

Contribution of intermolecular interactions to constructing supramolecular architecture: Synthesis, structure and Hirshfeld surface analysis of a new hybrid of polyoxomolybdate and ((1*H*-tetrazole-5-yl) methyl)morpholine

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ABSTRACT

A new soluble organic–inorganic hybrid based on polyoxomolybdate, $[\text{C}_6\text{H}_{12}\text{N}_5\text{O}]_3[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]\cdot 6\text{H}_2\text{O}$ (**1**), has been successfully synthesized and characterized by using elemental analysis, IR, UV spectroscopies, ^1H NMR technique, and single-crystal X-ray diffraction. According to the results of X-ray crystallography the anion $[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]^{3-}$ has a typical Keggin structure and the Mo–O distances of Mo–O–Mo bonds are alternately short and long in the polyoxoanion structure. Hirshfeld surface analyses, especially d_{norm} surface and fingerprint plots, are used for decoding intermolecular interactions in the crystal network and contribution of component units for the construction of the 3D architecture. The results indicate that in **1** the hydrogen bond interaction play a main role in the construction of the 3D architecture, especially the $\text{CH}\cdots\text{O}$ interaction which overruns the classic $\text{NH}\cdots\text{O}$, $\text{N}\cdots\text{HO}$ hydrogen bond interactions; van der Waals force between the peripheral atoms of component units cannot be ignored.

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Polyoxometalates (POMs) constitute a fascinating class of metal–oxygen cluster compounds with definite size and shape. They have been found to be extremely versatile inorganic building blocks in view of their potential applications in catalysis, medicine, materials science, and others [1–6]. In recent decades, POMs associated with organic donors have generated a series of important compounds [7–10]. They have led to the development of substances with interesting electric, magnetic and/or optical properties. On the other hand, the ((1*H*-tetrazole-5-yl)methyl)morpholine is a biological equivalent for carboxylic acid group. A literature survey discloses that tetrazoles are present in a number of biologically active molecules [11] and extensive works have been carried out in relation with them in the fields of medicinal chemistry [12]. Prompted by these reports and due to our interest in the synthesis of biologically important molecules [13,14] and to give birth to a variety of hydrogen-bonded frameworks with fascinating structures, here, we report the synthesis, molecular structure, and the Hirshfeld surfaces analyses [15,16] of a new organic–inorganic hybrid $[\text{C}_6\text{H}_{12}\text{N}_5\text{O}]_3[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]\cdot 6\text{H}_2\text{O}$ (**1**).

Hybrid **1** was prepared as follow: a solution of the $\text{C}_6\text{H}_{11}\text{N}_5\text{O}$ (0.14 g, 0.82 mmol) in 30 ml of water was added with vigorous

stirring, to a solution of $\alpha\text{-H}_3[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]\cdot 21\text{H}_2\text{O}$ (0.50 g, 0.27 mmol) in 25 ml of water. The yellow precipitate was formed after 5 h. The solid was filtered, washed with DMF and dried at RT. The precipitate was redissolved in hot acetonitrile and the solution was cooled to ambient temperature, yellow block crystals were obtained, filtered, washed several times with distilled water, and dried in air (yield 30% based on Mo) [17]. The single-crystal X-ray structure analysis [18] reveals that the title hybrid consists of one discrete anion $[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]^{3-}$, three $[\text{C}_6\text{H}_{12}\text{N}_5\text{O}]^+$ cations and six water molecules (Fig. S1). The anion $[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]^{3-}$ has a classic Keggin anion structure, that is, it is constructed by corner-sharing of four tri-metal clusters (Mo_3O_{13}) and arraying around the central (PO_4) tetrahedron. The tri-metal cluster (Mo_3O_{13}) is formed by edge-sharing connection of MoO_6 octahedrons. In the anion the Mo–O distances of all Mo–O–Mo bridging bonds are alternately short and long (Fig. S2), a characteristic of dodecamolybdates. Since the organic moieties are located on the two sides of $[(\text{PO}_4)\text{Mo}_{12}\text{O}_{36}]^{3-}$ clusters, one-dimensional inorganic zig-zag chain along the *a* axis can be described which is formed *via* strong interactions between the anions with distances of $\text{O}(15)\cdots\text{O}(32)$ 2.986 Å and $\text{O}(34)\cdots\text{O}(3)$ 3.017 Å (Fig. S3). The one-dimensional chains arrange in parallel fashion in the crystal lattice. Each anion forms several hydrogen bonds with water molecules (O2w, O4w, O5w, O6w) through its terminal oxygen atoms (O10, O21, O26, O32), in turn, each water molecule links more than two structural

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components, that is, the water molecules play an important role in constructing the supramolecular architecture. Their linking details are shown in Table S1 and Fig. S4.

In the **1**, organic bases, protonated organic structural components, not only play a space-filling and charge-compensating role but also are intimately involved in structural propagation in supramolecular architecture. They link the polyoxomolybdate chains and water molecules *via* electrostatic force and van der Waals force ($H_{\text{organic}} \cdots H$, $H_{\text{organic}} \cdots N$, $N \cdots O$), as well as various hydrogen bond interactions ($C-H_{\text{organic}} \cdots O_{\text{polyoxo}}$, $O_{\text{organic}} \cdots O_{\text{polyoxo/w}}$, $N_{\text{organic}} \cdots O_w$). In order to comprehend the role of the organic base in structural propagation, Hirshfeld surface analyses on **1** were carried out. 3D isosurface pictures of Hirshfeld surfaces, d_{norm} and d_e maps, of the organic moieties have been showed in Fig. 1. In Fig. 1a (i and ii) the region labelled **1** is an intermolecular contact between nitrogen atom of 1*H*-tetrazole ring of organic moiety (I) and oxygen atom of water molecule, $N(1) \cdots O(5W)$ 2.886 Å; hydrogen bond and $H \cdots H$ contact from the protonated tetrazole ring and water molecule can be seen in red hollow regions labelled **2** with distances of $N(3)-H(3C) \cdots H(3E)$ 1.571 Å and $N(3)-H(3C) \cdots O(3W)$ 2.058 Å; the hydrogen bonds from morpholine ring of organic component (I) and oxygen atoms of polyoxomolybdate with $C(1)-H(1B) \cdots O(13)$ 2.698 Å and $C(4)-H(4B) \cdots O(10)$ 2.552 Å can be seen

in red-yellow regions labelled **3** and **4**. In Fig. 1b (i)/(ii), the red concave areas denoted **5** reveal the strong interaction from nitrogen atom of tetrazole ring and water molecule in crystal network with $N(4) \cdots H(6C)-O(6W)$ distance of 1.924 Å; the regions labelled **6–9** show weak interactions of $C-H \cdots O_{\text{water/polyoxomolybdate}}$. For organic moieties II and III, same interactions have been observed (see Fig. 1c and d) but contributions of them in intermolecular interactions are different.

By using breakdown of fingerprint plots (existing techniques and tools based on the Hirshfeld surface and already incorporated in Crystal Explorer computer program) we can decompose fingerprint plots of organic components to highlight particular close contacts. This decomposition enables to separate contributions from different interaction types, which commonly overlap in the full fingerprint. It also facilitates a rapid comparison between related molecules in the same or different crystals. Fig. 2 illustrates this decomposition of the fingerprint plots for three organic components in crystal lattice, highlighting separately the $H_{\text{organic}} \cdots O$ (a), and $H_{\text{organic}} \cdots N$ (b) intermolecular contacts, Fig. S5 shows decomposition of the fingerprint plots of other interactions. To provide context, the outline of the full fingerprint is shown in grey and the blue area shows the separate contact. Fig. 3 shows the relative contributions to the Hirshfeld surface area coming from

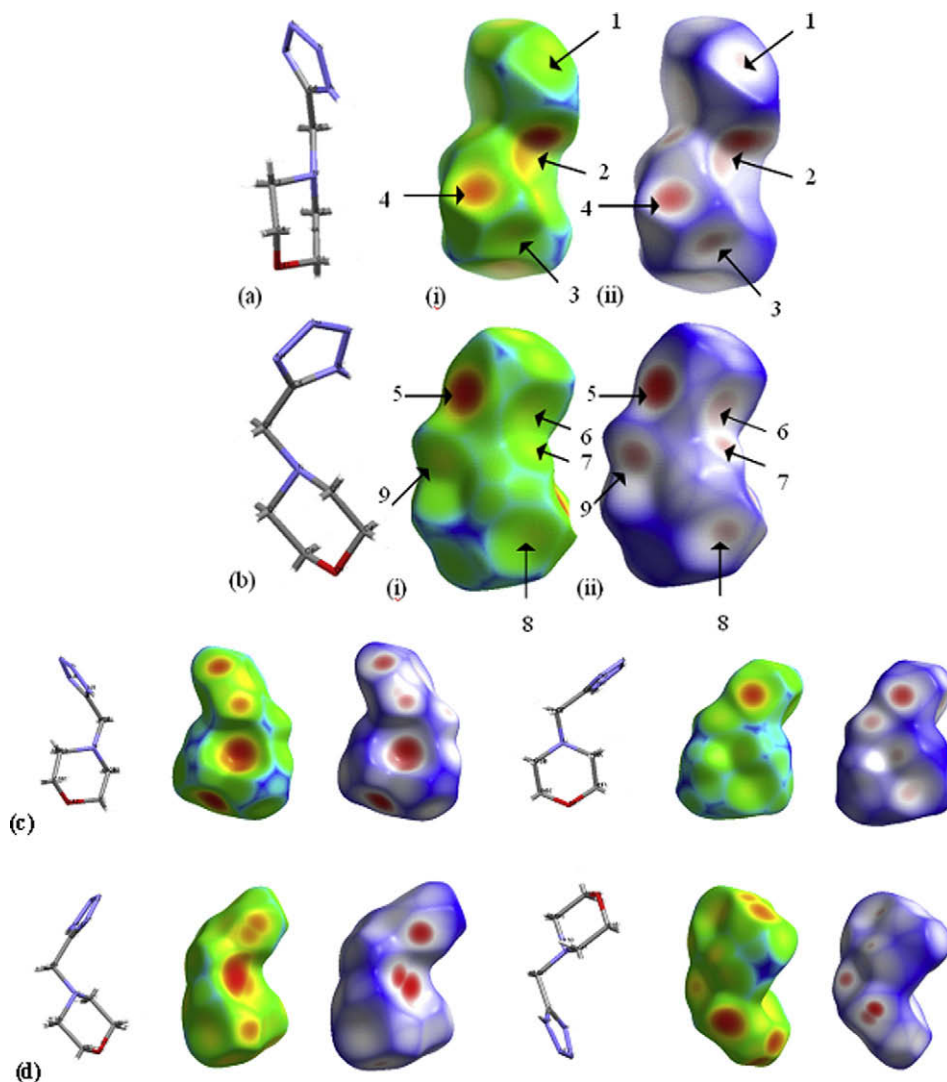


Fig. 1. The Hirshfeld surfaces of $[C_6H_{12}N_5O]$ (I), (a, b), $[C_6H_{12}N_5O]$ (II) (c) and $[C_6H_{12}N_5O]$ (III) (d), mapped with d_e (i) and the d_{norm} (ii) property in two orientation. The molecules in ball-stick representation beside the surface maps have been added for clarity.

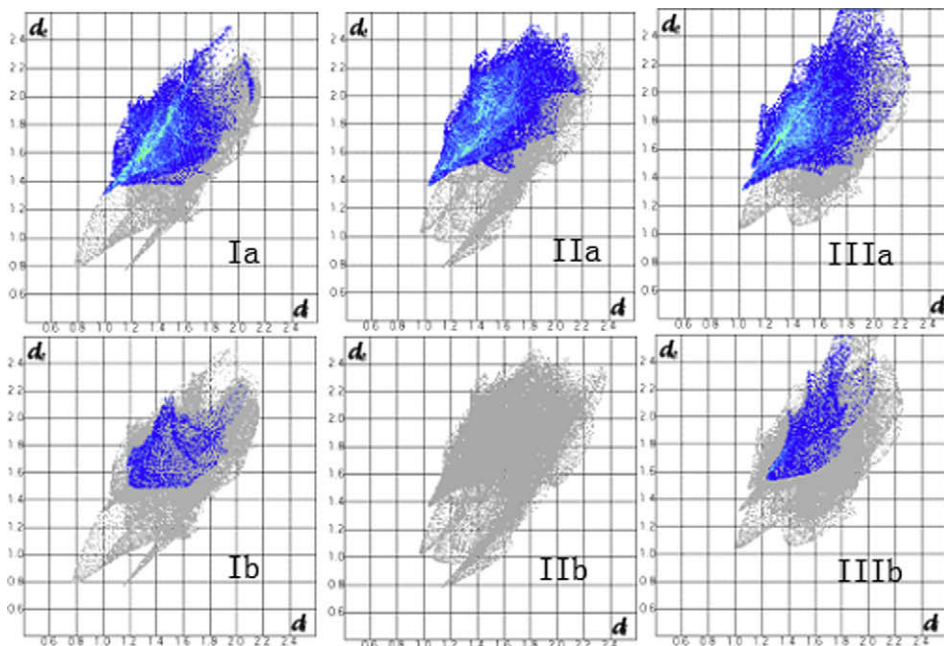


Fig. 2. Fingerprint plots for organic moieties (Ia), (IIa) and (IIIa) for $H_{\text{organic}} \cdots O$ contacts and (Ib), (IIb) and (IIIb) for $H_{\text{organic}} \cdots N$ (f) contacts. The full fingerprint appears beneath each decomposed plots as a grey shadow.

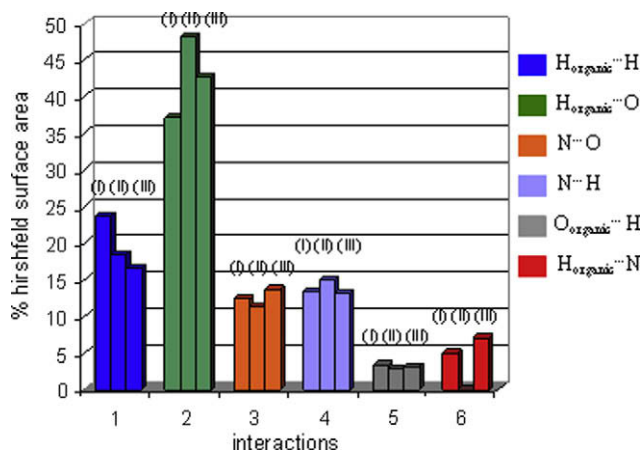


Fig. 3. Relative contributions to the Hirshfeld surface area for the various intermolecular contacts in ($H_{\text{organic}} \cdots H$, $H_{\text{organic}} \cdots O$, $N \cdots O$, $N \cdots H$, $O_{\text{organic}} \cdots H$ and $H_{\text{organic}} \cdots N$) organic moiety (I), (II) and (III).

$H_{\text{organic}} \cdots H_{\text{water}}$, $H_{\text{organic}} \cdots O_{\text{poa}}$, $N \cdots O$, $N \cdots H$, $O_{\text{organic}} \cdots H$ and $H_{\text{organic}} \cdots N$ contacts for three morpholine species. From this simple analysis, it immediately emerges that morpholine species are conspicuously contributor in $H_{\text{organic}} \cdots O$ interactions (37% area for organic moiety (I), 48% area for organic moiety (II) and 42% area for organic moiety (III)) (Fig. 2Ia, IIa, IIIa and Fig. 3). It is clear that the natures of the $H_{\text{organic}} \cdots O$ contacts in three organic molecules are strikingly similar to each other. $N \cdots H$ contacts in organic components (I) and (II) are comparable, 13.2% area for organic moiety (I) and 13.4% area for organic moiety (II) (see Fig. 3). Fig. 2Ib, IIb and IIIb) also reveals that, organic moiety (II) have not any $H_{\text{organic}} \cdots N$ intermolecular contacts in crystal lattice (4.9% $H_{\text{organic}} \cdots N$ area for organic moiety (I), 0.0% $H_{\text{organic}} \cdots N$ area for organic moiety (II), 7.0% $H_{\text{organic}} \cdots N$ area for organic moiety (III)). Also, it should be noted that the water molecules have important role in the observed interactions. From Fig. 3 it can be concluded that in **1** the hydrogen bond interaction play a main role in the

construction of the 3D architecture, especially the $CH \cdots O$ interaction which overruns the classic $NH \cdots O$, $N \cdots HO$ hydrogen bond interactions; van der Waals force between the peripheral atoms of component units cannot be ignored.

In summary, we have prepared and characterized structurally a novel organic–inorganic hybrid containing ((1*H*-tetrazol-5-yl)-methyl)morpholine and Keggin-type polyoxoanion: $[C_6H_{12}N_5O]_3-[(PO_4)_4Mo_{12}O_{36}] \cdot 6H_2O$. According to the crystal structure analysis, this material contains infinite zig-zag chains of inorganic moieties. The organic moieties play a space-filling and charge-compensating role and meanwhile are intimately involved in structural propagation in supramolecular architecture. Through this paper, we have demonstrated how Hirshfeld surfaces analyses (in particular d_{norm} surface) and breakdown fingerprint plots are a valuable and rapid tools for visualizing and analyzing intermolecular interactions in organic–inorganic hybrids based on polyoxometalate.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.07.002.

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- [17] Anal. Calcd. for $C_{18}H_{45}N_{15}O_{49}PMo_{12}$: C, 8.84; H, 1.84; N, 8.60. Found: C, 8.72; H, 1.68; N, 8.47. 1H NMR in D_2O : δ (ppm), 2.65 (t, 4H, $(CH_2)_2N$), 3.80 (t, 4H, $(CH_2)_2O$), 4.15 (s, 2H, $CH_2-N(CH_2)_2$). UV: 374 nm (abs = 2.49, $H_3[(PO_4)Mo_{12}O_{36}] \cdot 21H_2O$), 212 nm (abs = 2.04, (1*H*-tetrazole-5-yl) methyl morpholine), 278 nm (abs = 2.48, the title hybrid). IR (cm^{-1}): 3550(s), 1640(s), 1467(m), 1455(m), 1063(s), 961(s), 877(s), 789(w).
- [18] The diffraction data of yellow block crystal of $[C_6H_{12}N_5O]_3-[(PO_4)Mo_{12}O_{36}] \cdot 6H_2O$ were collected at 296 K on a Bruker Smart CCD diffractometer with graphite monochromatic Mo $K\alpha$ radiation ($\lambda = 0.07103 \text{ \AA}$) and ω -scan technique. 14,137 of 37,154 reflections are unique reflections ($R_{int} = 0.044$), 12,215 observed reflections in scan range of $1.61-28.25^\circ$. An empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 software. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrical calculated positions and thereafter allowed to ride on their parent atoms. Crystal and refinement data for the title hybrid are: $C_{18}H_{33}Mo_{12}N_{15}O_{49}P$, $Mr = 2425.84 \text{ g/mol}$, orthorhombic, space group $P2_12_12_1$, $a = 14.3502(7) \text{ \AA}$, $b = 15.4580(7) \text{ \AA}$, $c = 27.1062(13) \text{ \AA}$, $V = 6012.8(5) \text{ \AA}^3$, $Z = 4$, $\mu = 2.563 \text{ mm}^{-1}$, $S = 1.028$, final R indices [$I > 2\sigma(I)$] $R_1 = 0.0364$, $wR_2 = 0.0694$. X-ray crystallographic files in CIF format of the title hybrid (CCDC No. 657898) has been deposited in the Cambridge Crystallographic Data Center. Copy of this information may be obtained, free of charge, from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).