

Structural and electronic properties of MOF-74

Aline de Oliveira*, Guilherme Ferreira de Lima and Heitor Avelino De Abreu

Departamento de Química – Universidade Federal de Minas Gerais
 Av. Antônio Carlos, 6627 – Pampulha – Belo Horizonte – MG – Brazil, Zip Code 31270-901
 *alinetgui@yahoo.com.br

The Metal-Organic Frameworks (MOFs) compose a class of solids with diversified properties, justifying their potential application in different areas, such as gas storage, separation methods, catalysis, sensors, controlled drugs release devices and magnets [1]. The reticular chemistry (methodology that consists on the connection of molecular construction blocks to the formation of predetermined structures) combined with the understanding at molecular level of those solids in their application allow the design of materials with adjusted properties for more efficient technological applications. In this context, computational simulations to obtain structural and electronic information of MOFs are very important.

The MOF-74 is obtained from the combination of divalent metallic cations with the divergent organic ligand 2,5-dihydroxybenzene-1,4-dicarboxylate (DBDC). Its crystalline structure presents a honeycomb topology (Figure 1). A wide diversity of materials can be synthesized based on the topology of MOF-74 [2]. Besides the different divalent metallic cations which can be used to the

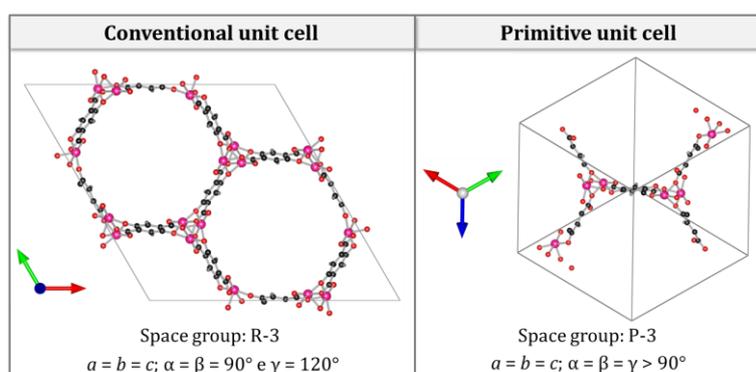


Figure 1. Unit cells of MOF-74. Legend of atoms: oxygen (red), carbon (black), metallic cation (pink), hydrogen (grey).

preparation of these solids, and even the combination of them (in the mixed metals MOFs), organic ligands with larger sizes and with other functional groups can also be employed. After the synthesis of the MOF, it is still possible to make post-synthetic modifications in its structure [3]. All of this justifies the importance to obtain structural and electronic information of the MOF-74, to better understand this solid at molecular level to assist the design of materials with optimized properties.

Computational simulations were performed based on Density Functional Theory (DFT) with plane waves methodology under periodic boundary conditions. The exchange-correlation functionals PBE and PW91 with pseudopotentials of ultrasoft type were used in the Quantum Espresso package [4]. The dispersion was included by the D2 method of Grimme. Cutoff energies of 50 and 500 Ry for plane waves and charge density and potential, respectively, were applied. The Monkhorst-Pack scheme was chosen to the Brillouin-zone integration in the Gamma point, besides Marzari-Vanderbilt 0.02 Ry smearing. The choice of these values for the calculation parameters guarantees a convergence for energy of 1 mRy. The solids Mg-MOF-74, Co-MOF-74 and Mn-MOF-74 were investigated using the primitive unit cell (Figure 1). The spin configuration utilized to simulate the solids constituted by open shell cations (Co(II) and Mn(II)) was the one resulting of an antiferromagnetic coupling among all the ions. Effective Hubbard parameters from 0.0 to 8.0 eV were evaluated to cobalt and manganese atoms, in order to obtain a properly description of the electronic correlation on *d* orbitals.

The levels of theory that best describe both structural (Table 1) and electronic parameters of these materials were PBE-D2/US, PBE-D2+U4+J1/US and PBE-D2+U5.5+J0 for Mg-MOF-74, Co-MOF-74 and Mn-MOF-74, respectively. These levels of theory were used to the detailed investigation of the solids.



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Table 1. Lattice parameters for the evaluated MOFs. The percentage errors in relation to the experimental data are in parenthesis.

MOF	Method	$a / \text{Å}$	$c / \text{Å}$	Work
Mg-MOF-74	PBE-D2/US	26.039 (0.46)	6.860 (-0.04)	This work
Mg-MOF-74	Neutron Powder Diffraction	25.921	6.863	Queen <i>et al.</i> [5]
Co-MOF-74	PBE-D2+U4+J1/US	26.166 (1.0)	6.836 (0.3)	This work
Co-MOF-74	X-Ray Powder Diffraction	25.906	6.817	Dietzel <i>et al.</i> [6]
Mn-MOF-74	PBE-D2+U5.5+J0/US	26.555 (1,2)	6.975 (-0.9)	This work
Mn-MOF-74	X-Ray Powder Diffraction	26.230	7.035	Zhou <i>et al.</i> [7]

The direct band gaps on the Γ point were 2.10, 1.97 and 2.00 eV for Mg-MOF-74, Co-MOF-74 and Mn-MOF-74, respectively. The experimental value for Co-MOF-74, which was obtained through diffuse reflectance UV-VIS spectroscopy, is 2,02 eV [8], indicating the good description of the material. The analyses of the electronic band structure show that the band gap with the lower energy variation is indirect from Γ to Z point, and occurs between states localized on carbon atoms. There is a significant contribution in the conduction band of states from metallic cations, indicating a possible Lewis acidic activity of these atoms, and a significant contribution in the valence band of states from oxygen atoms, indicating their possible Lewis basic activity.

The methods Electron Localization Function (ELF) and the Quantum Theory of Atoms in Molecules (QTAIM) were applied to the analyses of the electronic density topology obtained to the three solids. These methodologies indicated that the bonds between the metallic cations and the oxygen atoms are predominantly ionic while the other ones are predominantly covalent. Furthermore, through QTAIM analyses were possible to identify non-conventional hydrogen bonds in Mg-MOF-74 and Co-MOF-74, which were not observed to Mn-MOF-74 (Figure 2). This interaction occurs between the oxygen atoms of carboxylate group and the hydrogen atoms bonded to the aromatic ring of the organic ligand. The absence of this interaction in Mn-MOF-74 makes its structure more flexible than the others. The Bader charges to the metallic cations were +1.74, +1.56 and +1.41 a.u. to Mg(II), Mn(II) and Co(Mn), indicating that the increasing order of Lewis acidic strength is Co(II) < Mn(II) < Mg(II). In this way the catalytic activity of these materials, for example, is dependent of the combination of the flexibility of the structure to accommodate the substrates involved in the reaction process (highest to Mn-MOF-74) and of the Lewis acidic strength (highest to Mg(II)).

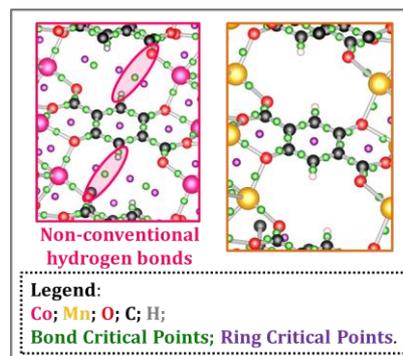


Figure 2. Critical points found to Co-MOF-74 and Mn-MOF-74.

In conclusion, the levels of theory suitable for computational simulations of Mg-MOF-74, Co-MOF-74 and Mn-MOF-74 were optimized, which provide data in agreement with the experimental ones. Besides that, it was exposed structural and electronic properties of the evaluated MOFs that allow to better understand these solids at molecular level, which can assist the design of new materials and even to recognize processes already described in literature.

Key-words: Metal-Organic Frameworks, MOF-74, DFT, ELF, QTAIM.

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