Preparation, spectral characterization, ESR measurements and DFT calculations of Schiff base copper(II) complex

Article *in* Inorganic and Nano-Metal Chemistry · December 2020

DOI: 10.1080/24701556.2020.1842768

CITATIONS
6

READS
391

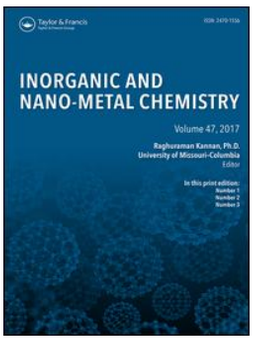
6 authors, including:

Sibel Tokdemir Ozturk
Gebze Technical University
29 PUBLICATIONS **114** CITATIONS
SEE PROFILE

Perihan Aksu
Gebze Technical University
12 PUBLICATIONS **32** CITATIONS
SEE PROFILE

Nevin Turan
Muş Alparslan University
75 PUBLICATIONS **1,093** CITATIONS
SEE PROFILE

Kenan Buldurun
Muş Alparslan University
65 PUBLICATIONS **943** CITATIONS
SEE PROFILE



Inorganic and Nano-Metal Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsrt21

Preparation, spectral characterization, ESR measurements and DFT calculations of Schiff base copper(II) complex

Sibel Tokdemir Öztürk , Perihan Aksu , Nevin Turan , Kenan Buldurun , Emine Tanış & Naki Çolak

To cite this article: Sibel Tokdemir Öztürk , Perihan Aksu , Nevin Turan , Kenan Buldurun , Emine Tanış & Naki Çolak (2020): Preparation, spectral characterization, ESR measurements and DFT calculations of Schiff base copper(II) complex, Inorganic and Nano-Metal Chemistry, DOI: 10.1080/24701556.2020.1842768

To link to this article: https://doi.org/10.1080/24701556.2020.1842768

INORGANIC AND NANO-METAL CHEMISTRY
https://doi.org/10.1080/24701556.2020.1842768

Preparation, spectral characterization, ESR measurements and DFT calculations of Schiff base copper(II) complex

Sibel Tokdemir Öztürk[a], Perihan Aksu[b], Nevin Turan[c], Kenan Buldurun[c], Emine Tanış[d], and Naki Çolak[e]

[a]Department of Physics, Gebze Technical University, Gebze, Kocaeli, Turkey; [b]Institute of Nanotechnology, Gebze Technical University, Gebze, Kocaeli, Turkey; [c]Department of Chemistry, Faculty of Arts and Sciences, Muş Alparslan University, Muş, Turkey; [d]Department of Medical Services and Techniques, Vocational School of Health Services, Kırşehir Ahi Evran University, Kırşehir, Turkey; [e]Department of Chemistry, Faculty of Arts and Sciences, Hitit University, Çorum, Turkey

ABSTRACT

The title compound ($[CuClL(H_2O)]\cdot 2H_2O$) were synthesized. The copper(II) complex in square planar geometry were identified by using elemental analysis, magnetic susceptibility, mass spectra, FT-IR, UV-Vis. and ESR techniques. DFT calculations at the UB3LYP/LANL2DZ level of theory were conducted to obtain vibrational and electronic properties of the copper(II) complex. Vibrational assignments of the observed infrared spectra of title compound were carried out based on the calculated potential energy distributions (PEDs). The sensitive measurement results indicated that the observed values were reasonable. The energy values were determined to describe electronic properties of the title molecules. Furthermore, NBO analysis was performed to analyze the hyperconjugative stability of the molecule, molecular orbital interaction and charge delocalization.

ARTICLE HISTORY
Received 8 June 2020
Accepted 18 October 2020

KEYWORDS
Copper(II) complex; UB3LYP/LANL2DZ level; ESR; HOMO-LUMO levels

Introduction

Schiff bases are extensively researched owing to their synthetic flexibility, selectivity and sensitivity to central metal ions. These ligands are often obtained directly by a synthetic easy method with high purity and yield. Therefore, the form of the synthesized ligands can offer a wide variety of chemical, electronic and kinetic properties.[1] Schiff base ligands, which contain N and O donor atoms, easily form complex compounds in atmospheric environments and high yields with numerous transition metal atoms.[2,3] Metal complexes have many different chemical and structural properties. Schiff base complexes of transitions metals are investigated because of their variety of applications, including biological[4,5] and catalytic,[6–9] optical memory devices,[10] sensors and photovoltaic materials.[11,12] Recently, the coordination chemistry of copper(II) oxygen-free and nitrogenous heterocyclic compounds has had great attention. This may be associated with their biological activity, stability and potential practices in many fields.[13] Many DFT (density functional theory) researches are given a systematic theoretical study on some Schiff base complexes. By means of computational chemistry, equilibrium geometries of the ligand and Schiff bases containing different metal ions and optimized geometry parameters of the complexes are obtained.[9,14]

Recently, DFT calculations have been widely used to study the electronic structure of large molecules, such as transition metal complexes, to give precise and reliable results. In this study, we also made extensive DFT calculations to optimize the structure of the copper(II) complex, to understand and analyze the spectral and electronic properties. Furthermore, NBO analysis were obtained with the DFT/B3LYP/6-31G(d,p) mixed basis set.

Experimental section

Materials and reagents

Electron spin resonance (ESR) spectra for solution at low temperature (105 K) was attained from a JEOL spectrometer operating at X-band (ca. 9.1 GHz) with appropriate microwave power (5–10 mW) and 100 kHz magnetic field modulation. DMF was used as solvent and concentration was around 2×10^{-3} M.

Elemental analyses (C, H and N) were determined using PerkinElmer 240B elemental microanalyses. FT-IR was performed using Perkin Elmer instrument applying KBr disk in the range 4000–400 cm^{-1}. Electronic spectra were measured on a Shimadzu UV-vis spectrophotometry in the range 200–800 nm. Mass spectra was determined on an AGILENT model 1100 MSD mass spectrophotometer. Furthermore, magnetic susceptibility was measured by a modified Gouy method and using $Hg[Co(SCN)_4]$ as a calibrate.

All chemicals and solvents used for the synthesis and analysis were of Sigma-Aldrich products, and they were used without purification.

CONTACT Nevin Turan nevintrn@hotmail.com; n.turan@alparslan.edu.tr Department of Chemistry, Faculty of Arts and Sciences, Muş Alparslan University, 49250 Muş, Turkey.

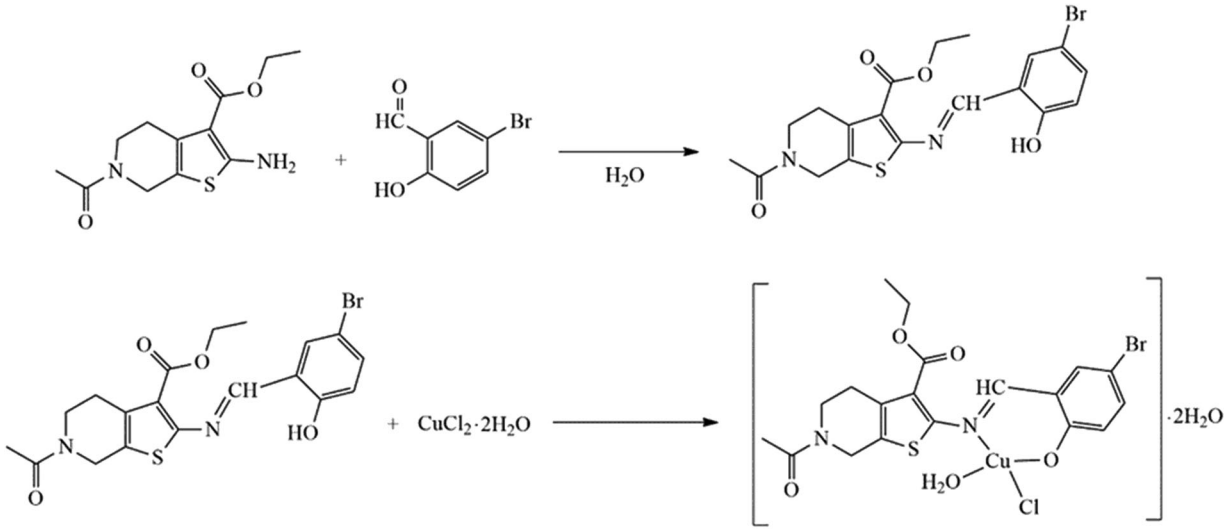


Figure 1. Synthesis scheme of free ligand and suggested structure of the copper(II) complex.

Synthesis of copper(II) complex

The copper(II) complex were obtained by refluxing the mixture of the corresponding metal chloride ($CuCl_2{\cdot}2H_2O$ (0.33 g, 2.2 mmol)) and 1.0 g, 2.2 mmol of the ligand ((*E*)-ethyl 6-acetyl-2-(5-bromo-2-hydroxybenzylideneamino)-4,5,6,7-tetrahydrothieno[2,3-*c*]pyridine-3-carboxylate) in 20 mL methanol until the complex precipitated out. The color complex was filtered, washed with methanol and then with diethyl ether. It was dried under vacuum. The structural formula of the complex was given in Figure 1. Yield 79%. mp.: 250–253 °C. IR (KBr, cm^{-1}): 3374, 3247 ν(OH), 3165 $\nu(C–H_{aro.})$, 2963 $\nu(C–H_{alip.})$, 1675 $\nu(C=O)$, 1608 $\nu(CH=N_{azomethine})$, 1535, 1541 $\nu(C=C_{aro.})$, 1139 $\nu(C–O_{phenolic})$, 775, 760 ν(C–S–C), 537 ν(Cu–O), 561, 601 ν(Cu–N). Anal. calc. for $C_{19}H_{24}BrN_2O_7SClCu$ (602.91 g/mol): C: 37.81, H: 3.98, N: 4.64, S: 5.30%; found: C: 38.10, H: 3.85, N: 4.70, S: 5.33%. UV-Vis. spectra (in ethanol): λ_{max}/nm (ε, L $mol^{-1}cm^{-1}$): 228 (2182), 294 (994), 332 (922), 803, 828, 881 (31), 921 (30), 978 (28),1052 (25). ESI-MS: (m/z) 600.91 (calc.), 600.90 (found) $[M-2H]^{2-}$. μ_{eff} (B.M.): 1.61. Color: Dark green.

Computational details

The Gaussian package program was used to make calculation for the copper(II) complex.[15] The results were determined with the help of the GaussView5 program.[16] To find the most stable structure of the copper(II) complex, it was primarily optimized using the DFT/UB3LYP/6-31G(d,p)+LANL2DZ hybrid method. The harmonic frequencies were multiplied by the scaling factor[17] to approximate the calculated vibration frequencies to the experimental vibration frequencies. These calculated vibration modes were assigned with the help of the VEDA 4 program.[18] Frontier molecular orbitals called HOMOs and LUMOs were identified and analyzed conductivity and reactivity in the complex. Molecular orbital interactions and coordination states around the copper(II) atom were determined by NBO analysis.

Results and discussion

The copper(II) complex was created in distorted square plane geometry such that it has three coordination with the ligand molecule, around the center of the copper metal ion, and one coordination with the chloro atom. The optimized geometrical structure of the copper(II) complex molecules were shown in Figure 2.

Spectroscopic characterization

Copper(II) complex were synthesized by reacting the ligand with metal ion in methanol medium in 1:1 molar ratio. The characterizations of the complex were given in experimental section. FT-IR, calculated IR spectrum and the potential energy distributions (PED values) of the vibrational modes for the title molecule were showed in Figures 3 and 4 and summarized in Table 1. The IR spectrum of the ligand was compared with the spectra of copper(II) complex to study the type of bonding in metal complex. The ligand acted as a bidentate coordinate through oxygen and nitrogen donor atoms. The FT-IR spectrum of the complex showed a sharp band at about 1605 cm^{-1}, which was attributed to the azomethine (CH = N) vibration. This band performed at 1601 cm^{-1} for Schiff base ligand.[19] The CH = N stretching band was calculated at 1610 cm^{-1} (43% PED). The FT-IR spectrum of the complex exhibited a sharp band at about 1675 cm^{-1} for C = O groups. It was also observed that the band associated with the C = O groups was at the region of 1636 and 1696 cm^{-1} for ligand, but these groups did not significantly affect the metal complex.[13] This suggested that C = O groups did not coordinate with the metals complexes. The comparison of copper(II) complex (1139 cm^{-1}) with the free ligand (1189 cm^{-1}) showed that phenolic C–O band was shifted to lower value by 50 cm^{-1}, which showed the participation of the oxygen atom of the phenolic group in coordination to the metal ions.[19] The C = O and C–O bands were computed at 1664 cm^{-1} (94% PED) and 1134 cm^{-1} (93% PED), respectively. Furthermore, the characteristic peak at 775 and 760 cm^{-1} were attributed to the stretching vibration

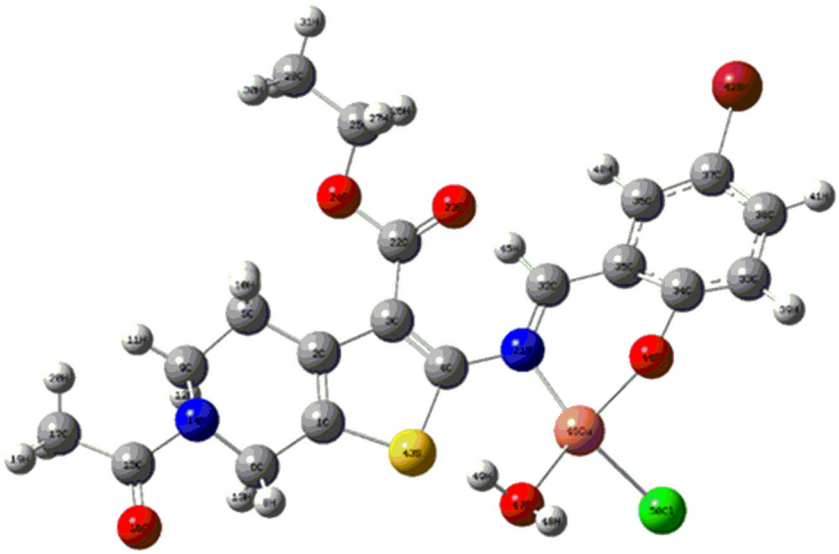


Figure 2. The optimized structures of the copper(II) complex.

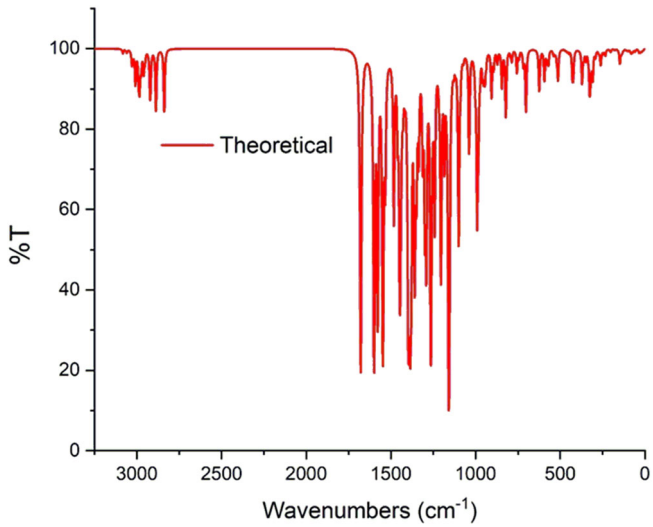


Figure 3. The calculated infrared spectra of the copper(II) complex.

of the C–S–C in the thiophene moiety. The IR spectra of copper(II) complex also showed a few new bands in the 537 and 561, 601 cm^{-1} fields, which were likely because of the formation of Cu–O and Cu–N bands, respectively.[20–22] As can be seen from the data in Table 1, both experimental and computational results are compatible with the literature.

UV-vis spectrum of copper(II) complex was recorded in ethanol (1×10^{-5} mol/L). In the copper(II) complex, the bands were shifted from 228 to 294 for the $\pi \rightarrow \pi^*$ transition and 332 to 1052 nm for the n $\rightarrow \pi^*$ transition. The transitions of $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ in the copper complex appeared to shift to longer wavelengths as a result of coordination of the metal atom to the ligand center. This indicated the formation of the M $\rightarrow$ L coordination bond.[19,23] Magnetic moment value of the copper(II) complex was measured as 1.61 B.M. This showed that the structure corresponded to square planar geometry.[19,20,24]

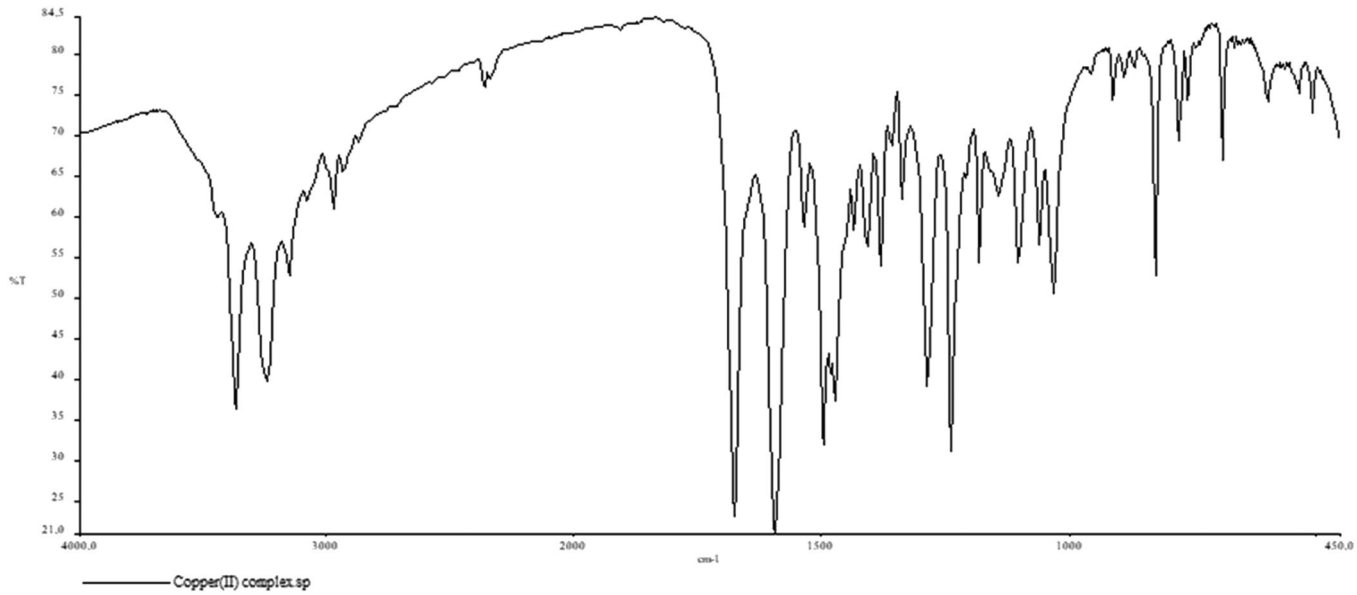


Figure 4. The experimental infrared spectra of the copper(II) complex.

Table 1. Comparisons of observed and calculated infrared spectra of copper(II) complex.

Copper(II) complex		
Experimental		Theoretical Frequency and Assignments
O-H	3374, 3247	3287 (82%)
Aromatic C-H	3165	3183 (100%)
Aliphatic C-H	2963	2953 (85%)
C = O	1675	1664 (92%)
CH = N	1605	1610 (43%)
Aromatic C = C	1535, 1541	1542 (60%)
C-O	1139	1134 (93%)
C-S	775	773 (75%)
S-C	760	754 (78%)
M-O	537	534 (54%)
M-N	561, 601	552, 601 (76%)

Frontier molecular orbitals and natural bonding orbital analysis

In a molecule, the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels, called frontier molecular orbitals (FMOs), are important for the electronic, optical and molecular charge transfer of the molecule.[25] While HOMO orbitals tend to give electrons, LUMO orbitals also tend to receive electrons. These molecular orbitals (MOs) are important because their interaction with other molecules is through HOMO-LUMO priority orbitals. The FMOs energy was calculated same method in ethanol. HOMO-LUMO shapes for the complex were given in Figure 5. In Figure 5, the HOMO orbitals were localized throughout the molecule, except from the ethyl acetate group, carbonyl group, and pyridine ring. The LUMO orbitals were localized throughout the molecule, excepting the Br, Cl atoms, carbonyl group, ethyl acetate group and pyridine ring. The energy gap (E_g) which is the energy difference between the HOMO and LUMO is a critical parameter in measuring electron conductivity and molecular reactivity. As shown in Figure 5, this value is 0.54 eV (2277 nm) in the ethanol solvent. It is seen that the complex studied with an energy range of 0.54 eV has a metal energy range.

The natural bonding orbital (NBO) analysis is used to calculate the distribution of bonds, donor-acceptor interactions and electron density between atoms, depending on the density of electrons. The value of E(2) indicates the magnitude of the interaction between the electron donors and their receptors, the tendency to electron donate between them. This value is calculated with the help of a second-order perturbation approach.[26,27] NBO calculations of the copper(II) complex was attained by using DFT/UB3LYP/LANL2DZ level and the results are reported in the Table 2. As shown from the Table 2, the strongest stabilization energy was calculated as LP(1)C36 → LP*(1)C35 interaction at 688.82 kcal/mol. Alike, the interaction energy of C22-O23 → C3-C4 is calculated to be 77.16 kcal/mol. Moreover, LP(2)O45 → LP*(6)Cu46, LP(1)N21 → LP*(6)Cu46 and LP(4)Cl47 → LP*(6)Cu46 interactions of Cu and Cl atoms are also among strong interactions (see Table 2). As seen from Table 2 that the stabilization for the title molecule is largely realized by the strong interactions of LP(1)C36 → LP*(1)C35 and C22-O23 → C3-C4 in the benzene ring. Similarly, we see that this stabilization is achieved by charge transfer between the bonding and anti-bonding orbitals.

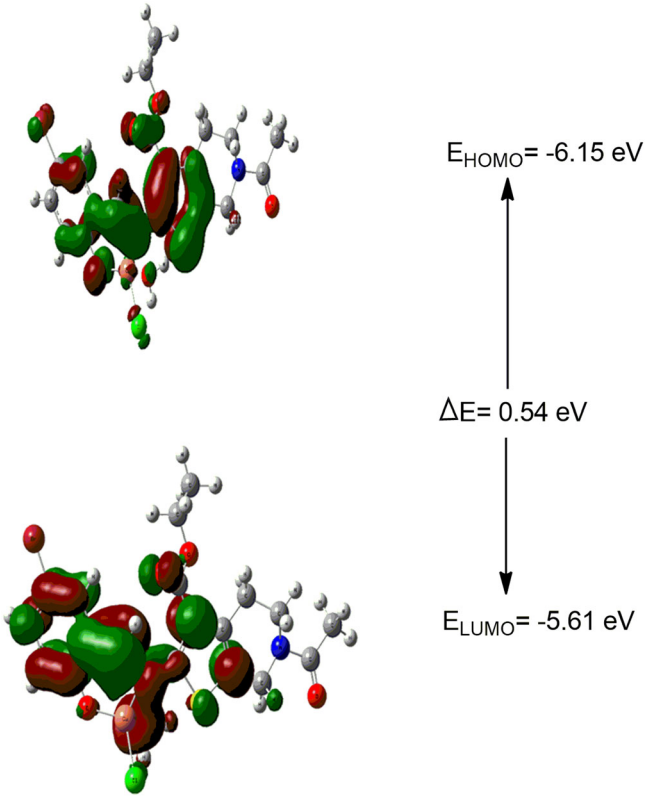


Figure 5. The HOMO and LUMO frontier molecular orbitals of the copper(II) complex.

Determination of g values by electron spin resonance measurements

ESR spectrum (simulated and experimental) of the copper(II) complex was given in Figure 6. The g value was distillated from the frozen liquid spectrum using the simulation program WinEPR Simfonia v1.25 (Bruker) and the components of the g value, $g_{//}$ and $g_{\perp}$, were the inputs for this program. The best-fitted $g_{//}$ and $g_{\perp}$ values were taken when the simulated and the experimental spectrums were matched, after optimization of the input values.

The g values were assigned to be $g_{//} = 2.294$ and $g_{\perp} = 2.061$. The measured ingredients of the g-factors showed that the paramagnetic copper center in copper(II) complex was axially symmetric, with $g_z = g_{//}$ and $g_x = g_y = g_{\perp}$.[28] The g values of copper were in the order of $g_{//} > g_{\perp} > g_e$ (free electron g value,$g_e = 2.0023$) which performed that the $d_{x^2-y^2}$ orbital was taken part by an unpaired electron.[29] Recorded low temperature ESR spectrum in solution gave better resolution and the possibility to distinguish hyperfine and super hyperfine splitting. In the low field region ESR spectrum of copper(II) complex in DMF exhibited resolved parallel hyperfine properties owing to copper (I = 3/2). The hyperfine interaction because of copper had also axial symmetry and values were assigned to be $A^{Cu}{}_{//} = 156$ G and $A^{Cu}{}_{\perp} = 5$ G. On the other hand, our simulations suggested

Table 2. Second order perturbation theory analysis of Fock matrix in natural bonding orbital basis for copper(II) complex.

Donor (i)	Type	ED/e	Acceptor (j)	Type	ED/e	$E^{(2)a}$ (kJ mol^{-1})	E(j)-E(i)[b] (a.u)	F(i,j)[c] (a.u)
C1-C2	σ	0.99	C2-C3	σ*	0.01	2.10	1.24	0.064
C1-C2	π	0.92	C3-C4	π*	0.21	6.38	0.28	0.058
C1-C2	σ	0.99	C1-S44	π*	0.02	0.26	0.95	0.020
C1-C6	σ	0.99	C1-C2	σ*	0.01	2.15	1.28	0.066
C1-C6	σ	0.99	N14-C15	σ*	0.04	1.40	1.14	0.051
C1-S44	σ	0.99	C1-C2	σ*	0.01	0.53	1.29	0.033
C1-S44	σ	0.99	C2-C5	σ*	0.01	2.63	1.10	0.068
C2-C3	σ	0.98	C1-C2	σ*	0.01	2.01	1.28	0.064
C2-C3	σ	0.98	C1-C6	σ*	0.01	2.68	1.06	0.068
C2-C3	σ	0.98	C5-C9	σ*	0.01	0.44	1.05	0.027
C2-C5	σ	0.98	C1-S44	σ*	0.01	2.39	0.83	0.056
C2-C5	σ	0.98	C5-H10	σ*	0.01	0.30	1.04	0.022
C3-C4	σ	0.98	C2-C3	σ*	0.01	2.41	1.23	0.069
C3-C4	σ	0.98	C22-O24	σ*	0.04	0.87	1.12	0.040
C3-C4	π	0.88	C1-C2	σ*	0.01	8.17	0.32	0.065
C3-C4	π	0.88	C22-O23	σ*	0.01	12.33	0.27	0.075
C3-C22	π	0.98	O24-C25	σ*	0.01	2.01	0.93	0.055
C3-C22	π	0.98	C22-O24	σ*	0.03	0.38	1.09	0.026
C9-H11	σ	0.99	C6-N14	σ*	0.01	2.27	0.84	0.055
C32-C36	σ	0.99	N21-C32	σ*	0.01	1.60	1.24	0.056
C34-C39	π	0.87	C35	LP*(1)	0.02	23.46	0.15	0.089
C37-C38	π	0.99	C34-C39	π*	0.01	9.52	0.32	0.069
N14	LP(1)	0.99	C15-O16	π*	0.01	29.90	0.28	0.116
O16	LP(2)	0.99	N14-C15	σ*	0.04	12.57	0.70	0.120
O23	LP(2)	0.99	C22-O24	σ*	0.04	10.15	0.80	0.116
O24	LP(2)	0.99	C22-O23	π*	0.01	27.19	0.31	0.121
C36	LP(1)	0.99	C35	LP*(1)	0.01	688.82	0.02	0.130
C36	LP(1)	0.99	N21-C32	π*	0.01	69.83	0.09	0.119
O45	LP(3)	0.99	C35	LP*(1)	0.02	66.79	0.16	0.152
C3-C4	π	0.21	C1-C2	π*	0.14	34.64	0.03	0.073
C22-O23	π	0.18	C3-C4	π*	0.21	77.16	0.02	0.082
C37-C38	π	0.15	C34-C39	π*	0.01	71.53	0.01	0.077
N21	LP(1)	0.91	Cu46	LP*(6)	0.14	13.58	0.56	0.113
N21	LP(1)	0.91	Cu46	LP*(7)	0.07	16.18	0.62	0.128
O23	LP(2)	0.96	Cu46	LP*(7)	0.07	1.08	0.62	0.033
O45	LP(2)	0.93	Cu46	LP*(6)	0.14	16.54	0.66	0.138
Cu46	LP(1)	0.99	N21-C32	π*	0.18	0.04	0.34	0.005
Cu46	LP*(8)	0.05	C4-N21	σ*	0.01	0.06	0.19	0.016
Cl47	LP(2)	0.99	C22-O23	σ*	0.01	0.03	0.78	0.006
Cl47	LP(4)	0.89	Cu46	LP*(6)	0.14	40.92	0.66	0.212

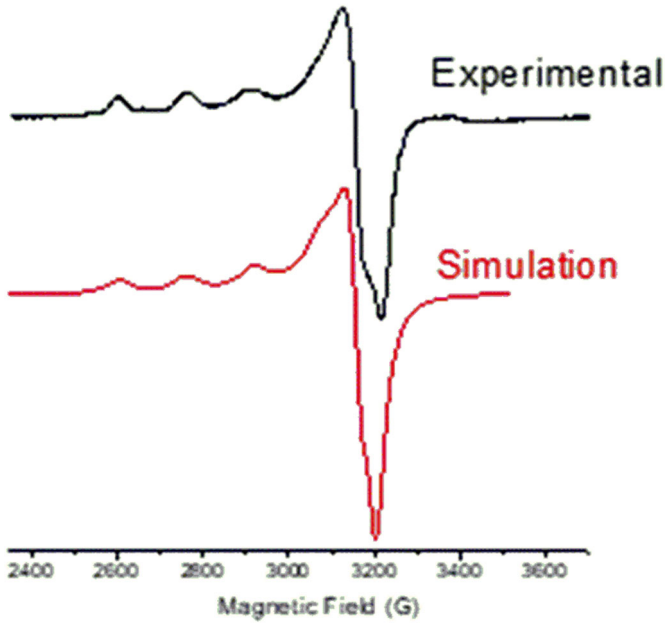


Figure 6. Experimental (black) and simulated (red) electron spin resonance spectra at 105 K of copper(II) complex in *N,N*-dimethylformamide solution.

that the superhyperfine interaction due to N (I = 1) and Cl (I = 3/2) were presented and determined as $A^{14N}{}_{//} = 7$ G and $A^{35Cl}{}_{//} = 10$ G respectively. This further split because of superhyperfine interaction with one nitrogen nuclei and one Cl nuclei could not be resolved owing to intermolecular dipolar interactions. The obtained values were shown in Table 3.

Conclusions

The copper(II) complex were successfully synthesized and characterized using various spectroscopic methods, element analysis, magnetic susceptibility measurements. Structural optimization and other calculations were performed using DFT calculations. Theoretical and experimental results were found to be compatible with each other. TD-DFT calculations were performed to obtain HOMO and LUMO orbitals of the synthesized crystal. E_{gap} energy difference value between HOMO-LUMO orbitals is calculated as 0.54 eV. This energy value indicates that the copper(II) complex is a metal material and it has high properties such as

Table 3. Electron spin resonance data for copper(II) complex.

	$g_{//}$	$g_{\perp}$	$A_{//}(Cu)$ (Gauss)	$A_{\perp}(Cu)$ (Gauss)	$A_{//}(^{14}N)$ (Gauss)	$A_{\perp}(^{14}N)$ (Gauss)	$A_{//}(^{35}Cl)$ (Gauss)	$A_{\perp}(^{35}Cl)$ (Gauss)
Cu(II) complex	2.294	2.061	156	5	7	0	10	0

conductivity and reactivity. Bonding and anti-bonding interactions that stabilize within the copper(II) complex were determined by NBO parameters. The strongest stabilization energy was calculated as LP(1)C36 → LP*(1)C35 interaction at 688.82 kcal/mol. ESR spectral data of copper complex showed that the complex had axial symmetry, which confirmed the oxidation states of metal ions.

ORCID

Kenan Buldurun http://orcid.org/0000-0002-2462-7006
Naki Çolak http://orcid.org/0000-0001-7181-9556

References

1. Teles, C. M.; Lammoglia, L. C.; Juliano, M. A.; Ruiz, A. L. T. G.; Candido, T. Z.; de Carvalho, J. E.; Lima, C. S. P.; Abbehausen, C. Novel Anticancer PdII Complexes: The Effect of the Conjugation of Transferrin Binding Peptide and the Nature of Halogen Coordinated on Antitumor Activity. *J. Inorg. Biochem.* **2019**, *199*, 110754. DOI: 10.1016/j.jinorgbio.2019.110754.
2. Ekennia, A. C.; Osowole, A. A.; Olasunkanmi, L. O.; Onwudiwe, D. C.; Ebenso, E. E. Coordination Behaviours of New (Bidentate N,O-Chelating) Schiff Bases towards Copper(II) and Nickel(II) Metal Ions: Synthesis, Characterization, Antimicrobial, Antioxidant, and DFT Studies. *Res. Chem. Intermed.* **2017**, *43*, 3787–3811. DOI: 10.1007/s11164-016-2841-z.
3. Radha, V. P.; Kirubavathy, S. J.; Chitra, S. Synthesis, Characterization and Biological Investigations of Novel Schiff Base Ligands Containing Imidazoline Moiety and Their Co(II) and Cu(II) Complexes. *J. Mol. Struct.* **2018**, *1165*, 246–258. DOI: 10.1016/j.molstruc.2018.03.109.
4. Zianna, A.; Geromichalos, G. D.; Pekou, A.; Hatzidimitriou, A. G.; Coutouli-Argyropoulou, E.; Lalia-Kantouri, M.; Pantazaki, A. A.; Psomas, G. A Palladium(II) Complex with the Schiff Base 4-Chloro-2-(N-Ethyliminomethyl)-Phenol: Synthesis, Structural Characterization, and In Vitro and In Silico Biological Activity Studies. *J. Inorg. Biochem.* **2019**, *199*, 110792. DOI: 10.1016/j.jinorgbio.2019.110792.
5. Mesbah, M.; Douadi, T.; Sahli, F.; Issaadi, S.; Boukazoula, S.; Chafaa, S. Synthesis, Characterization, Spectroscopic Studies and Antimicrobial Activity of Three New Schiff Bases Derived from Heterocyclic Moiety. *J. Mol. Struct.* **2018**, *1151*, 41–48. DOI: 10.1016/j.molstruc.2017.08.098.
6. Buldurun, K.; Turan, N.; Savcı, A.; Çolak, N. Synthesis, Structural Characterization and Biological Activities of Metal(II) Complexes with Schiff Bases Derived from 5-Bromosalicylaldehyde: Ru(II) Complexes Transfer Hydrogenation. *J. Saudi Chem. Soc.* **2019**, *23*, 205–214. DOI: 10.1016/j.jscs.2018.06.002.
7. Turan, N.; Buldurun, K.; Çolak, N.; Özdemir, İ. Preparation and Spectroscopic Studies of Fe(II), Ru(II), Pd(II) and Zn(II) Complexes of Schiff Base Containing Terephthalaldehyde and Their Transfer Hydrogenation and Suzuki-Miyaura Coupling Reaction. *Open Chem.* **2019**, *17*, 571–580. DOI: 10.1515/chem-2019-0074.
8. Iftikhar, B.; Javed, K.; Khan, M. S. U.; Akhter, Z.; Mirza, B.; Mckee, V. Synthesis, Characterization and Biological Assay of Salicylaldehyde Schiff Base Cu(II) Complexes and Their Precursors. *J. Mol. Struct.* **2018**, *1155*, 337–348. DOI: 10.1016/j.molstruc.2017.11.022.
9. Beigi, Z.; Kianfar, A. H.; Farrokhpour, H.; Roushani, M.; Azarian, M. H.; Mahmood, W. A. K. Synthesis, Characterization and Spectroscopic Studies of Nickel (II) Complexes with Some Tridentate ONN Donor Schiff Bases and Their Electrocatalytic Application for Oxidation of Methanol. *J. Mol. Liq.* **2018**, *249*, 117–125. DOI: 10.1016/j.molliq.2017.10.131.
10. Rodríguez, M. R.; Del Plá, J.; Piro, O. E.; Echeverría, G. A.; Espino, G.; Pis-Diez, R.; Parajón-Costa, B. S.; González-Baró, A. C. Structure, Tautomerism, Spectroscopic and DFT Study of o -Vanillin Derived Schiff Bases Containing Thiophene Ring. *J. Mol. Struct.* **2018**, *1165*, 381–390. DOI: 10.1016/j.molstruc.2018.03.120.
11. Parsaee, Z.; Joukar Bahaderani, E.; Afandak, A. Sonochemical Synthesis, In Vitro Evaluation and DFT Study of Novel Phenothiazine Base Schiff Bases and Their Nano Copper Complexes as the Precursors for New Shaped CuO-NPs. *Ultrason. Sonochem.* **2018**, *40*, 629–643. DOI: 10.1016/j.ultsonch.2017.08.010.
12. Turan, N.; Gündüz, B.; Körkoca, H.; Adigüzel, R.; Çolak, N.; Buldurun, K.; Mex, J. Study of Structure and Spectral Characteristics of the Zinc(II) and Copper(II) Complexes with 5,5-Dimethyl-2-(2-(3-nitrophenyl)hydrazono)cyclohexane-1,3-dione and Their Effects on Optical Properties and the Developing of the Energy Band Gap and Investigation of Antibacterial Activity. *Chem. Soc.* **2014**, *58*, 65–75.
13. Abdi, Y.; Bensouilah, N.; Siziani, D.; Hamdi, M.; Artur, M. S.; Kheddis, B. B. New Complexes of Manganese (II) and Copper (II) Derived from the Two New Furopyran-3, 4-Dione Ligands: Synthesis, Spectral Characterization, ESR, DFT Studies and Evaluation of Antimicrobial Activity. *J. Mol. Struct.* **2020**, *1202*, 127307. DOI: 10.1016/j.molstruc.2019.127307.
14. Sherif, O. E.; Abdel-Kader, N. S. DFT Calculations, Spectroscopic Studies, Thermal Analysis and Biological Activity of Supramolecular Schiff Base Complexes. *Arab. J. Chem.* **2018**, *11*, 700–713. DOI: 10.1016/j.arabjc.2015.07.008.
15. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E. *Gaussian 09, Revision B.01*; Gaussian, Inc.: Wallingford, CT, **2009**.
16. Dennington, R.; Keith, T.; Millam, J. *GaussView, Version 5*; Semichem Inc.: Shawnee Mission, KS, 2009.
17. Tamer, Ö.; Avcı, D.; Atalay, Y.; Çoşut, B.; Zorlu, Y.; Erkovan, M.; Yerli, Y. Synthesis, X-Ray Structure, Spectroscopic Characterization and Nonlinear Optical Properties of Triaqua(1,10-Phenanthroline-2,9-Dicarboxylato)Manganese(II) Dihydrate: A Combined Experimental and Theoretical Study. *J. Mol. Struct.* **2015**, *1100*, 605–613. DOI: 10.1016/j.molstruc.2015.07.043.
18. Jamroz, M. H. *Vibrational Energy Distribution Analysis VEDA4*; LSMMSD: Warsaw, 2004.
19. Mallikarjuna, N. M.; Keshavayya, J.; Maliyappa, M. R.; Ali, R. A. S.; Venkatesh, T. Synthesis, Characterization, Thermal and Biological Evaluation of Cu (II), Co (II) and Ni (II) Complexes of Azo Dye Ligand Containing Sulfamethaxazole Moiety. *J. Mol. Struct.* **2018**, *1165*, 28–36. DOI: 10.1016/j.molstruc.2018.03.094.
20. Rambabu, A.; Ganji, N.; Daravath, S.; Venkateswarlu, K.; Rangan, K. Mononuclear Co(II), Ni(II) and Cu(II) Complexes of the Schiff Base, 2-(((4-Trifluoromethoxy)phenylimino)methyl)-6-tert-butylphenol: Synthesis, Spectroscopic Characterization, X-ray Study and Biological Evaluation. *J. Mol. Struct.* **2020**, *1199*, 127006. DOI: 10.1016/j.molstruc.2019.127006.
21. Souza, I. V.; Machado, B. P.; Carvalho, A. B.; Binatti, I.; Krambrock, K.; Molphy, Z.; Kellett, A.; Pereira-Maia, E. C.; Silva-Caldeira, P. P. S. Exploring the DNA Binding, Oxidative Cleavage, and Cytotoxic Properties of New Ternary Copper(II) Compounds Containing 4-Aminoantipyrine and N,N-Heterocyclic co-Ligands. *J. Mol. Struct.* **2019**, *1178*, 18–28. DOI: 10.1016/j.molstruc.2018.10.004.
22. Kasumov, V. T.; Yerli, Y.; Kutluay, A.; Aslanoglu, M. Synthesis, Spectroscopy, Magnetic and Redox Behaviors of Copper(II) Complexes with Tert-Butylated Salen Type Ligands Bearing Bis(4-Aminophenyl)Ethane and Bis(4-Aminophenyl)Amide Backbones. *Spectrochim Acta A. Mol. Biomol. Spectrosc.* **2013**, *104*, 203–212. DOI: 10.1016/j.saa.2012.11.061.
23. El-Sonbati, A. Z.; Diab, M. A.; El-Bindary, A. A.; Abou-Dobara, M. I.; Seyam, H. A. Supramolecular Coordination and Antimicrobial Activities of Constructed Mixed Ligand

Complexes. *Spectrochim Acta A. Mol. Biomol. Spectrosc.* **2013**, *104*, 213–221. DOI: 10.1016/j.saa.2012.11.024.
24. Shahraki, S.; Razmara, Z.; Shiri, F. A Paramagnetic Oxalato-Bridged Binuclear Copper(II) Complex as an Effective Catalase Inhibitor. Spectroscopic and Molecular Docking Studies. *J. Mol. Struct.* **2020**, *1208*, 127865. DOI: 10.1016/j.molstruc.2020.127865.
25. Cankaya, N.; Tanış, E.; Gülbaş, H. E.; Bulut, N. A New Synthesis of Limonene Copolymer: Experimental and Theoretical Analysis. *Polym. Bull.* **2019**, *76*, 3297–33277. DOI: 10.1007/s00289-018-2543-3.
26. Altürk, S.; Tamer, Ö.; Avcı, D.; Atalay, Y. Synthesis, Spectroscopic Characterization, Second and Third-Order Nonlinear Optical Properties, and DFT Calculations of a Novel Mn(II) Complex. *J. Organomet. Chem.* **2015**, *797*, 110–119. DOI: 10.1016/j.jorganchem.2015.08.014.
27. Alkorta, I.; Perez, J. J. Molecular Polarization Potential Maps of the Nucleic Acid Bases. *Int. J. Quantum Chem.* **1996**, *57*, 123–135. DOI: 10.1002/(SICI)1097-461X(1996)57:1<123::AID-QUA14>3.3.CO;2-F.
28. Abragam, A.; Bleaney, B. *EPR of Transition Ions*; Dover Publications: New York, 1986, pp 157.
29. Di Mauro, E.; Domiciano, S. M. Covalent Bonding in NH4Br:Cu2+. *J. Phys. Chem. Solids* **1999**, *60*, 1849–1854. DOI: 10.1016/S0022-3697(99)00198-5.