

## On the Polymorphism of 12-Tungstoborate Heteropolyanion: Structure Determination and Its Functionalization with L-proline

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A new structure related to previously reported structure of 12-tungstoborate Keggin-type polyoxometalate,  $K_5[BW_{12}O_{40}]$ , BW12 (I) was synthesized and its characterization by single crystal X-ray diffraction shows the polymorph structure. Further attempts have been performed to provide three component compounds based on L-proline, lanthanoid and  $K_5[BW_{12}O_{40}]$  under hydrothermal conditions which is rarely reported in hybrid materials rather than other Keggin types. The proposed general structures contain lanthanoid dimers with amino acid bridges and BW12, which characterized by elemental analysis, FT-IR spectroscopy and ICP (Inductively coupled plasma) method. Various types of interactions are established, depending on the POM shape and charge, the amino acid side chain, peptide sequence or protein structure. Experimental conditions such as temperature, acidity, solvent, *etc.* are also important factors that influence the binding/reactivity of POM with biomolecules, as described recently [13]. This understanding allows the adequate design of the POM-biomolecule couple for tailoring and controlling mechanisms of action such as catalysis, inhibition, and aggregation, or the crystallizing agent.

**Keywords:** 12-Tungstoborate, L-proline, Polymorphism, Inorganic-organic hybrid, Hydrothermal reaction

### INTRODUCTION

Polymorphism and crystal growth are one of the most interesting areas of research in recent years due to their important effect and commercial interest in pharmaceutical solids and new materials. Although crystal formation governed fundamentally by varied intermolecular interaction ranging from hydrogen bond interactions to van der Waals forces which is considered as weaker ones, but the exact mechanisms needs to be elucidated even for simple organic molecules due to the complexity of which molecules interact with each other [1]. Moreover, polymorphism, the existence of the same chemical substance in more than one crystalline modification, has received considerable attention in recent years, particularly in the industrial and academic communities. In general, based on the geometry of molecular assembly in the crystal

lattice, polymorphs are classified into two major categories: conformational and packing polymorphs [2]. The isolation, identification and characterization of different crystal forms (polymorphs, solvates, salts and co-crystals) of the same molecule or of aggregates of the same molecule with other molecules represents one of the most active areas of modern solid state chemistry [3].

On the other hand polyoxometalates (POM) are typically consist of early-transition metal addenda ions such as W(VI), Mo(VI) and V(V) in their highest oxidation state bridged by oxo anions [4]. They are fascinating group of compounds in inorganic chemistry due to definite size and shape and their various and unique properties such catalysis (homogeneous and heterogeneous) [5,6], medicine (*e.g.*, as antiviral and anti-tumoral agents) [7,8], theoretical studies, nano-materials science [9] and others, which results in vast application potential in different areas ranging from catalysts to medicinal materials. So, investigation of POM

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structures and architects as well as their functionalization with organic molecules seized many inorganic and bio-inorganic chemists around the world. Due to previously reported capability of POMs to play important role in anti-tumor, anti-cancer and anti HIV disease areas, functionalization of POMs with special bio molecules are of great importance. Although POMs biological properties have been proved [7,8], the challenge prohibit rapid progress is to increase their selectivity and biocompatibility. Modifying POM properties with amino acids, as one of important biomolecules, is an appropriate approach to overcome this challenge [10,11]. So, following our group previous studies concerning different types of POMs and their hybrid compounds [12-15] including two and three component systems with various organic moieties and metal centers [16-23], we focused on boron-centered heteropoly anion. The  $K_5[BW_{12}O_{40}]$  salt was synthesized by Rocchiccioli-deltcheff *et al.* in 1983 [24] and its crystal structure was determined in 2001 by Fletcher [25]. We followed studies with 12-tungstoborate polyoxometalate and its derivatives synthesis including  $Ce^{3+}$  and  $Sm^{3+}$  lanthanoids and L-proline amino acid. Fortunately during this process, we got crystals of BW12 (II) polymorph structure.

Crystal polymorphs and *pseudo* polymorphs exhibit different physical and chemical properties as a consequence of their different molecular arrangements or conformations in the crystal [26]. We continued our study to form three component hybrid compounds based on new polymorph structure (BW12), which are investigated with spectroscopic methods and elemental analysis.

In spite of the huge efforts of many researchers about polymorphism, our knowledge of this phenomenon is still embryonic, and the relationship between growth of a crystalline phase and nucleation of the first crystallites is often mysterious. It is a fact that, despite the ambitions of the scientist, crystal construction is not yet strictly under human control [3].

## EXPERIMENTAL

### Instrumentation and Methods

The FT-IR spectra were recorded in the range 4000-400  $cm^{-1}$  on an AVATAR 370 Thermo Nicolet spectrometer

with a pressed KBr pellet. The C, H and N elemental analyses were performed on a Thermo Finnigan Flash model 1112EA microanalyzer. The Ce and Sm values detected by spectro arcsos system ICP-OES instrument model 76004553. Single crystal X-ray data were collected on a Rigaku diffractometer equipped with a Pilatus 200K area detector, a Rigaku MicroMax-007HF microfocus rotating anode with MoKa radiation and Confocal Max Flux optics and Apex DUO diffractometer equipped with a Kappa 4-axis goniometer, an APEX II 4K CCD area detector, a Microfocus Source E025 IuS using MoKa radiation and Quazar MX multilayer Optics as monochromator.

### Reagents and Synthetic Procedure

All chemicals were used as received from the suppliers and used without further purification. Commercial  $Sm(NO_3)_3$ ,  $Ce(NO_3)_3$  lanthanoid metal salts and L-proline amino acid were used. The boro-tungstate, BW12 (I) were prepared as described in the literature [25].

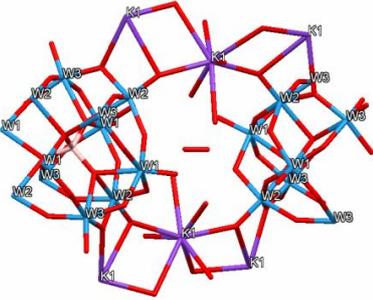
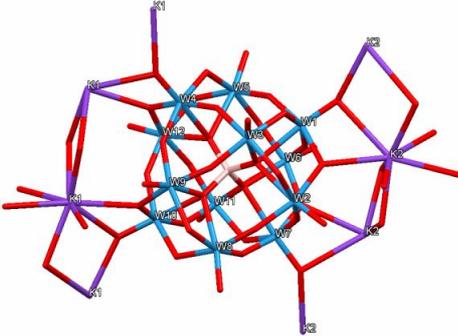
**$K_5[BW_{12}O_{40}].xH_2O$  (II).** The polymorph which used in later reactions was an unexpected product of a hydrothermal reaction between BW12 (I) and L-proline amino acid. Investigation of the result colorless crystals of this reaction showed that it is a polymorph structure of BW12.

**$(C_{40}H_{64}N_9O_{16}Ce_2)_n[BW_{12}O_{40}].6H_2O$  (I).** A solution of L-proline in distilled water (106 mg, 0.92 mmol, 10 ml) was added, with stirring, to a solution of  $Ce(NO_3)_3$  in the same solvent (41 mg, 0.092 mmol, 5 ml), at about 70-80 °C. After about 1 h, a BW12 solution in distilled water (281 mg, 0.092 mmol, 10 ml) was added drop-wisely, while stirring, to the previous solution, and the pH adjusted ( $pH \approx 2$ ) with few drops of HCl (3 M). A white powder precipitated after about 5 min which was filtered off. The mixture was transferred to 30 mL Teflon-lined reactor. The reactor was heated at 110 °C for 24 h and then cooled to room temperature within a day. Yellow precipitate was filtered off and the remaining solution was kept at ambient conditions. A month later pale-yellow block crystal obtained. Anal (%). Found (Calcd.) for  $K_5[BW_{12}O_{40}].(C_{40}H_{76}N_9O_{22}Ce_2)_n$ : C, 11.28 (11.52); N, 2.97 (3.02); H, 1.98 (1.84), Ce, 6.61 (6.72). IR ( $cm^{-1}$ ): (B-O<sub>a</sub>) 997 (s), (W-O<sub>t</sub> (terminal oxygen)) 959 (s), (W-O<sub>b</sub>(corner shared oxygen)-W) 890 (s), (W-O<sub>c</sub>(edge shared oxygen)-W) 833 (s).

**Table 2.** Different Crystal Structure Parameters in  $K_5[BW_{12}O_{40}] \cdot 1.6H_2O$  (I) and Related Polymorph (II)

Parameters	$K_5[BW_{12}O_{40}] \cdot 1.6H_2O$ (I)	$K_5[BW_{12}O_{40}] \cdot 1.6H_2O$ (II)
$M_r$	3340.72	
Space group	Hexagonal, $P6_222$	Trigonal, $P3_2$
$A$ (Å)	18.970 (4)	18.886 (2)
$C$ (Å)	12.414 (5)	12.421 (2)
$V$ (cm <sup>3</sup> )	3868.81	3836.79

**Table 2.** Comparison Between some of Bond Lengths (Å) of Two 12-Tungstoborate Polymorph Structures I and II

			
$K_5[BW_{12}O_{40}] \cdot 1.6H_2O$ (I)		$K_5[BW_{12}O_{40}] \cdot 1.6H_2O$ (II)	
		B1-O2	1.503(8) Å
		B1-O3	1.534(8)
B-O123	1.554(10) Å	B1-O1	1.519(9)
		B1-O4	1.522(6)
W1-O123	2.354(10) Å	W1-O1	2.352(5)
W1-O1	1.699(11)	W1-O8	1.708(6)
W1-O12	1.963(10)	W1-O5	1.947(8)
W2-O123	2.320(9)	W2-O1	2.360(2)
W2-O2	1.719(10)	W2-O9	1.695(8)
W2-O12	1.908(10)	W2-O5	1.893(4)
W3-O123	2.358(10)	W3-O1	2.387(9)
W3-O3	1.708(10)	W3-O10	1.720(2)
W3-O32	1.902(10)	W3-O6	1.882(8)

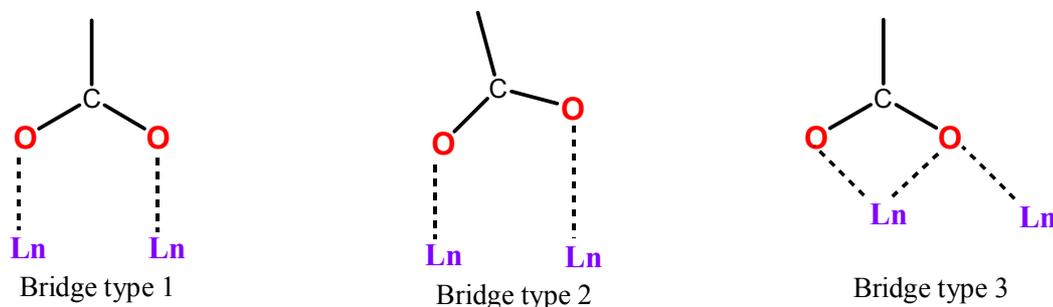


Fig. 1. Different coordination modes of amino acids toward lanthanoid metal centers.

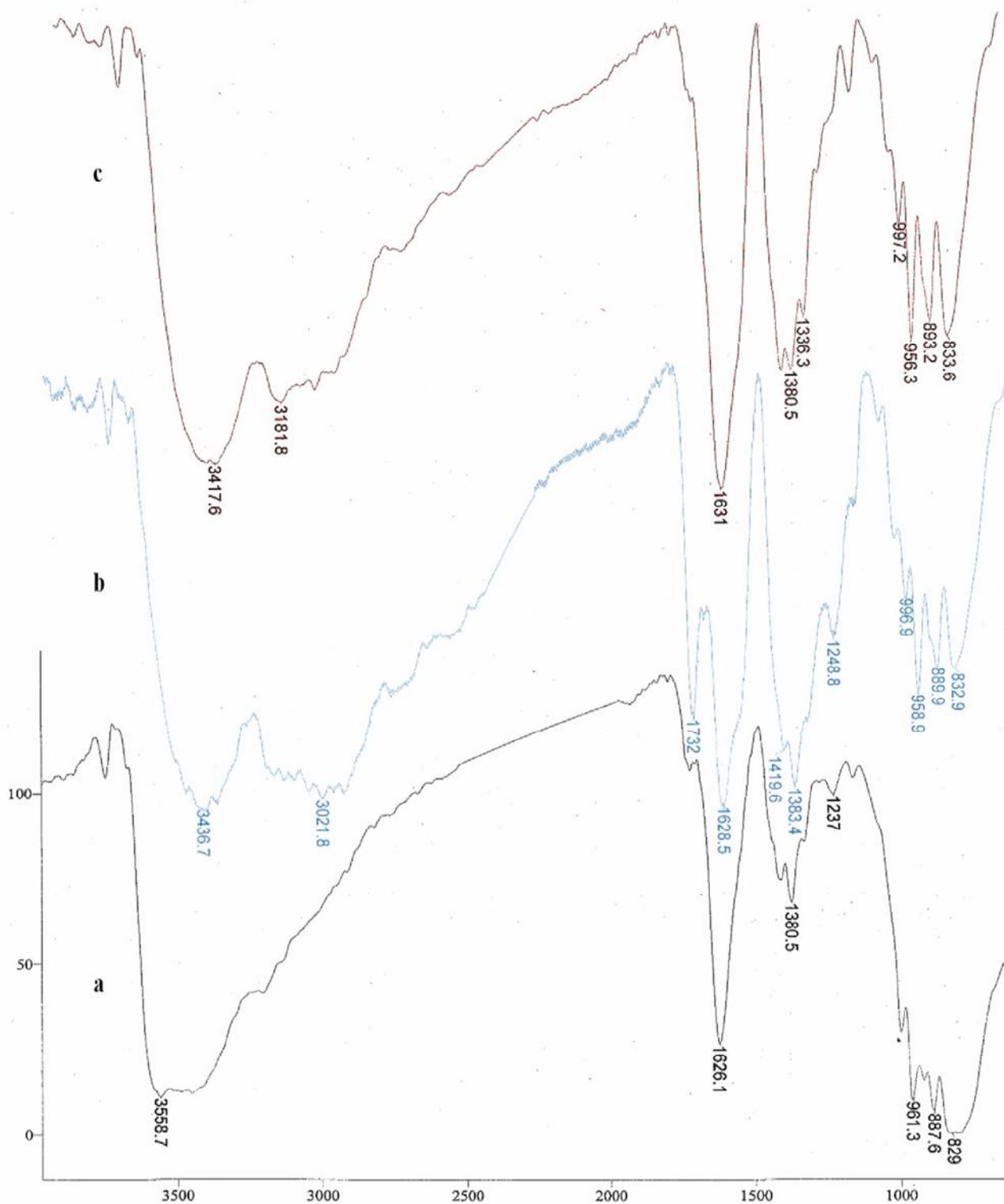
$(C_{40}H_{64}N_{10}O_{19}Sm_2)_n[BW_{12}O_{40}].4H_2O$  (**2**). Preparation of **2** was similar to that of **1** except that  $Sm(NO_3)_3$  (50 mg, 0.11 mmol) was used instead of  $Ce(NO_3)_3$ , and subsequently the amount of BW12 and L-proline changed to (335 mg, 0.11 mmol) and (129 mg, 1.12 mmol), respectively. Block light brown crystals were formed in the reactor. Anal (%). Found (Calcd.) for  $[BW_{12}O_{40}].(C_{40}H_{72}N_{10}O_{63}Sm_2)_n$ : C, 11.85 (11.39); N, 3.25 (3.32); H, 2.08 (1.72); Sm, 7.09 (7.13). IR ( $cm^{-1}$ ): (B-O<sub>a</sub>) 997 (s), mas (W-O<sub>d</sub>) 956 (vs), mas (W-O<sub>b</sub>-W) 893 (s), mas (W-O<sub>c</sub>-W) 834 (vs).

## RESULTS AND DISCUSSION

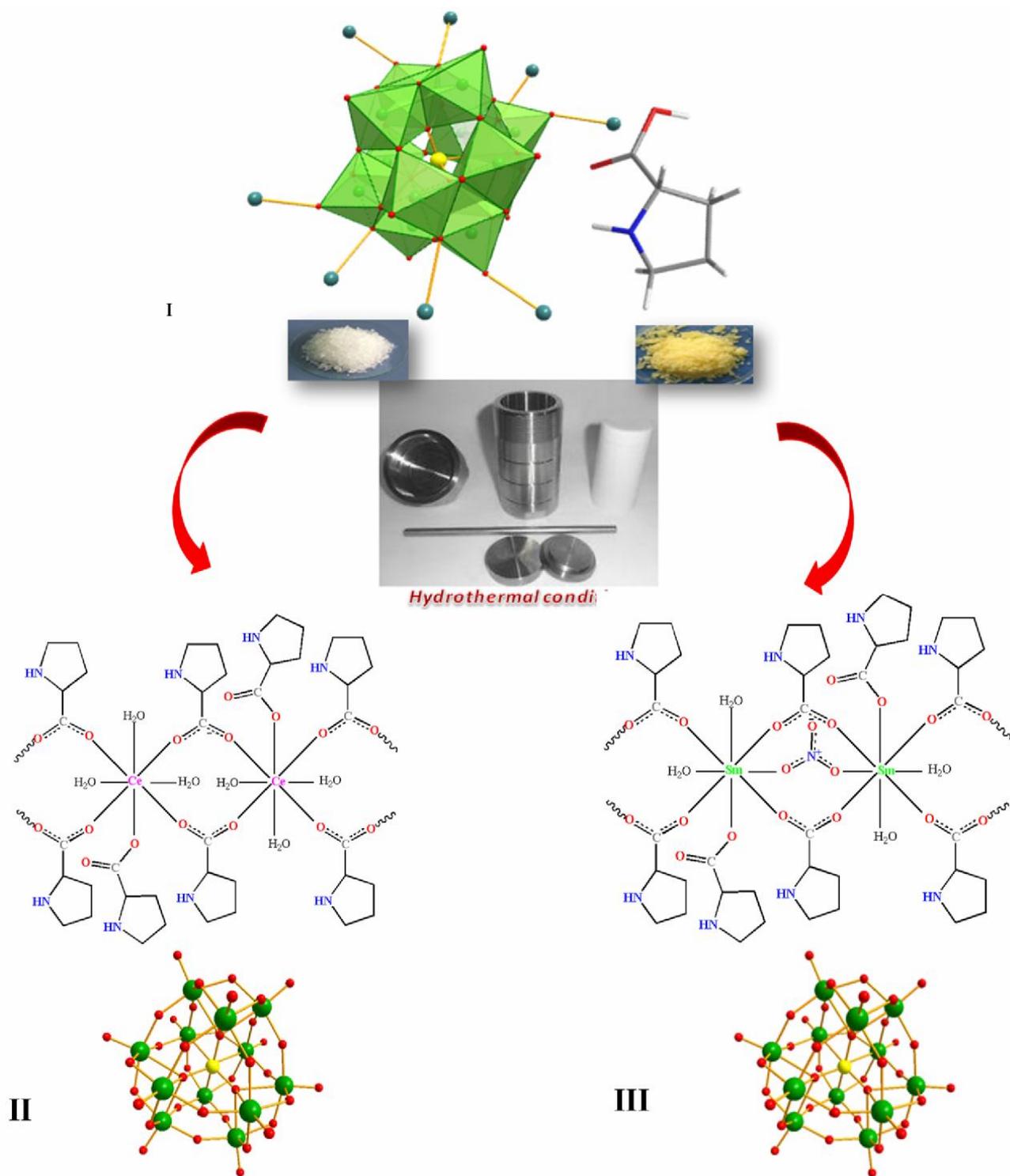
### Structure Determinations

Single-crystal X-ray analysis of BW12 (II) reveals that this compound is a polymorph structure of  $K_5[BW_{12}O_{40}]$  [25], which are different in some parameters such as space group, cell dimension and *Z* value which are listed in Table 1. Unless chiral L-proline amino acid has not been involved in final crystal structure, it had influence in the crystal structure. Similarly, the effect of amino acid in forming *pseudopolymorphs* has been reported previously [27]. More careful comparison of BW12; (II) and (I) shows different B-O bond lengths in (II), whereas in, BW12 (I) structure all of them are the same (see Table 2 for more detailed information). Comparing the W-O bonds suggests that distortion in B tetrahedral extend to all structure and results in various W-O bond lengths in each octahedral. While there are three symmetrically different W atoms in BW12 (I), all W atoms are different herein. It can be suggested that the presence of a chiral molecule, L-proline, tend the overall crystal structure to crystallize in  $P3_2$  chiral space group.

The infrared spectra of **1** and **2** (Fig. 2) are in consistent with their structural characteristics. All complexes display characteristic strong bands of the BW12 (II) unit about 960, 887, and 829  $cm^{-1}$  which are related to asymmetric stretching of B-O, and W-O<sub>b/c</sub>-W stretching vibrations, respectively, which are in good agreement with similar structures. As it is expected, the intensity of characteristic frequencies of 960  $cm^{-1}$  correspond to symmetric stretching vibration of B-O reduced, due to involvement of terminal oxygen atoms in H-bonds with amino acid and water molecules. The appearance of signals at 1200-1700  $cm^{-1}$  region related to the characteristic bands of L-proline moiety. The bands around 1420  $cm^{-1}$  were devoted to N-H vibration. Moreover, the bands at about 1300-1400 and 1500-1600  $cm^{-1}$  are, respectively, assigned to the symmetric and asymmetric stretching vibrations of carboxylate fragments. There are various possibilities of L-proline to coordinate to metal centers, but since, lanthanoids are typical hard metals, consequently, they preferentially interact with the harder residue of amino acids and peptides. Most reported data in either aqueous solution or solid state support this, also there are rare examples of this behavior in copper complex [28]. In the solid-state structure, carboxylate groups play a very important role. Different spatial arrangements are found, but the presence of COO-bridges is a common structural framework. As depicted in Fig. 1, there are different bridging modes of amino acid carboxylate group to lanthanoids, while investigating proline mode in reported structures, shows clearly its tendency to bridging as I and II modes [29]. Eventually bands at approximately 1620 and 3350  $cm^{-1}$  are assigned to the water molecules where the former is due to the



**Fig. 2.** FT-IR spectra of a) BW12, b) compound 1 and c) compound 2.



**Fig. 3.** Synthesis scheme and products; I) precursors including K<sub>5</sub>[BW<sub>12</sub>O<sub>40</sub>], l-proline and lanthanoid salts, II) proposed structure of compound 1 with Ce<sup>3+</sup> cation, and III) of compound 2 with Sm<sup>3+</sup> cation.

heteropoly acid crystalline water and the latter is a broad band corresponds to vibrations of coordinated waters and extended hydrogen bonding interactions. Considering all the above-mentioned analysis, previously reported complexes of L-proline and lanthanoids and also the first data of X-ray structure determination of compounds 1 and 2, which is now in progress, two structures proposed for them (Fig. 3 II and III) which are in good agreement with spectroscopic and analytical data.

## CONCLUSIONS

In this study two new three component inorganic-organic hybrid materials based on Keggin-type POM has been synthesized from 12-tungstoborate, and  $\text{Sm}^{3+}/\text{Ce}^{3+}$ -proline complexes. Hybrids based on the more negatively charged Keggin-type POM,  $\text{K}_5[\text{BW}_{12}\text{O}_{40}]$ , are rarely reported rather than other analogues. The reported 12-tungstoborate POM in this study, is a polymorph structure which has been analyzed and compared with previously reports one, and then used to synthesis three component inorganic-organic hybrids. Moreover, compounds 1 and 2 investigated and related structures suggested.

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