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Synthesis, crystal structure and desulfurization properties of zig-zag 1D coordination polymer of copper(II) containing 4-methoxybenzoic acid ligand

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ABSTRACT

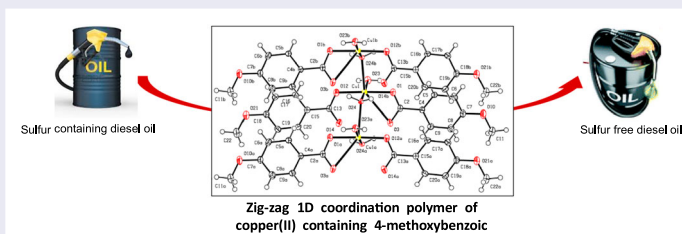
Combustion of fuels containing organosulfur compounds has resulted in the emission of sulfur oxides (SO_x) into the atmosphere, therefore, causing serious environmental and health hazards. Herein, slightly distorted octahedral zig-zag 1D coordination polymer of copper(II) [Cu(4-mba)₂(H₂O)₃] was synthesized by reacting copper sulfate pentahydrate with a carboxylate-containing ligand (H-4mba = 4-methoxybenzoic acid) and employed for sulfur compound uptake. The ligand coordinates to the copper(II) atom *via* two pairs of deprotonated ligating atoms (carboxylate oxygens) and two water molecules. Structural characterization also reveals that interplay of O–H...O, N–H...O, C–H...O and C–H...π interactions between lattice and coordinated water and ligands significantly contribute to the crystal packing leading to the formation and strengthening of three-dimensional supramolecular assembly. The complex, [Cu(4-mba)₂(H₂O)₃], show potential for desulfurization of fuel with an observed adsorption capacity of 9.6 mg/g at 32°C for 6 h. DFT calculations further revealed a transfer of electron sulfur-containing compounds and the complex, [Cu(4-mba)₂(H₂O)₃], thus leading to a stronger pi–pi interaction.

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1. Introduction

The deleterious effects of refractory polyaromatic hydrocarbons found in fuels such as organosulfur compounds (namely, dibenzothiophene (DBT) and its alkylated derivatives) are such that they emit SO_x to the environment when combusted, thereby reducing air quality, deactivating refining catalysts, poisoning catalytic converters of cars. Desulfurization of fuels is one of the main processes employed in a petroleum refinery to reduce sulfur content in order to meet environmental protection sulfur standards of 10 mg/L [1,2].

Hydrodesulfurization (HDS) process currently employed to remove sulfur suffers limitations such as the inability to efficiently eliminate refractory organosulfur compounds specifically DBTs and the alkyl substituted dibenzothiophenes [3]. DBT accounts for up to 70% of total organic sulfur in hydrotreated diesel [4]. Adsorptive desulfurization (ADS) is about the most recent method that is being applied to remove refractory organosulfur compounds from fuel oil. So far, various functionalized porous adsorbents such as activated carbon, zeolites, silica and MOFs have been employed for ADS [5–7].

In general, the development of a scalable adsorbent composed of inexpensive materials but possessing a large adsorption capacity as well as regeneration properties would be ideal for continuous operation in a desulfurization unit. MOFs is one of the most promising groups of these adsorbents that have been applied for ADS [8–12]. However, these MOFs are known to have low hydrolytic stability, thus, limiting their application in solvents having water molecules. Studies have shown that adsorbents such as activated carbon, zeolites, silica lack selectivity for targeted compounds despite their high surface area and porous molecular traps [13]. The shapes and sizes of pores within these adsorbents influences their selectivity to targeted compounds [14]. Recently, the introduction of metal ions unto porous adsorbents improved their selectivity for sulfur compounds during desulfurization [15–20]. In the design of potential adsorbent for the target compounds, the nature of metal ions and aromatic multicarboxylic acid are important factors to be considered. In this regard, the use of 4-methoxybenzoic acid ligand does not only offer carboxylate group for chelating with metal ion but also not provide steric hindrance (presence of rigid or flexible spacers), which offer wider surface for interaction. The presence of oxygen atoms and rich aromatic backbone of 4-methoxybenzoic acid offer various intermolecular interactions such as hydrogen bonding and π - π stacking [18–20]. The use of Cu^{2+} for organosulfur compound uptake has also attracted much attention due to the soft Lewis open metal sites it possesses [18–20].

In this paper, the removal of sulfur-containing aromatics, such as DBT, from fuel is investigated by employing a cost-effective copper(II) coordination polymer, $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$. A combined experimental and computational study was adopted to gain a fundamental understanding of the possible interactions responsible for adsorption of sulfur-containing compounds in fuels.

2. Results and discussion

The chemical reaction of 4-methoxybenzoic acid with the sulfate salt of Cu(II) at room temperature, led to the formation of a novel compound, $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$. The compound was subjected to different characterization techniques (such as FT-IR, SC-XRD and TGA) in order to determine their structural composition. The compounds consist of

metal ion which coordinates through the oxygen atom of the carboxylate of two molecules of 4-methoxybenzoic acid (one monodentate, the other bidentate) and with three water molecules.

2.1. *Bet surface area of activated [Cu(4-mba)₂(H₂O)₃]*

The BET surface area of activated [Cu(4-mba)₂(H₂O)₃] was observed to be 31.7 m²/g with a pore size (BJH) of 61.2 Å. Nitrogen adsorption-desorption isotherm of [Cu(4-mba)₂(H₂O)₃] is available in the supplementary data section (Figure S1).

2.2. *FT-IR of [Cu(4-mba)₂(H₂O)₃]*

The FT-IR spectra of the 4-methoxybenzoic acid and its crystal in the far IR region 4000–400 cm^{−1} were compared with one another. The comparison of the infrared spectrum of the crystal with that of the 4-methoxybenzoic acid shows less absorption bands with changes in their frequencies due to the disappearance of some characteristic frequencies that occurred at the coordination sites during chelation. 4-methoxybenzoic acid is a monocarboxylic acid having coordination sites at only the carboxylic acid functional groups. The carboxylate group (−COOH) is deprotonated and involved in coordination with a copper ion.

The slightly broad band at 3100 cm^{−1} characteristic of the carboxylate OH group in 4-methoxybenzoic acid were not observed in the IR spectra of the complex, this is attributed to the coordination of the ligand through the oxygen atom of this group after deprotonation [21].

The characteristic absorption bands of C=O (slightly broad) and C–O of the 4-methoxybenzoic acid ligand at 1720 and 1180 cm^{−1} have shifted to lower region (1685 and 1153 cm^{−1}) in the complex because of the coordinated copper atom on the carboxylate group [21–24]. The broad absorption band that appeared in crystal at 3424 cm^{−1} was due to the presence of water molecules. Similar coordination mode of oxalic acid was observed by Jin and his co-workers [25]. M–OH₂ peak at 658 cm^{−1} in crystal also confirm the presence of water in the system. New bands at 500 cm^{−1} in the crystal gives inference about ν(M–O) bonding (Figure 1).

2.3. *Thermal analysis of [Cu(4-mba)₂(H₂O)₃]*

The TG-DSC curves of [Cu(4-mba)₂(H₂O)₃] is shown in Figure 1. The crystal was thermally stable up to 75°C, followed by the first mass loss of 4.48%, between 75°C and 125°C, this was attributed to the loss of non-coordinated solvents [26]. The second thermal decomposition leading to the breakdown of the complex, [Cu(4-mba)₂(H₂O)₃], to copper salt and ligand as well as the loss of coordinated waters occurred between 135°C and 175°C. At this stage, a total weight loss of 75.21% was observed [26]. The final decomposition step (~ 15%) was ascribed the breakdown of aromatic rings followed by the formation of copper oxide as final product.

2.4. *Description of the crystal structure of [Cu(4-mba)₂(H₂O)₃]*

Copper(II) coordination polymer of 4-methoxybenzoic acid, [Cu(4-mba)₂(H₂O)₃], (Figure 2) is an interesting compound. When all six formal bonds coordinated to copper(II)

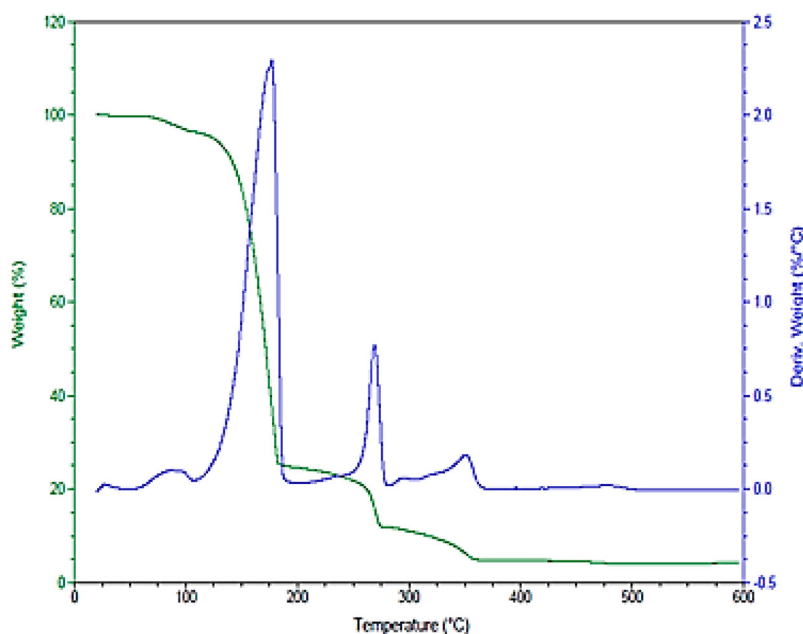


Figure 1. TG-DSC curves of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$.

are considered, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ without scrutinizing the bond lengths, the compound may be thought to be octahedral, with one carboxylate showing bidentate coordination while the other is monodentate. There are three water molecules coordinated, two acting as bridges between copper(II) ions, all Cu–O bonds being within the sum of van der Waals radii of Cu and O contact [27,28]. Therefore, these Cu–O bonds are considered as regular bonds, all contributing to the resulting coordination polyhedron. Hence, we are inclined to describe this compound, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, as having an octahedral coordination sphere [27,28]. A zig-zag complex of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ was observed *via* ORTEP view (Figure 2), the 1D units are held by strong hydrogen bonds (Figure S2). The selected interatomic bond distances and angles around Cu(II) are presented in Table 1. The complex crystallizes in monoclinic system, space group P21 with lattice parameters, $a = 7.3391(1) \text{ \AA}$, $b = 5.797(9) \text{ \AA}$, $c = 19.642(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.3^\circ$, $\gamma = 90^\circ$, $Z = 2$, $V = 833.603(4) \text{ \AA}^3$. The crystallographic data and the structure refinement parameters of the crystal are presented in Table S1.

The crystal structure of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ is presented in Figure 2. The copper(II) atom is octahedrally coordinated to two molecules of 4-methoxybenzoate (one monodentate, the other bidentate) and three water molecules. The values of Cu–O bond distances and angles (Table 1) are similar to those reported in the literatures [27–30]. The cis angles at the copper(II) atom range from 89.7° to 90.6° and the trans angles from 174.7° to 178.1° showing slight distortion.

Two of the coordinated water molecules form bridges to adjacent copper(II) ions, giving rise to a zig-zag 1D coordination polymer (Figure 2 and Figure S2). Crystal packing of zig-zag 1D unit of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ showing hydrogen bonds linking water molecules to carboxylate moieties on adjacent units of the polymer is also provided in Figure S2.

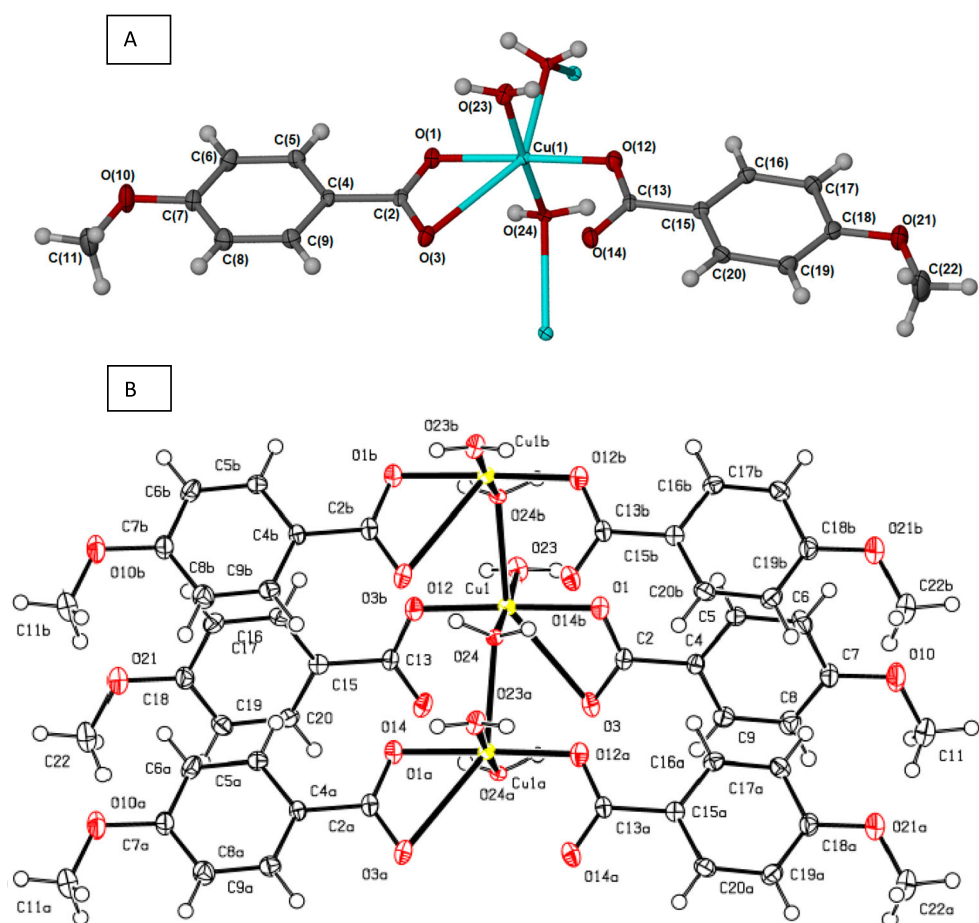


Figure 2. ORTEP diagram showing (A) crystal structure of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and (B) zig-zag 1D unit of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$.

Table 1. Interatomic bond distances (Å) and angles (°) of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$.

Bond lengths	(Å)	Bond angles	(°)
Cu1–O1	1.954(4)	O12–Cu1–O23	91.3(2)
Cu1–O3	2.784(5)	O1–Cu1–O23	89.7(2)
Cu1–O12	1.943(4)	O12–Cu1–O24	88.6(2)
Cu1–O23	1.957(3)	O1–Cu1–O24	90.6(2)
Cu1–O24	1.987(3)	O12–Cu1–O24 (1–x, ½ + y, –z)	89.0(2)
Cu1–O24 (1–x, ½ + y, –z)	2.454(5)	O1–Cu1–O24 (1–x, ½ + y, –z)	92.8(2)
		O23–Cu1–O24 (1–x, ½ + y, –z)	84.9(2)
		O24–Cu1–O24 (1–x, ½ + y, –z)	89.8(2)
		O23–Cu1–O3	89.2(2)
		O24–Cu1–O3	95.2(2)

2.5. Hirshfeld surface analyses

The molecular Hirshfeld surface; d_{norm} curvedness and shape index for $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ is demonstrated in Figure 4 and mapped over d_{norm} ranges -0.6742 to 1.1725 Å, shape index ranges -0.9957 to 0.9966 Å, and curvedness ranges -3.2532 to 0.8098

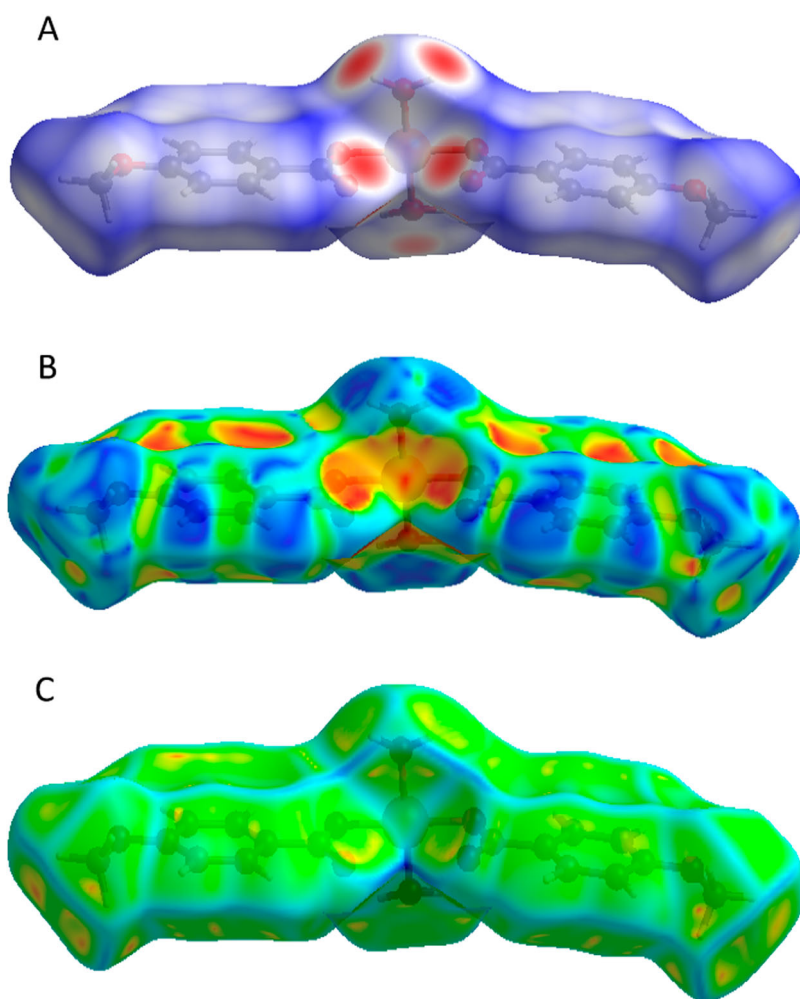


Figure 3. Molecular Hirshfeld surface: (A) d_{norm} (B) shape index and (C) curvedness for $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$.

Å, respectively. The d_{norm} mapping indicates that strong hydrogen bond interactions, such as $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding between coordinated/lattice water and carboxylato oxygen, this give the indication that the main interaction between complexes occurs around the region seen as a bright red area in the Hirshfeld surfaces (Figure 3). The 2D fingerprint plots for $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ (Figure 4(a)) shows that the intermolecular $\text{H}\cdots\text{H}$, $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ interactions are well dominated and are in complement to the Hirshfeld surfaces.

Shit *et al.* [29,30] reported that the shape index is the most sensitive to very subtle changes in surface shape, the red triangles on them (above the plane of the molecule) represent by concave regions indicating atoms of the π -stacked molecule above them, and the blue triangles represent by convex regions indicating the ring atoms of the molecule inside the surfaces [29,30]. The red triangles on the shape index mapping are referring to the $\text{C22A}-\text{H22A}\cdots\pi$ interaction with the contribution of 26.6% (Figure 4). The measure of the shape of the surface area of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ is defined by the

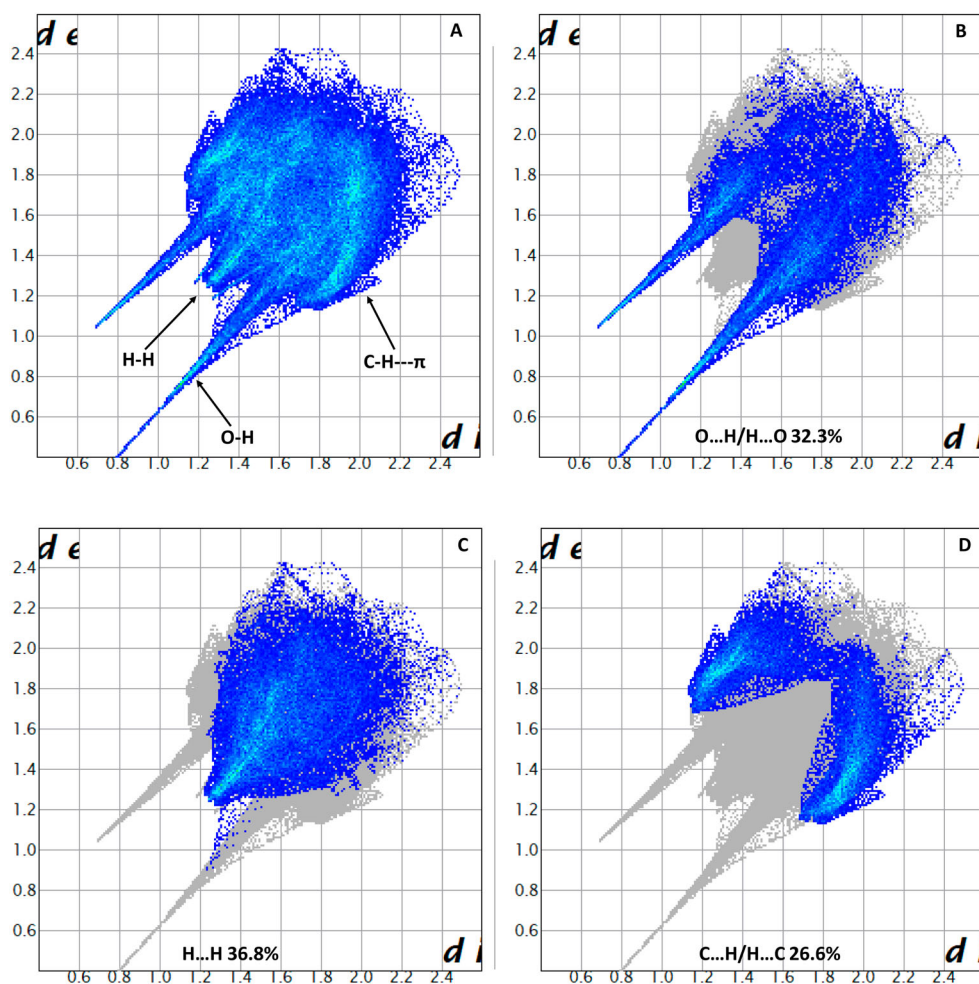


Figure 4. Fingerprint plot of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$: (A) full and resolved into (B) $\text{H}\cdots\text{O}$ (C) $\text{H}\cdots\text{H}$ and (D) $\text{H}\cdots\text{C}$ contacts showing the percentages of contacts contributed to the total Hirshfeld surface area.

curvedness [29,30]. The flat areas of the surface correspond to low values of curvedness, while sharp curvature areas correspond to high values of curvedness and usually tend to divide the surface into patches, indicating interactions between neighboring molecules. The large flat region which demarcated by a light blue outline refers to the $\pi\cdots\pi$ stacking interactions. The fingerprint plots were further analyzed to highlight particular atoms pair close contacts and enables separation of contributions from different interaction types.

Two sharp spikes pointing towards lower left of the plot are typical $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds. This portion corresponds to $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ interactions comprising 32.3% of the total Hirshfeld surfaces for $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$. $\text{C}\cdots\text{H}\cdots\pi$ interactions was observed at the top left of the plot. The fingerprint plots showed that $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ contacts comprise 26.6% of the total Hirshfeld surface area for $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$. They correspond to all $\text{C}\cdots\text{H}\cdots\text{C}$ interactions of which $\text{C}\cdots\text{H}\cdots\pi$ appear in the fingerprint plot in a characteristic

Table 2. Summary of various contacts and their contributions to the Hirshfeld Surface in $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$.

Types of contacts	Contributions in %
C...O	1.2
O...O	0.5
C...C	0.7
H...Cu	0.6
O...Cu	1.4
H...H	37.6
C...H	26.4
O...H	31.7

manner. The broad region bearing short and narrow spikes at the middle of plot is reflected as H...H interaction in $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ comprising 36.8% of the total Hirshfeld surfaces for $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$. Apart from these above, the presence of C...O, O...O, C...C, H...Cu, O...Cu and O...C interactions were observed and summarized in Table 2. Hirshfeld Surface Analyses laid the foundation for the use of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, for sulfur compound uptake due to H...H, O...H and C-H... π stacking interactions properties it possesses.

2.6. Desulfurization studies

The desulfurization ability of the synthesized crystal was thoroughly investigated on model fuel by varying initial concentration, contact time and temperature. The ability of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ to absorb sulfur from hexane solution at different optimized condition of concentration, time, temperature and dosage.

2.6.1. Effect of concentration

The effects of concentrations were studied at 32°C for 90 min using 0.02 g of adsorbent. Figure S3 indicated that the amount of sulfur adsorbed unto $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ increased with increase in concentration. The effect of the initial concentration factor depends on the immediate relation between the sulfur concentration and the available binding sites on an adsorbent surface [31,32]. The optimum adsorption capacity was found to be 9.2 mg/g. The result implies that at low concentrations of the sulfur solutions, there still existed unoccupied adsorption sites that might got occupied with increase in concentration [33]. The increase in adsorption capacity with increasing sulfur concentration could be due to the collision of the adsorbent surface with the adsorbed molecules [34].

2.6.2. Effect of contact time

The effect of contact time was studied at 32°C for different time (up to 6 h) with 0.02 g of adsorbent. The effect of contact time on the desulfurization over $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ at initial concentrations of 100 mg/L is depicted in Figure S4. The desulfurization over $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ was rapid at the initial stages of the contact period, and thereafter it approached to equilibrium. This may be due to the presence of huge number of available vacant surface sites for desulfurization during the initial stages of the adsorption [31,35]. As time passes, number of available vacant sites decreases, and the adsorption

sites become saturated. The desulfurization over $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$ attained equilibrium after 120 min and remain almost constant to 360 min. The optimum adsorption capacity was found to be 9.6 mg/g after 3 h.

2.6.3. Effect of temperature

The effect of temperature was studied using 0.02 g of adsorbent. The adsorption of sulfur usually depends on the temperature of desulfurization over $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$ was studied for a fixed time of 90 min. The result of studies of temperature effect as shown in Figure S5, reveal that the amounts of adsorbed sulfur decreased with increasing the temperature of the sulfur solution (this further confirms physical adsorption). The maximum uptake of 8.7 mg/g was adsorbed at temperature of 35°C.

2.6.4. Effect of adsorbent dosage

The results of studies of adsorbent dosage effect as shown in Figure S6, reveal that the amounts of adsorbed sulfur increase rapidly with an increase in the mass of the adsorbent. An increase in $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$ resulted in the availability of more sites for interaction, thus, more sulfur compounds are adsorbed on the surface of $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$.

2.7. Adsorption kinetic models

For sulfur compound adsorption studies using $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$, the pseudo-first-order and pseudo-second-order models were used to study the kinetics of the adsorption process (Equations 1 and 2).

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t, \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{1}{q_e} t \quad (2)$$

where q_e and q_t (mg/g) are the amounts of sulfur-containing compounds adsorbed on $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$ at equilibrium and time t , respectively.

K_1 (h^{-1}) is the pseudo-first-order adsorption rate constant and was calculated by plotting the $\log(q_e - q_t)$ versus t (Figure S7), while pseudo-second-order was obtained by plotting t/q_t versus time (Figure S7). Based on the obtained correlation coefficients (R^2), adsorption studies fitted the pseudo-first-order model, thus indicative of a physical adsorption interaction (weak interactions which are reversible) (Figure S7(a)). A high possibility of also obtaining chemical interaction *via* pi-pi interaction may occur due to the slightly lower correlation coefficients (Figure S7(b)).

2.8. Adsorption isotherms

The adsorption behavior of sulfur-containing compounds over $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$ was followed using the Langmuir and Freundlich isothermal equations (Equations 3 and 4).

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{K_d}{Q_m}, \quad (3)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K, \quad (4)$$

where q_e (mg/g) and C_e (mg/g) are the sulfur amounts adsorbed at equilibrium and the equilibrium concentration, (Q_m) is the theoretical maximum adsorption capacity at monolayer (mg/g) and K_d is the Langmuir constant (related to the affinity of adsorption sites) [36]. Freundlich constants k and n indicating adsorption capacity and intensity, respectively, were determined from the linear plot of $\log q_e$ against $\log C_e$ (Figure S8).

Langmuir equation obtained from a plot of C_e/q_e against C_e is probably proof of chemical adsorption, which may usually mean monolayer adsorption on the surface of adsorbents [36]. Freundlich isotherm indicated a multiple-layered adsorption on adsorbents, which may possibly infer sulfur compound-sulfur compound interactions on the adsorbent.

The regression coefficient values of Langmuir and Freundlich, models given in Table 3 indicated that Freundlich was the most suitable. The regression coefficient values R^2 show the applicability of the isotherms to the absorption process. It can be seen from Figure S8(a,b) that Freundlich isotherm has the highest R^2 value of 0.9992, therefore, it fits most to the absorption process. The isotherms parameters are given in Table 3.

From the slope and intercept of straight portion of the Freundlich plot, the values of Freundlich parameters, *i.e.* n to be $n = 1.478$. The numerical value of $n > 1$ indicates that sorption capacity is only slightly suppressed at lower equilibrium concentration and suggests multiple binding sites, with the highest strength sites binding the sorbate first. The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

2.9. Adsorption of model sulfur-containing compound (DBT) in model fuel

Adsorption studies using a solution mixture of model compound (DBT) in hexane was carried out under batch process by employing 0.02 g of conditioned $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$. The adsorbent, $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$, was packed into a screw-capped vial containing 2 mL DBT solution 575 mg/L (100 mg/L S) and stirred for 12 h. A reduction in the concentration of DBT was observed after adsorption with $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$ (Figure S9). In the batch adsorption process, DBT was reduced to 12.1 mg/L (2.1 mg/L S).

Adsorption capacity of copper(II) complex was compared to adsorption capacities reported in our previous study where molecularly imprinted polybenzimidazole nanofibers was employed [3]. It was observed that the current adsorbent, $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$, presented an adsorption capacity of 9.6 mg/g which is lower than capacities with the use of imprinted polybenzimidazole nanofibers (29.8 mg/g), high surface area

Table 3. Isotherm parameters with coefficient of determination (R^2) for the adsorption of sulfur-containing compounds at $30 \pm 2^\circ\text{C}$.

Langmuir isotherm			Freundlich isotherm		
Q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g(L/mg))	N	R^2
11.521	0.333	0.8676	2.302	1.478	0.9992

and available functionalities on nanofibers surfaces have influenced the reported adsorption capacities [3]. This phenomenon is also common to MOFs and other solid sorbents such as functionalized zeolite- they possess large surface areas and pores which enable the adsorption of high concentrations of organosulfur compounds.

2.10. Theoretical calculations

Since the analyzed fuel contained mostly alkylated DBT and benzothiophene, we undertook theoretical studies to understand the mechanism of adsorption. Studies reported in this section includes HOMO energy positions, LUMO energy positions, LUMO–HOMO energy gap (ΔE), hardness (η), softness (σ), electronegativity (χ) and chemical potential (μ)³⁷ of the adsorbent and adducts.

2.10.1. HOMO and LUMO positions

The octahedral geometry obtained for $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ (Figure 2) was further distorted when modeled in hexane, thus, creating an enabling environment for possible interaction of sulfur-containing compounds with $[\text{Cu}(\text{H-4mba})_2(\text{H}_2\text{O})_2]$. The observed bond angles for the modeled complex, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, were 170.28°, 176.15°, 85.23° and 94.18° for O23–Cu1–O24, O1–Cu1–O12, O1–Cu1–O23 and O1–Cu1–O24, respectively.

HOMO and LUMO represent the highest energy molecular orbital and the lowest energy empty molecular orbital, respectively. The molecular orbital energy diagram of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ showing the HOMO and LUMO positions are presented in Figure 5. With complex, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, the HOMO position centers around the methoxyl and aromatic rings of the co-ordinating ligand, while the LUMO position originates around the copper metal center atom (Figure 5).

Adducts formed when benzothiophene was brought in contact with $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ indicated that the HOMO originates from benzothiophene, while LUMO centers mostly around copper atom of the coordination polymer, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, (Figure 6). This clearly indicated that the interaction between the $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and benzothiophene is through electron donation from the HOMO to the LUMO (Figure 6). The possible formation of π – π interaction (π – π stacking) between aromatic rings of benzothiophene and 4-methoxybenzoic acid (ligand).

Adducts formed between DBT and $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ also indicated that the HOMO originates from DBT, while LUMO centers mostly around copper atom of the coordination polymer, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, (Figure 7). This clearly indicated that the interaction between the $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and DBT is through electron donation from the HOMO to the LUMO (Figure 7). The flat plane geometry between aromatic rings of DBT and 4-methoxybenzoic acid (ligand) indicated the possible formation of π – π stacking.

2.10.2. Energy gap (ΔE)

The HOMO–LUMO gap describes the stability and resistance of molecules, and it also predicts activity between species by providing the electrical transport properties as well as electron carrier and mobility in molecules. The HOMO and LUMO energies of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, are –7.99 and –7.21 eV, respectively. High ionization potential is indicated by low HOMO energy (better electron donor), while high electron affinity is indicated by

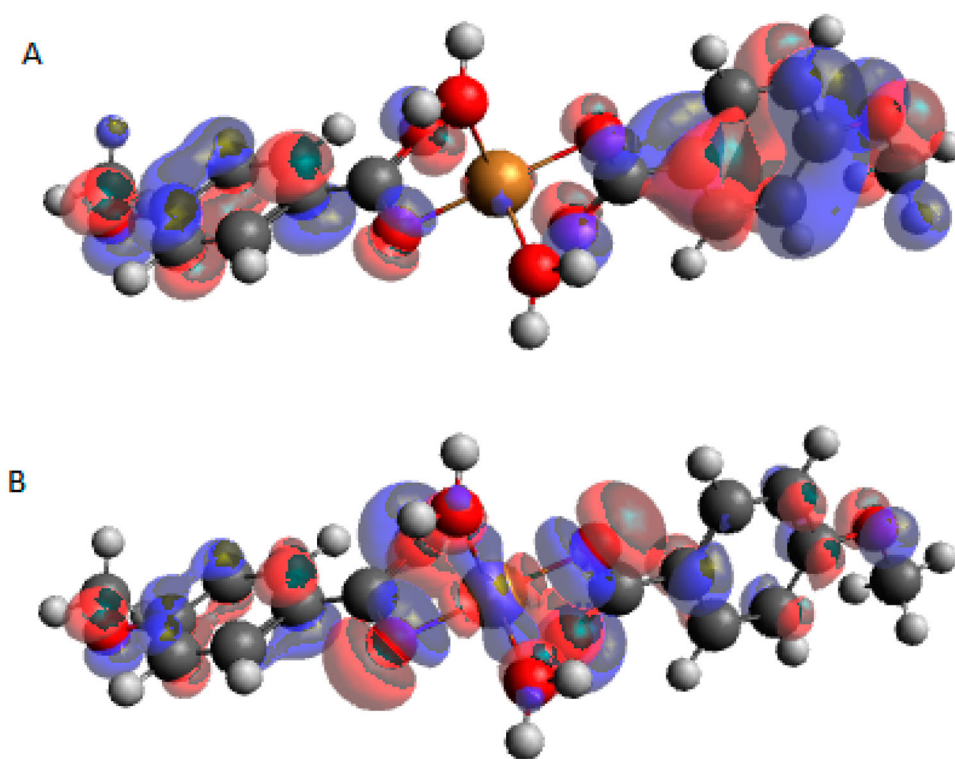


Figure 5. (a) HOMO and (b) LUMO location of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$.

high LUMO energy (better electron acceptor). The energy gap of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ which depends on the HOMO and LUMO energies was observed to be 0.79 eV.

The HOMO and LUMO energy values of adducts formed between benzothiophene with $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, is -7.55 and -6.30 eV, respectively, while the HOMO and LUMO energy values of adducts formed between dibenzothiophene with $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, is -6.48 and -5.79 eV, respectively. The energy gap of benzothiophene- $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ adduct and DBT- $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ adduct were observed to be 1.25 and 0.68 eV.

The interaction between DBT and $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ displayed the smallest HOMO–LUMO energy gap which is indicative of soft molecules, and this small gap leads to better polarizability and reactivity as observed in the experimental studies (Table 4).

Benzothiophene interaction on the other hand, displayed a higher HOMO–LUMO energy gap, however, it was observed that benzothiophene is highly electronegative as compared to DBT, hence presenting a higher tendency of benzothiophene to attract electrons towards itself from the complex, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ (Table 4). According to hard and soft acids bases (HSAB), hard acids interact more strongly with hard bases, while soft acids interact more strongly with soft bases [37]. This further indicated that benzothiophene would also interact more with benzothiophene. Benzothiophene also presented a much lower chemical potential as compared to DBT, thus indicative of a much reactive molecule.

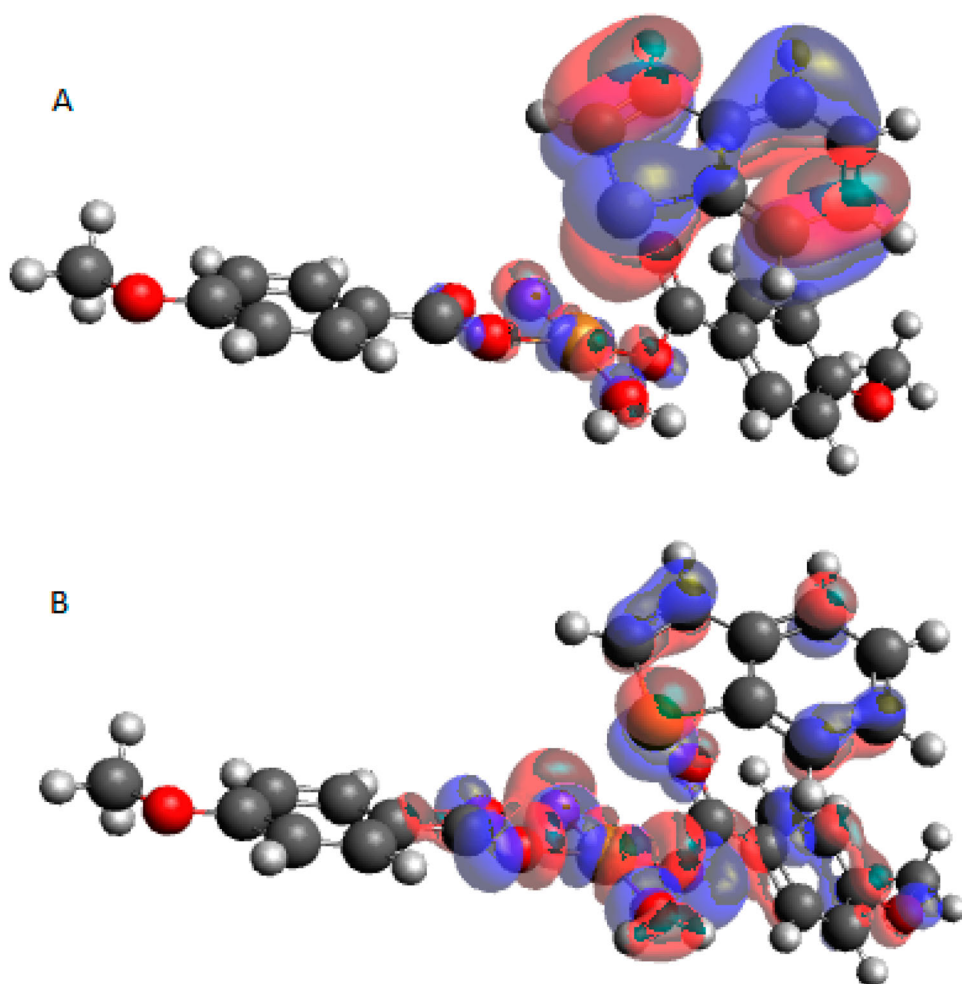


Figure 6. (a) HOMO and (b) LUMO location of adduct between $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and benzothiophene.

2.10.3. Gibb's energies of formation

The images showed that sulfur atoms of benzothiophene and DBT tend to interact more with then ligand of the complex, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ (Figures 6 and 7). The Gibbs free energy of formation of adducts between $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and sulfur-containing compounds (benzothiophene and DBT) shows that formation is favorable $\Delta G^\circ_{\text{F}} < 0$. Gibbs free energy of formation for DBT- $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ adduct and benzothiophene- $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ was observed to be -31.65 kcal/mol and -23.62 kcal/mol, respectively.

3. Conclusions

A novel octahedral $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ compound was synthesized using solvent-based technique by reacting copper sulfate and 4-methoxybenzoic acid. Structural

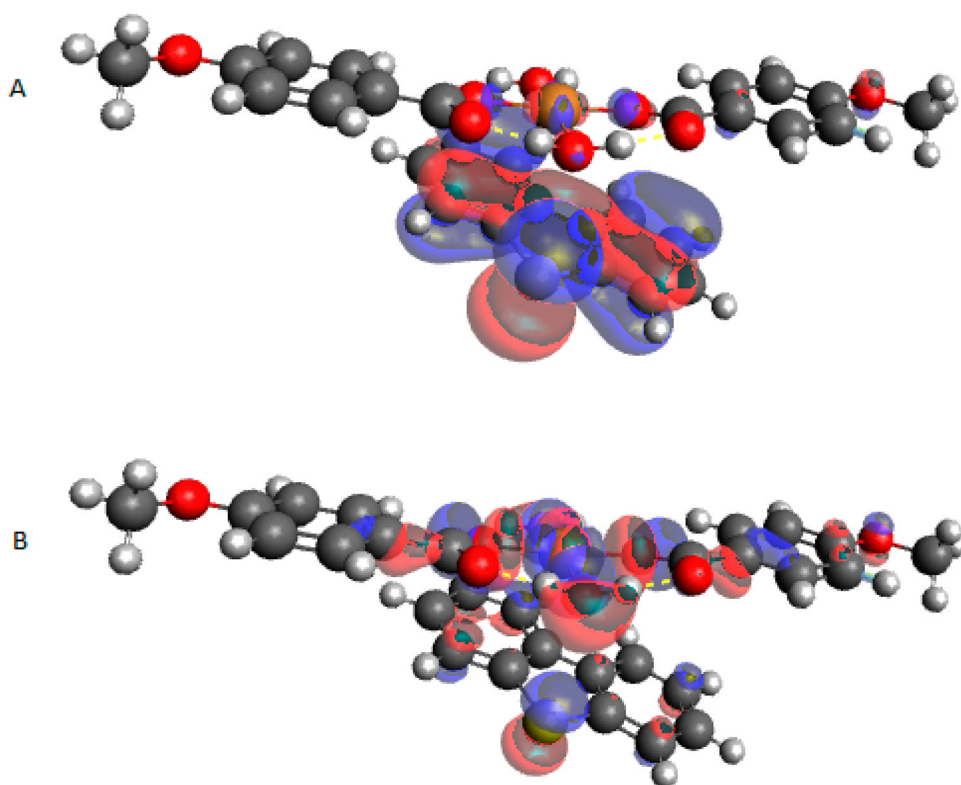


Figure 7. (a) HOMO and (b) LUMO location of adduct between $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and dibenzothiophene.

Table 4. Some electronic structure identifiers of the studied adducts.

	Cu	DBT	BT	Cu-DBT	Cu-BT
Hardness (η)	0.396	2.415	1.513	0.341	0.625
Softness (σ)	2.525	0.414	0.661	2.933	1.600
Electronegativity (χ)	7.603	3.729	5.123	6.134	6.925
Chemical potential (μ)	-7.603	-3.729	-5.123	-6.134	-6.925

Note: Cu = $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$; CuDBT = dibenzothiophene- $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ adduct; Cu-BT = benzothiophene- $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ adduct; DBT = dibenzothiophene; BT = benzothiophene.

characterization of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ further revealed that the net supramolecular arrangements are dictated by $\text{H}\cdots\text{H}$, $\text{O}\cdots\text{H}$ and $\text{C-H}\cdots\pi$ stacking interactions. The molecular Hirshfeld surface and 2D fingerprint plots were used for quantitative mapping out these interactions. The compound, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$, shows potential for the adsorption of sulfur-containing compounds. A better regression R^2 presented by Freundlich isotherm confirmed multilayer adsorption attributed to the interactions between $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and sulfur-containing compounds. Molecular modeling also confirmed hydrogen bond interactions within $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ as well as electron transfer between sulfur-containing compounds and adsorbent, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$. Further DFT calculations also confirmed the feasibility of π - π interactions between the aromatic rings of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ and sulfur compounds (DBTs and benzothiophenes).

4. Experimental section

4.1. Materials

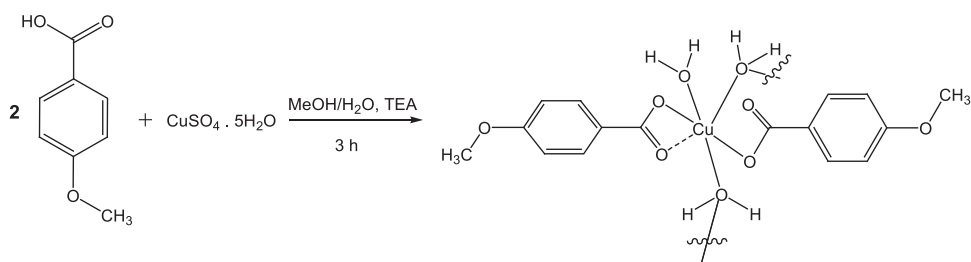
All reagents and solvents were commercially sourced and were used as obtained without further purification. High purity 4-methoxybenzoic acid and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Sigma-Aldrich.

4.2. Synthesis of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$

This compound was prepared by adding a solution containing 1 mL triethylamine (TEA), and 4-methoxybenzoic acid (0.304 g, 2 mmol) in methanol (10 mL) to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.160 g, 1 mmol) in water (10 mL). The mixture was stirred at room temperature for 3 hours; a clear blue solution was obtained and left standing for slow evaporation at room temperature (Scheme 1). Single blue crystal suitable for X-ray analysis was obtained after two weeks. The blue crystal formed was separated out by filtration and washed with a mixture of water and methanol in ratio 1:1 and dried at room temperature. Yield: 69.18%. FT-IR (KBr pellet, cm^{-1}) 3424, 1685, 1153, 658, 500.

4.3. Physical measurements

FT-IR spectra in the range of $4000\text{--}400\text{ cm}^{-1}$ were obtained from samples using KBr pellets on FTIR-8501 Shimadzu Spectrometer. A Bruker D8 Advance X-ray diffractometer was used for the XRD patterns analysis while the thermo-gravimetric analyses (TGA) were carried out a TGA Q500 V20.13 build-39 instrument under a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from room temperature up to a temperature of $600\text{ }^\circ\text{C}$. A JENWAY 6405 UV-VIS spectrophotometer was used for the UV-VIS spectra and GC-FID was employed to follow the progress of adsorption. The BET surface area measurements of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ was performed by using a Micromeritics ASAP 2020 surface area analyzer. Prior to analysis, $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$ were degassed for 4 h at $50\text{ }^\circ\text{C}$. Nitrogen gas (N_2) was employed as adsorption gas for the surface area measurements. Adsorption studies on the model compound (DBT) were monitored by employing an Agilent 7890A gas chromatograph fitted with flame ionization detector (GC-FID). The GC condition for adsorption analyses was started with an oven temperature of $50\text{ }^\circ\text{C}$ ramping to $80\text{ }^\circ\text{C}$ for 2 min, and then increased to $300\text{ }^\circ\text{C}$ at a rate of $20\text{ }^\circ\text{C/min}$, and finally held for 1 min. Results obtained from both the UV-VIS and GC-FID analysis were in good agreement.



Scheme 1. Synthesis of zig-zag 1D coordination polymer of $[\text{Cu}(\text{4-mba})_2(\text{H}_2\text{O})_3]$.

4.3.1. Crystallographic data collection and structural analysis

Single crystals suitable for X-ray crystallography were obtained by slow evaporation of aqueous/methanolic solution. Details of the crystal parameters, data collection and refinements were listed in Table 1. Data were collected on a Bruker D8 Venture Dual Source diffractometer equipped with a CMOS-detector using graphite-monochromated Mo K α ($\gamma = 0.71073$ Å) radiation at 293 K. The structure was solved by Charge Flipping using SUPERFLIP and refined by full-matrix least-squares methods based on F^2 using SHELXL [38,39]. Molecular graphics or complete structure solution, refinement and analysis program were achieved using OLEX2 [40,41]. Table 2 lists selected molecular parameters.

4.4. Desulfurization experiment

Batch equilibrium technique was used to study desulfurization of diesel fuel on [Cu(4-mba) $_2$ (H $_2$ O) $_3$]. A stock solution of hydrotreated diesel fuel (~ 100 mg/L) was obtained from the Nigerian National Petroleum Corporation (NNPC). Organic solutions with different concentrations of the sulfur compounds (1–100 mg/L) were prepared by successive dilution of the stock solution with N-hexane. Preliminary investigations through GCMS analysis revealed that the fuel contains mostly alkylated DBT, as main sulfur-containing compound [3,4]. The concentration of sulfur compounds was determined using the absorbance (at $\lambda_{\text{max}} = 381$ nm) of the solutions after getting the UV spectra of the solution with a spectrophotometer (SHIMADZU UV-1650pc UV-VIS spectrophotometer). The calibration curve was obtained from the spectra of the standard solutions (0–200 mg/L).

Prior to adsorption, the crystal, [Cu(4-mba) $_2$ (H $_2$ O) $_3$], was activated by drying under vacuum at 60°C for 30 min and kept in a desiccator. An exact amount of 0.02 g of the crystal (adsorbent) was brought in contact with fuel solution dissolved in hexane solution (2 mL) with the fixed sulfur concentration from 1 to 100 mg/L. The organic sulfur solutions in a screw-capped vial containing adsorbents were mixed well with an incubator shaker at 165 rpm and were maintained for a fixed time (10 min to 6 h) at 32°C. After adsorption for a pre-determined time, the solutions were separated from adsorbent [Cu(4-mba) $_2$ (H $_2$ O) $_3$] using syringe filter and the sulfur concentration was calculated with the absorbance that was obtained from the UV spectrophotometer. Physicochemical parameters namely initial concentration of the adsorbent, contact time, temperature and adsorbent dosage were varied to maximize the adsorption efficiency. Adsorption capacity, q_e (mg/g) was calculated from Equation (5).

$$q_e = \frac{V(C_o - C_e)}{W}, \quad (5)$$

where C_o , C_e , W and V are the initial concentration (mg/L), equilibrium concentration (mg/L), dry weight of adsorbent, [Cu(4-mba) $_2$ (H $_2$ O) $_3$] (g) and solution volume (L), respectively. Conditioning of adsorbents was carried out by pre-wetting adsorbents with hexane.

4.5. Theoretical studies

Molecular interactions between [Cu(4-mba) $_2$ (H $_2$ O) $_3$], and sulfur-containing compounds (benzothiophene and DBT) were modeled in hexane using B3LYP functional with a basis

set SDD, using the Gaussian09 software (calculated at 298 K) [42]. Semi-experimental or ab-initio calculations such as HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), LUMO-HOMO energy gap (ΔE), hardness (η), softness (σ), electronegativity (χ) and chemical potential (μ) were calculated using the following equations;

$$\eta = \frac{I - A}{2}, \quad (6)$$

$$\sigma = \frac{1}{\eta}, \quad (7)$$

$$\chi = \frac{I + A}{2}, \quad (8)$$

$$\mu = -\chi. \quad (9)$$

According to the Koopmans theorem, the ionization energies and the electron affinities of the chemical species were estimated using the following equations:

$$I = -E_{\text{HOMO}}; A = -E_{\text{LUMO}}.$$

Finally, LUMO-HOMO energy gap (ΔE) was calculated using the following formula:

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}.$$

4.5.1. Interaction studies

The interactions on a molecular level depend basically on the following interactions; HOMO and LUMO orbitals, π - π interaction, hydrogen bond interaction and van der Waals forces. A molecule with low HOMO energy indicates a better electron donor (high electronegativity), while a molecule with high LUMO energy indicates better electron acceptor (high electron affinity).

4.5.2. Gibbs formation energies

The atomic level interaction of the DBT with $[\text{Cu}(4\text{-mba})_2(\text{H}_2\text{O})_3]$ was predicted by molecular interaction studies using B3LYP functional with a basis set SDD, using the Gaussian09 software (calculated at 298 K) [42]. The Gibbs formation energies were calculated by using Equation (10).

$$\Delta G_{\text{formation}} = \Delta G_{\text{adduct}} - (\Delta G_{\text{SCs}} + G_{\text{Cu-complex}}), \quad (10)$$

where SCs is sulfur-containing compounds and Cu(II) complex.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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