



# CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF A ONE-DIMENSIONAL COORDINATION ORGANIC/INORGANIC HYBRID [(MoO<sub>3</sub>)(biim)]<sub>n</sub>



## ANÁLISE DE ESTRUTURA CRISTALINA E SUPERFÍCIE HIRSHFELD DE UMA COORDENAÇÃO UNI-DIMENSIONAL HÍBRIDA ORGÂNICA/INORGANICA [(MoO<sub>3</sub>)(biim)]<sub>n</sub>

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### RESUMO

Um novo híbrido orgânico/inorgânico unidimensional [(MoO<sub>3</sub>)(biim)]<sub>n</sub> foi sintetizado por método hidrotérmico em um reator Parr. Sua estrutura foi caracterizada por estudos espectroscópicos FT-IR e difração de raios-X de um único cristal. Este composto cristaliza no sistema ortorrômbico com o grupo espacial Cmc2<sub>1</sub>, Z = 4 e os parâmetros da célula unitária **a** = 6.9834(4) Å, **b** = 9.8771(6) Å, **c** = 13.6740(8) Å e β = 103.861(1)°, V = 1026,64(18) Å<sup>3</sup>. A estrutura molecular e a embalagem de cristal são estabilizadas principalmente por fortes ligações de hidrogênio intermoleculares com átomos N-H...O que podem ser descritos pelo símbolo de conjunto de grafos R<sup>2</sup><sub>2</sub>(9) e sua disposição de embalagem reforçada por empilhamento de π-π. Os intercontatos na estrutura do cristal são analisados usando o método computacional de superfícies de Hirshfeld.

**Palavras-chave:** Síntese hidrotermal; Híbrido inorgânico/orgânico; Análise da estrutura de cristal; Análise de superfície de Hirshfeld.

### ABSTRACT

A new one-dimensional organic/inorganic hybrid [(MoO<sub>3</sub>)(biim)]<sub>n</sub> has been synthesized by a hydrothermal method in a reactor Parr. Its structure was characterized by FT-IR spectroscopic studies and single-crystal X-ray diffraction. This compound crystallize in the orthorhombic system with space group Cmc2<sub>1</sub>, Z = 4, and unit cell parameters **a** = 6.9834(4) Å, **b** = 9.8771(6) Å, **c** = 13.6740(8) Å, and β = 103.861(1)°, V=1026.64(18) Å<sup>3</sup>. The molecular structure and crystal packing are stabilized mainly by a strong intermolecular hydrogen bonds with atoms N-H...O which can be described by graph set symbol R<sup>2</sup><sub>2</sub>(9) and its packing arrangement reinforced by π-π stacking. The intercontacts in the crystal structure are analyzed using Hirshfeld surfaces computational method.

**Keywords:** Hydrothermal synthesis; Inorganic/organic hybrid; Crystal Structure analysis; Hirshfeld surface analysis.

## INTRODUCTION:

Within the most interesting nanostructured porous solid materials are organic metal structures (MOFs) which are composed of center metallic and, organic ligands. These last can act either as spacer or bridges inside the crystal structure, and its proper choice allows the design of new architectures with properties made to order like as applications in the area of catalysis, magnetism and particularly in gas storage (Pope, 1991; Cheetham, 1994).

For this reason, countless efforts have been invested in designing optimal strategies for the synthesis of this kind of materials. One of the strategies used in the synthesis of organic metal structures (MOFs) is to assemble together with organic species under hydrothermal conditions, in order to reduce the use of solvents and decrease the reaction time (Zhang *et. al.*, 1997; Tong, 2000; Lu, 2002, Zapf, 1997). However, still under these conditions, it has been demonstrated that functionalization or modification of the metal topology is determined by the stereochemical characteristics of the organic component (Hagrman *et. al.*, 1999).

Therefore, knowing that the hydrothermal synthesis offers a powerful synthetic route for the design of novel materials (Stupp, 1997; Hagrman *et. al.*, 1999) we will explore the capabilities of 2,2-biimidazole as a potential building block for the synthesis of organic metal structures under these synthesis conditions. Here, we report the application of this technique to the cooperative assembly of molybdenum oxide / organic phases that have resulted in the formation of [(MoO<sub>3</sub>)(biim)]<sub>n</sub> (**1**) a new one-dimensional chain which was synthesized by hydrothermal methods structurally characterized by spectroscopic method (FT-IR), X-ray diffraction and analysis of intercontacts by Hirshfeld surfaces.

## PARTE EXPERIMENTAL

All reagents for the synthesis were purchased as reagent grade and used without further purification. The FT-IR spectrum for the title compound was recorded on a Perkin Elmer Spectrum GX spectrometer employing a KBr disc, in the region from 400 to 4000 cm<sup>-1</sup>. FT-IR (KBr),  $\nu$  cm<sup>-1</sup>: 3481,51 [N-H], 1670 [C=C], 1436,97 [C=N], 1217 [C-H], 887,26 [Mo=O], 744,52 [Mo-O].

Elemental analysis (C, H, N) were determined with TruSpec CHN Leco instrument and the analyses indicate the following stoichiometry C<sub>6</sub>H<sub>6</sub>MoN<sub>4</sub>O<sub>3</sub>: Calculated: C, 25.92; H, 2.16; N, 20.16%. Experimental: C, 25.71; H, 2.44; N, 19.78 %.

### Synthesis of complex 1.

A mixture of Molibdeno oxide [MoO<sub>3</sub>](3 mmol) and 2,2 biimidazole (3 mmol) in water (8 ml) was placed in a Teflon vessel which was inserted into a stainless steel reactor and sealed, then heated to a temperature of 180 °C for 48 hours. The reaction mixture was cooled and filtered, washed with cold water and finally dried. The best suitable crystals were chosen for the single crystal X-ray diffraction characterization. Blue rectangular crystal (0.18, 0.11 and 0.022 mm) was used for data collection.

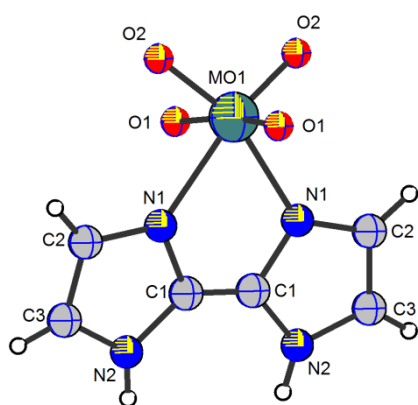
### X-ray single-crystal crystallography

The single crystal X-ray diffraction analysis was carried out on a KAPPA APEX II DUO Diffractometer with a graphite monochromator and Mo-K $\alpha$  radiation ( $\lambda=0.71069$  Å) operating at 50 kV and 30 mA. A total of 3528 frames were collected with  $\phi$  and  $\omega$  scans' every 0.30° for 10 s each (Bruker 2004). The structure was solved and refined using the SHELX Software Package (Sheldrick, 2015). In the resolution of the crystal structure the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms bound to C-atoms were placed geometrically and refined using a riding model, with C-H = 0.93 Å, Uiso(H) = 1.2 Ueq(C) for aryl H; N-H = 0.86 Å and Uiso(H) = 1.2 Ueq(N) and O-H = 0.82 Å and Uiso(H) = 1.2 Ueq(O). The final refinement values converge to R1 = 0.0896, wR2 = 0.2455 and S = 1.172 respectively. Table 1 contains the crystal data and refinement, as well as, bond distances and angles for this compound in Table 2. All the figures (ORTEP, packing and hydrogen bonding) were plotted using Diamond program (Brandenburg, 2001). All geometrical calculations were done using the Platon program (Spek, 2003). X-ray crystallographic data for this structure has been deposited at the Cambridge Crystallographic Data Center under code CCDC 1527112. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: þ44-1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Hirshfeld surface analyses were carried out and fingerprint plots were plotted using CRYSTAL EXPLORER program (Wolff *et al.*, 2007).

## RESULTS AND DISCUSSION:

Compound (1) crystallizes in space group  $Cmc_2$ , with cell parameters  $a = 18.1535(18)$ ,  $b = 3.8379(4)$ ,  $c = 14.7354(15)$  Å,  $V = 1026.64(18)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_c = 1.489$  g cm<sup>-3</sup>. The molecular structure and its atom-labeling scheme are presented in figure 1. A search previous in the Cambridge Structural Database (CSD, version 5.37, Feb. 2016) (Allen, 2002) no produced any results of similar structures.

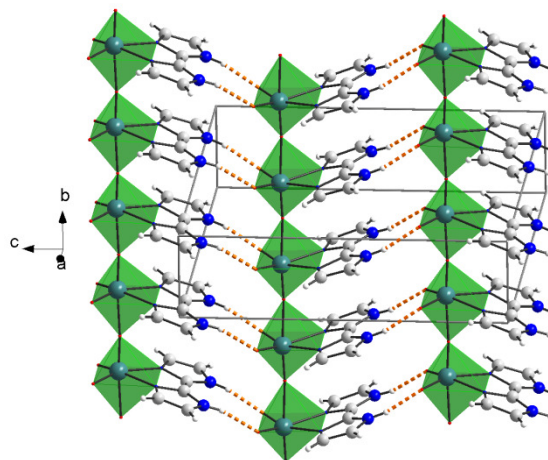


**Figure 1.** View of compound (1) with its atom-labeling scheme.

In the structure molecular of Compound (1), the Mo(1) atom center lies on a (0, 0, 0) inversion center and is coordinated by the two nitrogen atoms from bidentate ligand 2,2'-biimidazole and four oxygen atoms, two of them located in the equatorial plane (forming a polymer of coordination) and the other two in axial position, adopting a distorted octahedral geometry with a volume of 9.420 Å<sup>3</sup>. Two identical Mo-N distances are observed at 2.234 Å and the Mo-O distances are in the range between 1.66 (3) and 1.67 (2) Å. The rings from the structure of 2,2'-biimidazole show planar conformation, however, in the complex it is observed the formation of a 5-membered ring formed by the bond of the molybdenum atom with the 2,2'-biimidazole structure; this 5-membered ring exhibits a conformation envelope on Mo(1).

As shown in Table 3, compound (1) present one strong conventional hydrogen bond between the N-H group from 2,2'-biimidazole molecule and the oxygen atoms of the neighbor coordination complex, thereby this hydrogen

bond pattern N2-H2a...O2 [x,1-y,-1/2+z] bond each the polymer chains that grown along c-axis (Figure 2). These hydrogen bond patterns can be described by graph set symbol  $R^2_2(9)$ .



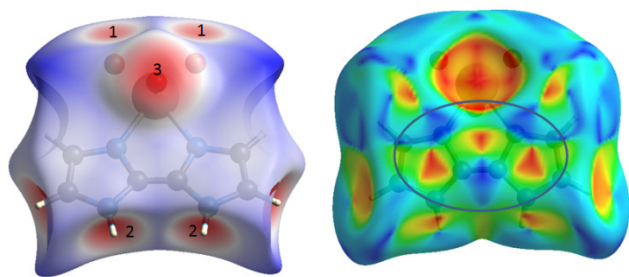
**Figure 2.** View of hydrogen bond pattern with graph  $R^2_2(9)$  in the packing arrangement of compound (1). For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

On the other hand, these polymer chains are bonded between them by  $\pi$ -stacking interactions between each one of 2,2'-biimidazole molecule which presents a distance of the ring-centroids of 3.838(8) Å. These  $\pi$ -stacking interactions are hence crucial for the crystal packing stabilization and are largely responsible for the thermodynamic stability of the crystal system because keeping the 2,2'-biimidazole molecules in the polymer chain in *cis*-position.

The crystallographic unit does not show any coordinated solvent molecules, however, the packing arrangement of title compound present a potential solvent area with a volume of 184.9 Å<sup>3</sup> corresponding to 18.0% of total unit cell volume.

All these intermolecular interactions are quantified using Hirshfeld surface analysis (Spackman *et al.*, 2002, 2008, 2009; McKinnon, 2007; Hirshfeld, 1977). The close-contact interactions, like hydrogen bond contacts, are represented in figure 3, by the large and deep red spots on the 3D Hirshfeld surfaces (Parkin, *et al.*, 2007; Rohl *et al.*, 2008). The small red spots on the surfaces of 2,2'-biimidazole molecule represent the C-H... $\pi$  interactions. The 2-D fingerprint plots are shown in figure 5. With the help of these analysis results, different interactions can be separated from each other that would commonly overlap in full fingerprint

plots.

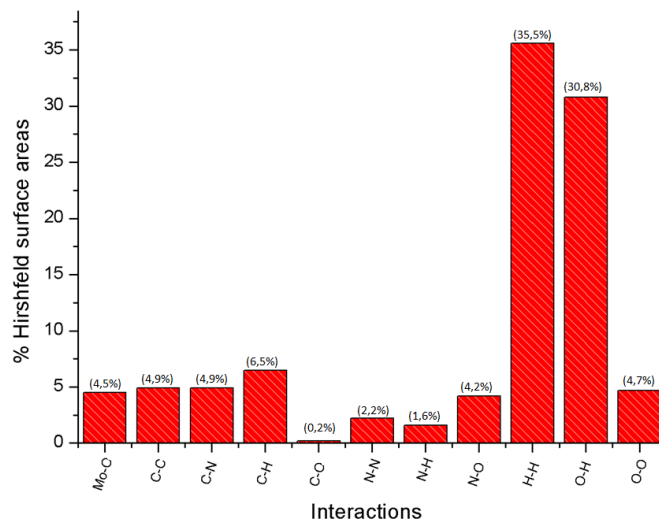


**Figure 3.** (a) Left: *dnorm* mapped on Hirshfeld surface for visualizing the intercontacts of the title compound. (b) Right: Shape index for the title compound (1).

Figure 4 indicates the contribution of intercontacts to the Hirshfeld surfaces, H-H (35,5%), O-H (30,8%), C-H (6,5%), C-N (4,9%), C-C (4,9%), O-O (4,7%), Mo-O (4,5%), N-O (4,2%), N-N(2,2%), N-H (1,6%), and C-O (0.2%). In compound (1) the H-H interactions, which are reflected in the middle of scattered points in the 2-D fingerprint plots, exhibit the most significant contribution (35,5%) to the total Hirshfeld surfaces. It is possible to observe two highly directional contributions demonstrated by the elongated and fine peaks observed in the fingerprint, corresponding to Mo-O interactions (4.5%) which are responsible for the formation of the chain polymeric; as well as the O-H interactions (30.8%), which are responsible for the formation of hydrogen bonds N-H...O with graph-set symbol  $R^2_2(9)$  linking each polymer chain. These last ones are highlighted by conventional mapping of *dnorm* on molecular Hirshfeld surfaces are shown in Figure 3a (labels 1-2). The red spots on the surface indicate the intercontacts involved in the hydrogen bonds N-H...O described above.

In order to evaluate the presence of  $\pi$ -stacking interactions, a close examination with *Shape index* generally used to identify planar stacking arrangements was performed. These interactions are identified by the adjacent red and blue triangles on the shape index surfaces, as can be seen in figure 3b when is possible to observe the pattern of red and blue triangles on the same region of the shape index surface, demonstrating that the molecules overlap and make contact with each other. Blue triangles represent convex regions due to ring carbon atoms of the molecule inside the surface, while red triangles represent concave regions due to

carbon atoms of the  $\pi$ - $\pi$  stacked molecule above it. Figure 4, that contains the percentages of contributions of intermolecular contacts, it can be seen that the C-C contacts, associated with  $\pi$ -stacking interactions which are minimal in the compound under study, representing only 4.9% of the total Hirshfeld surface area.



**Figure 4.** Percentage of various intermolecular contacts contributed to the Hirshfeld surface

## CONCLUSIONS:

In conclusion, it demonstrates that the formation of the hydrogen bond pattern N-H...O, with graph-set symbol  $R^2_2(9)$ , are the majority responsible for the supramolecular assembly of compound (1) in comparison to the  $\pi$ -stacking interactions. These quantitatively authenticated observations display the effectiveness of Hirshfeld surface to gain insights into the intermolecular interactions in the context of crystal engineering as well as, it is evidenced that the hydrothermal synthesis is a method effective for the preparation of a new compound and a new branch for the application of polyoxometalates.

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**Table 1.** Crystal Data and Details of the Structure Determination for compound (1).

Crystal Data		Data Collection	
Formula	C <sub>6</sub> H <sub>6</sub> Mo N <sub>4</sub> O <sub>3</sub>	Temperature (K)	296
Formula Weight	278.028	Radiation [Å] MoKα	0.71073
Crystal System	Orthorhombic	Θ range (°)	1.4, 26.4
Space group	Cmc2 <sub>1</sub> (No. 36)	hkl range	-22: 21 ; -4: 3 ; -18: 18
a, b, c [Å]	18.1535 (18) 3.8379 (4) 14.7354 (15)	Tot., Uniq. Data, R(int)	6222, 1054, 0.039
V [Å <sup>3</sup> ]	1026.64 (18)	Observed Data [I > 0.0 sigma(I)]	995
Z	4	Refinement	
D(calc) [g/cm <sup>3</sup> ]	1.489	Nref, Npar	1054, 60
Mu(MoKa) [/mm]	0.681	R, wR2, S	0.0834, 0.2283, 1.16
F(000)	460	Flack x	0.07(3)
Crystal Size [mm]	0,18 x 0,11 x 0,022	Hooft y	0,27(0,05)
CCDC	1527112	Min /Max. Δρ [e/ Å <sup>3</sup> ]	-0.67, 0.84

**Table 2.** Bond distances and angles (Å, °) for compound (1).

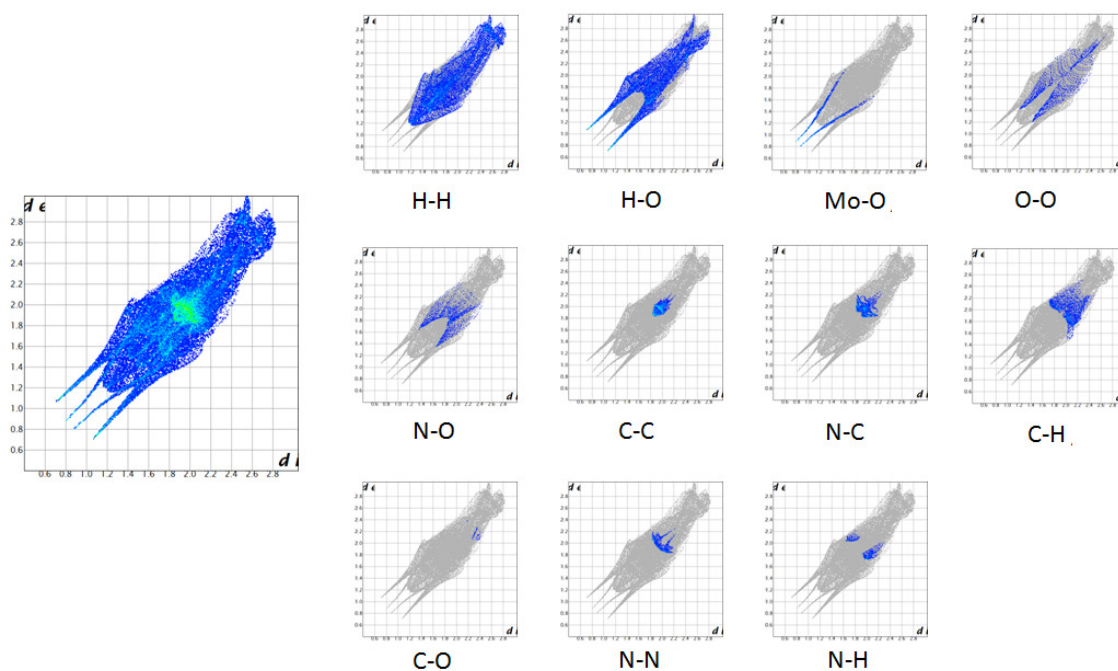
Mo1-O1	1.66(3)	N2-C1	1.420(16)
Mo1-O2	1.67(2)	N2-C3	1.421(16)
Mo1-N1	2.234(11)	C1-C1_c	1.278(13)
Mo1-O1_b	2.18(3)	C2-C3	1.42(2)
Mo1-O2_c	1.67(2)	N2-H2A	0.8600
Mo1-N1_c	2.234(11)	C2-H2	0.9300
N1-C1	1.421(16)	C3-H3	0.9300
N1-C2	1.421(17)		
O1-Mo1-O2	97.9(17)	Mo1-N1-C1	115.8(8)
O1-Mo1-N1	95(2)	Mo1-N1-C2	135.3(9)
O1-Mo1-O1_b	175(3)	C1-N1-C2	108.0(10)
O1-Mo1-O2_c	97.9(17)	C1-N2-C3	108.0(11)
O1-Mo1-N1_c	95(2)	N1-C1-N2	108.0(9)
O2-Mo1-N1	91.3(8)	N1-C1-C1_c	117.8(11)
O1_b-Mo1-O2	85.0(14)	N2-C1-C1_c	134.2(12)
O2-Mo1-O2_c	103.2(11)	N1-C2-C3	108.0(10)
O2-Mo1-N1_c	159.3(8)	C1-N2-H2A	126.00
O1_b-Mo1-N1	81.6(16)	C3-N2-H2A	126.00
O2_d-Mo1-N1	159.3(8)	N2-C3-C2	108.1(10)
N1-Mo1-N1_d	71.3(4)	N1-C2-H2	126.00
O1_b-Mo1-O2_c	85.0(14)	C3-C2-H2	126.00
O1_b-Mo1-N1_c	81.6(16)	N2-C3-H3	126.00
O2_d-Mo1-N1_c	91.3(8)	C2-C3-H3	126.00
Mo1-O1-Mo1_a	175(4)		

Symmetry transformations used to generate equivalent atoms:

a = x, -1+y, z    b = x, 1+y, z    c = 1-x, y, z

**Table 3.** Hydrogen bonds patterns for compound (1) ( $\text{\AA}$ ,  $^\circ$ )

H-Bond	D-H	H-A	D-A	D-H-A	Symmetry	Motif
N2-H2...O2	0,8600	1.9100	2.75(2)	165,00	x, 1-y, -1/2+z	R <sup>2</sup> <sub>2</sub> (9)



**Figure 5.** Detailed view of 2-D fingerprint plots with the main interactions showed inside the Hirshfeld surface for the title compound (1).