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Synthesis, characterization, and theoretical calculations of mononuclear copper(II) benzoate complex with 2-propylimidazole, $[Cu(PIM)_2(PhCOO)_2]$

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ABSTRACT

A mononuclear copper(II) complex, $[Cu(PIM)_2(PhCOO)_2]$ (**1**) [where PIM = 2-propylimidazole] has been synthesized and characterized by elemental analysis, IR, UV–Vis, TGA, and single crystal X-ray diffraction. The structural analysis indicated that Cu(II) atom in the complex is six-coordinated in a distorted octahedral geometry by two N atoms from two 2-propylimidazole and four O atoms from two benzoate ligands. In addition, based on crystal structural data, quantum chemistry calculation in DFT/B3LYP level has been used to reoptimize and explore the electronic structure of the compound **1**; time-dependent DFT (TD-DFT) calculations have also been performed in order to elucidate its spectroscopic properties. All parameters from the calculations are in well accordance with our experimental result.

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1. Introduction

The design, synthesis, and crystal engineering of coordination complexes continue to be a quite active research field because of their enchanting structures and potential applications as functional materials [1–7]. Especially, the coordination chemistry of imidazole and its derivatives has captured the considerable attention of chemists for several decades [8,9]. The investigations in biological importance, supramolecular chemistry, electronic spectra, gas adsorption separation, and the artificial nuclease activity under appropriate conditions have been well represented [10–16]. On the other hand, copper is an essential trace element required by all living organisms, and plays a key role as an integral component of many enzymes [17,18]. Thus, the biological functional Cu(II) complexes with imidazole-based ligands have been widely studied and reported. With the further research of the series, various substituted imidazoles have been also used as the co-ligand so that the structural and electronic effects on the biologically important Cu–N (imidazole) bond could be well-elucidated [19,20].

However, the complexes of 2-propylimidazole (PIM), a 2-substituted derivative of the imidazole, have rarely been reported. In order to obtain more insight into the metal complexes of 2-propylimidazole ligand, we herein report the successful preparation and structural characterization of the $[Cu(PIM)_2(PhCOO)_2]$ (**1**) complex. Furthermore, the electronic structure of the compound has been estimated by using the density functional theory (DFT) method, and time-dependent DFT (TD-DFT) calculations have also been used for analysis of the electronic spectrum and spectroscopic properties. At present, DFT is commonly being used to assess the electronic structure of transition metal complexes [21–25]. It meets with the requirements of being accurate, easy to use, and being fast enough to allow the study of relatively large molecules of transition metal complexes.

2. Experimental

2.1. Materials and general methods

All the reagents and solvents were purchased from commercial sources and used without further purification. Elemental analyses were performed on Perkin–Elmer 240C automatic analyzer. The Infrared (IR) spectrum was recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet FT-IR 170SX spectrometer. The UV–Vis spectra were recorded on Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller in the range of 190–1100 nm. Thermal stability (TG-DTA) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 700 °C under N_2 atmosphere with a heating rate of 10 °C min^{-1}.

2.2. Synthesis of complex

$[Cu(PIM)_2(PhCOO)_2]$ (**1**). Basic copper(II) carbonate (221 mg, 1 mmol) was treated with an aqueous solution (10 mL) of benzoic

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acid (488 mg, 4 mmol) in a steam bath until the solid disappeared. The solution was then filtered and diluted to approximately 40 mL with water. An ethanol solution (10 mL) of 2-propylimidazole (441 mg, 4 mmol) is then added to above solution. The resultant clear-blue solution is warmed on a steam bath for 1 h. The volume is kept constant by periodic addition of water. Then the solution is filtered and allowed to stand at room temperature. Blue single crystals of **1** were harvested after 5 days. They are filtered, washed with water and ethanol and then air-dried. Yield: 58% (based on basic copper(II) carbonate). Anal. Found (%): C 59.50, H 5.81, N 10.72. Calc.(%) for $C_{26}H_{30}N_4O_4Cu$ ($Fw = 526.09$): C 59.31, H 5.70, N 10.65. FT-IR (cm^{-1}): 3100 (m), 2976 (s), 1600 (s), 1535 (vs), 1473 (m), 1391 (vs), 1152 (w), 1051 (w), 1023 (w), 847 (m), 729 (s). UV–vis peaks (λ_{max}, nm): 731.3, 265.7.

2.3. X-ray crystallographic

Suitable single crystal of the title complex was mounted on glass fibers for X-ray measurement. Reflection data were collected at 20 °C on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) and a ω–2θ scan mode. Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT [26], using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. All the measured independent reflections were used in the structure analyses, and semi-empirical absorption corrections were applied using the SADABS program [27]. Crystal structure was solved by the direct method and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. All the hydrogen atoms were positioned geometrically and refined using a riding model for the title complex. All the calculations were performed using the program SHELXTL program [28]. Atomic scattering factors were those incorporated in the computer programs. The crystallographic data and experimental details of the data collection and the structure refinement were given in Table 1.

Table 1
Crystal data and structure refinement for $[Cu(PIM)_2(PhCOO)_2]$.

Empirical formula	$C_{26}H_{30}N_4O_4Cu$
Formula weight ($g\ mol^{-1}$)	526.09
Crystal colour/habit	Blue block
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	7.8338(16)
b (Å)	8.3275(17)
c (Å)	11.503(2)
α (°)	84.88(3)
β (°)	70.14(3)
γ (°)	63.00(3)
Volume (Å^3)	627.0(2)
Z	1
D_{calc} ($Mg\ m^{-3}$)	1.393
Absorption coefficient (mm^{-1})	0.910
F(000)	275
Crystal size (mm)	0.24 × 0.23 × 0.16
θ range for data collection (°)	1.89–28.08
Index ranges	$-10 \leqslant h \leqslant 10$, $-10 \leqslant k \leqslant 10$, $-13 \leqslant l \leqslant 15$
Reflections collected/Independent [R_{int}]	9179/2949 [0.0206]
Completeness to $\theta = 28.08°$	96.6%
Data/restraints/parameters	2949/0/160
Goodness-of-fit on F^2	0.999
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0271$, $wR_2 = 0.0750$
R indices (all data)	$R_1 = 0.0287$, $wR_2 = 0.0761$
Largest difference in peak and hole (e Å^{-3})	0.222 and −0.306

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2=\{\Sigma[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$, $[F_o > 4\sigma(F_o)]$.

2.4. Computational details

The gas phase geometry of the $[Cu(PIM)_2(PhCOO)_2]$ was optimized without any symmetry restriction in the doublet state with the DFT method using the hybrid B3LYP functional of GAUSSIAN-03. The calculation was performed by using the standard 6-31G* basis set for C, H, N, and O atoms, and effective core potentials basis set LanL2DZ for Cu atom in the title complex [29]. The optimized geometry of the complex was verified by performing a frequency calculation. All the vibrations in the calculated vibrational spectrum of the complex were real, thus the optimized geometry corresponds to true energy minimum. The optimized geometry along the coordinates was further verified by frozen distance optimizations, which also served to obtain information about the charge/spin distributions and molecular orbital information. Net atomic charges had been obtained using the Natural bond orbital (NBO) analysis of Weinhold and Carpenter [30]. All calculations were carried on a Pentium IV computer with the GAUSSIAN-03 suite of software packages [31].

3. Results and discussion

3.1. Synthesis and spectral characterization of 1

The title complex **1** was synthesized by the reaction of basic copper(II) carbonate with benzoic acid and 2-propylimidazole in a 1:4:4 M ratio in water/alcohol mixed solvent. The result of elemental analyses for the complex is in good agreement with the theoretical requirements of their compositions (X-ray analysis). This compound is stable in air. In the IR spectrum, the characteristic bands of the C=C and C=N stretching modes of 2-propylimidazole was observed at ∼1600 and ∼1473 cm^{-1}. Bands at 2976 and 729 cm^{-1} can be assigned to the N–H stretching and bending frequencies of the PIM ligand, respectively. Asymmetric and symmetric C=O stretching modes of the coordinated benzoate moieties were evidenced by very strong, slightly broadened bands at ∼1535 and ∼1381 cm^{-1}. In comparison with benzoic acid, it can be found that the stretching characteristic bands of all carboxylate groups in the title complex are of redshift being due to the coordination of O atom to copper(II) atom, which is consistent with the results of the X-ray analysis.

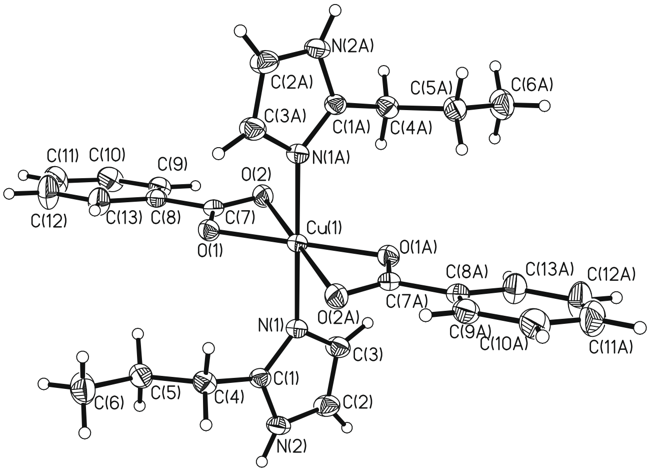


Fig. 1. A view of the molecular structure of the $[Cu(PIM)_2(PhCOO)_2]$.

Table 2
The selected experimental and optimized bond lengths (Å) and angles (°) for [Cu(PIM)$_2$(PhCOO)$_2$].

Parameters	Experimental values	Optimized values
Cu(1)–O(1)	1.9753(12)	1.9746
Cu(1)–O(1A)	1.9753(12)	1.9746
Cu(1)–N(1)	1.9882(14)	2.0066
Cu(1)–N(1A)	1.9882(14)	2.0066
Cu(1)–O(2)	2.6404(13)	2.5396
Cu(1)–O(2A)	2.6404(13)	2.5396
O(1A)–Cu(1)–O(1)	180.0	179.99
O(1A)–Cu(1)–N(1A)	90.73(6)	90.17
O(1)–Cu(1)–N(1A)	89.27(6)	89.83
O(1)–Cu(1)–N(1)	90.73(6)	90.17
O(1A)–Cu(1)–N(1)	89.27(6)	89.83
N(1A)–Cu(1)–N(1)	180.0	180.0
O(1A)–Cu(1)–O(2)	124.89(4)	122.32
O(1)–Cu(1)–O(2)	55.11(4)	57.68
N(1A)–Cu(1)–O(2)	88.87(5)	93.36
N(1)–Cu(1)–O(2)	91.13(5)	86.64
O(1A)–Cu(1)–O(2A)	55.11(4)	57.68
O(1)–Cu(1)–O(2A)	124.89(4)	122.32
N(1A)–Cu(1)–O(2A)	91.13(5)	86.64
N(1)–Cu(1)–O(2A)	88.87(5)	93.36
O(2)–Cu(1)–O(2A)	180.0	179.99

Symmetry code: A – x, $-y + 1$, $-z + 1$.

Table 3
Intermolecular H-bonding contacts detected in the [Cu(PIM)$_2$(PhCOO)$_2$] complex.

D–H…A	d(D–H) (Å)	d(H…A) (Å)	d(D…A) (Å)	∠DHA (°)
N(2)–H(2 N)…O(2)^i	0.860	2.072	2.861	152.22

^{i} The O(2) atom from adjacent benzoate ligand of another same unit connected by intermolecular H-bonding, $i = 1 + x, y, z$.

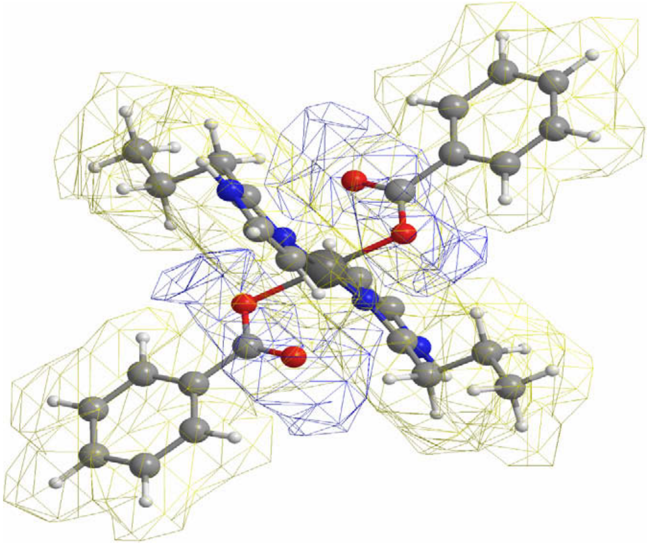


Fig. 3. Electrostatic potential map of the [Cu(PIM)$_2$(PhCOO)$_2$]. Yellow denotes the positive regions. Blue indicates the negative regions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Description of the crystal structure of complex **1**

[Cu(PIM)$_2$(PhCOO)$_2$] (**1**). The mononuclear complex **1** crystallizes in the triclinic space group $P\bar{1}$ and has an inversion centric symmetry with the Cu(II) atom being in the center of inversion. The asymmetric unit of the complex consists of half of a central Cu(II) ion, one benzoate, and one PIM ligand. Fig. 1 gives a perspective view of the molecular structure with atoms labeling. The selected bond lengths and angles are listed in Table 2. In the structure of **1**, the Cu(II) atom occupies the center of a Jahn–Teller distorted octahedral geometry and is six-coordinated by two N atoms of two PIM [1.9882(14) Å for Cu(1)–N(1)] and four carboxylate O atoms from two benzoate groups [1.9753(12) Å for Cu(1)–O(1), 2.6404(13) Å for Cu(1)–O(2)]. The two-N-donors from two PIM and two-O-donors from two benzoates form the basal plane; the remaining two benzoate-O-donors constitute the axial directions. The axial Cu–O [Cu(1)–O(2)] distances are longer than those on the equatorial positions being comparable to the values reported in the literature [16b], indicating that the O(2)-donor is more loosely bound with the metal center.

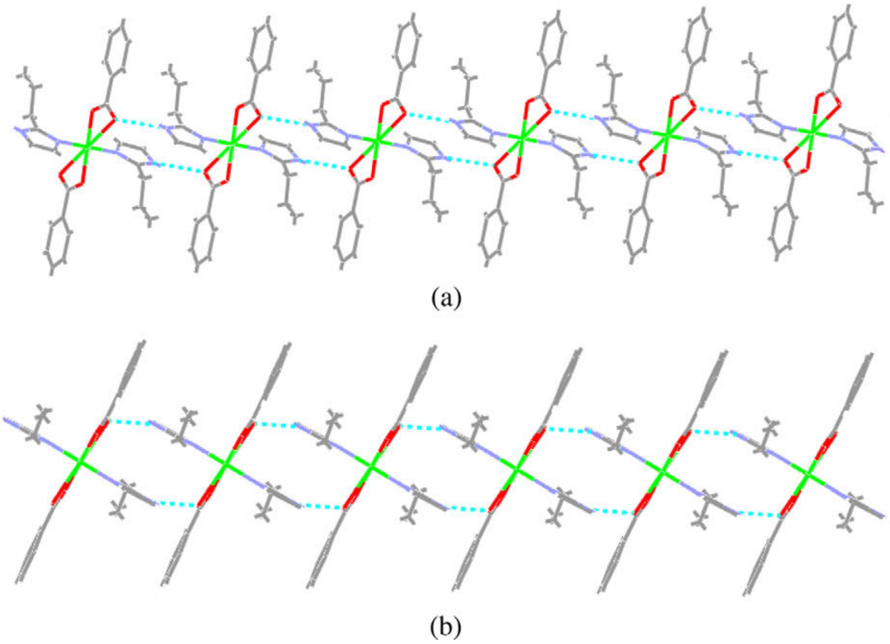


Fig. 2. 1D double-bridged chain structure of the title complex constructed by intermolecular H-bonds: (a) viewed along the *b*-axis and (b) viewed along the *c*-axis.

Table 4
Natural atomic charges and natural electron configuration of part atoms in the $[Cu(PIM)_2(PhCOO)_2]$ complex.

Atoms	Net Charge	Electron Configuration
Cu(1)	1.32497	[core]4s(0.33)3d(9.30)4p(0.01)4d(0.02)5p(0.01)
O(1)	−0.77747	[core]2s(1.72)2p(5.04)3p(0.01)3d(0.01)
O(1A)	−0.77738	[core]2s(1.72)2p(5.04)3p(0.01)3d(0.01)
O(2)	−0.74343	[core]2s(1.72)2p(5.00)3p(0.01)3d(0.01)
O(2A)	−0.74332	[core]2s(1.72)2p(5.00)3p(0.01)3d(0.01)
N(1)	−0.57808	[core]2s(1.36)2p(4.19)3p(0.02)
N(1A)	−0.57813	[core]2s(1.36)2p(4.19)3p(0.02)

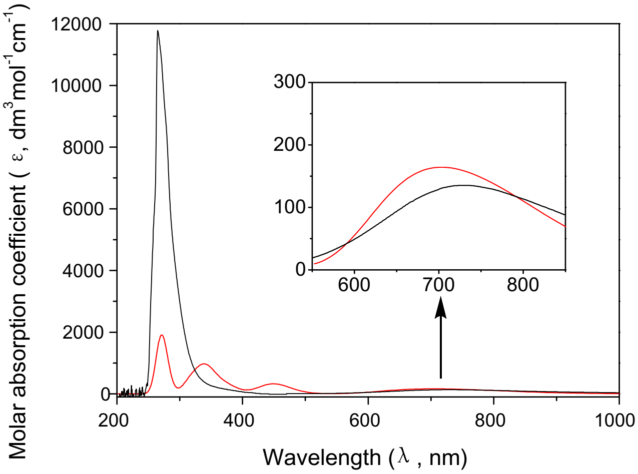


Fig. 4. The experimental (black) and calculated (red) electronic absorption spectra of $[Cu(PIM)_2(PhCOO)_2]$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Analysis of the crystal packing of **1** shows that a 1D chain is formed by the linkage of hydrogen bonds between O atoms of benzoate ligand and the H atoms of the imidazole ring [N(1)–H(2B)···O(2)^i ($i = 1 + x, y, z$)] (Fig. 2). The related hydrogen-bonding bond distance and angle are as follows: H(2B)···O(2) = 2.861(2) Å and N–H···O = 152°, being in the normal range of such interactions (Table 3). Another noteworthy structural feature of **1** is that one ortho-H atoms (H4B) from the side chain of imidazole point towards the centre of an imidazole ring (Cg: N1–C1–N2–C2–C3, symmetry related by the transformation of 1 − x, 1 − y, 1 − z) to form additional weak interactions. Comprehensive analysis C–H···π interaction carried out with the program PLATON [32] shows that the H···ring centroid (H···Cg) distance is 2.84 Å, C···Cg distance is 3.6195(19) Å, H···ring plane perpendicular distance is 2.785 Å, and the C–H···Cg angle is 138°, being below the optimal value (180°) for the strongest C–H···π interaction, which may be due to the steric constraint in the molecular packing. The γ angle is found to be 11.47°.

The bond valence theory is an effective and important method for understand the intensity of coordinate bonds. In order to explore the coordination bonds of the complex, the bond valences were calculated by the formula of $S_{ij} = \exp[(R_{ij} - r_{ij})/B]$, where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single bond length between i and j atoms), r_{ij} is bond length between i and j atoms and B was taken as 0.37 [33].

The R_{Cu-O} and R_{Cu-N} were taken as 1.679 [34] and 1.713 [35], respectively. The computed bond valences of the copper(II) center are $S_{Cu(1)-O(1)} = 0.449$, $S_{Cu(1)-O(2)} = 0.075$ and $S_{Cu(1)-N(1)} = 0.475$, thus the computed valence of the Cu atom is 1.998 valence units. The deviation of valence sum range larger than 0.5–0.1 valence units can indicate omission or misinterpretation of coordination sphere. It can be considered that in the complex the copper atom is six-coordinated even weak interactions are included. In addition, it is noteworthy that Cu(1)–O(2) bond-valence is smaller than Cu(1)–O(1) and Cu(1)–N(1), indicating that Cu(1)–O(2) bond is a reasonably weak coordination.

3.3. Geometry optimization and population analysis

The geometry of $[Cu(PIM)_2(PhCOO)_2]$ was optimized in doublet state using the DFT method with the B3LYP functional. The optimized geometric parameters are collected in Table 2. In general, the predicted bond lengths are somewhat longer than the values from the X-ray crystal structure data, and the general trends observed in the experimental data are well reproduced in the calculations. The differences both the calculated and experimental value are 0.1 Å smaller for all the selected bond lengths and 5° for all the selected bond angles. Some discrepancies between the theoretical and experimental structural parameters could be attributed to the intermolecular hydrogen bonding in the crystal, because the theoretical study has been done on an isolated molecule.

The calculated net charge on the Cu atom in $[Cu(PIM)_2(PhCOO)_2]$ is equal to 1.32497 deviating significantly from the formal charge +2, being a result of charge donation from the donor atoms of ligands. Namely, the net charge of coordinated N and O atoms

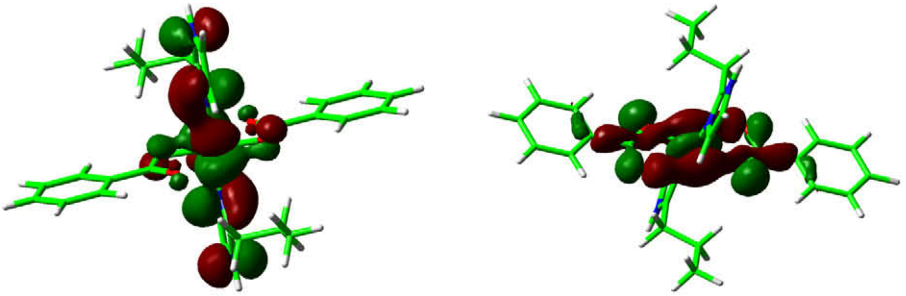
Table 5
The assignments of the calculated transitions to experimental absorption bands and electronic transition properties of the title complex.

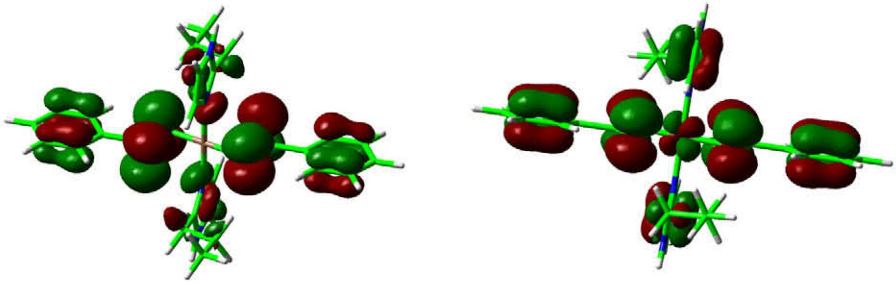
The most important orbital excitations	Transition character	Calculated (nm)	E (eV)	Oscillator strength	Experimental (nm)
HOMO-6(β)→LUMO(β)	π(benzoate)/d_{yz}/π(PIM)→$d_{x^2-y^2}$	832.9	1.49	0.0002	–
HOMO-8(β)→LUMO(β)	π(benzoate)/d_{xy}/π(PIM)→$d_{x^2-y^2}$	740.3	1.67	0.0013	731.3
HOMO-11(β)→LUMO(β)	π(benzoate)/d_{z2}→$d_{x^2-y^2}$	614.5	1.85	0.0007	–
HOMO-3(β)→LUMO(β)	π(benzoate)/π(PIM)→$d_{x^2-y^2}$	541.2	2.23	0.0003	–
HOMO-1(β)→LUMO(β)	π(benzoate)/d_{yz}/π(PIM)→$d_{x^2-y^2}$	493.1	2.43	0.0005	–
HOMO-2(β)→LUMO+1(β)	π(benzoate)/π(PIM)→$d_{x^2-y^2}$				
HOMO-14(β)→LUMO(β)	π(PIM)/d_{yz}→$d_{x^2-y^2}$	444.2	2.87	0.0035	–
HOMO-2(β)→LUMO+1(β)	π(benzoate)/π(PIM)→$d_{x^2-y^2}$				
HOMO-3(β)→LUMO(β)	π(benzoate)/π(PIM)→$d_{x^2-y^2}$	339.0	3.41	0.0116	–
HOMO-1(β)→LUMO(β)	π(benzoate)/d_{yz}/π(PIM)→$d_{x^2-y^2}$				
HOMO-4(α)→LUMO+1(α)	π(benzoate)→π*(benzoate)	314.6	3.94	0.0007	–
HOMO-9(β)→LUMO(β)	(P, σ)/π(benzoate)→$d_{x^2-y^2}$	281.9	4.39	0.0036	–
HOMO-5(α)→LUMO(α)	π(benzoate)→π*(benzoate)				
HOMO-3(β)→LUMO(β)	π(benzoate)/π(PIM)→$d_{x^2-y^2}$	271.3	4.56	0.0264	265.7
HOMO-2(β)→LUMO+1(β)	π(benzoate)/π(PIM)→$d_{x^2-y^2}$				
HOMO(α)→LUMO+4(α)	π(PIM)→π*(PIM)	259.4	4.78	0.0002	
HOMO-5(β)→LUMO+2(β)	π(PIM)/d_{xy}→π*(PIM)				

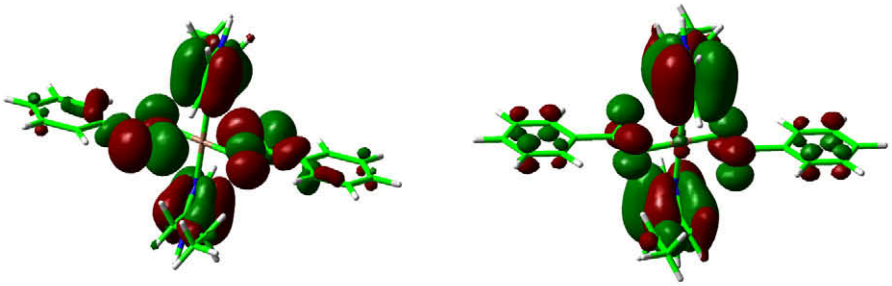
range from −0.77747 to −0.57808, showing that part electrons transfer from N and O atoms to Cu atom and the coordinate bonds come into being. The obtained positive charges of every benzoate ligand and every PIM ligand from Cu(II) ion are 0.21055 and 0.12684, respectively, indicating that the interaction of copper ion and benzoate ligand is stronger than that of PIM ligand. Moreover, the electrostatic potential also demonstrates that such strong coordination behavior of the benzoate ligands with Cu atom and the benzoate ligands are yet quite well activity after coordinated (Fig. 3).

As shown in Table 4, the electron number of Cu 3d orbit is 9.30 and that of 4s orbit is 0.33 (the electron numbers of 4d, 4p and 5p are so small that can be omitted). From the above analysis we can conclude that the Cu atom coordination with N and O atoms is on 3d ($3d_{x^2-y^2}$ and 3 d_{z^2} are revealed by NBO orbital analysis) and 4s orbits. The electron number of N 2s orbit is 1.36 and 2p that of orbit is 4.19, showing that the N atoms form coordination bonds with Cu atom by using 2s and 2p (mainly from $2p_x$ orbit indicated by NBO orbit analysis) orbits. In the same way, all O atoms supply electrons of 2s (1.72) and 2p (range from 5.00 to 5.04) to Cu and form the coordination bonds. Thus, according to Valence-bond theory the $[Cu(PIM)_2(PhCOO)_2]$ complex shows covalent-type Cu-ligand interactions.

The energy of the title complex in ground state is -1.99×10^6 kcal/mol. The HOMO(β) and LUMO(β) energies of molecular orbitals are −5.74 eV and −1.25 eV, respectively, indicating that this config-


HOMO-14 (-7.75 eV) HOMO-11 (-7.43 eV)


HOMO-9 (-6.70 eV) HOMO-8 (-6.60 eV)


HOMO-3 (-6.30 eV) HOMO-1 (-6.22 eV)

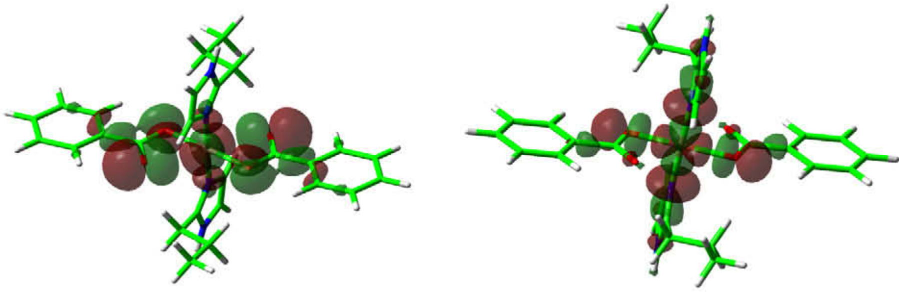

HOMO (-5.74 eV) LUMO (-1.25 eV)

Fig. 5. Contour plots and energy of the selected β-spin HOMO and β-spin LUMO orbitals active in the electronic transitions for the title complex.

uration is stable. Dipole moment of the complex is 0.0001 Debye, indicating the nonpolarization.

3.4. Electronic spectrum and spectroscopic properties

The nature of the transitions observed in the UV–vis spectrum of the title complex has been studied by the time-dependent density functional (TD-DFT) method. The calculated electronic spectrum of $[Cu(PIM)_2(PhCOO)_2]$ in comparison with the experimental one is presented in Fig. 4. The most important calculated electronic transitions and their assignments to the observed absorption bands of the complex were presented in Table 5. The UV–vis spectra of the complex display clearly the two absorption bands at 731.3 and 265.7 nm. The selected β-spin electron orbitals and energies of the title complex are given in Fig. 5.

TD-DFT calculations showed that the calculated absorption maxima (740.3 and 271.3 nm) are based on the β-spin LUMO frontier orbital as the main arrival orbital of transitions and the ligand π bonding orbitals as the main starting ones of transitions. Because of the Cu $3d_{x^2-y^2}$ orbital character of the β-spin LUMO (mentioned above), these absorption bands should be mainly ascribed to similar $\pi \rightarrow d_{x^2-y^2}$ ligand-to-metal charge transfer (LMCT). As shown in Table 5, the TD-DFT calculated results are in well agreement with experimental ones.

In general, the absorption bands in experimental UV–vis spectra originate from the transitions from ground state to excited states with higher energy [36–38]. According to our TD-DFT calculations, the absorption band at 740.3 nm with an oscillator strength 0.0013 can be correlated to the 731.3 nm band in experimental electronic spectrum. This absorption maximum is mainly associated with the transition from HOMO-8(β) to LUMO(β) with configuration interaction coefficient up to 0.93, and can be reasonably ascribed to π(benzoate)/π(PIM)$\rightarrow d_{x^2-y^2}$ ligand-to-metal charge transfer (LMCT) and $d_{xy} \rightarrow d_{x^2-y^2}$ ligand field (LF) transitions. Similarly, the calculated absorption maximum at 271.3 nm with an oscillator strength 0.0264 can be correlated to the band at 265.7 nm absorption band in experimental spectrum. This absorption maximum is mainly associated with transition from HOMO-3(β) to LUMO(β) with configuration interaction coefficient up to 0.88 and transition from HOMO-2(β) to LUMO+1(β) with configuration interaction coefficient up to 0.31, thus it can be mainly ascribed to π(benzoate)/π(PIM)$\rightarrow d_{x^2-y^2}$ ligand-to-metal charge transfer (LMCT).

In addition, some predicted absorption bands could not been observable in experimental UV–vis spectrum, being mainly due to their relatively low oscillator strengths and higher transition energies required. These calculated absorption bands mainly arise from π(benzoate)/π(PIM)$\rightarrow d_{x^2-y^2}$ ligand-to-metal charge transfer (LMCT) and $d_{yz} \rightarrow d_{x^2-y^2}$ ligand field (LF) transitions of β-spin electron orbitals and π(benzoate)$\rightarrow \pi^*$(benzoate) intraligand (IL) transition of α-spin electron orbitals.

In summary, our TD-DFT calculations predict the all absorption bands in experimental UV–vis spectrum for the title complex. Meanwhile, it can be conclude that the low-lying absorption bands are $\pi \rightarrow d_{x^2-y^2}$ and/or $(P, \sigma) \rightarrow d_{x^2-y^2}$ ligand-to-metal charge transfer (LMCT) without almost d→d ligand field (LF) transition in nature.

3.5. Thermal properties

The thermal stability of the complex **1** in N_2 atmosphere was examined by the TG-DTA techniques in the temperature range of 20–1000 °C. The thermal decomposition process of the complex can be divided into two steps from the TG curve. The first weight loss of 51.77% between 191.6 and 270.5 °C corresponds to the release of two PIM ligands and one CO_2 molecule (50.28% theoretical weight loss). The DTA curve of the complex indicates that it is an endothermic process. The second weight loss of 31.03% was observed in the temperature range of 270.5–584.5 °C, which is attributed to the release of one benzoate group and one benzene ring residue (33.04% theoretical weight loss) leading to the decomposition of the complex to CuO with a residual mass of 17.20% (in good agreement with the calculated value of 16.68%).

4. Conclusion

A mononuclear copper(II) complex with both benzoate and 2-propylimidazole ligands has been synthesized and structurally characterized and its geometric parameters, electronic structure, spectroscopic property, and thermal property were investigated by combining X-ray crystallography, spectroscopy, DFT/TD-DFT theoretical calculations and TG-DTA test. The optimized geometry from calculations is in well agreement with that from X-ray single-crystal structural determination. In addition, the electronic structure is well evaluated on the calculation, as well as the spectroscopic characterizations from experiments and calculations also march well. In summary, this work has combined the theoretical calculation and experimental characterizations into the investigation of coordination complex, a strategy being useful for similar systems in coordination chemistry.

5. Supplementary Materials

CCDC-750290 contains the supplementary crystallographic data for **1**. This data can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

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