

## Three new inorganic-organic hybrid materials based on inorganic cluster, [(PO<sub>4</sub>)M<sub>12</sub>O<sub>36</sub>].nH<sub>2</sub>O (M = Mo, W)

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Received 5 July 2010, revised and accepted 20 December 2010

Three new inorganic-organic hybrid materials based on heteropolyoxometalates, [L-C<sub>6</sub>H<sub>14</sub>NO<sub>2</sub>]<sub>3</sub>[(PO<sub>4</sub>)Mo<sub>12</sub>O<sub>36</sub>].3H<sub>2</sub>O (**1**), [L-C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>]<sub>3</sub>[(PO<sub>4</sub>)W<sub>12</sub>O<sub>36</sub>].H<sub>2</sub>O (**2**), and [C<sub>2</sub>H<sub>7</sub>N<sub>2</sub>O]<sub>3</sub>[(PO<sub>4</sub>)W<sub>12</sub>O<sub>36</sub>].4H<sub>2</sub>O (**3**), where C<sub>6</sub>H<sub>14</sub>NO<sub>2</sub>, C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>, and C<sub>2</sub>H<sub>7</sub>N<sub>2</sub>O are protonated L-leucine, L-proline, and methyl urea, respectively, have been synthesized and structurally characterized by some physico-chemical methods. Elemental analyses, IR, Raman, mass, UV, and <sup>1</sup>H NMR spectroscopies of the title hybrid materials indicate that there are van der Waals interactions between O atoms of the heteropolyoxometalates and water molecules, as well as the N and O atoms of the amino acids and methyl urea moieties. The molecular structures of synthesized hybrid materials contain discrete entities of L-leucinium, L-prolinium or methyluronium and water molecules that surround every [(PO<sub>4</sub>)M<sub>12</sub>O<sub>36</sub>]<sup>3-</sup> anion, over the extended crystalline network. The observed bands in Raman spectra of (**2**) and (**3**) demonstrate that the [(PO<sub>4</sub>)W<sub>12</sub>O<sub>36</sub>]<sup>3-</sup> anion retains its "Keggin structure". At pH = 4 – 7, the characteristic bands of the Keggin anion [(PO<sub>4</sub>)M<sub>12</sub>O<sub>36</sub>]<sup>3-</sup> (M = Mo, W) appear at 210 and 260 nm in the UV spectra, respectively.

**Keywords:** Polyoxometalates, Metalates, Hybrids, Inorganic-organic hybrids, Amino acids, L-Leucine, L-Proline, Methyl urea

Polyoxometalates (POMs) constitute an interesting class of metal–oxygen cluster hybrids with definite size and shape. These hybrids have been found to be extremely versatile inorganic building blocks in view of their potential applications in catalysis, medicine, materials science, and others<sup>1-6</sup>. In recent decades, POMs associated with organic ligands have generated a group of privileged hybrids<sup>7-10</sup>. They have led to the development of substances with interesting electric, magnetic and/or optical properties. Many POMs have

been used as building blocks to construct a variety of organic–inorganic solid-state hybrid materials, following several strategies, viz., the use of entities capable of acting as charge compensating cations in the syntheses of salt-like hybrids and of organically functionalized POM clusters. Examples of the former are hybrids with POMs and cationic porphyrins, propane sulfonate functionalized organic cations, surfactants, organic radical ions and transition metal or lanthanide complex cations or coordination polymers with organic ligands. The reported association of POMs with amino acids is a result of either (i) functionalization of the heteropolyanions with the amino acids, or, (ii) electrostatic and/or hydrogen bonding interactions. For different purposes, materials have been prepared with the Keggin heteropolyanions ([XM<sub>12</sub>O<sub>40</sub>]<sub>n</sub>, M = Mo, W, X = P, Si, B) and several amino acids, viz., glycine, tyrosine, ornithine, alanine, histidine, lysine, proline, cysteine and also with amino acidate copper complexes. However, crystal structure of only a few has been determined<sup>11</sup>. To the best of our knowledge, there are no reports published on the titled Keggin anions and L-leucine, L-proline and methyl urea.

Research on amino acid salts of POMs continues to be an interesting subject both in respect of discovery of new crystalline supramolecular architectures (assemblies) and of the study of their properties. This prompted us to investigate hybrids resulting from the reaction between amino acids and heteropolyacids. In continuation of previous works on the synthesis of biologically active hybrids<sup>12-14</sup>, herein we have carried out the reaction of L-leucine and methyl urea with 12-tungsto- and molybdo-oxoanions. This contribution describes for the first time the syntheses and characterization of three inorganic-organic hybrid materials based on heteropolyoxometalates: [L-C<sub>6</sub>H<sub>14</sub>NO<sub>2</sub>]<sub>3</sub>[(PO<sub>4</sub>)Mo<sub>12</sub>O<sub>36</sub>].3H<sub>2</sub>O (**1**), [L-C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>]<sub>3</sub>[(PO<sub>4</sub>)W<sub>12</sub>O<sub>36</sub>].H<sub>2</sub>O (**2**) and [C<sub>2</sub>H<sub>7</sub>N<sub>2</sub>O]<sub>3</sub>[(PO<sub>4</sub>)W<sub>12</sub>O<sub>36</sub>].4H<sub>2</sub>O (**3**).

### Experimental

α-H<sub>3</sub>[(PO<sub>4</sub>)M<sub>12</sub>O<sub>36</sub>].nH<sub>2</sub>O (M = Mo, W) were prepared by the well-known procedures<sup>15</sup>. Other chemicals were commercially available and used without further purification. A Buck-500 scientific spectrometer was employed to record IR spectra using

KBr discs.  $^1\text{H}$  NMR spectra was recorded on a Bruker BRX-100 Avance spectrometer. Elemental analyses were performed on a Thermo Finnigan Flash-1112EA microanalyzer. Mass spectra were obtained from a Varian CH-7 instrument at 70 eV. The UV spectrum was obtained on an Agilent 8453 single beam photodiode array spectrometer in the range of 190-350 nm. The Raman spectrum was collected employing a  $180^\circ$  back scattering geometry and a Bomem MB-154 Fourier transfer spectrometer which was equipped with a ZnSe beam splitter and TE cooled in GaAs detector. A column containing Dowex 50WX8 in the  $\text{H}^+$  form was used to prepare the related heteropolyacid of molybdenum and tungsten. The Mo, W, and P contents were measured by ICP method. Distilled water was used throughout.

$\alpha\text{-H}_3[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]\cdot 21\text{H}_2\text{O}$  was prepared as follows: To 100 mL of water at  $60^\circ\text{C}$ ,  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$  (10 g, 41 mmol) was slowly added and then 1 mL (0.01 mmol) orthophosphoric acid 85 % and 8 mL (0.10 mmol) conc. HCl were added dropwise with stirring. The precipitate was dissolved by vigorous stirring and kept overnight. The solution was filtered and precipitate was washed with warm water and dried in a desiccator (Yield: 40 % based on Mo). The free acid was prepared by passing a solution of 10 g of the sodium salt in 20 mL of water through a column (50 cm  $\times$  1 cm) of Dowex 50WX8 in the  $\text{H}^+$  form and evaporating the eluate to dryness in vacuo.

$\alpha\text{-H}_3[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]\cdot 19\text{H}_2\text{O}$  was prepared similarly by the above procedure using 100 mL water at  $60^\circ\text{C}$ ,  $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$  (10 g, 30 mmol), 1 mL (0.01 mmol) orthophosphoric acid 85 %, and 8 mL (0.10 mmol) conc. HCl.

$[\text{L-C}_6\text{H}_{14}\text{NO}_2]_3[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]\cdot 3\text{H}_2\text{O}$  (**1**) was prepared as follows: Water 4 mL,  $\alpha\text{-H}_3[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]\cdot 21\text{H}_2\text{O}$  (0.3 g, 0.14 mmol), and L-leucine (0.1 g, 0.76 mmol) were mixed in a small bottle and the mixture was kept at room temperature under stirring for 2 h. The contents were then filtered and the resulting yellow precipitate was isolated and air-dried. It was redissolved in minimum amount of water. Slow evaporation at room temperature for several days yielded large yellow crystals of (**1**) in about 35 % yield based on Mo. Anal.: Calc. for (**1**): C, 10.01; H, 2.07; N, 1.94; P, 1.43; Mo, 53.33. Found: C, 9.95; H, 2.16; N, 2.03; P, 1.35; Mo, 52.82 %.

$[\text{L-C}_5\text{H}_{10}\text{NO}_2]_3[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]\cdot \text{H}_2\text{O}$  (**2**) was prepared similarly by the above procedure using  $\alpha\text{-H}_3[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]\cdot 19\text{H}_2\text{O}$  (0.5 g, 0.17 mmol) and

L-proline (0.1 g, 0.86 mmol) and stirred for 5 h. The resulting colorless precipitate was redissolved in minimum amount of DMF and after slow evaporation of DMF for 4 weeks, pure colorless precipitate of (**2**) in about 30 % yield was obtained. Attempts to obtain the single crystal were not successful. Anal.: Calc. for (**2**): C, 5.48; H, 1.09; N, 1.28; P, 0.94; W, 66.84%. Found: C, 5.53; H, 1.01; N, 1.15; P, 0.90; W, 65.42 %.

Synthesis of  $[\text{C}_2\text{H}_7\text{N}_2\text{O}]_3[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]\cdot 4\text{H}_2\text{O}$  (**3**) was accomplished by dissolving the  $\alpha\text{-H}_3[(\text{PO}_4)\text{W}_{12}\text{O}_{36}]\cdot 19\text{H}_2\text{O}$  (0.2 g, 0.07 mmol) in 10 mL water. This solution was then added dropwise to a solution containing of methyl urea (0.05 g, 0.70 mmol) in 5 mL 2N HCl. The solution was kept at room temperature under stirring for 24 h. After adjusting the pH to 2.5 with 2N HCl, the resulting clear solution was left for a week. The white precipitate of (**3**) was redissolved in water and filtered. The filtrate was kept for several days at ambient conditions. White block crystals of (**3**) were isolated in about 40 % yield based on W. Anal.: Calc. for **3**: C, 2.27; H, 0.85; N, 2.64; P, 0.97; W, 69.63. Found: C, 2.21; H, 0.80; N, 2.80; P, 0.90; W, 68.45 %.

## Results and discussion

The structural assignments of hybrids (**1**) to (**3**) were based on the spectral and microanalytical data. Generally, there are four types of oxygen atoms in any Keggin unit. Four  $\text{X-O}_a$  oxygens are bonded to a heteroatom (e.g., phosphorus) in the central tetrahedron. Twelve  $\text{M-O}_b\text{-M}$  oxygen atoms are in a corner-sharing arrangement between the  $\text{MO}_6$  octahedrons. Twelve  $\text{M-O}_c\text{-M}$  oxygens exist in an edge-sharing arrangement between the neighboring  $\text{MO}_6$  octahedrons. Finally, there are twelve  $\text{M=O}_d$  terminal oxygen atoms<sup>1</sup>. Characteristic IR bands of L-leucine remain unchanged. IR bands arising from the POM anions, on the other hand, are altered in intensity and position, compared to those of the free  $\alpha\text{-H}_3[(\text{PO}_4)\text{M}_{12}\text{O}_{36}]\cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Mo}, \text{W}$ )<sup>15</sup>. In hybrid (**1**) the vibrational bands of the  $\text{P-O}_a$ , and  $\text{Mo=O}_d$  show red-shift from 1067 and 963  $\text{cm}^{-1}$  to 1061 and 958  $\text{cm}^{-1}$  respectively.

The  $\text{Mo-O}_b\text{-Mo}$  and  $\text{Mo-O}_c\text{-Mo}$  bands of (**1**) are blue-shifted from 870 and 785  $\text{cm}^{-1}$  to 879 and 788  $\text{cm}^{-1}$ , respectively. The apparent weakening of the two bonds and strengthening of the other two bonds in (**1**) is likely to be due to different hydrogen bonding interactions between POM oxygens and the hydrogen atoms of L-leucine nitrogen and, to a lesser extent, the hydrogen atoms of L-leucine carbons. Characteristic

bands of L-leucine are as expected. For example, the  $1460\text{ cm}^{-1}$  band is typical of N–H vibration, the one at  $1734\text{ cm}^{-1}$  is characteristic of the carbonyl group and the featured  $2953\text{ cm}^{-1}$  band is attributed to  $\text{CH}_2$  groups.

In hybrid (2), characteristic IR bands of L-proline remain unchanged. IR bands arising from the POM cation, on the other hand, are altered in intensity and position compared to those of the uncombined heteropoly acids with the exception of vibrational bands of  $\text{P-O}_a$  and  $\text{W=O}_d$  at  $1080$  and  $982\text{ cm}^{-1}$ , respectively. In fact these oxygens do not have any role in the van der Waals interactions between POMs and amino acid. The  $\text{W-O}_c\text{-W}$  is red shifted from  $810\text{ cm}^{-1}$  to  $804\text{ cm}^{-1}$  and  $\text{W-O}_b\text{-W}$  band is blue shifted from  $890\text{ cm}^{-1}$  to  $895\text{ cm}^{-1}$ . The apparent weakening of one bond and strengthening of another in the title hybrid is likely to be due to different hydrogen bonding interactions between POM oxygens and the hydrogen atoms of nitrogen in L-proline, and to a lesser extent, the hydrogen atoms of carbons in L-proline. Characteristic bands of L-proline are as expected. For example, the  $1460\text{ cm}^{-1}$  band is typical of N–H vibration, the one at  $1728\text{ cm}^{-1}$  is characteristic of the carbonyl group and the featured  $2950\text{-}2970\text{ cm}^{-1}$  band is attributed to  $\text{CH}_2$  and CH groups.

In hybrid (3), the  $\text{W=O}_d$  bond is blue-shifted from  $982$  to  $984\text{ cm}^{-1}$  and the  $\text{W-O}_b\text{-W}$  bond is red-shifted from  $890$  to  $885\text{ cm}^{-1}$ , while the other bonds, viz., the  $\text{P-O}_a$  and  $\text{W-O}_c\text{-W}$  bonds, are unchanged. Also, the characteristic bands of methyl urea molecules are observed. For example the bands at  $1336\text{-}1730$  and

$2916\text{-}2943\text{ cm}^{-1}$  are characteristic of methyl urea molecules. The  $1453\text{ cm}^{-1}$  feature is characteristic of N–H vibration,  $1711\text{ cm}^{-1}$  is characteristic of the C=O group and the band at  $2953\text{ cm}^{-1}$  is attributed to the methyl group. This seems contradictory, because one would expect to observe some changes in the wave numbers (absorption energy) due to the POM-methylurinium interaction. However, the “contradiction” may be rationalized by the fact that we are looking at the literature values for the vibrational frequencies of methyl urea and not methylurinium. Furthermore, the observed wave numbers are obtained from a crystal lattice that exerts its unique influence, not present in the uncombined “ligand”, i. e., methyl urea.

The  $^1\text{H}$  NMR shifts for hybrid (1) are 4.0 (t, 1H,  $\text{C}_1\text{H}$ ); 1.8 (q, 4H,  $\text{C}_2$ , 3H); 0.9 (t, 6H,  $\text{C}_4$ , 5H). Hybrid (2): 4.30 (t, 1H,  $\text{C}_2\text{H}$ ); 3.40 (t, 2H,  $\text{C}_3\text{H}$ ); 2.03 (m, 4H,  $\text{C}_3\text{H}$ ,  $\text{C}_4\text{H}$ ). These shifts and patterns are consistent with the seven hydrogen atoms that are covalently bonded to the carbon atoms of the L-proline. The  $^1\text{H}$  NMR spectrum of (3) reveals the signal of protons of the methyl group at  $\delta$  2.5. The bands for  $\text{NH}_2$  and NH protons are masked by the solvent resonance absorptions. According to the above data, it is concluded that van der Waals interactions reduce electron density around the C–H groups. Hence, these protons appear at lower magnetic field. The bands for  $\text{NH}_2$  protons are masked by the solvent resonance absorptions. The UV spectra of the title hybrids measured in aqueous solution, is similar to that of  $\alpha\text{-H}_3[(\text{PO}_4)_M\text{M}_{12}\text{O}_{36}]\cdot n\text{H}_2\text{O}$  ( $M = \text{Mo}, \text{W}$ ) in the same

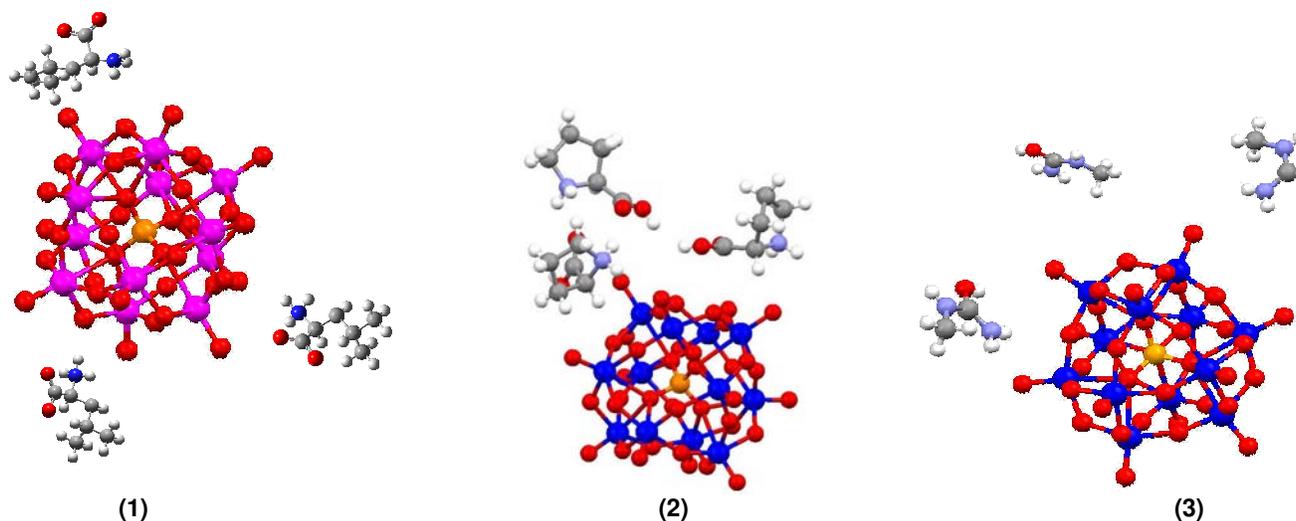


Fig. 1 — Schematic representation of proposed structures for 1-3. [Colour codes: phosphorus, orange; oxygen, red; carbon, gray; hydrogen, white (a: molybdenum, pink; nitrogen, blue; b and c: tungsten, blue; nitrogen, light blue)].

solutions. Between  $pH = 4 - 7$ , these spectra exhibit two absorption bands at 210 and 260 nm, ascribed to  $p_{\pi}(O_d) \rightarrow d_{\pi^*}(W)$  transitions in the  $W=O$  bonds and transitions  $d_{\pi}-p_{\pi}-d_{\pi}$  between the energetic levels of the  $W-O-W$  tricentric bonds. These results indicate that the polyanions in the title hybrid materials still retain the basic Keggin structure, but are distorted due to the effect of hydrogen bonding interactions.

Raman spectra of (2) and (3) were recorded in the range of  $1050-200\text{ cm}^{-1}$ . There are three prominent bands at 1007, 987 and  $217\text{ cm}^{-1}$  for (3) that can be attributed to  $\nu_s(W=O_d)$ ,  $\nu_{as}(W=O_d)$ , and  $\nu_s(W-O_a)$ , respectively. These bands demonstrate that  $[(PO_4)W_{12}O_{36}]^{-3}$  anion retains its "Keggin structure"<sup>15</sup>. Raman bands for methyl urea molecules have low intensity and could not be assigned unambiguously.

The  $^1H$  NMR spectral data and elemental analyses are in good agreement with mass data.  $M^+$  ions at  $m/z = 130, 115, \text{ and } 73$  indicate the presence of  $C_6H_{12}NO_2$ ,  $C_5H_8NO_2$ , and  $C_2H_5N_2O$  molecular formulas and suggest the loss of one hydrogen atom. Further,  $m/z = 114, 99, \text{ and } 57$  suggest the loss of  $NH_2$  (M-16), which is confirmed by neutral loss mass data and indicate the presence of N-H bond in the title hybrid materials. Schematic representations of proposed structures for (1), (2) and (3) are shown in Fig. 1.

In the present study, combination of the POM cluster and the organic substrate resulted in hybrids (1), (2) and (3), which have been fully characterized by elemental analyses, UV IR, Raman and  $^1H$  NMR and mass spectral data. According to the molecular structural analyses, these materials contain infinite planes of inorganic moiety. The arrangement of these planes with respect to each other creates space for the organic molecules to enter. The van der Waals interactions hold the organic moieties in the vacancies in the POM crystalline network. The synthesis and characterization of these new organic-inorganic

hybrid compounds is an important continuous step to incorporate organic molecules of biological significance into the network of inorganic cluster-hybrids. A combination of electrostatic forces and hydrogen bonding keeps this "adduct" stable in the solid state. The fact that in the solution phase the hybrid is also stable makes it a viable candidate for application as homogeneous catalysis. There may be potential pharmaceutical benefits that are yet to be explored. Our future efforts will be devoted to the growth of large crystals and related X-ray studies and biological activity tests on these compounds.

## References

- 1 Pope M T, *Heteropoly and Isopoly Oxometalates*, (Springer, Berlin) 1983.
- 2 Hill C L, *Chem Rev*, 98 (1998), Special issue on Polyoxometalates, Guest Editor.
- 3 Uchida S & Mizuno N, *Coord Chem Rev*, 251 (2007) 2537.
- 4 Alizadeh M H, Eshtiagh-Hosseini H, Mirzaei M, Salimi A R & Razavi H, *Struct Chem*, 19 (2008) 155.
- 5 Fukaya K & Yamase T, *Angew Chem Int Ed*, 115 (2003) 678.
- 6 Kögerler P & Cronin L, *Angew Chem Int Ed*, 117 (2005) 866.
- 7 Mialane P Dolbecq A & Sécheresse F, *Chem Commun*, (2006) 3477.
- 8 Yang X D, Chen Y G, Mirzaei M, Salimi A R & Yao F, *Inorg Chem Commun*, 12 (2009) 195.
- 9 Nikpour M, Eshtiagh-Hosseini H, Mirzaei M, Aghaei Kaju A, Chen Y G & Zarinabadi S, *Chin Chem Lett*, 21 (2010) 501.
- 10 Nikpour M, Mirzaei M, Chen Y G, Aghaei Kaju A & Bakavoli M, *Inorg Chem Commun*, 12 (2009) 879.
- 11 (a) Wang S & Du D, *Sensors Actuat B - Chem*, 94 (2003) 282.  
(b) Santos F M, Brandão P, Félix V, Cavaleiro A M V, de Matos Gomes E & Belsley M S, *J. Mol Struct*, 963 (2010) 267.
- 12 Bakavoli M, Nikpour M, Rahimizadeh M, Saberi M R & Sadeghian H, *Bioorg Med Chem*, 15 (2007) 2120.
- 13 Bakavoli M, Sadeghian H, Tabatabaei Z, Rezaei E, Rahimizadeh M & Nikpour M, *J Mol Model*, 14 (2008) 471.
- 14 Nikpour M, Sadeghian H, Saberi M R, Shafiee Nick R, Seyedi S M, Hosseini A, Parsaei H & Taghian A, *Bioorg Med Chem*, 18 (2010) 855.
- 15 Deltcheff C R, Fournier M, Franck R & Thouvenot R, *Inorg Chem*, 22 (1983) 207.