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Combined Experimental and Molecular Simulation Study on The Hydrogen Storage Properties of Cu(II) and Ni(II) Metal-Organic Compounds

Cu(II) Ve Ni(II) Metal-Organik Bileşiklerin Hidrojen Depolama Özellikleri Deneysel ve Moleküler Simulasyon Çalışmaları

Research Article

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ABSTRACT

For the purpose of investigating alternative adsorbents, new metal-organic compounds were synthesized, characterized and examined for their hydrogen storage capabilities. First, the compounds were synthesized and then the molecular structures of the compounds were determined experimentally by using thermal, FT-IR, solid-UV and powder-XRD analysis. Then, the crystal structures were solved using theoretical calculations. At last, the simulated maximum hydrogen storage capacities of the compounds were 3.62 and 0.64 wt. % at 77 K and 100 bars, while the numbers less than 0.1 wt. % for 1 bar and same temperature. In brief, crystal structures of inorganic compounds are determined with combined experimental and computational techniques, then, hydrogen storage abilities are investigated

Key Words
Molecular Structure, Hydrogen Storage, Molecular Simulation Calculation .

ÖZET

Alternatif depolayıcılar geliştirme amacıyla yeni metal-organik bileşikler sentezlenmiş, karakterize edilmiş ve hidrojen depolama özellikleri belirlenmiştir. Öncelikle, bileşikler sentezlenmiş ve sonra, termal, FT-IR, katı-UV ve toz-XRD deneysel analiz teknikleri kullanılarak moleküler yapıları karakterize edilmiştir. Daha sonra, kristal yapıları teorik hesaplamalarla çözümlenmiştir. Sonuç olarak, bileşiklerin simule edilmiş hidrojen depolama performansları 77 K ve 1 bar basınçta kütlece % 1'in altındayken aynı sıcaklık ve 100 bar basınçta kütlece % 3.62 ve 0.64'tür. Sonuç olarak, inorganik bileşiklerin kristal yapıları aynı zamanda teorik ve deneysel olarak belirlenmiş, sonrasında hidrojen depolama yetenekleri araştırılmıştır.

Anahtar Kelimeler
Moleküler yapı, Hidrojen Depolama, Moleküler Simulasyon Hesaplamaları.

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INTRODUCTION

The investigations increased incrementally to discover convenient sorbate for hydrogen storage during the last decade, because the great majority of the scientists who are working to solve energy problems, believe that the best candidate to solve the storage problem of hydrogen are sorbates in their solid state. In addition to other potential options, metal-organic compounds such as Metal Organic Framework (MOF)s are very popular, due to their high gas sorption capacities. MOFs also have great potentials for catalysis [1], photo luminescence [2], photo catalysis [3], gas separation [4] and support material [5] in addition to other specific applications. MOFs are mainly formed with 1D, 2D or 3D crystalline structures. In the frameworks, second and third dimensions could be formed by covalent interactions, resulting in strong crystals and good thermal stability, as seen in crystalline zeolitimidazolate frameworks [6]. Additionally, the second and third dimensions could be formed with hydrogen bonds, causing weak crystal structures in comparison with covalent three-dimensional structures [7]. It is reasonable to try to synthesize three dimensional crystals connected with covalent interactions to each other, but sometimes this method does not work. On the other hand, if the compounds do not form as a single crystal (which is more convenient for the collection of single crystal XRD data), characterization of the compound gets significantly more difficult. To characterize the structure correctly scientists used a combination of techniques, like experiments and simulations, which were evaluated together [8]. Kitaura et al. published a MOF structured three-dimensional metal-organic compound that was solved using Rietveld refinement via powder XRD data. The authors also reported the crystal structure parameters of the metal-organic compound. The R_{wp} value which describes the discrepancy between simulated and experimental XRD data was 3.04% in their work [9].

Storing hydrogen in metal-organic compounds by using simulation calculations is another option to compare hydrogen storage performances of synthesized compounds. In addition to metal-organic compounds, researchers are also performing the hydrogen storage calculations for other types of potential materials. To investigate hydrogen storage performances of metal-organic buckyballs, Zhao et al. constructed and simulated structures, then calculated the hydrogen storage performances [10]. In another work, Weck et al. determined the metal-organic structure that stores hydrogen chemically (known as metal-hydride system), and then calculated the storage performances. The authors reported maximum retrievable 9.3 wt% for ScC_4H_4 and 9.1 wt% for TiC_4H_4 hydrogen in the metal-hydride systems [11]. Furthermore, Deng et al. reported the gravimetric and volumetric hydrogen uptake capacities at ambient temperatures of lithium-doped MOF impregnated with lithium-coated fullerene. Volumetric and gravimetric uptakes were 42 g/L and 6.3 wt% at 100 bars and 243K [12].

EXPERIMENTAL

Materials

$NiNO_3.6H_2O$, $CuNO_3.6H_2O$, 1,10- phenantroline (Phen), trimesic acid (TMA), teraphtalic acid (TFA), dimethyl formamide (DMF) and $NaHCO_3$ were purchased from Sigma-Aldrich (St. Louis, MO) and were not purified for the synthesis.

Synthesis of Compounds Compounds were synthesized according to room temperature synthesis procedure. In the procedure, all reactions were actualized at the room temperature without heating. First, the 3 mmol acids were mixed with $NaHCO_3$ (6 mmol for TFA and 9 mmol for TMA) to form sodium salt of carboxylic acids in 10 ml of water. A Phen (1 mmol) solution in the 5 ml of DMF was added to the salt solution which was formed according to following reaction ($TMA+3NaHCO_3 \rightarrow 3H_2O+3CO_2+Salt$). Lastly, metal nitrate (3 mmol) solution in 5 ml of water was added drop by drop to the mother solution with continuous stirring. After 6 hours, the stir compounds were filtered off and washed with water and ethanol several times. Finally, the compounds dried in an oven at 85°C overnight. The final products with Cu(II) and Ni(II) metals are coded as I and II respectively.

Characterization; FT-IR analysis using the KBr disc method in the range of 400-4000 cm^{-1} (Perkin Elmer Spectrum One; Waltham, MA), solid UV-visanalysis in the range of 200-900 nm with 1 nm resolution (Shimadzu UV-3600; Nakagyoku, Kyoto, Japan), TGA/DTA/DrTGA simultaneous analysis in the nitrogen atmosphere at temperatures up to 1273 K with 5°C/min heating rate (Shimadzu DTG 60H, Nakagyoku, Kyoto, Japan), elemental analysis to determine gravimetric existence of N, C and H atoms (Thermo Scientific Flash2000; Waltham, MA) and powder-XRD analysis to collect diffraction peaks at 296 K, were realized within fixed monochromater and continuous scanning to determine molecular structure and some characteristics of compounds.

Molecular Simulation

Molecular simulation calculations were realized by using different modules of Materials Studio7.0 (MS) to calculate hydrogen storage performances. After that, geometries of estimated molecular structures which were drawn by using GaussView 4.1 software, were optimized by using MS-Forcite module with COMPASSII force field. Current charges and the ABNR algorithm [13] were used within ultrafine calculation quality (2.0 E-5 kcal/mol energy, 0.001 kcal/mol/Å Force, 1.0E-5 Å displacement with 500 iterations for convergence tolerance). COMPASSII force field was used because it is capable of describing intramolecular and intermolecular interactions in chemical systems. In the other calculation, crystal parameters (a, b, c, alpha, beta, gamma, cell volume, and extinction class and crystal system) of potential crystal structures were indexed using MS-Reflex Powder-indexing tool with the X-Cell program [14] and experimental powder-XRD spectrums. In the indexing calculations, cubic, hexagonal, tetragonal, orthorhombic, monoclinic and triclinic crystal systems were researched for the convenient crystal parameters. Here, convenience means the similarity of the experimental and simulated diffraction peaks. The differences between experimental and simulated XRD peaks are being described with the value of R_{wp}, which also describes the suitability of the simulated space group. In the calculation output, the stability and the impurity levels are being calculated in addition to discovered peaks in comparison to selected ones. Geometry optimized [15] molecules in MS-Forcite were used to build crystals by using the MS visualizer build tool with the calculated suitable crystal parameter by using MS-Reflex. Then, the crystal structures were refined by using MS-Reflex Powder Refinement tool. Rietveld type refinement was used in the tool with ultra-fine convergence quality in the range of 5 to 70 degrees of 2-Tetha. In the refinement motion groups, torsions and angels of the molecules or the parts/groups of molecules are set for refinement parameters or, in other words, as the components of degrees of freedom. In another option, in the same calculation, all atoms and crystal parameters were set for refinement. Peak profile function was Pseudo-Voigt [16] in all refinement calculations. Refined crystal structures were used for hydrogen storage calculations using MS-Sorption module. The metropolis method [17] and Universal force field were used with ultra-fine quality in the sorption calculations. Adsorption isotherms were calculated in range of 0.1 to 100 bars and 0.1 to 1 bar of pressure. The temperatures were at 77, 273 and 298 K.

RESULTS AND DISCUSSION

Characterization Studies

Experimental results were interpreted together, and the final molecular structures were determined. Thermal stabilities and the decomposition steps were determined according to the thermal analysis of coded compounds I and II (Figure 1a). After removing aqua molecules, I and II decomposed in three and four steps respectively. Mono-dentate binding of carboxylic acids to the metals resulted in the difference between asymmetric and symmetric carbonyl stretches bigger than 200 cm^{-1}, while the number was smaller for bi-dentate complexes [18]. The difference for I was 191 cm^{-1} and it showed a single bond between carboxylic acid and metal. The number for II was 201 cm^{-1}, which represents a bi-dentate complex. FT-IR spectra are given in Figure 1.b. d→d electronic transitions at 714 and 740 nm, as overlapped broad solid state UV peaks, represent a structural change from octahedral to square pyramid that is commonly seen for Cu(II) complexes. Similar structures were reported previously by Kose et. al. and Kose and Necefoglu [19,20].

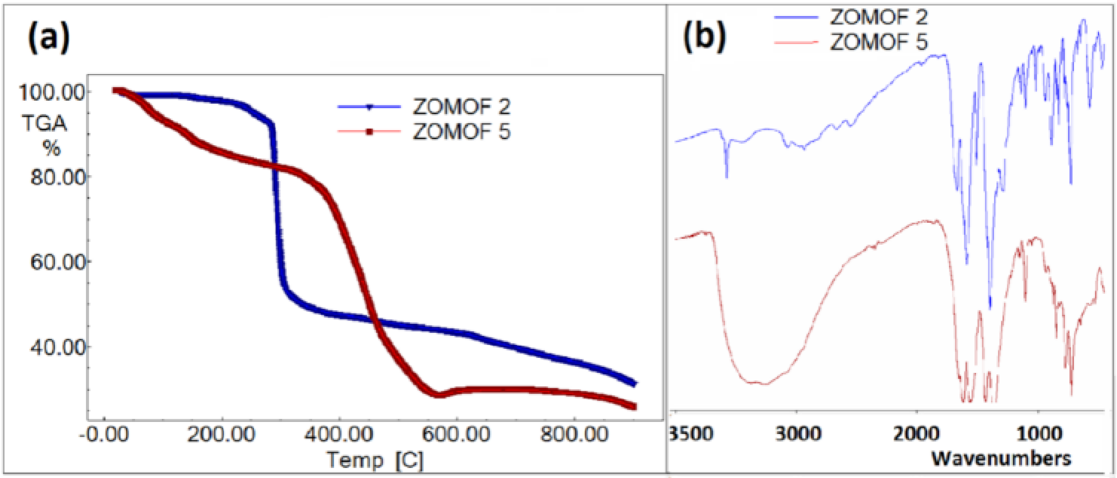

Figure 1. (a) Thermal decomposition (TGA) curves and **(b)** FT-IR spectrums of the compounds.

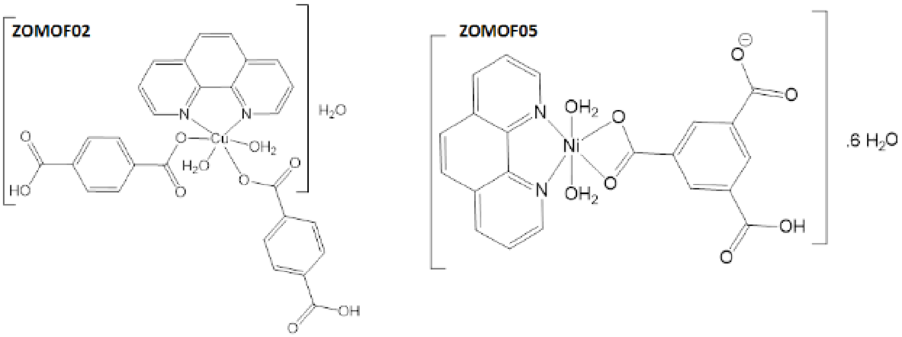

Figure 2. Molecular structures of compounds.

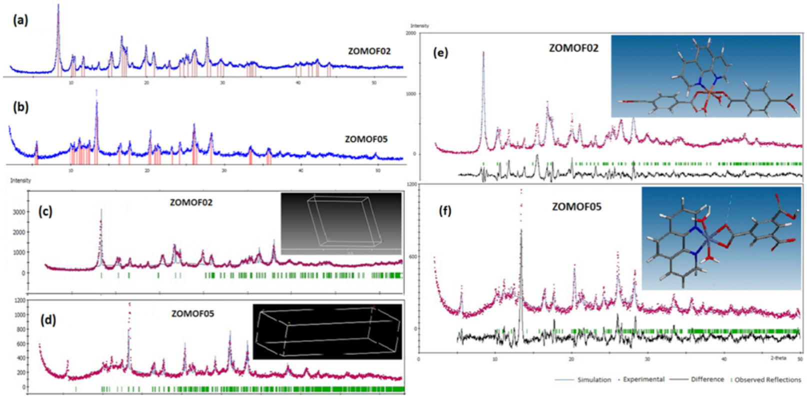

Figure 3. Selected characteristic PXRD peaks for (a); I, (b); II, refinements results according to lowest Rwp of (c); I, (d); II, Rietveld refined structures with (hydrogen bonded crystals on the corner of figures) with simulated and experimental PXRD spectrums, difference and observed reflections of (e) I and (f) II.

According to elemental analysis (EA) and other characterization studies, the final molecular structures were determined, as seen in Figure 2. EA experimental results have similar results to the calculated percentages of C, N and H atoms by using ChemDraw software. The numbers were C% 53.48 (52.95), N% 4.46 (4.62) and H %3.82 (3.12) for I, where the calculations are in brackets,

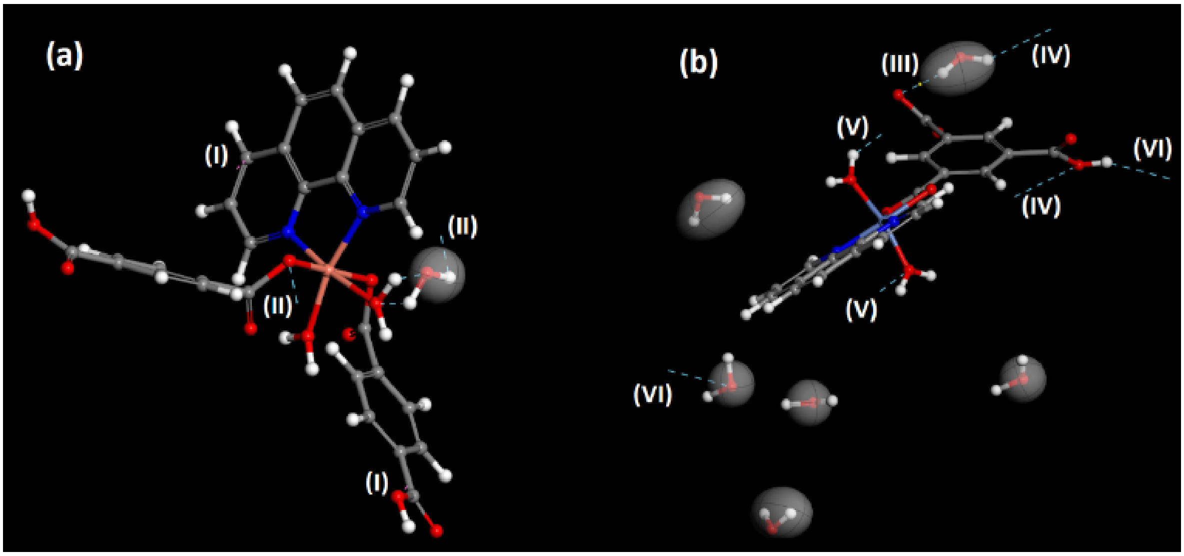

Figure 4. Crystal structures of compounds and bonding schme of (**a**); I and (**b**); ZOMOF03.

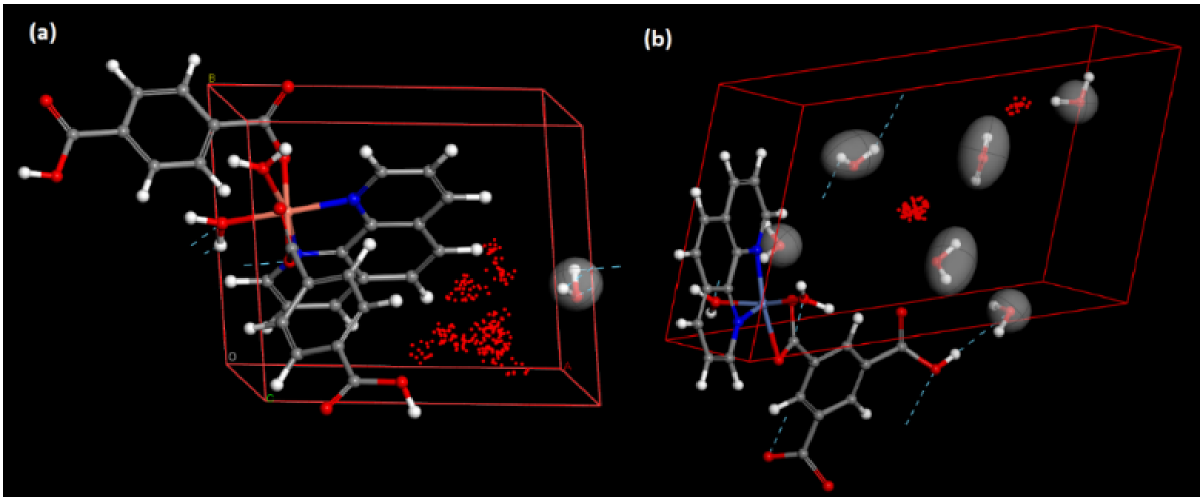

Figure 5. Possible places in red dots for hydrogen storage inside (**a**); I and (**b**); II.

while the calculated molecular weight of the compound was 628.25 g/mol. They were C%: 42.63 (41.96), N%: 4.74 (4.63) and H% 4.74 (3.72) and 591.15 g/mol for II.

Molecular Simulation; Characteristic powder X-Ray diffraction (PXRD) peaks were selected manually and indexed using MS Reflex module. The software filtered out the best results. Then, three convenient crystal systems and parameter results were selected for both compounds (Figure 3a, b). The crystal systems were triclinic with P1 space group. It was found that the resulted unit cell parameters represent 90-95% of selected experimental PXRD peaks. Pawley refinement, which only refines crystal structure parameters by using experimental PXRD data, was used and refined results were kept to use later with molecules. The best structures were selected according to R_{wp} calculations. R_{wp} values of compounds were 24.35, 23.27, 23.74% and 17.79, 20.00, 21.32% for I and II respectively. Convenient crystal cells were selected according to the lowest R_{wp} which are shown in Figure 3c and d. Figure 3. Selected characteristic PXRD peaks for (a); I, (b); II, refinements results according to lowest R_{wp} of (c); I, (d); II, Rietveld refined structures with (hydrogen bonded crystals on the corner of

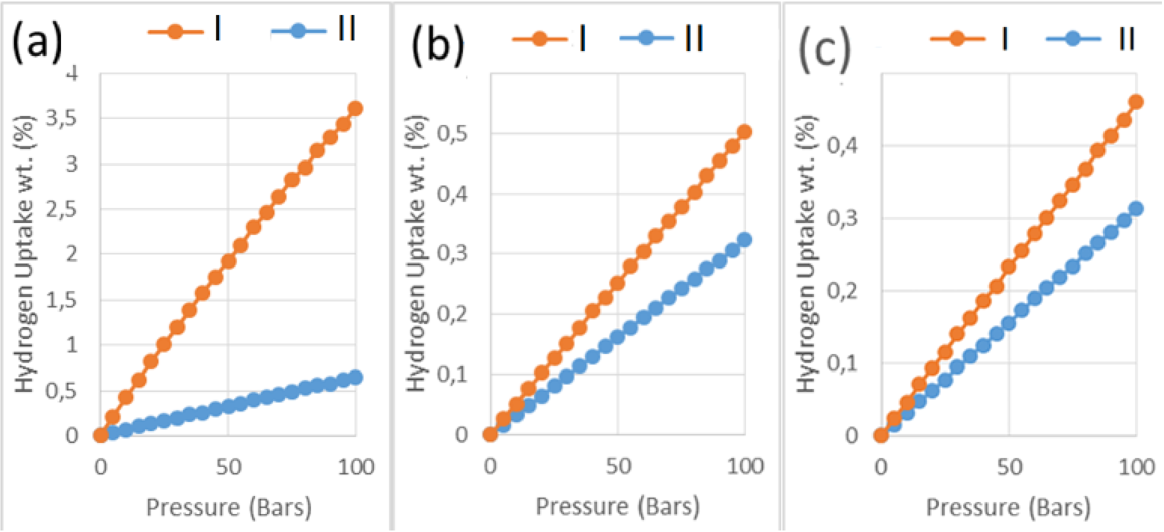

Figure 6. Hydrogen storage capacities of compounds in the pressures up to 100 bars at; (a) 77 K, (b) 273 K and (c) 298 K.

figures) with simulated and experimental PXRD spectrums, difference and observed reflections of (e) I and (f) II The difference between experimental results and calculated results for the compounds are shown in Figure 3e and 3f. Blanton et al. reported that they refined the simulated crystal structure of less complicated silver carboxylate dimer with 8.66% R_{wp} [21]. In another study, Tasner et al. reported an oxomolybdenum (V) dinuclear complex refinement with 5.7% R_{wp} by using experimental single crystal XRD which makes it easy to solve the crystal structure [22]. After rietveld refinement to final R_{wp} numbers, a bonding scheme was simulated. Some hydrogen bonds and one close covalent contact were found for I. The close covalent contact between two neighbour molecules, shown in Figure 4a. with the number of (I), enables second dimension for the crystal structure.

Bond number (II) shows the hydrogen bonds over free aqua molecules that enable a third dimension for I in Figure 4a. There was only one aqua molecule inside I, and it works as a bridge between neighbour molecules to construct 3D crystals. Accordingly, the bonds with the numbers of (III) and (IV) form a bridge over free aqua molecules between two neighbour II molecules with hydrogen bonding in Figure 4b. Bond number (V) was the hydrogen bond interaction between main molecules, in addition to (III) and (IV), that constracts second and third dimensions as in (I) and (II) for I. The bond number (VI) in Figure 4.b. represents the single hydrogen bond between free aqua and the II body. Hydrogen Storage; Hydrogen storage properties were investigated after the determination of the final crystal structures of the compounds. The possible places for storing hydrogen were simulated and shown in Figure 5a and 5b for I and II respectively. Red dots represents the spaces that the hydrogen could be placed. Hydrogen storage values for the molecules were 0.403, 0.055 and 0.051 at the temperatures of 77, 273 and 298 K respectively at 100 bars for I.

The numbers shows that the I does not have large spaces for hydrogen storage. If the units are converted from loading per cell to weight percentage, the number changes to 3.62, 0.51 and 0.46 wt. %. These figures are very promising and comparable with the most wellknown MOF structured adsorbents. Gravimetric uptakes for II were 0.63, 0.32 and 0.31 wt. % for the same order and conditions (Figure 6). Gravimetric hydrogen uptake in the range of 0-1 bar were also calculated for both molecules to find out the maximal hydrogen storage performances under the most promising conditions. The values were 0.042, 0.0052 and 0.0046 wt. % for I and 0.0065, 0.0032 and 0.0031 wt. % for ZOMO05 at 1 bar pressure at the temperatures of 77 K, 273 K and 298 K respectively.

Pan et al. measured approximately 0.95 wt. % hydrogen storage capacity at room temperature (298 K) and 50 atm (≈50 bars) pressure for micro porous MOF structured compound. The values were 0.23 and 0.15 wt. % for I and II respectively while SWCNT storing 0.18 wt. % hydrogen at the same conditions [23]. Accordingly, in another work, Dinca et al. [24] reported 1,4-benzeneditetrazolate(BDT) incorporated microporous MOF structured $Mn_2(BDT)Cl_2$ with 0.7 wt.% hydrogen storage capability at 77K and 900 torr(≈1 bars) pressure . The values were 0.042 and 0.0065 wt. % in the present work for I and II respectively Li et al. [25] reported 3.42 and 2.05 wt. % hydrogen storage capacity for Ni and Co based mix ligand metal-organic compounds at 77 K and 70 bars pressures. I and II uptake 2.64 and 0.45 wt. % hydrogen at the same conditions while the values were 3.62 and 0.64 wt. % at 77 K and 100 bars.

CONCLUSIONS

The molecular and crystal structures that were solved in this study combined both experimental and theoretical techniques. In conclusion, two novel mix ligand metal-organic Cu and Ni compounds were synthesized, characterized experimentally, and determined theoretically (in terms of crystal structure). Different numbers of free aqua molecules were placed inside the compounds at simulations. The decomposition steps at experimental TGA prove the situation. Crystal structures of the compounds were solved in the degree of 19 and 12.5 percent difference with experimental diffraction data. Finally, hydrogen storage capacities of the compounds were investigated. Additionally, it was found that the columbic interactions enable extra hydrogen uptake ability in contrary CNTs which don't have polar sites, an explanation for why the compounds in the present work take up so much hydrogen. The maximal hydrogen storage abilities of the compounds were 3.62 and 0.64 wt. % for I and II respectively. These numbers are commensurate with the literature.

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