Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstr

[Diaquo{bis(p-hydroxybenzoato- $\kappa^1 O^1$)}(1-methylimidazole- $\kappa^{1}N^{1}$)}copper(II)]: Synthesis, crystal structure, catalytic activity and DFT study

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ARTICLE INFO

Article history: Received 27 June 2021 Revised 11 August 2021 Accepted 15 August 2021 Available online 18 August 2021

Kevwords: Single crystal DFT Hirshfeld 1-methylimidazole Benzimidazole Catalysis

1. Introduction

Functional hybrid materials such as metal organic framework by virtue of their applications as catalyst, optical material, gas storage, separations, magnetism and chemical sensors have gained interest worldwide [1-9]. One of the advantages of this type of functional hybrid material is due to the presence of both the tunable inorganic and organic component. Thus by varying the organic and inorganic components in such materials, the diversity in the properties of such material can be tuned for their potential uses in many fields [10]. In last few decades a variety of flexible organic linkers consisting of carboxylate and heterocyclic tethers such as pyridine, imidazole, 1,10-phenanthroline, etc, have shown the most significant development in the field of synthesis of tunable metal organic framework and supramolecular structure [11–14]. Among these organic linkers, carboxylate ligands have great importance in the construction of coordination architectures because such ligand possesses special metal coordinating ability, versatile coordination modes and also the diverse topologies [15–17]. On the other hand, copper is one of the essential biological elements found in a number of enzymes which catalyzes certain biological processes.

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ABSTRACT

Metal-organic hybrid complexes often exhibit large surface area, pore volume, fascinating structures and potential applications including catalytic applications. Hence a new metal-organic hybrid complex $[Diaquo{bis(p-hydroxybenzoato-\kappa^1O^1)}(1-methylimidazole-\kappa^1N^1)}copper(II)]$ was synthesized using conventional method. Physico-chemical characterization of the complex was performed with FTIR spectroscopy, single crystal X-ray diffraction, TGA, EPR and FESEM. Single crystal X-ray diffraction study suggests it to be three dimensional with space group P2₁2₁2₁ (orthorhombic). The crystal achieves its threedimensional structure and stability through extensive intermolecular hydrogen bonding. Hirshfeld surface analysis, catalytic activity and DFT study of the complex was also performed. The synthesized complex acts as good catalyst in benzimidazole synthesis with good recyclability as catalyst up to 5th run.

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Amongst the transition metals, copper is probably the most favorite element for designing and synthesis of metal-organic hybrid materials; since its ions [Cu(I) and Cu(II)] in combination with various organic linkers can form fascinating network structures and packing motifs [18-21]. Again the architecture of low dimensional metal organic framework can easily be formed by various benzoic acid derivatives, since these derivatives can serve both as hydrogen bond donor and hydrogen bond acceptor for the construction of such frameworks [22,23]. One of the key features of the organic carboxylate ligand is that they can bind a metal ion through various coordination modes and this unique feature of the carboxylate ligands have been employed to prepare a large number of coordination polymers of different dimensionality and different properties [24,25]. Moreover, many metal organic hybrid complexes of Cu(II) ion containing derivatives of benzoic acid have been reported in the literature, where the substituent were halogen, nitro, hydroxy and cyano groups [26,27]. Therefore, herein this paper the synthesis, crystal structure, Hirshfeld surface analysis, catalytic activity and DFT study of a new Cu(II) complex derived from 4-hydroxybenzoic acid and 1-methylimidazole using conventional method has been reported.







2. Experimental section

2.1. Materials and methods

Copper nitrate [Cu(NO₃)₂·3H₂O, 99%], 4-hydroxy benzoic acid (99%), 1-methylimidazole (98.5%) and triply distilled de-ionized water (with specific conductance $< 1.10^{-6}~S~cm^{-1}$ at 25 °C) were used in this synthesis. All these chemicals were of analytical reagent (A. R.) grade and used without further purification. All the solvents used were of spectroscopic grade. Elemental microanalysis of the complex (C, H and N) was carried out using Perkin-Elmer (Model 240C) analyzer. Cu-content in the complex was determined using AAS (Varian, SpectrAA 50B), calibrated with standard Cu-solution (Sigma-Aldrich, Germany). IR spectrum was obtained from a Perkin-Elmer FT-IR spectrometer (RX-1) in the region 4000 to 400 cm⁻¹ at ambient temperature. The sample was diluted with IR grade KBr (Sigma-Aldrich, Germany) and pressed into a pellet. EPR data of the single crystal of the complex in the X-band was obtained from EPR magnetometer (JEOL, JES-X3 FA200) for the field range of -10 to 990 mT. The mass spectra of the synthesized compounds have been analyzed using WATERS O-TOF Premier HAB-213 mass spectrophotometer in methanol solvent. Single crystal X-ray diffraction study was performed using Xcalibur, sapphire3 (manufactured by Oxford diffraction, Poland) equipped with CCD camera. X-ray powder diffraction (PXRD) study has been carried out in analytical X'pert powder X-ray diffractometer using Cu- $K\alpha$ radiation of wavelength 1.54 Å and the data were recorded for the 2θ range varied from 5° to 90° at room temperature. The melting point of the synthesized compounds was determined by open capillary method. Thermal stability of the complex was studied by thermogravimetric (TGA) and differential thermogravimetry (DTG) analysis. The thermal data were recorded using TGA instrument (Q500 V20.10 Build 36) in N₂ atmosphere with an initial weight of the complex (6.619 mg) subjected to a heating rate of 10 °C min⁻¹. The electronic spectra were recorded with a JascoV-530 double beam Spectrophotometer in methanol. ¹H-NMR spectra of the synthesized benzimidazole derivatives (1-18) were recorded at room temperature on a FT-NMR (Bruker Avance-II 400 MHz) spectrometer by using DMSO-d₆ as solvents and chemical shifts are quoted in ppm downfield of internal standard tetramethylsilane (TMS). The morphology of the crystal was studied using Field Emission Scanning Electron Microscopy (FESEM, INSPECT F50, FEI, The Netherland). The magnetic moment measurements of the copper complex were carried out on Sherwood Scientific magnetic susceptibility balance (UK) using $Hg[Co(NCS)_4]$ as the calibrant.

2.2. Synthesis of [Diaquo{bis(p-hydroxybenzoato- $\kappa^1 O^1$)}(1-methylimidazole- $\kappa^1 N^1$)]copper(II)] dry CH₃OH

To a 50 mL round bottom flask containing a solution of 4hydroxy benzoic acid (0.277 g, 2 mmol) in dry methanol (20 mL), copper nitrate (0.2417 g, 1 mmol) was added. The light blue solution was then stirred at room temperature for 30 min. To this solution 1-methyl imidazole (0.082 g, 1 mmol) was added dropwise. The color of the solution changed from light blue to dark blue. To this dark blue solution, few drops of triethyl amine were added and then refluxed for 4 h at 160 °C. The mother liquor was then transferred in 50 mL beaker and allowed to stand at room temperature. After few days the compound was obtained as a blue crystal. The compound was then collected by filtration and washed repeatedly with triply distilled de-ionized water followed by diethyl ether. Single crystals suitable for X-ray diffraction were collected by hand picking under a microscope (40x). The synthesized copper complex was soluble in most of the polar solvent except water and it did not melt up to 280 °C. Yield: 0.383 g, 78% (based on Cu), ESI-MS 491.95 (M⁺). Elemental analysis calcd (%) for

Table 1

Crystal data collection and structure refinement for copper complex 1.

Crystal data	
Chemical formula	$[Cu(C_{18} H_{20} N_2 O_8).2H_2O]$
M _r	491.93
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	298.8 (7)
Colour, habit	Blue, Parallelepiped
Size, mm	$0.50 \times 0.40 \times 0.20$
a, b, c (Å)	7.0603 (3), 12.1658 (5), 24.2757 (8)
α, β, γ (°)	90
V (Å ³)	2085.14 (14)
Z	4
Radiation type	Μο Κα
Density (calculated), Mg/m ³	1.567
Absorption coefficient, mm ⁻¹	1.106
Data collection	
Diffractometer	xcalibur, sapphire3
T _{min} , T _{max}	0.608, 0.809
$\theta_{\max}, \theta_{\min}$	29.271, 3.453
h	-9→7
k	- 16 →15
1	-25 →32
Reflections collected	6703
Unique reflections	4513
Observed reflections (> $2\sigma(I)$)	4110
R _{int}	0.0363
Refinement	
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	451 /12/308
Final R indices $[I>2\sigma(I)]$	$R_1 = 0.0363, wR_2 = 0.0859$

 $[Cu(C_{18}H_{20}N_2O_8).2H_2O]\colon$ C 43.94, H 4.92, N 5.69, Cu 19.91; found: C 43.77, H 4.69, N 5.55, Cu 12.96.

2.3. X-ray crystallographic measurements

Crystal data collection and structure refinement are summarized in Table 1. Data collection of the synthesized copper(II) complex were carried out on an Oxford Diffraction Xcalibur 3/Sapphire3 CCD diffractometer (manufactured by Oxford diffraction, Poland) equipped with CCD (with Mo K α , $\lambda = 0.71073$ Å) at 299 K using ω scan technique. Data refinement and reduction were carried out using CrysAlisPRO(Agilent Technologies, version 1,171.37.35, 2014). The crystal system was determined by Laue symmetry and the space groups was assigned on the basis of systematic absences using XPREP. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined on F² by full-matrix least-squares methods with SHELXL-2014 crystallographic software package [28]. All the non-hydrogen atoms were anisotropically refined and all hydrogen atoms were placed in the calculated positions and refined isotropically with a rigid model. The hydrogen atoms bound to water molecules were found via Fourier difference map and these hydrogen atoms were then restrained at a fixed positions and refined isotropically. The crystal of copper (II) complex was twinned (inversion); its twin law was found via TWIN/BASF instructions included in the SHELXL2014 instruction file [28]. All calculations and molecular graphics were carried out with the SHELXL-2014/7 PC programme package. The data collection, structure refinement parameters and crystallographic data for the complex is given in Table 1. Some selected bond lengths, bond angles and non-covalent interaction parameters (H-bond) are presented in Tables 2 and 3, respectively.

2.4. Catalytic activity for benzimidazole synthesis

In a typical procedure a mixture of 1,2-phenylenediamine (1.0 mmol), substituted benzaldehyde (1.0 mmol) and TLC grade silica gel (silica gel G) were thoroughly grinded and mixed with the help of motor and pastle to make a homogenous mixture. The

Table 2

Selected bond lengths (A)andbond angles (°) for (1).				
Cu1-07	1.956 (3)	01-C7	1.279 (5)	
Cu1-01	1.961 (2)	02-C7	1.243 (5)	
Cu1-04	1.961 (2)	04-C14	1.274 (5)	
Cu1-N1	1.966 (3)	05-C14	1.245 (5)	
Cu1-08	2.351 (4)	C15-N1	1.317 (6)	
C15-N2	1.328 (6)	C17-N1	1.361 (6)	
C16-N2	1.385 (7)	C4-03	1.362 (4)	
C11-06	1.355 (4)	C1-C7	1.496 (5)	
C8-C14	1.494 (5)			
07-Cu1-01	88.96 (12)	04-Cu1-08	87.67 (13)	
07-Cu1-04	88.89 (12)	N1-Cu1-08	95.78 (15)	
01-Cu1-04	174.44 (11)	Cu1-07H107	128 (3)	
07-Cu1-N1	167.72 (14)	Cu1-07H2O7	117 (4)	
01-Cu1-N1	91.06 (13)	07-Cu1-08	96.48 (14)	
04-Cu1-N1	92.13 (13)	01-Cu1-08	87.47 (13)	

Table	3
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Hydrogen bonded geometries in (1).

_					
	D - H…A	D - H	H…A	DA	D - H…A
	03-H1-03…010 ⁱ	0.82	1.99	2.751 (5)	154.4
	06-H1-0609 ⁱ	0.82	1.92	2.685 (6)	155.4
	07-H1-07…05 ⁱⁱ	0.885 (13)	1.764 (16)	2.643 (5)	172 (6)
	07-H2-07…02 ⁱⁱ	0.886 (13)	1.790 (17)	2.671 (5)	172 (2)

Symmetry codes: (i) -x+1/2, -y+1, z-1/2, (ii)-x+3/2, -y+1, z-1/2.

mixture was transferred to a 50 mL round bottomed flask. To this mixture 5 mol% of the title complex was added. The reaction mixture was stirred for 20 min at room temperature. TLC was used to monitor the progress of the reaction. After completion of the reaction, the reaction mixture was extracted with dry ethylacetate and filtered. The filtrate was evaporated in vacuum and subsequently dried to afford crude product which was purified by column chromatography using n-hexane/ethylacetate (v/v, 80:20) as eluent to afford pure benzimidazole derivatives (2a-2s) as shown in Scheme 1.

2.5. Theoretical study

All DFT calculations were carried out using Gaussian 16, Revision A.03 programme package [29]. The molecular structure of the representative complexes in the ground state were optimized by the DFT method using B3LYP hybrid functional [30,31] combined with LANL2DZ basis sets for ligand and Cu(II) ion, respectively. One of the prominent features of the LANL2DZ basis set is its inclusion of relativistic effect that is prerequisite for heavy elements. The total energy calculations within the DFT framework were carried out to ascertain the interaction of copper ion with the O and N coordination environment. The optimized structures, vibrational frequencies, electronic spectra, HOMO-LUMO energies, chemical potential (μ), global hardness (η) and global electrophilicity power (ω), Mulliken charge and MESP [32] properties are the main theoretical assessments that have been emphasized herein this work. The Hirschfield surface analysis has also been carried out using crystal explorer 17.5 programme [33] to explore the types of intermolecular interactions prevailing in the molecule.

3. Results and discussion

3.1. Structural description of $[Cu(C_{18}H_{20}N_2O_8).2H_2O]$

The single crystal X-ray analysis show that the synthesized complex has molecular formula $[Cu(C_{18}H_{20}N_2O_8).2H_2O]$ and crystallizes in an orthorhombic space group, $P2_12_12_1$ with four formula unit in the unit cell (Z = 4). The asymmetric unit contains one Cu(II) ion, two carboxylate anion, one 1- methyl imidazole and



Fig 1. Coordination geometry of Cu(II) ion in the complex. Color scheme: green, Cu; red, O; yellow, S; blue, N; grey, C and sky blue, H.



Fig 2. Crystal packing and hydrogen bonding (green dotted lines) within the framework.

two coordinated water molecule. The asymmetric unit also contains two guest water molecules (Fig. 1). The penta-coordinated Cu(II) adopts a square pyramidal geometry comprising of two oxygen atoms from the two carboxylate ligand (01, 04), one nitrogen atom from the 1-methyl imidazole (N1) and two oxygen atom from the two coordinated water molecule (07, 08). Furthermore, the bond lengths of the metal atom Cu and the ligands are Cu1-01 1.961(2), Cu1-O4 1.961 (3), Cu1-N1 1.966 (3), Cu1-O7 1.956 (3) and Cu1-O8 2.351 (4), respectively. The bond length of coordinated water molecule Cu1-O8 at the apical position is 2.351 (4) and it is larger than the other water molecule Cu1-07, 1.956 (3) coordinated to the square plane. Thus the water molecule at the apical position could be described as a weakly coordinated as the other water molecule of the square plane. The three dimensional packing arrangement of the title compound has been shown in Fig. 1. The complex forms the supramolecular framework through intramolecular and intermolecular hydrogen bonding between coordinated water molecules and the guest water molecules as evident by Fig. 2.

3.2. FTIR spectroscopic study

The Infra-red spectra of the synthesized compound give valuable information about the metal ligand bonding. The FTIR spectrum of the synthesized Cu(II) complex has been shown in Fig. 3. From the spectra, it is evident that the band appearing at 1595 cm⁻¹ and 1389 cm⁻¹ can be attributed to the asymmetric stretching (v_{as}) and symmetric stretching (v_s) vibrations of the (COO-) group, respectively. The large separation $\Delta v = (v_{as}-v_s)$ between v_{as} (COO-) and v_s (COO-) is 206 cm⁻¹ and it indicates an un-symmetrical monodentate mode of bonding of the carboxylate group [34,35] in the synthesized complex which in turn substantiated by the single crystal structure of the complex. Again the band in the region 3459–3222 cm⁻¹ for the complex is attributed to the presence of coordinated and the lattice water molecule. The appearance of medium intensity band at ~958 cm⁻¹ in the spectrum of the molecule is characteristic to the carboxylate bridging (M–O–



Fig 3. FTIR spectrum of the complex.

M) in the complex [36]. The peak appearing at 632 cm^{-1} indicates the presence of Cu-N bond [37]. The bands in the region 1282– 632 cm⁻¹ are attributed to the CH in plane or out of plane bending, or ring deformation absorptions of the benzene ring, respectively. Again the Infra-red spectra of the complex have been calculated theoretically using B3LYP/LANL2DZ basis sets [30,31]. The theoretical infra-red spectra of the complex is shown in Fig. S1.

From a perusal of the Figs. 3 and S1 it is evident that the bands appeared at around 1595 cm⁻¹1389 cm⁻¹, 1282–632 cm⁻¹, 3459–3222 cm⁻¹ and around 632 cm⁻¹ in theoretically calculated IR spectra match well with the experimental spectra and hence this validates the level of theory used for theoretical calculation.

3.3. Magnetic moment and EPR analysis

The room temperature magnetic moments of the complex (μ_{eff}) measured with magnetic susceptibility balance is found to be 1.92 B.M [38,39] and this indicates the presence of a single unpaired electron in the title Cu(II) complex. The X-band EPR spectrum (Fig. S2) of the complex appeared to be slightly broadened with g_{\perp} = 2.15 and g_{\parallel} = 2.215 and this is characteristic of a square pyramidal geometry. Also a perusal of the g-values $[g_e < g_{\perp} < g_{\parallel}]$ (2.002 < 2.15 < 2.215)] suggests that $d_{x^2-y^2}$ orbital is in the ground state and the d^9 configuration is $(e_g)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1$. The 'g' values are related to the axial symmetry and the fact, $g_{||} > g_{\perp}$, supports square pyramidal geometry for Cu(II) complex [38] as mentioned above. The magnetic moment obtained using s = 1/2 and g = 2.215 (best fitted curve of EPR data) was also 1.92 B.M (i.e., $\mu_{\rm eff}=\mu_{\rm cal}$). All these facts support square planar geometry and presence of single unpaired electron in $d_{x^2-y^2}$ orbital for Cu(II) ion in the title complex [38,39].

3.4. Thermogravimetric analysis (TGA)

The synthesized complex is air stable. Thermal stability of the complex was studied using thermogravimetric technique in the temperature range 0–890 °C. The thermogram (shown in Fig. 4) has mainly three weight loss stages. The two sharp stages followed by a slow but gradual weight loss stage. The sample shows an initial mass loss of 16% (calcd: 14.6%) from around 100 to180 °C due to loss of two coordinated and two non-coordinated water molecules. The second weight loss stage occurs from 200 to 380 °C with a sharp weight loss of 57% (calcd: 55.7%). The DTG curve (in blue) also well corroborates with the TGA curve (in green) for the complex. This sharp weight loss is probably due to loss

of coordinated 4-hydroxy benzoic acid moieties. This stage is accompanied by subsequent weight loss of 16% (calcd: 16.7%) 420 to 870 °C. This weight loss is probably due to the loss of coordinated 1-methyl imidazole fragment and finally the sample decomposes to corresponding metal oxide at about 890 °C. Hence the complex has an appreciable thermal stability at ambient to moderately high temperatures. The complex started degrading at 90°C and continued to decompose to 890 °C until a metal oxide residue was obtained. So the complex is thermally stable up to 100 °C, thereafter it suffers stepwise successive thermal degradation.

3.5. PXRD and SEM analysis

To check the purity and homogeneity of the bulk product of the synthesized copper complex, the X-ray powder diffraction studies were carried out at room temperature. The simulated and experimental X-ray powder diffraction (XRPD) pattern of the synthesized complex are shown in Fig. 5. From the Fig. 5 it is evident that the major peak positions of the diffraction pattern of the bulk solid of Cu(II) complex matched well with that of the simulated pattern obtained from the single crystal data. This indicates the presence of mainly one crystalline phase and homogeneity of the synthesized complex has been evaluated using FESEM analysis (Fig. S3). The FESEM micrograph of the catalyst before and after the reaction (up to 5th) run is shown in Fig. 6.

The FESEM micrograph shows that the Copper complex has a rectangular box like morphology with the average length of the boxes lies between 90–160 μ m. Again the FESEM micrograph of the catalyst revealed that the surface morphology of the catalyst has changed from rectangular boxes to a more or less 2 dimensional flat wafer like structures with the length ranging from 15 to 55 μ m during the reaction time (up to 5th run) (Fig. 6).

3.6. DFT study

The geometrical structure of the complex was optimized at B3LYP level of theory using LANL2DZ basis set and the optimized geometry of the complex is in consistent with the structure obtained from single crystal X-ray diffraction study. The optimized geometry of the Cu(II) complex is shown in Fig. 7. The Cu(II) ion in the complex is situated at the center of the square plane which is coordinated by two carboxylate ion (mono-dentate binding mode), two water molecule and one 1-methylimidazole molecule. The penta-coordinated Cu(II)complex adopts a square pyramidal geometry and this is in consistent with the structure obtained from single crystal X-ray diffraction study.

3.7. Frontier molecular orbitals

The Frontier Molecular Orbitals (HOMO and LUMO) can qualitatively predict the excitation properties and electron transport in the studied system, therefore, the parameter HOMO and LUMO can offer a reasonable prediction of molecular reactivity. Thus the energies of the HOMO and LUMO orbitals of the Cu(II) complex have been calculated using density functional theory (DFT). The energy of HOMO and LUMO orbitals has been found to be -6.31 and -1.03 eV, respectively. Since the energy of HOMO and LUMO orbitals are negative, it indicates that the studied complex is stable [40]. Again the energy gap (ΔE) between HOMO and LUMO of the complex can be correlate with its stability and the energy gap (ΔE)=(E_{LUMO} - E_{HOMO}) for the studied system is found to be 5.28 eV and this large HOMO-LUMO energy gap reveals that the



Fig 4. Thermogram of the complex in the temperature range 0-890 °C.



Fig 5. Comparison of experimental with Theoretical PXRD Spectra.



Fig 6. FESEM micrograph of the catalyst after 1st run, 3rd run and 5th run of the reaction.

Cu(II) complex is highly stable [40]. However, the DFT based descriptors (HOMO-LUMO orbital energy) could be used in order to understand the structure and reactivity of molecule by calculating different properties such as Chemical potential(μ), Global hard-

ness (η) and global electrophilicity power (ω). The HOMO-LUMO orbital energies are directly related to ionization energy (I = - E_{HOMO}) and electron affinity (A = - E_{LUMO}). Similarly, the chemical potential (μ), Global hardness (η) and global electrophilicity power (ω) are related to HOMO-LUMO orbital energies by the following relations: chemical potential (μ) = (E_{HOMO}+E_{LUMO})/2, Global hardness $(\eta) = (-E_{HOMO} + E_{LUMO})/2$ and global electrophilicity power (ω) = $\mu^2/2\eta$. Alternatively, chemical potential (μ) and Global hardness ($\eta)$ are given by the following relations: μ = -(I+A)/2 and $\eta = (I-A)/2$, where I and A are the first ionization potential and electron affinity of the chemical species [32,41]. For the title compound, the values of first ionization potential (I), electron affinity (A), Chemical potential (μ), Global hardness (η) and electrophilicity power (ω) are 6.31, 1.03, -3.67, 2.64 and 2.55 eV, respectively. Since the chemical potential (μ) of the studied complex is negative and it signifies that the compound is stable and



Fig 7. HOMO-LUMO of the synthesized complex.

 Table 4

 Physical parameters obtained theoretically for the complex.

Parameters	Energy (eV)
Еномо	-6.31
E _{LUMO}	-1.03
ΔE	5.28
Chemical potential (μ)	-3.67
Global hardness (η)	2.64
Electrophilicity power (ω)	2.55

do not decompose spontaneously into its elemental form. The HOMO-LUMO orbital energies, chemical potential (μ), Global hardness (η) and global electrophilicity power (ω) are summarized in Table 4.

3.8. Mulliken charges

Atomic charge of a molecular system is an important parameter; thus the calculation of atomic charges has an important role in quantum mechanical calculations. The mulliken charges are a function of electron density population and thus, the mulliken charges are usually calculated by determining the electron population of each atom as defined in the basis function. The charge distribution on the studied Cu(II) complex has been calculated for the equilibirium geometry of the studied complex and the value of mulliken charges of the complex is given in Table 5. From the table it is evident that the mulliken charges in the neighborhood of C_{14} , C_{19} , C_{24} , C_{25} , C_{30} and C_{35} are more positive and thus this positive value indicates the direction of delocalization.

3.9. Molecular electrostatic potential

The Molecular Electrostatic Potential surface diagram is used to understand the reactive behavior of a molecule. The negative regions of the MESP can be regarded as nucleophilic centers, whereas the positive regions are potential electrophilic sites [32,42]. MESP is an Electron Density dependent property and it is a very valuable descriptor in understanding sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [32,43]. Hence in order to predict the reactive sites of electrophilic and nucleophilic attack for the studied Copper (II) complex, MEP at the B3LYP/LANL2DZ optimized geometry was calculated. The Molecular Electrostatic Potential surface diagram of the Cu(II) complex is shown in Fig. 8.

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Table 5

Charge distribution calculated by the Mulliken.

Atoms	Atomic charges (Mulliken)	Atoms	Atomic charges (Mulliken)
Cu1	0.623	C26	-0.229
02	-0.503	H27	0.241
03	-0.496	C28	-0.372
04	-0.818	H29	0.211
05	-0.436	C30	0.302
06	-0.440	C31	-0.329
07	-0.463	H32	0.248
H8	0.357	C33	-0.321
09	-0.464	H34	0.276
H10	0.358	C35	0.272
N11	-0.271	C36	-0.030
012	-0.701	H37	0.304
N13	-0.101	C38	-0.219
C14	0.280	H39	0.265
C15	-0.320	C40	-0.130
H16	0.276	H41	0.280
C17	-0.329	C42	-0.565
H18	0.249	H43	0.240
C19	0.303	H44	0.240
C20	-0.373	H45	0.231
H21	0.209	H46	0.453
C22	-0.296	H47	0.453
H23	0.228	H48	0.443
C24	0.282	H49	0.378
C25	0 274		



Fig 8. Molecular electrostatic potential surface diagram of the Cu(II) complex.

From the Fig. 8 it is evident that oxygen atom of the carboxylic group is the most negative potential region (red), oxygen atom of the water and hydroxyl group is the region of moderate negative potential (yellow), while the hydrogen and carbon atoms of the compound bear positive potentials (blue). The negative (red and yellow) region of MEP [32], McKinnon et al. [41–43] is related to the electrophilic reactivity whereas the positive (blue) region corresponds to nucleophilic reactivity. From the figure, it shows that the most reactive part in the molecule is the oxygen atom of the carboxylic group and the high reactivity of this group may be due to the more electronegative character of oxygen atom of the carboxylic group.

3.10. Hirshfeld surface analysis

In order to quantify the various intermolecular interactions, Hirshfeld surface analysis has been carried out for the synthesized complex and their associated two-dimensional fingerprint plots have been used to predict the possible intermolecular interactions. The descriptor d_{norm} , which incorporates two factors: (i) d_e , signifying the distance of any surface point nearest to the internal atoms, and (ii) d_i , signifying the distance of the surface point nearest to the exterior atoms and also with the van der Waals radii of the atoms has been used for mapping the Hirschfeld surface of a molecule [32,44]. The parameter d_{norm} is given by a math-



Fig 9. Molecular Hirschfeld surface: (a) d_{norm} , (b) shape index, (c) curvedness and (d) O-H/H-O for the complex.

ematical expression as $d_{\text{norm}} = (d_i - r_i^{\text{vdw}})/r_i^{\text{vdw}} + (d_e - r_e^{\text{vdw}})/r_e^{\text{vdw}}$, where r_i^{vdw} and r_e^{vdw} are the van der walls radii of atoms. The parameter d_{norm} may have negative or positive value depending on the types of intermolecular contacts. If the value is positive, then the intermolecular contacts are shorter and if the value is positive the contacts are larger than the van der walls separations [45]. The descriptor d_{norm} displays a surface with bright red, white and blue spots for shortest contact, contact around the van der walls separation and devoid of close contacts, respectively appear as a primary interaction in the complex [Fig. 9a]. Crystals with spherical atomic electron densities, the Hirshfeld surface is unique and it gives an idea about the intermolecular interactions occurring in the studied molecular crystals. In order for better visualization of the molecular moiety around which they are calculated, the surfaces have been shown as transparent. The molecular Hirschfeld surface for Cu(II); d_{norm} , shape index and curvedness for the Cu(II) complex is depicted in Fig. 9, respectively and mapped over d_{norm} ranges – 0.7184 to 1.7801 Å, shape index ranges -1.0000 to 1.0000 Å, and curvedness ranges -4.0000 to 0.4000 Å, respectively. The d_{norm} mapping for the studied Cu(II) complex shows a bright red area in the Hirshfeld surfaces indicating the strong hydrogen bond interactions, such as O-H--O between coordinated/lattice water and carboxylate oxygen and these hydrogen bond interactions. The intermolecular interactions of the Cu(II) complex are shown in the 2D fingerprint plots shown in Fig. 10. H...H contacts make the

Table 6



Fig 10. 2D Fingerprint plots of the complex.



largest contribution to the Hirshfeld surfaces (42.3%) [32,41–46]. The O...H/H.O interactions are represented by blue spikes on top and bottom of the pale yellow NH/HN (8.8%) interactions are near the CH regions while the green CH/HC interactions (34.2%) are between the N–H and O–H regions.

Optimization of	reaction condition.		
	$H_{2N} + H_{2N} = \frac{1}{R_{0}}$	Catalyst om Temperature	\mathbb{A}
Entry	Catalyst (mol%)	Time (mins)	Yield (%) of C
1	0	60	20
2	1	60	42
3	1.5	60	58
4	2	45	68
5	3	45	72
6	4	45	89
7	5	30	91
8	5	20	96
9	7	20	89
10	7	30	92
11	7	40	93

Reaction conditions: 2-itrobenzaldehyde (1 mmol), orthophenylenediamine (1 mmol), copper complex (5 ol%) at room temperature.

Table 7The yield of the catalysed products.



3.11. Catalytic activities

Among the various nitrogen based heterocyclic compounds, benzimidazole scaffold because of their wide spectrum of biological activities are ubiquitous in nature and these are often useful bioactive intermediates for the preparation of pharmacological and biological active molecules. A good number of literature methods have been reported for the synthesis of 2-substituted benzimidazoles using ortho-phenylenediamines and different aldehydes as precursors. Many of the reported methods for the synthesis of such compound require long reaction time, expensive catalysts and organic solvents. The recent trend towards development of green reaction conditions encouraged us to study an efficient and ecofriendly synthesis of 2-arylbenzimidazoles at room temperature in solvent free condition using silica gel as a solid medium. Therefore, in this work an attempt has been made to develop the solvent free green reaction condition for the synthesis of 2-substituted benzimidazole using ortho-phenylenediamine and aromatic aldehyde as

Table 8

Recyclability of copper catalyst in model reaction.

$ \begin{array}{c} & H \\ & H_2N \\ & H_2N \\ & H_2N \\ & H_2N \end{array} $	$\frac{1}{B} \frac{Cata}{Room T}$	$\stackrel{\text{lyst}}{\underset{\text{remperature}}{\overset{\text{lyst}}{\underset{\text{NO}_2}{\overset{\text{NO}_2}{\overset{\text{NO}_2}{\overset{\text{NO}_2}{\overset{\text{C}}{\overset{\text{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}}{\overset{NO}_2}{\overset{NO}_2}{\overset{NO}_2}}{\overset{NO}_2}{\overset{NO}_2}}{\overset{NO}_2}{\overset{NO}_2}}{\overset{NO}_2}}{\overset{NO}_2}{\overset{NO}_2}}{\overset{NO}_2}}{\overset{NO}_2}}{\overset{NO}_2}{\overset{NO}_2}}{\overset{NO}_$
Entry	No of runs	Isolated yield (%)
1	0	96
2	1	95
3	2	93
4	3	92
5	4	90
6	5	88
7	6	82
8	7	73

precursors over silica gel (TLC grade) in open air. In order to optimize the catalyst and reaction conditions, 1,2-phenylenediamine (1 mmol) and 2-nitrobenzaldehyde (1 mmol) were taken as precursors for initial model reaction. The results of optimization of reaction condition and catalyst are summarized in Table 6. The feasibility of the developed methodology was scrutinized for a series of aryl and heteroaryl aldehydes and it has been found that all the aldehyde gave excellent yield up to 98% under the reaction condition as mention above. The spectral data of the synthesized benzimidazole derivatives are in full agreement with data reported in the literature. The yield of the compounds (1–18) is given in Table 7.

The recyclability of the catalyst was then investigated and it has been found that the catalyst can be recovered after completion of the reaction and it can be used further up to 5th run with no significant loss of activity Table 8. However, the scanning electron micrograph of the catalyst taken before and after the reaction has revealed that the catalyst has lost its morphology to some extent during the reaction condition [Fig. 11].

4. Conclusion

The blue colored newly synthesized metal-organic hybrid complex has Parallelopiped shaped orthorhombic crystals with space group $P2_12_12_1$. The three-dimensional structure of the complex was stabilised due to extensive inter- molecular hydrogen bonding interactions. Thermogravimetric and magnetic studies revealed its thermal stability and weak paramagnetic behavior, respectively. The purity structure of the synthesized complex was well supported by FESEM, X-ray diffraction and DFT study. The synthesized complex acts as good catalyst in benzimidazole synthesis with good recyclabilty as catalyst up to 5th run.

CCDC 1823,459 contains the supplementary crystallographic data of this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc. cam.ac. uk/data_request/cif.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Amarjit Kamath: Conceptualization, Investigation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Dhiraj Brahman:** Resources, Writing – original draft. **Sailesh Chhetri:** Conceptualization, Methodology. **Patrick McArdle:** Funding acquisition, Methodology, Software. **Biswajit Sinha:** Funding acquisition, Investigation, Methodology, Project administration, Software, Supervision, Validation, Visualization.

Acknowledgments

The authors would like to acknowledge Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (SAP-DRS-III, No. 540/12/DRS/2013) & University of North Bengal, Department of Biotechnology, Govt. of West Bengal for financial and instrumental support. The authors also acknowl-edge "Centre de Diffractometrie Henri Longchambon" at Universite Claude Bernard Lyon 1 for Single crystal X-ray diffraction studies.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.131323.

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