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New 5-bromo-2-hydroxybenzaldehyde *S*-ethyl-isothiosemicarbazone and its mixed-ligand Cu(II) complex with imidazole: synthesis, characterization and DFT calculation

Research Article

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Abstract: A new Schiff base ligand of 5-bromo-2-hydroxybenzaldehyde *S*-ethyl-isothiosemicarbazone (H_2L) was synthesized and its mixed-ligand Cu(II) complex was also prepared by reaction of $Cu(NO_3)_2$•$3H_2O$ with H_2L and imidazole. Their structures were fully characterized by elemental analysis, FT-IR, molar conductivity and UV–Vis methods. The analytical data suggest that the metal, H_2L and imidazole ratios in the Schiff base complex are 1:1:1. Single crystal diffraction was also used to better understand the molecular structure of the Cu(II) complex. The results of physico-chemical analyses of the Schiff base complex reveal the coordination geometry around the central atom is square planar. The H_2L ligand (NNO donor) is coordinated to the metal center as a tridentate bionegatively agent. Another position of the square planar geometry is occupied by the imidazole ligand. Furthermore, computational studies of the new complex were performed by carrying out DFT calculations. Geometry optimization and natural band analysis of the complex is discussed in further detail.

Keywords: *Schiff base • Isothiosemicarbazone • Cu(II) complex • Crystal structure • DFT*

1. Introduction

There has been increasing interest in research on copper complexes because of their photophysical behavior [1], as well as electrochemical and corrosion inhibiting properties [2,3]. Copper complexes show great potential in the area of organic chemistry [4]. From a bioinorganic perspective, copper complexes have been extensively studied due to their similarity to metalloproteins. This has introduced copper compounds as significant active sites [5]. In addition, a large number of copper(II) complexes with Schiff base ligands have also been prepared and their catalytic abilities have been investigated [6].

The chemistry of imidazole derivatives has attracted attention due to its wide application in medicine [7], and its presence in important biological building-blocks such as histidine and histamine [8,9], antifungal drugs [10], fuel cell membranes [11] and luminescent materials [12]. The most important property is that the

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interaction of small molecules such as imidazole with DNA has shown suitable quality in recent years [13]. The facile redox behavior of Cu(II) has made the ion an intriguing target for artificial nuclease design [14]. In this work, we have described the syntheses and characterizations of 5-bromo-2-hydroxybenzaldehyde *S*-ethyl-isothiosemicarbazone ligand and (5-bromo-2-hydroxybenzaldehyde *S*-ethyl-isothiosemicarbazonato-N,N',O)-(imidazole)-copper(II) complex (Cu(L)Im, Im:imidazole) as two new compounds by spectral properties and micro analysis. The solid-state structure of the Cu(II) complex was also investigated. In addition, we use density functional theory to predict geometry optimization and natural band analysis. More recently, DFT (Density Functional Theory) calculations were used to investigate natural band behavior [15,16].

2. Experimental procedure

2.1. Physical measurements

All solvents and metal salt were of analytical reagent grades and used without any further purification. The infrared spectra were recorded on an 8400-SHIMADZU FT-IR spectrometer. Solid samples were examined as KBr discs. The electronic spectra were recorded on a SHIMADZU model 2550 UV–Vis spectrophotometer at concentrations of $2×10^{-5}$ and $1×10^{-3}$ M. ^{1}H NMR spectra were recorded on a Bruker BRX 100 AVANCE spectrometer in DMSO-d_6. C, H and N elemental analyses were performed on a Thermo Finnigan Flash Elemental Analyzer 1112EA instrument. Electric conductance measurements were carried out with a Metrohm 712 Conductometer at a concentration of $1×10^{-3}$ M in methanol. Diffraction data were measured using a Bruker APEX II CCD diffractometer.

2.2. Preparation of 5-bromo-2-hydroxybenzaldehyde S-ethyl-isothiosemicarbazone (H_2L)

Thiosemicarbazide (0.91 g, 10 mmol) was treated with ethyl iodide (1.72 g, 11 mmol) in 10 ml ethanol for 1 h at 90°C until all solid vanished. 5-bromo-2-hydroxybenzaldehyde (2.01 g, 10 mmol) was added to the reaction and reflux continued for one hour extra. A yellow precipitate was filtered off. After completely drying, it was dissolved in 50 mL of chloroform, and 10 mL of aqueous $Na_2CO_3•10H_2O$ (2.68 g, 10 mmol) was added to neutralize hydrogen iodide in constant stirring at room temperature. The two layers were separated and the organic layer left to stand overnight. A colorless precipitate separated. It was washed several times with ethanol and chloroform and dried *in vacuo* over silica gel.

Yield: 2.48 g (82%). M.p. 137°C. FT-IR (film): v_{as} = 3286 (NH_2), v_{sy} = 3203 (NH_2), v = 3062 (OH), 2854-293 (CH), 1639 (v(C=N) + δ(NH_2)), 1600 & 1516 (C=N + C=C), 1473 (C=C), 1184 (C-O), 1080 (N-N), δ = 648 (CH). ^{1}H NMR (100 MHz, DMSO-d_6): δ = 11.7 (s, 1H, O1H), 10.8 (s, H, N3bH), 8.4 (d, 1H, C7H), 7.9 (d, 1H, N2bH), 7.7 (d, 1H, C5), 7.4 (dd, 1H, C3), 7.1 (s, 2H, N3H_2), 6.8 (d, 1H, C2), 3 (q, 2H, C9), 1.3 (t, 3H, C10). Anal. Calc. for $C_{10}H_{12}BrN_3OS$: C, 39.75; H, 4.00; N, 13.91. Found: C, 39.31; H, 4.06; N, 13.76%. UV/Vis (methanol): λ_{max} (lg ε_{max}): 224 nm (4.43), 240 nm (4.35), 298 nm (4.28), 344 nm (4.22). Molar conductivity (1.0Í10^{-3} M; methanol): 23 Ω^{-1} cm^2 mol^{-1}.

2.3. Preparation of (5-bromo-2-hydroxybenzaldehyde S-ethyl-isothiosemicarbazonato-N,N',O)-(imidazole)-copper(II)

H_2L (0.30 g, 1 mmol) was dissolved in 5 mL of ethanol and added dropwise to a 5 mL ethanolic solution of a mixture of $Cu(NO_3)_2•3H_2O$ (0.24 g, 1 mmol) and imidazole (0.07 g, 1 mmol) at room temperature. The solution color gradually turned back to red after three hours. The clear solution was put in a refrigerator to produce suitable crystals. The appropriate single crystals were obtained after one week. They were separated and washed several times with cold ethanol and dried in vacuo over silica gel.

Yield: 0.24 g (55%). M.p. 186°C. FT-IR (film): v = 3409 $(NH)_{Im}$, 3117 (N3H), 3039-3050 $(CH)_{Im}$, 2854-2931 $(CH)_{ar}$, 1597 & 1497 (C=N + C=C), 1452 (C=C), 1157 (C-O), 1064 (N-N), δ = 656 (CH). Anal. Calc. for $C_{13}H_{14}BrCuN_5OS$: C, 36.16; H, 3.27; N, 16.22. Found: C, 36.51; H, 3.16; N, 16.06%. UV/Vis (methanol): λ_{max} (lg ε_{max}): 222 nm (4.36), 242 nm (4.4), 340 nm(4.06), 392 nm(4.22), 580 nm (2.3). Molar conductivity ($1.0×10^{-3}$ M; methanol): 11 Ω^{-1} cm^2 mol^{-1}.

2.4. Crystal structure determination

Data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo Ka radiation (λ = 0.71073 Å). Data collection, cell refinement, data reduction and absorption correction were performed using multi scan methods with Bruker software [17]. The structure was solved by direct methods using SIR2004 [18]. The non hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL [19]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to remain on their parent atoms. The crystal data, data collection parameters, and structure solution and refinement details for the determined structure is reported in Table 1.

2.5. Computational methods

The geometry of the copper(II) structure was optimized at the DFT level by using the B3LYP method [20,21] with the Gaussian 98 program [22]. In the unrestricted calculations, the 6-311++G(d,p) basis set was employed on C, H, N, S and O atoms and LANL2DZ [23] was selected on the central ion. The full optimization of the initial geometry was modified by frequency calculation that does not show any imaginary frequency, confirming geometry optimization was carried out successfully. In addition, natural band orbital (NBO) analysis was done with the NBO code included in Gaussian 98 [24].

3. Result and discussion

In ethanol, the reaction of 5-bromo-2-hydroxybenzaldehyde *S*-ethyl-isothiosemicarbazone (H_2L) with copper(II) nitrate trihydrate and imidazole, using a (1:1:1) molar ratio, yields a new Cu(II) mixed-ligand complex. The molar conductivities of the ligand and the complex are 23 and 11 Ω^{-1} cm^{2} mol^{-1} in methanol respectively, indicating H_2L is neutralized successfully and a neutral Cu(II) complex is formed [26]. The two new compounds have good solubility in DMF and DMSO, less solubility in common organic solvents like methanol, acetone, chloroform and diethyl ether, and are insoluble in benzene and *n*-hexane.

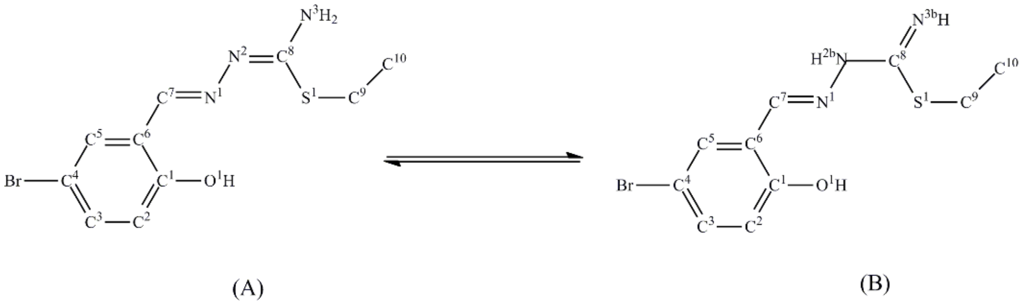
3.1. Spectral properties

All spectra of the H_2L and Cu(II) complex are presented in the supplementary material. H_2L has two characteristic IR absorption bands at 3286 cm^{-1} and 3203 cm^{-1}, indicative of asymmetric and symmetric vibrations of the NH_2 group respectively [27]. The OH stretching vibration is located at 3062 cm^{-1} [28]. The IR spectrum of ligand also exhibited four strong bands related to v(C=N) + $\delta(NH_2)$ at 1639 cm^{-1}, v(C=N) + v(C=C) at 1600 cm^{-1}, 1516 cm^{-1} and v(C=C) at 1473 cm^{-1}. A band with medium intensity at 1184 cm^{-1} is assigned to the v(C-O) vibration band [29,30]. The IR spectrum of the complex shows two sharp bands at 3409 cm^{-1} and 3117 cm^{-1} attributed to v(NH) of imidazole and deprotonated NH_2 respectively, in agreement with the coordination of the Schiff base to the metal ion through the thioamide nitrogen and imidazole nitrogen atoms respectively [31,32]. Two intensive bands at 1597 cm^{-1} and 1497 cm^{-1} are ascribed to the conjugation of v(C=N) + v(C=C) stretching vibrations [33]. The stretching vibration of the C-O band appears at 1157 cm^{-1} which shows a 27 cm^{-1} blue shift as compared to the free ligand, modifying coordination through the oxygen atom that is also supported by elimination of the v(O-H) peak [34].

Table 1. Crystal data and structure refinement for Cu(II)-complex.

Empirical formula	$C_{13}H_{14}BrCuN_5OS$
Formula weight	431.80
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.5705(3) Å α = 76.946(2)° b = 8.9644(3) Å β = 88.597(2)° c = 12.9346(5) Å δ = 70.021(2)°
Volume	802.33(5) Å^{3}
Z, Calculated density	2, 1.787 Mg m^{-3}
Absorption coefficient	3.989 mm^{-1}
F(000)	430
Crystal size	0.14×0.08×0.05 mm
Theta range for data collection	2.49° to 27.55°
Limiting indices	-9<=h<=9, -11<=k<=11, -16<=l<=16
Reflections collected / unique	15392 / 3698 [$R_{(int)}$ = 0.0238]
Completeness to theta = 27.55	99.8%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3698 / 0 / 200
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0907
R indices (all data)	R1 = 0.0406, wR2 = 0.0969
Largest diff. peak and hole	0.608 and -0.662 e. Å^{-3}

In the UV-Vis spectrum of H_2L, the two bands at 224 nm and at 240 nm are attributed to the $\pi \rightarrow \pi^*$ transition of the benzene ring of 5-bromo-salicylaldehyde. The azomethine and thioamide chromophore $n \rightarrow \pi^*$ transitions are observed at 298 nm and 344 nm, respectively [35]. For the Cu(II) complex, the two bands at 222 nm and 242 nm in the UV-Vis spectrum are attributed to the $\pi \rightarrow \pi^*$ transition of the aromatic ring. The lower energy band at 340 nm is related to the $n \rightarrow \pi^*$ transition [36]. Similar to other square planar Cu(II) complexes, the fourth band at 392 nm reveals coordination of the ligand to metal center. The high epsilon value of log ε= 4.22 confirms this band is due to MLCT (metal to ligand) and LMCT (ligand to metal) charge transfer transitions [37]. Three spin transitions are possible for four-coordinated Cu(II) complexes



Scheme 1. The two tautomeric forms of H_2L with numbering view used for the assignment of ^1H NMR.

that are assigned as follows: $^2A_{1g}\rightarrow{}^2B_{1g}$, $^2B_{2g}\rightarrow{}^2B_{1g}$ and $^2E_g\rightarrow{}^2B_{1g}$. The high intensity charge transfer bands masked $^2A_{1g}\rightarrow{}^2B_{1g}$ and $^2B_{2g}\rightarrow{}^2B_{1g}$ transitions and only the $^2E_g\rightarrow{}^2B_{1g}$ transition displays at 580 nm with a low intensity of log ε = 2.3 [38].

The ^1H NMR spectrum of H_2L was recorded in DMSO solvent. Two tautomeric forms of H_2L along with their numbering are depicted in Scheme 1. The ^1H NMR spectrum shows a broad peak at 11.7 ppm, corresponding to the OH proton resonance; two singlet signals due to the $N^{3b}H$ and $N^{2b}H$ resonance at 10.8 ppm and 7.9 ppm; and a broad signal recorded at 7.1 ppm corresponds to N^3H_2, which corroborate the existence of both tautomeric forms in solution. The OH, $N^{3b}H$, $N^{2b}H$ and N^3H_2 signals disappear in the presence of D_2O, which is evidence of their exchangeability. A sharp single peak appears at 8.4 ppm, corresponding to the azometinic proton. The signals of aromatic protons corresponding to C5, C3 and C2 appear at 7.7, 7.4 and 7.1 ppm as a doublet, doublet- doublet and singlet respectively. Finally, the C9 and C10 protons appear as triplet and quartet peaks at 3 and 1.3 ppm.

3.2. Crystal structure of Cu(II) complex

The best resolution of the structure of the Cu(II) complex was achieved by single crystal X-ray diffraction. An ORTEP diagram of molecular structure and a unit cell of the complex by 30% thermal ellipsoids are presented in Fig. 1. Selected bond lengths and angles around the central ion are summarized in Table 2. [Cu(L)Im] crystallizes in the triclinic P-1 space group with unit cell parameters a = 7.5705(3) Å, b = 8.9644(3) Å, c = 12.9346(5) Å , α = 76.946(2)°, β = 88.597(2)°, γ = 70.021(2)° with two molecules in the unit cell. The complex has the expected square planar arrangement around the central metal ion. The *S*-ethyl fragment is in the *trans* position with respect to the N3 atom, indicating that the ligand coordinated to the metal center is in the *syn* configuration. The ligand behaves as a NNO donor tridentate bi-negative agent. The coordination is through the anionic phenol oxygen atom, the neutral azomethine nitrogen and the anionic thioaminenitrogen atoms. The remaining site of the square planar geometry is occupied by imidazole.

The donor-copper bonds are Cu1-O1, Cu1-N1, Cu1-N3 and Cu1–N4 with bond lengths of 1.892(2) Å, 1.956(2) Å, 1.920(3) Å and 1.981(2) Å, respectively, which conform with observed values in this class copper(II) complex [39]. The bond distances and bond angles found in the aromatic ring and *S*-ethyl fragments are in good agreement with corresponding values for the related compound [40]. The bond distances C8-N2 = 1.332(3) Å and C8-N3 = 1.315(3) Å are between the double and single C-N bond comparing with some transition metal complexes with tridentate *S*-alkyl-lisothiosemicarbazones, indicating a large electron delocalization in the iosthiosemicarbazone fragment [41]. The four bond angles N3-Cu1-N4, N3-Cu1-N1, N1-Cu1-O1 and O1-Cu1-N4 around the copper(II) center are 96.84(9)°, 80.64(9)°, 92.92(9)° and 89.92(9)° respectively. The significant discrepancy between N3-Cu1-N1 and the other angles is due to formation of a five membered chelating ring. This observation is also noted in a related copper(II) complex [42]. It is interesting that the imidazole ring is shifted toward the O atom, as shown by the angle O1-Cu1-N4 of 89.92(9)° compared with N3-Cu1-N4 of 96.84(9)°. This phenomenon may be due to steric effects. The weak interactions between C13 with C7 and N1 make a dimer that associates with other molecules through hydrogen bonding. The dimer has an inversion center and one molecule (sym. Code x,y,z) converts to another (-x,-y,-z) via inversion at [0,0,0]. These dimers form a one-dimensional chain with N5 and N2 interaction along the *ab* plane bisector (Fig. 2).

3.3. Geometry optimization and NBO analyses

The geometry of the Cu(II) complex was optimized completely. Some important bond lengths and angles around the central ion of the Cu(II) complex are shown in Table 2. Generally, the calculated bond lengths and angles are fairly consistent with the X-ray crystal

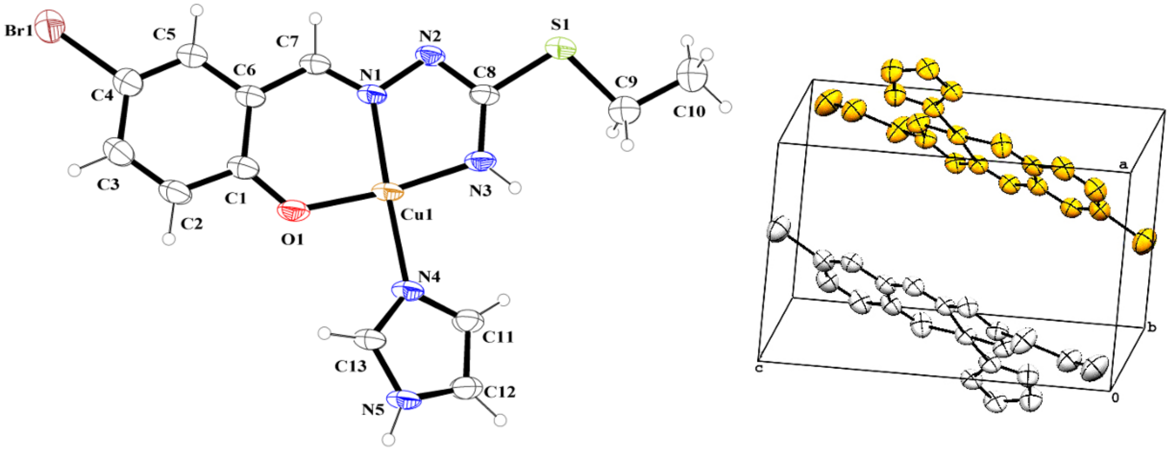


Figure 1. ORTEP drawing of the molecular structure and unit cell of the complex [Cu(L)Im].

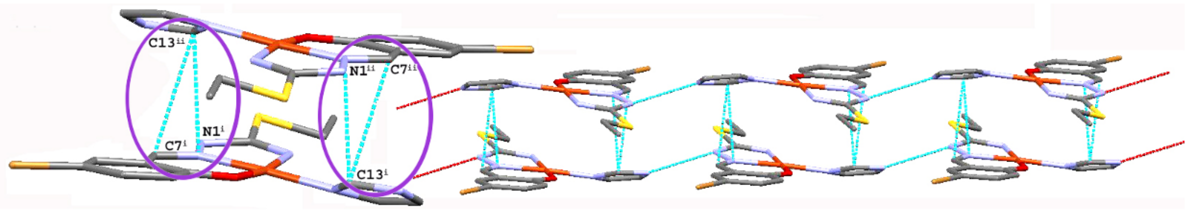


Figure 2. Crystal packing diagram (sym. code i: x,y,z ii: -x,-y,-z).

Table 2. Selected bond lengths (Å) and angles (°) in the experimental and at the B3LYP/6-311++G calculation.

type	Exp.	Calc.	Type	Exp.	Calc.
Cu1-O1	1.892(2)	1.937	O1-Cu1-N4	89.92(9)	88.7
Cu1-N4	1.981(2)	2.063	O1-Cu1-N1	92.92(9)	92.4
Cu1-N1	1.956(2)	1.987	O1-Cu1-N3	171.11(9)	172.3
Cu1-N3	1.920(3)	1.969	N4-Cu1-N1	175.91(9)	178.2
S1-C8	1.756(3)	1.788	N4-Cu1-N3	96.84(9)	98.9
S1-C9	1.803(3)	1.837	N1-Cu1-N3	80.64(9)	79.8
O1-C1	1.295(3)	1.309	C8-S1-C9	104.1(2)	102.8
N1-N2	1.391(3)	1.371	Cu1-O1-C1	127.9(2)	128.0
N1-C7	1.275(3)	1.295	N1-N2-C8	109.0(2)	110.2
N2-C8	1.332(3)	1.319	Cu1-N3-C8	112.2(2)	110.6
N3-C8	1.315(3)	1.335	N2-C8-N3	122.8(2)	123.5
C7-C6	1.436(4)	1.439	N1-C7-C6	124.2(2)	125.5

structure result. Maximum deviations are 0.082 Å and 2.3° for the Cu1-N4 bond and the N4-Cu1-N1 angle, respectively, at the B3LYP/6-311++G(d,p) level. The deviations between experiments and calculations may be due to choice of an approximate basis set in the calculations. The X-ray crystal diffraction was applied in the solid state, whereas the theoretical calculations were performed in the gas phase without considering effects of the chemical environment [43]. The dipole moment of the Cu(II) complex was evaluated to be 11.74 Debye into the XY plane, which shows that all electronegative atoms (Cu, N, O, Br and S) lie in the plane frame in the square planar environment and they do not show significant displacement toward the Z axis. Table 3 presents additional results obtained from the NBO analysis. There are more spin densities around the

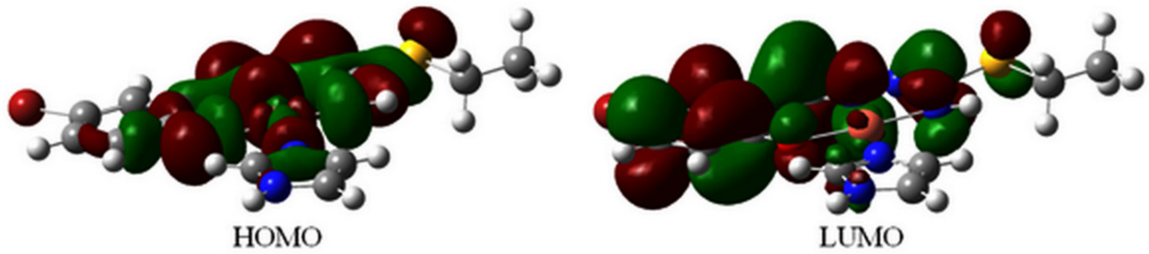


Figure 3. Contour plots of the HOMO and LUMO orbitals of the Cu(II) complex.

Table 3. Electron population, spin densities and charge of central ion, nitrogen and oxygen atoms.

atom	Electron population of the valence core	spin densities	Charge
Cu1	4S (0.32), 3d (9.39)	0.512	0.080
O1	2S (1.67), 2p (5.08)	0.109	-0.324
N4	2S (1.36), 2p (4.17)	0.058	0.001
N1	2S (1.31), 2p (3.99)	0.177	-0.005
N3	2S (1.40), 2p (4.47)	0.116	0.230

copper atom as compared to the nitrogen and oxygen donor atoms. The formal charges calculated from the natural population analysis on the central ion, O1, N1, N3 and N4 were found to be 0.08 a.u., -0.324 a.u., 0.001 a.u., -0.005 a.u. and 0.23 a.u. respectively, which indicate that donor atoms transmit electrons toward the central atom.. The calculated formal charge of Cu(II) is much lower than the expected +2, indicating charge donation of donor atoms toward the central ion. No bonds were detected between the central ion and donor atoms N1 and N2 in the NBO analysis, which may be due to weak interactions between Cu(II) with N1 and N2 atoms [44]. Fig. 3 depicts the HOMO and LUMO orbitals of the copper(II) complex. As can be seen in Fig. 3, a substantial contribution of electron density is localized toward the tridentate NNO donor ligand and the central ion in the HOMO orbital. The majority of the LUMO is also located on the ligand, though a little is also located on the Cu(II) atom. However, the HOMO and LUMO act primarily as electron donor and electron acceptor respectively. The transition state from the HOMO to the LUMO can be predicted by a combination of inter-ligand and MLCT charge transfer [45].

4. Conclusion

A new asymmetric tridentate NNO donor Schiff base ligand (H_2L) and its copper(II) complex with the general composition [Cu(L)Im] were prepared. The ligand and the metal complex were characterized by elemental analysis, FT-IR and UV–Vis spectroscopy. In addition, X-ray diffraction was employed for characterization of the metal complex. From the X-ray diffraction and spectral properties, it was concluded that the ligand is coordinated to metal as tridentate, bi-negatively chelating through the azomethine-N and deprotonated phenolic-O and deprotonated thioamide-N atoms and one imidazole ligand was also coordinated to the metal ion. Finally, DFT calculations were applied successfully to predict the structural geometry and interpret the natural band analysis. The geometry of the complex can be reproduced with minimum discrepancy with X-ray crystallography information. NBO analysis predicted a formal charge of 0.08 a.u. on the central ion Cu(II), indicating electron transmission from donor atoms N and O. Finally, the Cu(II) complex is air stable and soluble in most solvents, which may lead to increasing interest in research on its biological and catalytic activities.

Supplementary data

Crystallographic data for the structural analysis was deposited in the Cambridge Crystallographic Data Centre, CCDC No. 879871 for the Cu(II) complex. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, Cb2 1EZ, UK (fax: +44 1223 336 033); e-mail: deposit@ccdc.cam.ac.uk.

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