

## A Novel Hybrid Material Based on Two Symmetrically Independent *Keggin* Polyoxoanions: $[\text{NH}_3\text{-CH}(\text{CH}_3)\text{COOH}][\text{H}_3\text{O}]_8[\text{PMo}_{12}\text{O}_{40}]_3\cdot 4\text{NH}_3\text{CH}(\text{CH}_3)\text{COO}$

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Novel polyoxometalate-based organic-inorganic hybrid  $[\text{NH}_3\text{-CH}(\text{CH}_3)\text{COOH}][\text{H}_3\text{O}]_8[\text{PMo}_{12}\text{O}_{40}]_3\cdot 4\text{NH}_3\text{CH}(\text{CH}_3)\text{COO}$  was synthesized and characterized by  $^{31}\text{P}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and IR spectroscopies, elemental analysis and single crystal X-ray determination. Two of the  $\text{PMo}_{12}\text{O}_{40}^{3-}$  anions in the title hybrid are symmetrically equivalent. They are crystallographically independent from the third  $\text{PMo}_{12}\text{O}_{40}^{3-}$  polyoxoanion, in the case of various interactions with neighboring components in the crystal network (*i.e.*  $^+\text{NH}_3\text{-CH}(\text{CH}_3)\text{-COOH}$  and  $\text{H}_3\text{O}^+$  cations,  $^+\text{NH}_3\text{CH}(\text{CH}_3)\text{COO}^-$  zwitterions and polyoxoanions). The compound crystallizes in an orthorhombic C222 space group with  $a = 16.0392(16)$  Å,  $b = 34.480(4)$  Å,  $c = 12.8968(13)$  Å and  $Z = 2$ .

**Keywords:** Hybrid material, Symmetrically independent *Keggin* polyoxoanions, Crystal structure, Alanine

### INTRODUCTION

It has been shown that many different structures and extent properties for polyoxometalate (POM) compounds [1-3] and POM-based organic inorganic hybrids [4,5] have attracted much interest in crystal engineering [6,7]. The synthetic design of hybrid materials remain as a challenging task in material chemistry, since evolution of a hybrid material gives information on synthesizing new solids with unique structures and properties. Studies on design, synthesis and application of composite materials, which are based on the nanosized discrete metal-oxygen cluster anions (polyoxometalates), have been reported [8-11].

The POM-based organic-inorganic hybrids are important due to their applications to catalysis, sorption, electrical conductivity, magnetism, and photochemistry [12,13]. The use of some molecules having potential ability to produce various

non-covalent interactions and H-bonding with polyoxometalates is a method of approaching design [14,15]. Different orientation and shuffling resulting from non-rigid units in some molecules and salts and the presence of different H-bonds or other short contacts may result in two or more conformers in solid state [16-18]. In the previous studies, we reported on the structures of  $\text{Na}_3\text{PMo}_{12}\text{O}_{40}\cdot 16\text{H}_2\text{O}$ ,  $[\text{C}_2\text{H}_6\text{NO}_2]_3[\text{PMo}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$  and  $[\text{C}_8\text{H}_{10}\text{N}_5][\text{H}_2\text{PMo}_{12}\text{O}_{40}]\cdot 2.5\text{CH}_3\text{OH}\cdot 4\text{H}_2\text{O}$  [19] salts. In this work, we wish to report on the synthesis, spectroscopic characterization and crystal structure of a novel POM-based organic-inorganic hybrid,  $[\text{NH}_3\text{-CH}(\text{CH}_3)\text{COOH}][\text{H}_3\text{O}]_8[\text{PMo}_{12}\text{O}_{40}]_3\cdot 4\text{NH}_3\text{CH}(\text{CH}_3)\text{COO}$  which contains two symmetrically independent *Keggin* polyoxoanions.

### EXPERIMENTAL

#### Materials and Instrumentation

All chemicals were purchased commercially and used

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without further purification. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were determined on a Bruker Avance DRS 500 spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were determined relative to internal TMS, and the  $^{31}\text{P}$  chemical shifts relative to 85%  $\text{H}_3\text{PO}_4$  as an external standard. The infrared spectrum was recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

**Synthesis of  $[\text{NH}_3\text{-CH}(\text{CH}_3)\text{COOH}][\text{H}_3\text{O}]_8[\text{PMo}_{12}\text{O}_{40}]_3 \cdot 4\text{NH}_3\text{CH}(\text{CH}_3)\text{COO}$**

A solution of alanine (0.136 g, 1.53 mmol) in a mixture of HCl (2 ml, 1 M)- $\text{H}_2\text{O}$  (8 ml) was added dropwise to a solution containing  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (1.387 g, 0.76 mmol) in  $\text{H}_2\text{O}$  (25 ml) and was stirred for 1.5 h at room temperature. After filtering, the solution was hold in a beaker at room temperature; it takes few days to obtain the yellow crystals from this solution. IR (KBr) frequencies ( $\text{cm}^{-1}$ ): 771vs, 872s, 956vs, 1055vs, 1382m, 1466m, 1608m, 1726m, 3180m, 3395m.  $^{31}\text{P}$  NMR ( $(\text{D}_6)$ DMSO): -3.86.  $^1\text{H}$  NMR ( $(\text{D}_6)$ DMSO): 1.33 (d,  $^3\text{J}(\text{H},\text{H}) = 7.3$  Hz, 15H, 5 $\text{CH}_3$ ), 3.98 (b,  $\text{H}_2\text{O}$ , 8 $\text{H}_3\text{O}^+$ , 1 $\text{COOH}$  and 5CH), 8.18 (b, 15H, 5 $\text{NH}_3^+$ ).  $^{13}\text{C}$  NMR ( $(\text{D}_6)$ DMSO): 172.25 (s,

**Table 1.** Crystal Data and Structure Refinement for Title Hybrid Material

|   |  |
|---|--|
| Empirical formula                                       | $\text{C}_{15}\text{H}_{60}\text{Mo}_{36}\text{N}_5\text{O}_{138}\text{P}_3$                         |
| Formula weight  | 6065.43  |
| Temperature   | 120(2) K   |
| Wavelength ( $\text{\AA}$ )                             | 0.71073  |
| Crystal system  | Orthorhombic   |
| Space group   | C222   |
| Unit cell dimensions                                    | $a = 16.0392(16)$ $\text{\AA}$ ,<br>$b = 34.480(4)$ $\text{\AA}$ ,<br>$c = 12.8968(13)$ $\text{\AA}$ |
| Volume  | 7132.3(12) $\text{\AA}^3$  |
| Z   | 2  |
| Density (calculated)                                    | 2.824 $\text{g cm}^{-3}$   |
| Absorption coefficient                                  | 3.197 $\text{mm}^{-1}$   |
| F(000)  | 5692   |
| Crystal size  | 0.34 $\times$ 0.25 $\times$ 0.22 $\text{mm}^3$   |
| Theta range for data collection                         | 2.11 to 27.00 $^\circ$   |
| Index range   | -19 $\leq h \leq 20$ , -43 $\leq k \leq 38$ , -16 $\leq l \leq 15$                                   |
| Reflections collected                                   | 19109  |
| Independent reflections                                 | 7732 [R(int) = 0.0238]   |
| Completeness to $\theta = 27.00^\circ$                  | 99.0%  |
| Absorption correction                                   | Semi-empirical from equivalents  |
| Max. and min. transmission                              | 0.498 and 0.396  |
| Refinement method                                       | Full-matrix least-squares on $F^2$   |
| Data/restraints/parameters                              | 7732/2/456   |
| Goodness-of-fit on $F^2$                                | 1.052  |
| Final R indices [for 7390 refl. with $I > 2\sigma(I)$ ] | R1 = 0.0433, wR2 = 0.1241  |
| R indices (all data)                                    | R1 = 0.0456, wR2 = 0.1270  |
| Absolute structure parameter                            | 0.01(6)  |
| Largest diff. peak and hole                             | 3.344 and -1.884 $\text{e.}\text{\AA}^{-3}$  |

C=O), 47.96 (s, CH), 15.69 (s, CH<sub>3</sub>). Anal. Calc. for C<sub>15</sub>H<sub>60</sub>Mo<sub>36</sub>N<sub>5</sub>O<sub>138</sub>P<sub>3</sub>: C, 2.97; H, 1.00; N, 1.15; found: C, 2.94; H, 0.99; N, 1.16.

## RESULTS AND DISCUSSION

### IR Spectroscopy

The IR spectrum of title compound contains the characteristic bands at 771 (Mo-O<sub>c</sub>-Mo), 872 (Mo-O<sub>b</sub>-Mo), 956 (Mo-O<sub>d</sub>) and 1055 cm<sup>-1</sup> (P-O<sub>a</sub>) which demonstrate the *Keggin* structure of Mo atom (O<sub>a</sub>, O<sub>b</sub>, O<sub>c</sub> and O<sub>d</sub> are different kind oxygen atoms in *Keggin* polyoxoanion). The band at 1726 cm<sup>-1</sup> is assigned to C=O group.

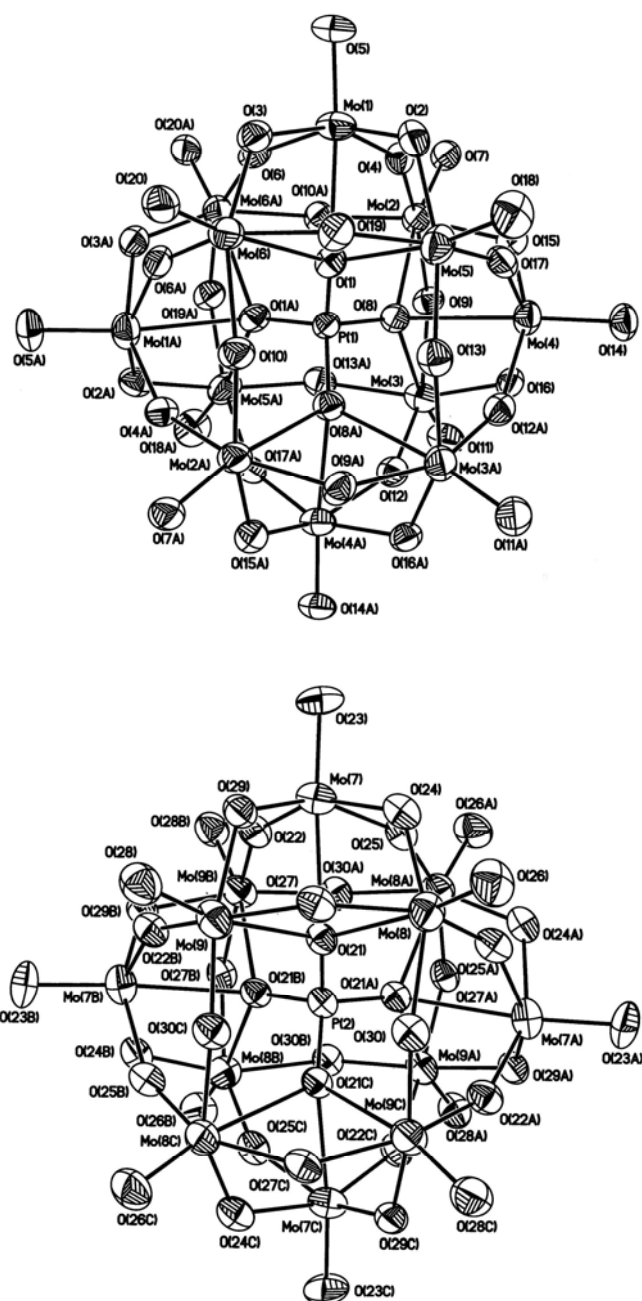
### NMR Spectroscopy

The phosphorus-31 NMR spectrum of title compound shows one signal at -3.86 ppm indicating the *Keggin* type polyoxoanions of Mo. The CH<sub>3</sub> protons appear at 1.33 ppm (doublet) in <sup>1</sup>H NMR spectrum. The signals at 15.69, 47.96 and 172.25 ppm in <sup>13</sup>C NMR spectrum are assigned to CH<sub>3</sub>, CH and C=O carbon atoms.

### Description of the Crystal Structure

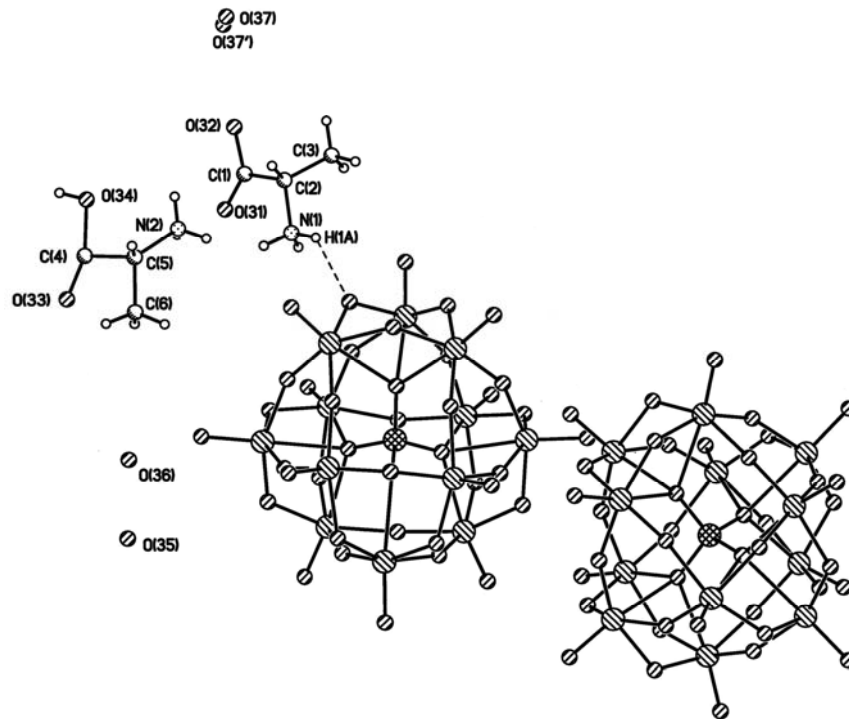
The crystal data and the details of X-ray analysis are given in Table 1. There are three PMo<sub>12</sub>O<sub>40</sub><sup>3-</sup> anions in title compound, two of them as the form of Fig. 1, top and the other as Fig. 1, bottom. The inorganic anions in the title hybrid have a *Keggin* structure with 4 different kinds of O atoms: i) 12 terminal oxygens, ii) 4 bonded oxygen to P and Mo, iii) the 12MoO<sub>6</sub> octahedra corner-shared oxygens and iv) the 12MoO<sub>6</sub> octahedra edge-shared oxygens. The P-O bonds in the polyoxoanions are single [1.530(5) Å to 1.539(6) Å], the P atoms have a tetrahedral configuration and the O-P-O angles are in the range of 109.0(4)° to 109.9(4)°. Selected bond lengths and angles are given in Table 2.

The Organic cation, <sup>+</sup>NH<sub>3</sub>-CH(CH<sub>3</sub>)COOH, and zwitterions, <sup>+</sup>NH<sub>3</sub>CH(CH<sub>3</sub>)COO<sup>-</sup>, produce different electrostatic interactions with the two symmetrically different inorganic anions. A view of two crystallographically independent polyoxoanions, organic cation <sup>+</sup>NH<sub>3</sub>-CH(CH<sub>3</sub>)COOH, zwitterion <sup>+</sup>NH<sub>3</sub>CH(CH<sub>3</sub>)COO<sup>-</sup> and symmetrically non-equivalent H<sub>3</sub>O<sup>+</sup> oxygen atoms is shown in Fig. 2. The unit cell packing of title hybrid material is shown

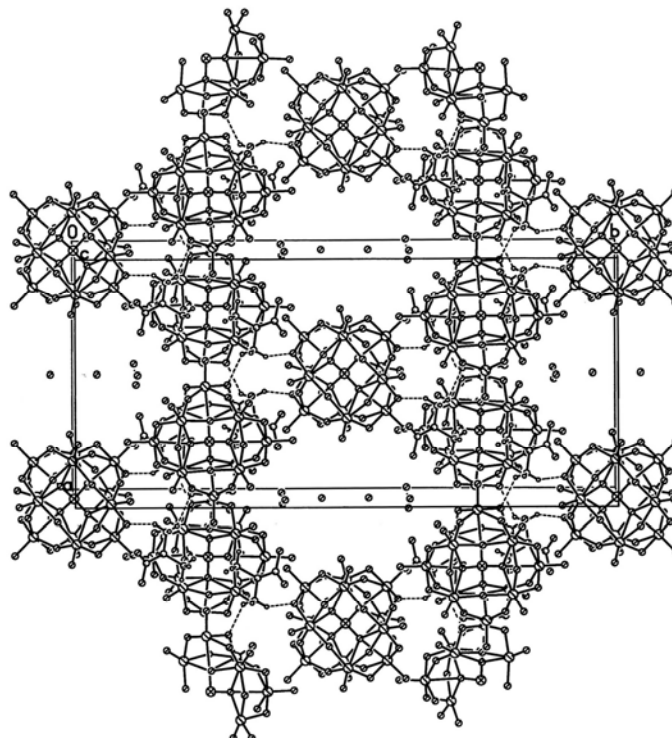


**Fig. 1.** Two symmetrically different *Keggin* polyoxoanions in compound [NH<sub>3</sub>-CH(CH<sub>3</sub>)COOH][H<sub>3</sub>O]<sub>8</sub>[PMo<sub>12</sub>O<sub>40</sub>]<sub>3</sub>·4NH<sub>3</sub>CH(CH<sub>3</sub>)COO.

in Fig. 3. The *Keggin* anion in the unit cell center, which is symmetrically equivalent to four *Keggin* anions in the unit cell edges (see the *Keggin* anion in the cross which is caused by



**Fig. 2.** A view of two symmetrically independent polyoxoanions,  ${}^+\text{NH}_3\text{-CH}(\text{CH}_3)\text{COOH}$  organic cation,  ${}^+\text{NH}_3\text{CH}(\text{CH}_3)\text{COO}^-$  zwitterion and the oxygen atoms of symmetrically different  $\text{H}_3\text{O}^+$ .

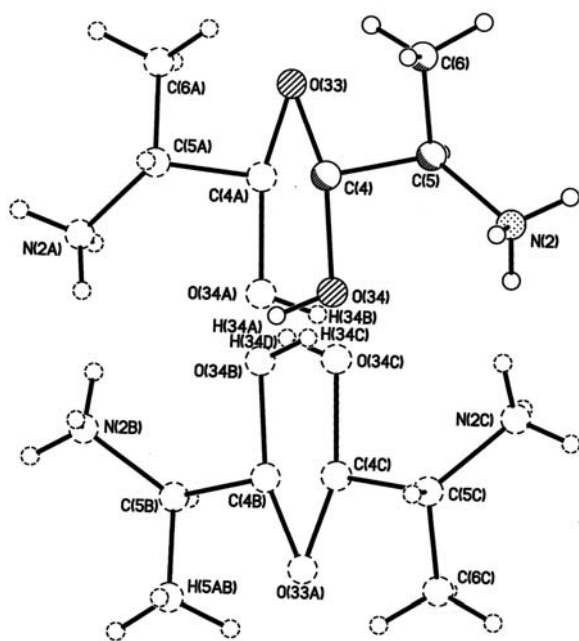


**Fig. 3.** A view of unit cell packing of the title hybrid material.

**Table 2.** Selected Bond Lengths and Angles

|                      |           |                  |           |
|----------------------|-----------|------------------|-----------|
| Mo(1)-O(4)           | 1.847(6)  | P(2)-O(21)#4     | 1.539(6)  |
| Mo(1)-O(3)           | 1.987(6)  | P(2)-O(21)#2     | 1.539(5)  |
| Mo(1)-O(1)           | 2.390(6)  | O(31)-C(1)       | 1.22(2)   |
| Mo(6)-O(6)#1         | 1.892(6)  | O(32)-C(1)       | 1.333(18) |
| Mo(8)-O(25)#2        | 1.827(6)  | N(1)-C(2)        | 1.463(13) |
| Mo(9)-O(28)          | 1.680(7)  | O(33)-C(4)#5     | 1.37(7)   |
| Mo(9)-O(30)#3        | 1.811(7)  | O(33)-C(4)       | 1.37(7)   |
| Mo(9)-O(21)          | 2.421(5)  | O(33)-C(6)#5     | 1.88(5)   |
| P(1)-O(1)            | 1.530(5)  | O(34)-C(4)       | 1.61(8)   |
| P(1)-O(8)            | 1.535(5)  | N(2)-C(5)        | 1.57(7)   |
| O(5)-Mo(1)-O(4)      | 106.0(3)  | P(1)-O(1)-Mo(6)  | 125.5(3)  |
| O(5)-Mo(1)-O(2)      | 100.5(3)  | Mo(1)-O(1)-Mo(6) | 89.11(17) |
| O(28)-Mo(9)-O(30)#3  | 104.8(3)  | Mo(5)-O(1)-Mo(6) | 88.61(18) |
| O(28)-Mo(9)-O(29)    | 97.6(3)   | P(1)-O(8)-Mo(4)  | 126.0(3)  |
| O(27)-Mo(9)-O(29)    | 84.9(3)   | P(1)-O(8)-Mo(2)  | 125.8(3)  |
| O(1)#1-P(1)-O(1)     | 109.9(4)  | P(2)-O(21)-Mo(8) | 125.9(3)  |
| O(1)#1-P(1)-O(8)     | 109.7(3)  | O(31)-C(1)-O(32) | 126.6(16) |
| O(21)#4-P(2)-O(21)#2 | 109.5(4)  | O(31)-C(1)-C(2)  | 121.4(12) |
| O(21)#4-P(2)-O(21)   | 109.8(4)  | N(1)-C(2)-C(3)   | 111.1(10) |
| Mo(1)-O(1)-Mo(5)     | 89.74(19) | N(1)-C(2)-C(1)   | 107.6(10) |

Symmetry transformation used to generate equivalent atoms: (#1)  $-x+3/2, -y+3/2, z$ , (#2)  $-x+1, -y+1, z$ , (#3)  $-x+1, y, -z+1$ , (#4)  $x, -y+1, -z+1$ , (#5)  $x, -y+2, -z+2$ , (#6)  $-x+2, y, -z+2$ , (#7)  $-x+2, -y+2, z$ .

**Fig. 4.** Organic cation in the title compound.

the planes (010) and (100)) is surrounded with 4 *Keggin* anions; these two kinds *Keggin* polyoxoanions are symmetrically different. The organic cation in this compound is disordered over 4 positions with equal occupancies (Fig. 4).

### Supplementary Material

CCDC 604766 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via*: [www.ccdc.cam.ac.uk/data-request/cif](http://www.ccdc.cam.ac.uk/data-request/cif).

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