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Structure of functionalized porous metal-organic frameworks by molecular orbital methods

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Abstract

The molecular structures of the $Zn_4O(RCOO)_6$, $R = CH_3$ and Ph, complexes, the model compounds $(CH_3COO)_5(Zn_4O)(OOC–C_6H_3X–COO)_6(Zn_4O)(CH_3COO)_5$, $X = H$, Br and NH_2, which represent a capped edge of the unit cell and the methyl capped unit cell of IRMOF-1, -2 and -3 were calculated with AM1 and PM3, with HF/6-31G and HF/6-31G**, with B3LYP/6-31G and B3LYP/6-31G** and with the two-layers ONIOM(HF/6-31G:PM3) methods. Comparisons with crystallographic results show that these structures were fairly well reproduced by the semiempirical methods and very well reproduced by the HF and B3LYP methods. Electronic correlation effects and polarization functions in the basis sets play minor roles in the results for the calculated structures, probably due to their rigidity. Vibrational frequencies and intensities for the $Zn_4O(OOC)_6$ core of the $Zn_4O(CH_3COO)_6$ complex were (semi-) quantitatively described by the AM1, PM3 and HF/6-31G methods. The two-layers ONIOM(HF/6-31G:PM3) method is appropriate for structural calculations and improvements at the ab initio or DFT level yields a methodology that can properly describe the interaction between a sorbate and the edge of the IRMOF cavities.

Keywords: μ^4-*oxo*; Semiempirical; Ab initio; Vibrational spectra

1. Introduction

Porous metal-organic frameworks (MOFs) are becoming an important class of materials for gas adsorption and storage and catalysis [1–3]. These MOFs, through finely tuned experimental conditions [4], can yield isorecticular MOFs (IRMOFs), whose properties, such as, cavity radius, density and free volume can almost be continuously varied from 51 to 91%, for the latter, leading to the lowest known density for a crystalline material [4]. In addition, the organic part can be easily functionalized before the synthesis to yield different chemical environments within the IRMOF's cavities. As a result, these materials can also be used as new reaction media with controlled spatial, chiral and chemical properties [5]. These IRMOFs can be viewed as composed of a secondary building unit (SBU) containing tetrahedral μ^4-*oxo* moieties (OZn_4) linked by rigid dicarboxylate bridges. Being crystalline, the X-ray crystallography has been the most important characterizing experimental tool. However, for disordered systems as the ones obtained after adsorption of, for instance, organic molecules, this technique becomes impractical, so alternative approaches have to be sought. Computational chemistry tools based upon classical force fields and quantum chemical methods (semiempiricals, DFT and ab initio) have been successfully used to calculate equilibrium molecular structures of a wide range of systems. However, as far as we know, these methods have not yet been employed for IRMOFs. Also, these materials present unusual μ^4-*oxo* groups (OM_4, $M = Zn$, Cu, Fe) that have not been included in the parametrization data set of either molecular mechanics or semiempirical methods. Thus, it would important to ascertain the reliability of these methods as well as DFT and ab initio ones in providing structural information about these IRMOFs. As a result, the main concern of this contribution is the study of the structures of the SBUs modeled by $Zn_4O(RCOO)_6$, $R = CH_3$ and Ph, sections of the IRMOFs modeled by an edge of the capped unit cell

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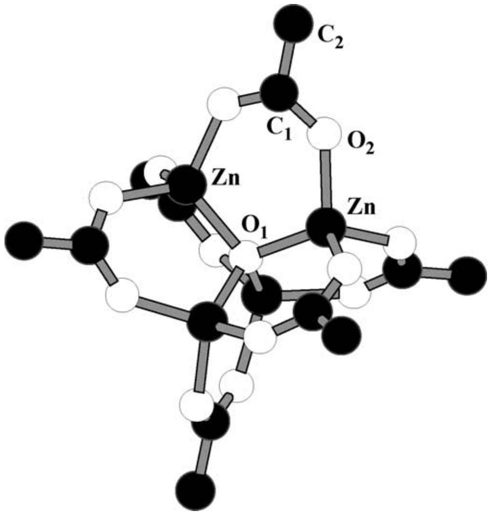

Fig. 1. Molecular structure of $Zn_4O(CH_3COO)_6$ and the atomic labels. The hydrogen atoms were omitted for clarity.

$(CH_3COO)_5(Zn_4O)(OOC–C_6H_3X–COO)_6(Zn_4O)(CH_3COO)_5$, X = H, Br and NH_2 and the methyl capped unit cell of functionalized IRMOF-1, -2 and -3 [4], calculated with the semiempirical methods AM1 and PM3, hybrid DFT (B3LYP) and ab initio Hartree–Fock (HF) methods. Also, the two-layers ONIOM approach has been tested using the combined HF:PM3 methods.

2. Computational procedure

The AM1 [6] and PM3 [7] semiempirical calculations have been performed with the either MOPAC 2000 [8] or PSQ2.5 programs [9] and HF [10], B3LYP [11] and ONIOM [12] calculations have been performed with either GAUSSIAN 98 [13] or PSQ2.5 programs [9]. The default parameters and criteria of the programs without any symmetry constraints were used. The basis sets used were: 6-31G, 6-31G* and 6-31G** [10].

3. Results and discussions

We have started this study by the SBU modeled by $Zn_4O(CH_3COO)_6$, (μ^4-*oxo*)hexakis(μ^2-acetato)tetrazinc or hexakis(μ^2-acetato-O,O′)-(μ^4-*oxo*)-tetrazinc, as depicted in Fig. 1.

This complex has already been studied by a LDS-DFT method [14] and by several experimental techniques, namely, photoelectron spectroscopy [14], vibrational spectroscopy [15], mass spectrometry [16] and X-ray crystallography [17]. The $Zn_4O(CCOO)_6$ core has tetrahedral symmetry, but the hydrogen atoms of the methyl groups should lower the symmetry. However, this symmetry lowering is not observed in the vibrational spectra of $Zn_4O(CH_3COO)_6$ and $Zn_4^{18}O(CH_3COO)_6$ in solution, since the $\nu_{as}(Zn_4O)$ vibration, which is the most sensitive to the symmetry-lowering is still t_2 [15]. The X-ray crystallography also yields a highly symmetric structure with a tetrahedral $Zn_4O(CCOO)_6$ core. It should be noted that both GAUSSIAN 98 and PQS 2.5 programs were unable to cope with the symmetry of this complex, because it tried to recognize the T_d symmetry and failed, despite the symmetry-lowering due to the hydrogen atoms of the methyl group. So, we have performed all calculations without symmetry. The results for the structure of this complex are presented in Table 1 and compared to the experimental data. It should also be noted that there are no significant differences between the results obtained with the PQS 2.5 program compared to the results obtained with either GAUSSIAN 98 or MOPAC 2000 programs.

All theoretical methods yielded an overall structure in very good agreement with the experimental data, namely, the tetrahedral structure of the $Zn_4O(CCOO)_6$ core as well as planar rings formed with the O_1–Zn–O_2–C_1–O_2'–Zn′ atoms. The PM3 method yielded slightly non-planar rings when the gradient norm was larger than $200\ kJ\ mol^{-1}\ pm^{-1}$, but with tighter convergence criteria the planar rings were obtained. From Table 1, it can be observed that the PM3 method yielded better results than AM1, mainly for the O_1–Zn and Zn–O_2 bond distances and both methods yielded the observed result that the bond distance O_1–Zn is slightly smaller than the Zn–O_2 one. This qualitative result is not reproduced by the ab initio (HF/6-31G and HF/6-31G**) nor the hybrid DFT (B3LYP/6-31G and B3LYP/6-31G**) methods, even though these methods yielded better average quantitative results for bond distances and bond angles.

Since we are interested in the structure of IRMOF-1, which has a dicarboxylate–benzene bridge, we have also determined the molecular structure of the $Zn_4O(PhCOO)_6$

Table 1
Selected bond distances (pm) and bond angles (deg) for $Zn_4O(CH_3COO)_6$

Method	Zn–O_1	Zn–O_2	O_2–C_1	O_1–Zn–O_2	Zn–O_2–C_1
AM1	205.7	211.5	128.3	110.0	134.0
PM3	195.3	204.3	127.5	112.1	130.5
HF/6-31G	202.4	196.7	126.8	109.2	134.9
HF/6-31G**	198.0	196.6	124.5	110.2	132.8
B3LYP/6-31G**	195.6	194.8–195.1	126.8	111.4	130.8
X-ray [17]	193.6	194.6	125.2	111.1	132.4

See Fig. 1 for atomic numbering.