate, $Na_{10}[\alpha\text{-}SiW_9O_{34}]$, was prepared according to the reported method [10] and was recrystallized three times from triply distilled water before use. Chemicals were readily available from commercial sources and were used as received without further purification. $CuCl_2.2H_2O$ (AR Loba, India) and ethylene diammine (Merck, India) were of reagent grade and used as received. Deionized water was used as the solvent.

Synthesis of bis(ethylene diamine) copper (II) silicotungstate $[Cu(en)_2 (H_2O)]_2[SiW_{12}O_{40}]$ (1)

The complex was synthesized hydrothermally from an aqueous mixture of $Na_{10}[\alpha\text{-}SiW_9O_{34}]$, cupric chloride $CuCl_2.2H_2O$ and ethylene diammine. The pH of the resulting mixture was adjusted with 0.5 mL of 1M HCl to approximately 2. As expected, control of the pH of the reaction mixture is critical for the crystallization of compound (1). It can be crystallized in a narrow pH at around 2 and in a temperature range of 130-150°C. The detailed procedure is as follows: $Na_{10}[\alpha\text{-}SiW_9O_{34}]$ (0.614 g, 0.25 mmol) was dissolved in hot water (20 ml). Then solid $CuCl_2. 2H_2O$ (0.153 g, 0.9 mmol) was added to the solution. The mixture was heated with stirring for 30 minutes. Liquid ethylene diammine (en) (0.06 g, 0.5 mmol) was then added dropwise with constant stirring. The resulting ink-blue solution was stirred at 80°C for another 30 minutes. The mixture was then transferred with subsequent pH adjustment into a Teflon jacket stainless steel pressure vessel and kept in an oven at 160°C for 5 days under autogenous pressure. The solution was cooled by decreasing the temperature at a regular interval of 5°C over 1 day. The resulting dark blue rhombic crystals of $[Cu(en)_2(H_2O))_2]_2[SiW_{12}O_{40}]$ were filtered off, washed with water, and dried at room temperature. Yield: 60% (based on Cu). Elemental analysis: calculated for $C_8H_{40}N_8O_{44}Cu_2SiW_{12}$: C, 2.89; H, 1.21; N, 3.38; found: C, 2.85; H, 1.03; N, 3.33%.

Physical measurements

The composition of the starting material ($Na_{10}[\alpha$-$SiW_9O_{34}]$) and the final polyoxo product [Cu(en)$_2$(H$_2$O))$_2$]$_2$[SiW$_{12}$O$_{40}$] with respect to the atom% of W and Si were estimated by SEM-EDX method and found to be 9:1 and 12:1 respectively. Elemental analyses were carried out using a Perkin–Elmer 240 elemental analyzer. Spectral measurements were made in a Varian Cary 1E UV-visible spectrophotometer with 1.00 cm glass cells. IR (400–4000 cm^{-1}) was recorded in KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer.

Crystal data collection and refinement

For better structural elucidation, both powder and single crystal XRD were done. Powder XRD patterns were obtained by Bruker D8 advance diffractometer with monochromatic CuKα (λ = 1.5418 Å) with step size of 0.02° s^{-1}, whereas X-ray diffraction data for compound 1 were collected on a Bruker Kappa Apex II CCD diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073Å) at 293 K. The structures were solved by the direct methods and refined by full-matrix least squares on F2 using the SHELXTL-97 software. The hydrogen atoms were treated as riding on their parent carbon atoms with d(C-H)= 0.93-0.95Å and U$_{iso}$= 1.2Ueqv(C). All the non-hydrogen atoms were refined anisotropically. A summary of crystal data and relevant refinement parameters for complex1are given below in Table1 and selected bond distances are given in Table 2. Molecular graphics were prepared with the aid of WinGx [11] packages.

Table 1: crystal data and relevant refinement parameters

Crystal Data and details of structure refinements for complex 1.	
Empirical formula	C$_8$H$_{40}$N$_8$O$_{44}$Cu$_2$SiW$_{12}$ (**1**)
Formula weight	3313
Crystal system	Tetragonal
Space group	I 4$_1$/α
a, b, c (Å)	20.16 (5), 20.75 (5), 21.85 (12)
α, β, γ (°)	90, 90, 90
Volume (Å^3)	4230(8)
Z	4
Density (calculated) Mg/m^3	3.079
Absorption coefficient mm^{-1}	16.6
No of observed data	23196
Independent reflections	7775[R$_{int}$=0.088]
Data / restraints / parameters	7775/ 0/592
Goodness-of-fit on F^2	1.190
Final R indices [I>2sigma(I)]	R_1=0.0706, wR_2 = 0.1512
Final R indices (all data)	R_1=0.0865, wR_2 = 0.1583
Largest diff peak and hole (e.Å^{-3})	2.034 and –3.662

Compound 1 crystallizes in the tetragonal space group I 41/α. The structure of complex 1 consists of Keggin cluster anion $[SiW_{12}O_{40}]^{4-}$ and charge balancing complex cation $[Cu(en)_2(H_2O)_2]^{2+}$. The copper-chelate cationic complex part of the compound 1 exhibits a distorted octahedral geometry with four nitrogen atoms of two chelating en ligands and two oxygen atoms of water molecules are axially coordinated to central Cu(II) ion. The coordination around the central copper atom is octahedral with the copper atom 0.78(4) Å above the equatorial plane of the four nitrogen atoms of the ligand molecule. The Cu — N equatorial plane bond lengths are 1.975 and 2.031Å. The axial positions of the co-ordination octahedron are occupied by two oxygen atoms of the respective water molecules. The two Cu —O bond lengths are more or less equal i.e. 2.32 Å and 2.33 Å respectively. Crystal structure of the complex is stabilized by collective interplay of various non-covalent interactions such as O–H···O, N–H···O and C–H···π interactions, apart from electrostatic attraction. At the center of the $[SiW_{12}O_{40}]^{4-}$ anion, the SiO_4 tetrahedron is disordered over two positions related by an inversion center at the site of Si atom (Si–O distances are in the range of 1.46(1) -1.77(1) Å). The classic $[SiW_{12}O_{40}]^{4-}$ Keggin cluster ion consists of twelve WO_6 octahedra with the three types of W−O bond lengths in normal range [12]. As usual, the W–O bond lengths decrease with the decreasing coordination number of the oxygen atom, with values averaging 2.389(2)Å for four coordination $(O_{\mu4})$,1.869(7) Å for two coordination $(O_{\mu2})$and1.644(4) Å for the terminal oxygen atoms (O_t) (Table-2). Bond valence sum calculations indicate all W atoms have the oxidation number 6^+ while the copper atoms is in the +2 oxidation state, also confirmed by their octahedral coordination environments and blue crystal color..From the variations of Si-O, W-O distances and the bond angles around the Si and W atoms it is evident that there is considerable distortion in the SiO_4 tetrahedra and WO_6 octahedra in the complexes.This is consistent with structural features of polyoxotungstates exhibiting Keggin structures. Even though there are no "classical hydrogen bonds" between the $[Cu(en)_2(H_2O)_2]^{2+}$ cations and the Keggin ion $[SiW_{12}O_{40}]^{4-}$ anion in compound 1, there are several CH…O contacts in the range 2.28–2.60 Å between these units (Table 3). These interactions involve both terminal and bridged oxo groups of Keggin ions. Through Cu-O bonds, each of the SiW_{12} anions connects two neighboring $[Cu(en)_2(H_2O)_2]^{2+}$ complexes, while each of $[Cu(en)_2(H_2O)_2]^{2+}$ complexes links two adjacent SiW_{12} anions. Consequently, a 1D chain is formed by repeating these connections. Besides, the adjacent chains are further inter-connected through hydrogen bondings among the terminal/bridge oxygen atoms of SiW_{12} anions and the hydrogen atoms of ethylenediamine molecule to generate a 3D supermolecular structure. Each $[SiW_{12}O_{40}]^{4-}$

anion is hydrogen bonded to eight $[Cu(en)_2(H_2O)_2]^{2+}$ cations, and in turn each $[Cu(en)_2(H_2O)_2]^{2+}$ cation is hydrogen bonded to four $[SiW_{12}O_{40}]^{4-}$ anions to form a three-dimensional network. The unit cell depicts the one formula unit of the complex where two $[Cu(en)_2(H_2O)_2]^2$cations counter balance the large $[SiW_{12}O_{40}]^{4-}$ polyanion as mentioned in ortep view of the complex (Fig1a). The H atoms on water molecules in (1) could not be found from the residual peaks and were directly included in the final molecular formula.

Table 2: List of bond distances in complex 1

W–O$_t$	1.626(5)–1.664(1)
W–Oμ$_2$	1.767(8) –1.971(6)
W–O μ$_4$	2.191(5) –2.586(6)
Si–O	1.464(7) –1.766(5)
Cu(1) – N(1)	2.012(3)
Cu(1) – N(2)	2.014(3)
Cu(1)– N(3)	1..96(3)
Cu(1) – N(4)	1.98(3)
Cu(1) – O(1)	2.32(3)
Cu(1) – O(2)	2.33(4)

Table 3. Atomic distance (Å) and angles (°) of O$_{POM}$ … H$_{en}$ interactions in the crystal structure of compound 1.

Donor…H…Acceptor	d(D…H)	d(H…A)	d(D…A)	∠DHA
C(9)…H(9)…O(2)	0.94	2.60	3.34(5)	137°
C(24)…H(24)…O(5)	0.93	2.28	3.19(5)	165°
C(27)…H(27)…O(22)	0.93	2.41	3.26(5)	153°
C(31)…H(31)…O(12)	0.93	2.53	3.38(7)	153°
N1–Cu1–O1				95.35° (12)
N2–Cu1–O1				92.00° (11)
N2–Cu1–N1				84.10° (12)
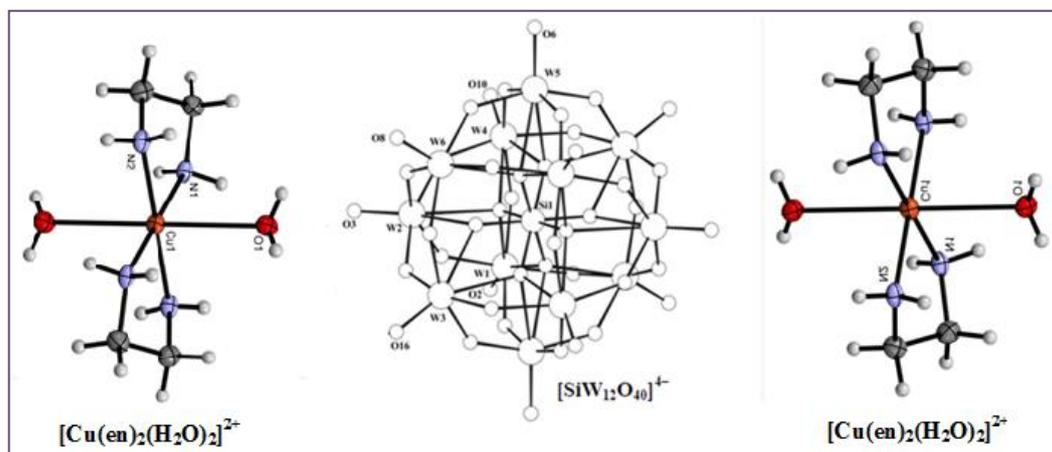
Fig.1a. Ortep diagram of of one formula unit of [Cu(en)$_2$(H$_2$O)$_2$]$_2$[SiW$_{12}$O$_{40}$] where Displacement ellipsoids are drawn at the 50% probability level.

The purity of compound 1 was confirmed by comparing the powder X-ray diffraction (PXRD) patterns of the pristine sample and the simulated pattern from the crystal structure. Purity of compound 1 was confirmed based on the basis of agreement of their PXRD diffraction patterns and the simulated patterns. (Fig.2)
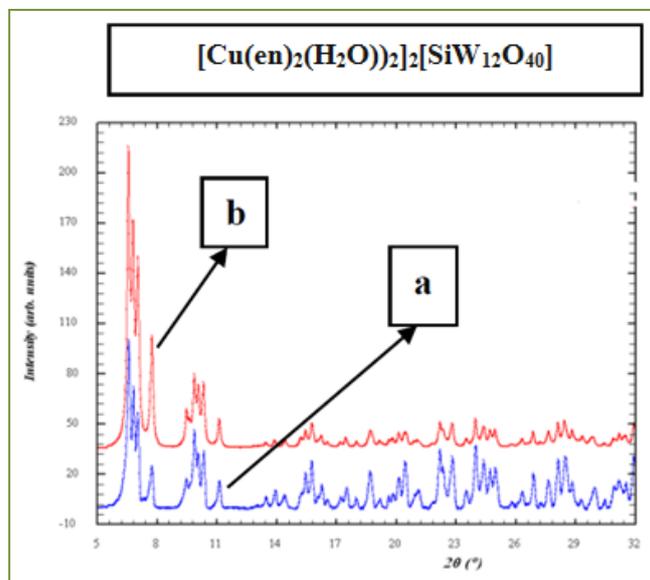

Fig.2.The powder X-ray diffraction patterns (blue line, a) and the simulated patterns (red line, b) of compound 1

Results and discussion

Vibrational and UV-vis spectra

For better reasoning of IR spectral values, Keggin anion $[SiW_{12}O_{40}]^{4-}$ needs a further elucidation. The oxygen atoms in the Keggin fragment of complex 1 can be classified into three groups i.e. the unshared or terminal O atoms 'O_t', the bridging O atoms (O_b) connecting two W atoms, and the O atoms (O_c) of the central SiO_4 moiety. The IR spectra of the compound (1) gives the characteristic peaks of Keggin anion at 930, 893, 798, and 703 cm^{-1} which are attributed to ν(W–Ot), ν(Si–Oa), ν(W–Ob) and ν(W–Oc) respectively. The higher energies for the W–O and Si–O stretches are consistent with a strong interaction existing between POM anion with Cu-en cationic complex. The bands at1105, 1020 and 990cm^{-1} can be ascribed to the vibration of Si-O. The bands at 893 and 798 cm^{-1} are ascribed to the vibration of W=O and W-O-W, respectively. The bands at 1640, 1587, 1397 and 1265 cm^{-1} can specifically be assigned to the bending vibrations of OH, CH, NH, or the chelate ring stretching frequency of the en ligands. The peaks near 3500 cm^{-1} are ascribed to the stretching vibration of ν(O-H) which indicates the presence of coordinated water (Fig-3). The optical absorption spectrum of compound 1 was characterized by a broad band in the visible domain around 445 nm and a band peaking at 270 nm. The visible absorption band is

attributed to a metal-to-ligand charge transfer (MLCT) transition in which an electron located in a metal-based d orbital is promoted into a ligand-centered π^* orbital [13].The UV absorption band corresponds to the band of ligand-to-metal charge-transfer (LMCT) transitions for W(VI) (O→W). Additionally, the bands in the region of 1000–1719 cm^{-1} could be ascribed to the en ligands, which are of low intensity with respect to those of the Keggin-type polyoxoanions. In the IR spectrum, the region of the NH$_2$ stretching vibrations is relatively broadened by partial superposition with the O-H vibrations of the coordinated and uncoordinated water molecules. The bands at 3370 and 3050 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the NH$_2$ groups of the coordinated and uncoordinated en ligands. The vibrational frequencies the CH$_2$ groups of the en ligands appear at 800 cm^{-1}. This is in agreement with literature data [13]. The Cu–N stretching frequency was observed at 750 cm^{-1}.
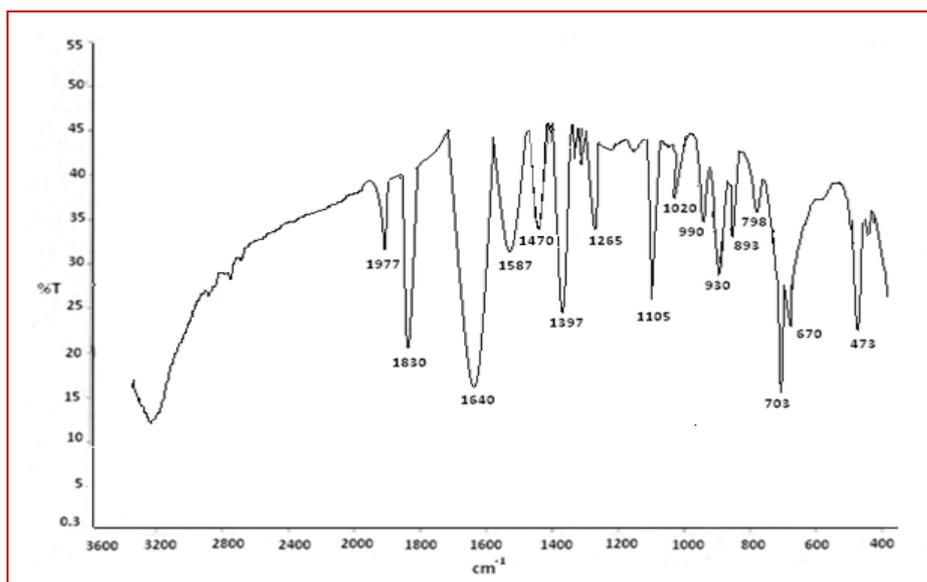

Fig.3. FTIR spectrum of complex 1, taken as KBr pellet

Thermo gravimetric analysis

The thermal stability of compounds 1 was investigated on powder samples in an air atmosphere in the temperature range 30-1000°C. The thermal dehydration occurred in two steps with endothermic effects at 40°C and 132°C (Fig. 1). One mole of coordinated water is removed at these stages (exp. 8.89%; calcd. 7.81%). A color change from blue to black was noted on removal of the water molecules. Further heating causes evaporation of one of the ethylenediamine molecules, resulting in an endothermic DTA peak at 154° C (exp.12.89%; calcd. 12.18%). The product is very unstable and undergoes further decomposition by release of the remaining ethylenediamine molecules. The exothermic peak at 480°C can be explained by the burning of the organic residue formed in the previous stages. The final solid product of

thermal decomposition was identified as a mixture of CuO, SiO_2 and WO_3.(exp. 86.85%; calcd. 88.50%).
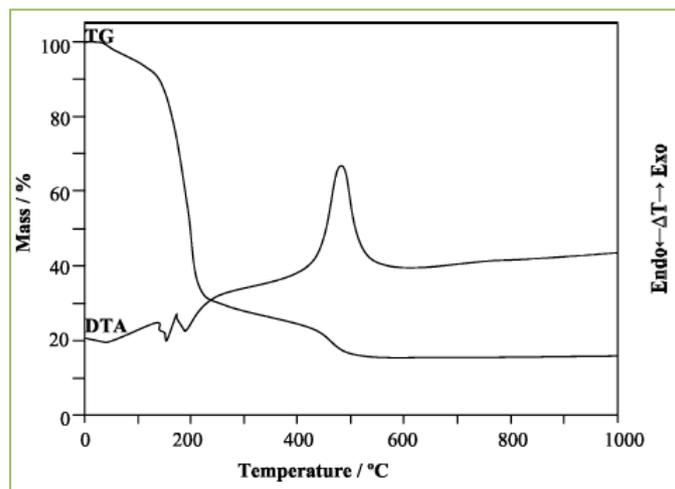

Fig.4. TG and DTA curves of the [Cu(en)$_2$(H$_2$O))$_2$]$_2$[SiW$_{12}$O$_{40}$]complex

Conclusion

In summary, a new inorganic-organic hybrid based on the Keggin ion $[SiW_{12}O_{40}]^{4-}$ was prepared hydrothermally. In this research paper, the synthesis, structure and properties of hybrid solid materials containing copper-(en) chelate complex and polyoxometalate anion have been described. Till date, Mn hybrid POM have been successfully synthesized and characterized [14]. The successful isolation of compound 1 demonstrates that the hydrothermal method can also be used for the incorporation of a stable cationic complex like $[Cu(en)_2(H_2O)_2]^{2+}$ cations into solid compounds through an electrostatic interaction to form hybrid materials. The non-covalent interactions play an important role in the assembly of the building blocks into solids which in turn direct the arrangement of these building units in the 3D space and the formation of 3D structures. There is an increasing interest and need to develop a deeper understanding of the 3D nature and behavior of organic-inorganic hybrid in chemistry. This is driven by the increased use of engineered hybrid POM and the increased pressure to commercialize this growing technology. Chatterjee et al [15] in this regard tried new crystal engineering in accordance to POM chemistry. Keeping in mind the greener side of technology, in this research article, we want to emphasize on a new synthetic methodology of the basic one-pot synthesis of polyoxometalates. In short, we have successfully constructed organic–inorganic hybrid by grafting POM with a metal-organic frame work.

References

Pope, M. T. (1983) Heteropoly and Isopoly Oxometalates. Springer Verlag, Berlin.

Gouzerh P, Proust A, (1998) Chemical Reviews. 98: 77–111

Hagrman P J, Hagrman D, Zubieta J (1999) Angew. Chem. Int. Ed. 38: 2638

Sun L., Akermark B., Ott S. (2005) Coordination Chemistry Reviews. 249: 1653-1663

Ritchie C, Cronin L, (2011) Chemical Record, 11: no. 3, 158–171

Kalyani V., Satyanarayana V.S., Singh V., Ghosh S. (2015) Chem. Eur. J. 21: 2250–2258

Keggin J.F. (1934): Proceedings of the Royal Society of London. Series   A 144: 75-100

Zorrilla J M, Reinoso S, Vitoria P, Lezama L (2003) Inorg. Chem. 42: 3709

Dolbecq A., Dumas E., Mayer C.R., Mialane P. (2014) Chem. Rev. 110: 6009-6048

Ginsberg A.P. (Editor in Chief) (1990) Inorganic synthesis, Wiley, 27:87

Sheldrick G.M (1998) SHELXTL PLUS. PC Version. A.

Keggin, J.F. (1933): Nature131: 908-909

Yesilel O Z, Olmez H, Naumov P, (2003) Synth. React. Inorg. Metal-Org. Chem. 33: 77

Chatterjee R., Drew M.G.B. (2009) Trans Met Chem. 34(1):1-5

Chatterjee R., Hazra D. (2014) Polyhedron 68: 265–271