



Synthesis, Characterization and DFT Studies of Some Co(II) and Cu(II) Complexes of 12-Membered Tetradentate [N₄] Macrocyclic Schiff Base Derived from 9,10-Phenanthrenequinone

AFREEN ANJUM^{1,*}, SIKANDAR PASWAN¹, MANOJ KUMAR¹, HABIB ALI² and RAJ KUMAR DUBEY¹

¹Synthetic Inorganic and Metallo-Organic Research Laboratory, Department of Chemistry, University of Allahabad, Prayagraj-211002, India

²Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India

*Corresponding author: E-mail: aanjum700@gmail.com

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The structures of some coordination compounds of cobalt(II) and copper(II) with macrocyclic Schiff bases obtained by the reaction of 9,10-phenanthrenequinone with diamines synthesized in 1:1 molar ratio(s) have been elucidated by various physico-chemical methods viz. elemental analysis, IR, UV-visible, mass, ESR. The surface morphology was determined by SEM analysis. Infrared spectra suggested that ligand was coordinated to the metal ion in a tetradentate manner through azomethine nitrogen atom by the change in its stretching frequency. ESR spectra of copper(II) complexes indicates the presence of unpaired electron in the $d_{x^2-y^2}$ by calculating the g values. The optimized geometries which were calculated using the DFT/B3LYP method were compared with the molecular geometries obtained experimentally.

Keywords: Macrocyclic ligands, Tetrahedral, Square planar, Co(II), Cu(II) complex, 9,10-Phenanthrenequinone.

INTRODUCTION

Over the past years, there had been development of a new group of synthesis of macrocyclic complexes has been a fascinating area of research at a fast pace owing to their analytical, industrial and medicinal applications [1-4]. Coordination complexes of macrocyclic ligands have gained attention due to its structural resemblance with many other natural systems like cobalamines, porphyrins *etc.* [5]. These macrocyclic Schiff base complexes are also used as dyes, pigments, metalloenzymes [6], magnetic resonance imaging [7], sensors [8], catalyst [9,10], as well as a NMR shift reagent [11]. Schiff base macrocyclic ligands are of significant interest due to their vast biological application such as antibacterial [12], antifungal [13], anticancer [14], antiviral [15], antitumor [16] *etc.* The structure of 9,10-phenanthrenequinone resembles with the phenanthroline compounds which are capable of undergoing intercalating interactions with DNA resulting in cell antiproliferative activities have drawn our attentions [17]. As compared to catecholates, unlike other *o*-quinones, 9,10-phenanthrenequinone is a weaker chelating agent and a limited number of coordination compounds of it with transition-metal ions has been reported [18].

In the present work, we report the synthesis and characterization of macrocyclic Schiff base complexes of cobalt(II) and copper(II). The molecular geometries obtained by different spectral analysis in the ground state were compared with the optimized geometries, which were calculated using the DFT/B3LYP method. The 6-31G* basis set for C, H, N, O, Cl atoms and B3LYP basis set for Cu atom were chosen in all theoretical calculations.

EXPERIMENTAL

9,10-Phenanthrenequinone, ethylene diamine, propyl diamine, copper(II) chloride and cobalt(II) chloride were purchased from Sigma Aldrich and SRL Chem and all are of reagent grade. All the reagents purchased were used without further purification. The C, H and N were analyzed on CHN-932 on Perkin-Elmer 7300 DV elemental analyzers. Electronic spectra were recorded in methanol on a JASCO V-670 UV-visible spectrophotometer at the range (200-800 nm). IR spectra were recorded from KBr disks of the samples over the range 4000-400 cm^{-1} on Bruker VI-FTIR spectrometer. Copper was estimated gravimetrically [19]. HRMS were recorded in ESI

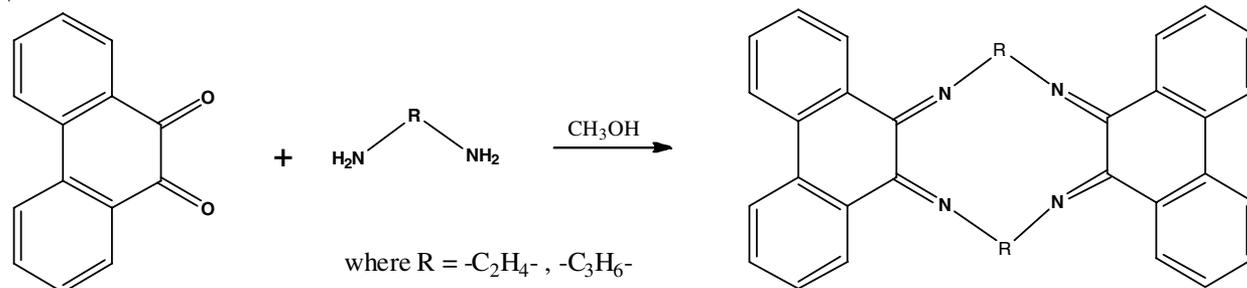


Fig. 1. Synthesis of the macrocyclic Schiff base ligands

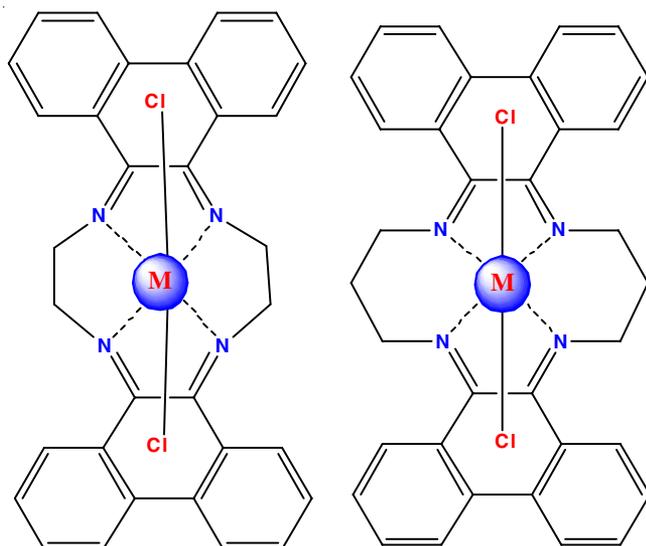
positive mode. Powder X-ray diffraction (PXRD) was recorded on X'Pert Pro XRD. X band ESR spectra were done on JES-FA200 Spectrometer. SEM-EDAX was recorded on JEOL, Japan (JFC 1600, Auto Fine Coater).

Synthesis of macrocyclic Schiff bases: All the tetradentate Schiff base ligands were prepared by condensations between diamines and 9,10-phenanthrenequinone in ethanol or methanol in 1:1 molar ratio(s) and were purified by recrystallization (Fig. 1). Ligands were characterized by elemental analyses, mass spectra, IR and UV.

(L₁): C₃₂H₂₄N₄, Yield, 82.68 %; Analytical calc. found (calcd.); C, 82.5 (82.73); H, 5.02 (5.21); N, 12.4 (12.06); m.p.: 156 °C; colour, light yellow.

(L₂): C₃₄H₂₈N₄, Yield, 81.3 %; Analytical calc. found (calcd.); C, 82.3 (82.90); H, 5.1 (5.73); N, 11.01 (11.37); m.p.: 170 °C; colour, green.

Synthesis of metal complexes: A template reaction was carried out to synthesize the complexes. A methanolic solution of the respective divalent metal halide (CoCl₂ and CuCl₂) was mixed with the methanolic solution of the macrocyclic Schiff base. The reaction mixture was stirred and was left under reflux for about 4-5 h. The metal complexes were precipitated out on cooling the reaction mixture overnight. It was further collected by filtration and washing with methanol and then dried in vacuum under pressure. The general structure for the complexes is given in Fig. 2.



where, M = Co & Cu

Fig. 2. Structure of the complexes

[CoL₁Cl₂]: C₃₂H₂₄N₄Cl₂Co, Yield, 52.08 %; Analytical calc. Found (calcd.); C, 63.05 (64.66); H, 4.01 (4.07); N, 9.3 (9.43); colour, light brown.

[CuL₁Cl₂]: C₃₂H₂₄N₄Cl₂Cu, Yield, 41.86 %; Analytical calc. Found (calcd.); C, 62.5 (64.16); H, 4.02 (4.04); Cu, 10.56 (10.61); N, 9.4 (9.35); colour, dark brown.

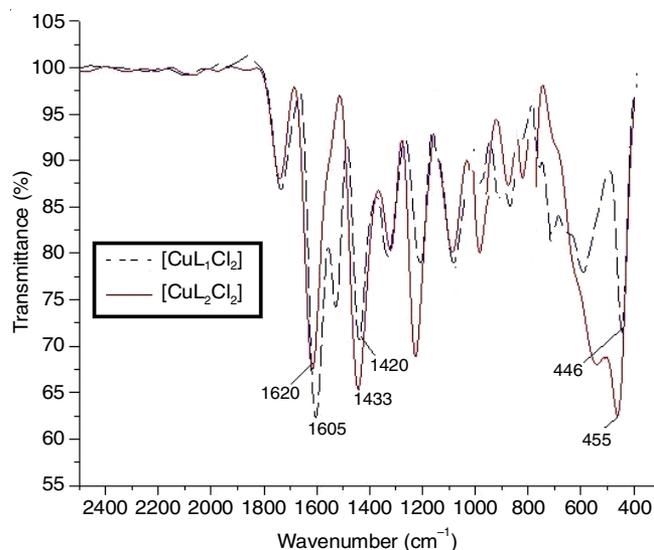
[CoL₂Cl₂]: C₃₄H₂₈N₄Cl₂Co, Yield, 42.98 %; Analytical calc. Found (calcd.); C, 65.5 (65.61); H, 4.32 (4.53); N, 8.8 (9.00); colour, greenish brown.

[CuL₂Cl₂]: C₃₄H₂₈N₄Cl₂Cu, Yield, 53.78 %; Analytical calc. Found (calcd.); C, 64.9 (65.12); H, 4.28 (4.5); Cu, 10.09 (10.13); N, 8.4 (8.93); colour, dark green.

RESULTS AND DISCUSSION

All the complexes obtained are stable to air and moisture and are appreciably soluble in many organic solvents such as methanol, ethanol, acetonitrile, DCM, DMSO *etc.* All the complexes were characterized by elemental analysis, UV, PXRD, ESR spectroscopy and mass spectrometry. The optimized geometries of the ligands as well as their complexes were calculated using the DFT/B3LYP method were compared with the molecular geometries obtained experimentally.

IR spectroscopy: The IR spectral bands (4000-400 cm⁻¹) of the free ligand and its metal complexes (Fig. 3) show strong intensity absorption band at 1600 ± 20 cm⁻¹ assigned to C=N stretching mode in the ligand, which shifts towards the weak intensity absorption band in the frequency range 1530 ±

Fig. 3. IR spectra of [CuL₁Cl₂] and [CuL₂Cl₂]

10 cm⁻¹ for the coordinated imine function $\nu(\text{C}=\text{N})$ for similar complexes as compared to their free ligands [20]. Therefore, it was concluded that both the ligands acted as in tetradentate fashion and binds to metal ions through imine nitrogen atoms. The absence of band characteristic of $\nu(\text{C}=\text{O})$, aromatic primary amine bands $\nu(\text{N}-\text{H})$ expected to appear in free 9,10-phenanthrenequinone and ethylene diamine/propyl-1,3-diamine respectively, confirms the formation of the proposed macrocyclic skeleton of the compounds. The medium intensity band due to $\nu(\text{M}-\text{N})$ vibrations was observed in the range 445 ± 10 cm⁻¹ [21] also indicates that metal was binded to azomethine nitrogen (Table-1).

Ligands/ complexes	$\nu(\text{C}=\text{C})$ (aromatic ring)	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$
L ₁	1454	1582	—
L ₂	1443	1597	—
[CoL ₁ Cl ₂]	1450	1602	452
[CuL ₁ Cl ₂]	1420	1605	446
[CoL ₂ Cl ₂]	1459	1605	436
[CuL ₂ Cl ₂]	1433	1620	455

Electronic spectroscopy: The electronic spectra of the ligands and their metal complexes were recorded in DMSO (Fig. 4). The electronic spectrum of all the complexes in DMSO shows essentially similar patterns of band in 400-250 nm [22] region due to intra-ligand and charge transfer transitions. The six coordinated octahedral Co(II) ion can be tentatively proposed by the observation of two bands, one in about 1100 nm region and the other in 515-510 nm region assignable to $4T_{1g}(\text{F}) \rightarrow 4T_{2g}(\text{F})$ and $4T_{1g}(\text{F}) \rightarrow 4T_{1g}(\text{P})$ transitions, respectively [23].

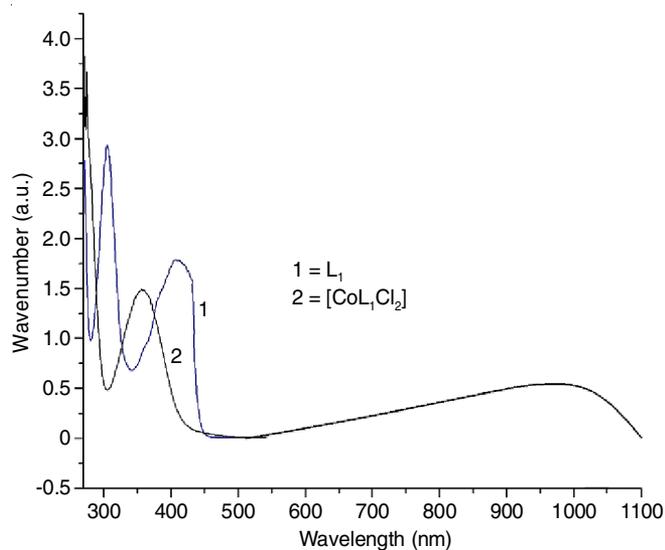


Fig. 4. UV spectra of L₁ with its Co complex

EPR spectroscopy: EPR spectra [24] of the copper (II) complexes were recorded at room temperature (Fig. 5), on X band at 9.1 GHz frequency in a polycrystalline state under the magnetic field strength of 3000G. Copper(II) complexes showed well resolved signals in the parallel and perpendicular regions (Table-2). The observed g values were found in the range 2.046-2.176 it was well known that the value of g is less than 2.003 for transition metal complexes having less than half filled d orbital, whereas g value is greater than 2.003 for those having more than half filled d orbitals. It had been observed that the value of g_{||} is a moderate function for indicating the nature of mode of binding. Thus, g_{||} > 2.3 is attributed to anionic surroundings and g_{||} < 2.3 is attributed of covalent surroundings in M-L binding*. It was observed for the complexes shows octahedral geometry.

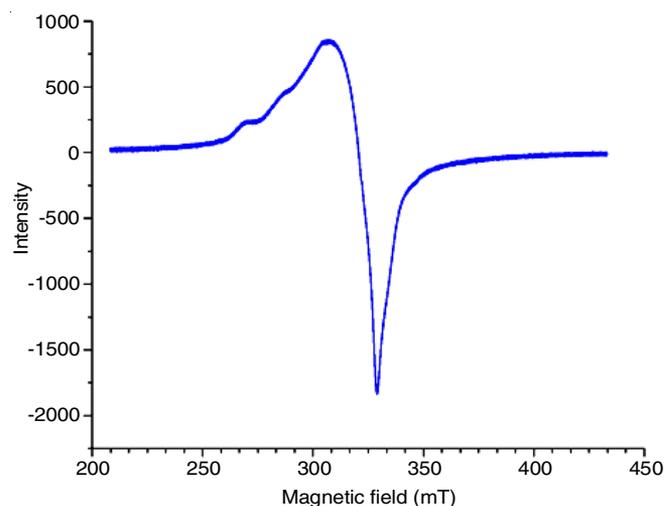
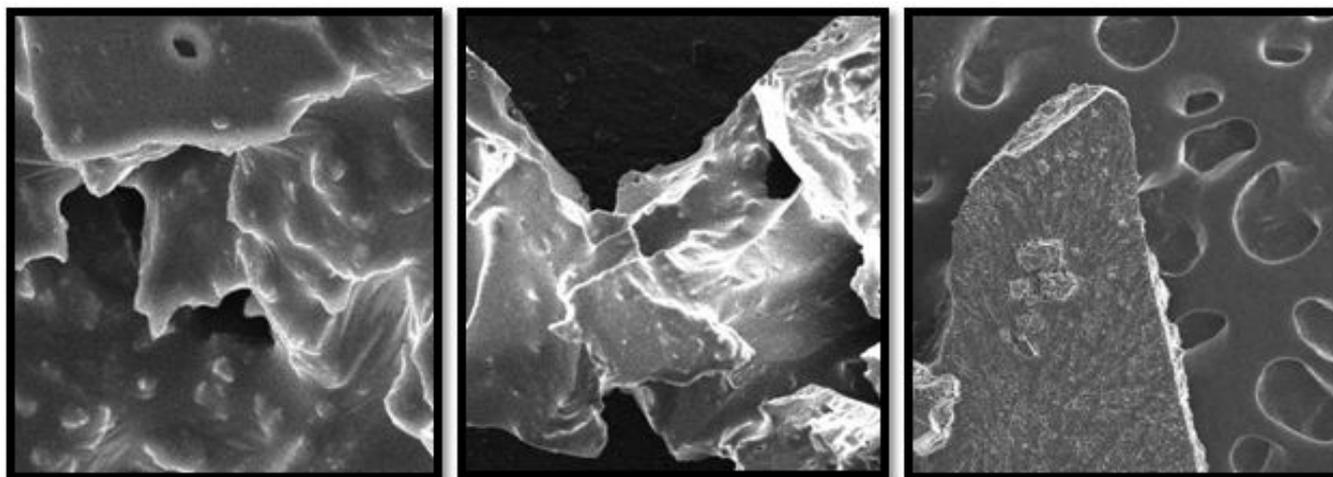
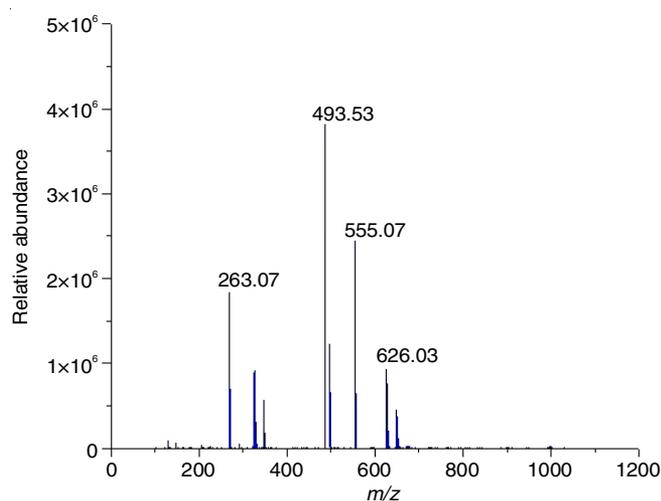


Fig. 5. EPR spectra of [CuL₁Cl₂]

SEM studies: SEM is a simple method can be used to check the deposited, which clearly indicated that the complexes have been formed. SEM uses a high energy electron beam but the beam is scanned over the surface and the back scattering of the electrons is looked at. It measures particle size and also gives the images of the surface of the complexes. The surface of the compound is shiny showing semi crystalline nature. The images of both the cobalt complexes are different with each other due to the presence of different ligands moiety present similarly in copper complexes. Fig. 6 shows SEM images of both cobalt and copper complexes.

Mass studies: The spectrum of the copper complex with L₂ (Fig. 7) shows a molecular ion peak at $m/z = 626.03$ (100 %) corresponding to the formula [CuL₂Cl₂] where the metal is coordinated to two equivalent ligands and two chloride ions. A good confirmation of the complex molecular weight was obtained from the base peak at $(m/z) = 493.53$ which corresponds to the formula C₃₄H₂₈N₄ which is in good agreement with the infrared results.

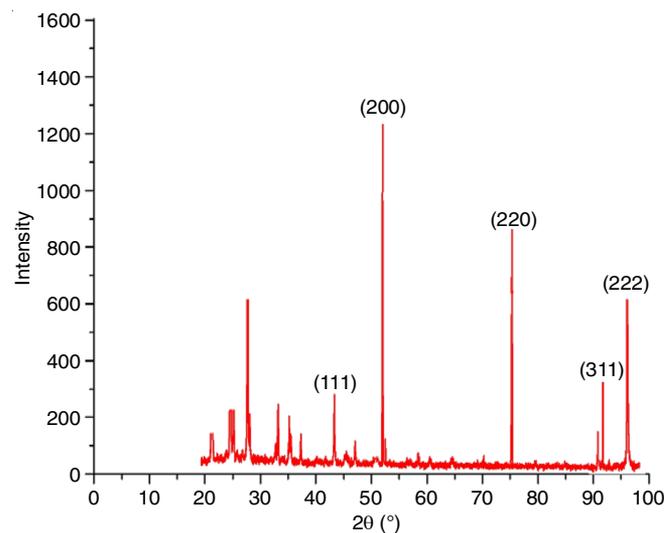
Complexes	H (mT)	H _⊥ (mT)	g	g _⊥	g _{av}	G
[CuL ₁ Cl ₂]	308.932	332.169	2.176	2.046	2.092	3.974
[CuL ₂ Cl ₂]	311.23	329.26	2.169	2.051	2.090	3.487

Fig. 6. SEM images of [CoL₁Cl₂], [CoL₂Cl₂] and [CuL₂Cl₂] respectivelyFig. 7. Mass spectrum of [CuL₂Cl₂]

PXRD studies: The X-ray diffraction patterns of both cobalt and copper complexes are given in Table-3. Single crystals of the complexes could not be isolated from any solvents. The powder XRD patterns of Co(II) complexes show sharp crystalline peaks indicating its crystalline nature. Phase and unit cell parameters were found using trial and error methods. All the Co(II) complexes show triclinic crystal system. The strong diffraction peaks at 2θ values of 51.65° , 75.95° , 92.35° and 97.75° corresponding to (200), (220), (311) and (222) crystal planes indicate formation of face-centered cubic crystalline

cobalt (JCPDS card no 15-0806) [25] whereas 44.316° and 50.493° corresponding to (111) and (200) relates to face-centered cubic copper (JCPDS card no 04-0836) [26]. Based upon the characteristic peak obtained (2θ value taken from Fig. 8), the particle size of the crystal was calculated using the formula,

$$D = \frac{0.91\lambda}{\beta \cos \theta}$$

Fig. 8. PXRD analysis of [CoL₁Cl₂]TABLE-3
PXRD STUDIES OF THE COBALT(II) AND COPPER(II) COMPLEXES

Parameter	Complex 1 [CoL ₁ Cl ₂]	Complex 2 [CuL ₁ Cl ₂]	Complex 3 [CoL ₂ Cl ₂]	Complex 4 [CuL ₂ Cl ₂]
Formula	C ₃₂ H ₂₄ CoN ₄ Cl ₂	C ₃₂ H ₂₄ CuN ₄ Cl ₂	C ₃₄ H ₂₈ CoN ₄ Cl ₂	C ₃₄ H ₂₈ CuN ₄ Cl ₂
F.W.	594.40	599.01	622.45	627.06
Temperature (K)	298	298	298	298
Wavelength	1.540598	1.540598	1.540598	1.540598
Radiation	Cu K _α	Cu K _α	Cu K _α	Cu K _α
Space group	Fm3m (225)	Fm3m (225)	Fm3m (225)	Fm3m (225)
Crystal system	Triclinic	Cubic	Triclinic	Cubic
Cell Parameters	a ≠ b ≠ c; α ≠ β ≠ γ	a = b = c; α = β = γ	a ≠ b ≠ c; α ≠ β ≠ γ	a = b = c; α = β = γ
Unit cell	fcc	Fcc	fcc	fcc
2θ	10-100°	10-100°	10-100°	10-100°

where constant 0.91 is the shape factor, k is the X-ray wavelength of $\text{CuK}\alpha$ radiation (1.5406 Å), D represents the average size of the particle, θ corresponds to Bragg diffraction angle and β represents full width at half maximum of peak (FWHM).

Computational studies: In this study, the 3D structure of the macrocyclic Schiff base ligands and their Co(II)/Cu(II) complexes are optimized using density functional theory (DFT) calculations were carried out by (B3LYP/6-31G/SDD/

LANL2DZ) basis set with Gaussian 09W program (Figs. 9-11) by using a selection of unrestricted modern density functional [27-29]. The basis set 6-31G was used for the N, C and H atoms and LANL2DZ was applied for the Co(II)/Cu(II) ion respectively [30]. The HOMO (highest occupied molecular orbital) energy represents the ability to donate an electron while the LUMO (lowest unoccupied molecular orbital) as an electron acceptor represents the ability to get an electron. The chemical

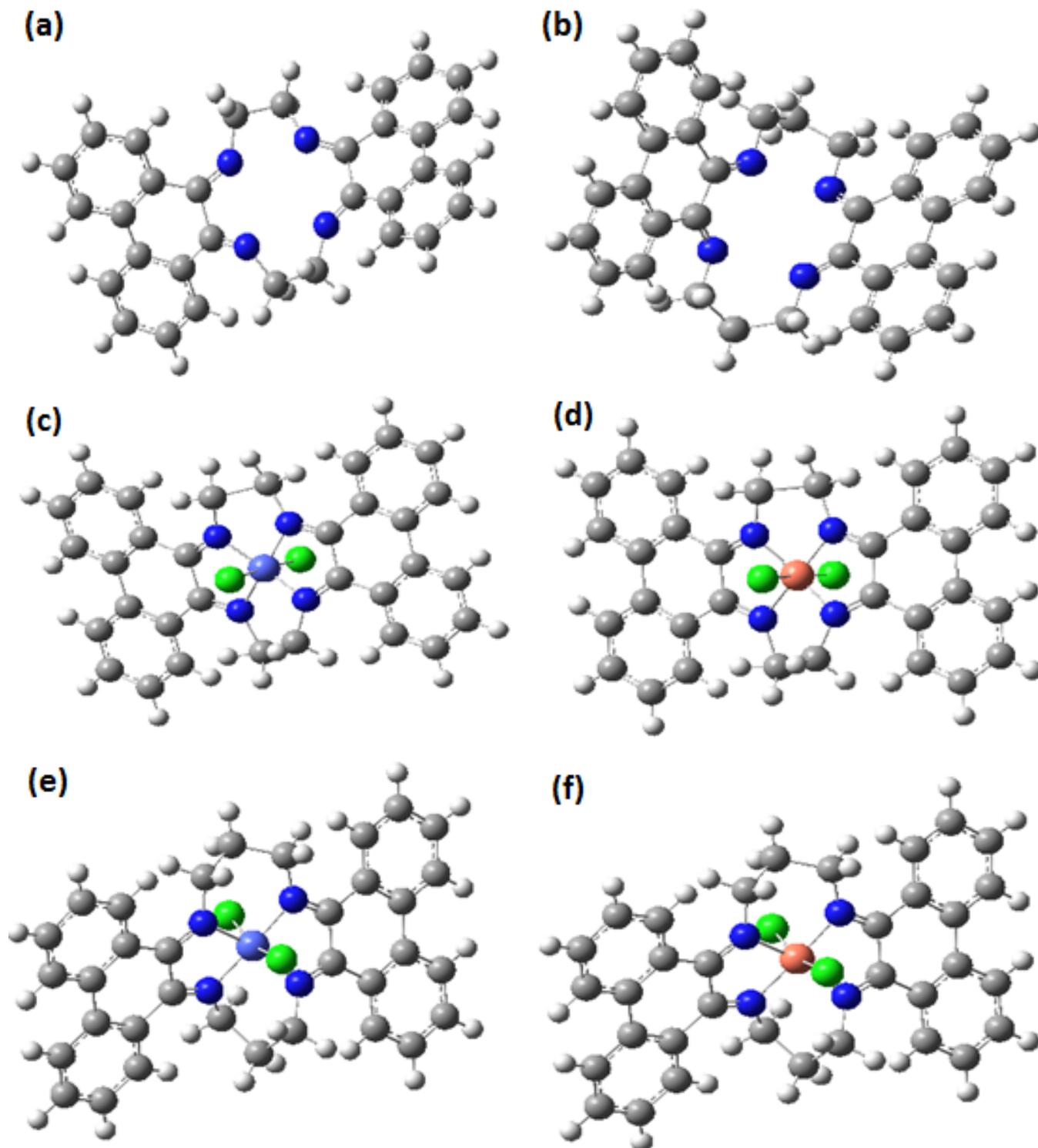


Fig. 9. 3D optimized structure of the (a) Schiff base ligands (L₁) (b) (L₂) and their complexes (c) [CoL₁Cl₂], (d)[CuL₁Cl₂], (e) [CoL₂Cl₂] and (f) [CuL₂Cl₂]

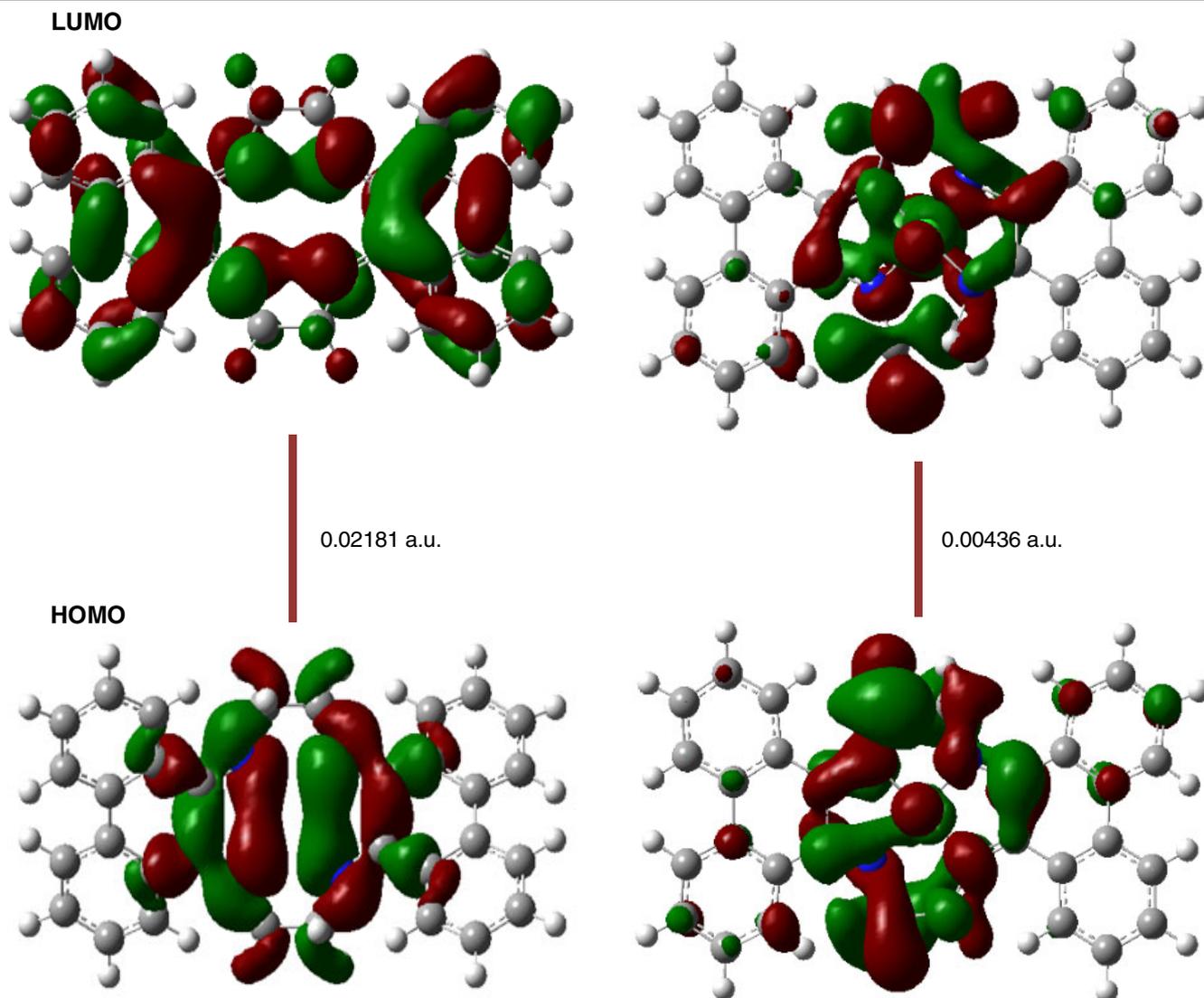


Fig. 10. Frontier molecular orbitals of Schiff base ligand L_1 and its copper complex (from left to right)

TABLE-4
COMPUTED ELECTRONIC VALUES OF LIGANDS AND THEIR METAL COMPLEXES USING DFT/B3LYP METHOD

Ligand/complex	Total energy (au)	Dipole moment (D)	HOMO (au)	LUMO (au)	HOMO-LUMO energy gap (au)
L_1	-1452.392	4.0034	-0.01072	0.03253	0.02181
L_2	-1530.857	5.2797	-0.01021	0.02135	0.01114
$[\text{Co}L_1\text{Cl}_2]$	-1626.912	2.1077	-0.00107	0.00842	0.00735
$[\text{Cu}L_1\text{Cl}_2]$	-2569.686	1.2381	-0.00323	0.00759	0.00436
$[\text{Co}L_2\text{Cl}_2]$	-3802.051	3.4320	-0.03809	0.08422	0.04613
$[\text{Cu}L_2\text{Cl}_2]$	-2956.897	2.5643	-0.02314	0.06854	0.04540

reactivity and the kinetic stability of a molecule can characterize by using value of the HOMO-LUMO energy gap.

Conclusion

In summary, two macrocyclic Schiff base ligands (L_1 and L_2) and their Co(II)/Cu(II) complexes were synthesized and characterized by conventional spectroscopic as well as computational investigations. The chemical structures of the Schiff base ligands and the ground state electronic structures complexes were tentatively proposed IR, ESR and mass spectroscopy. IR bands predicts the M-N bond in the complexes which

were absent in the ligands whereas copper ESR proposed the octahedral geometry of copper complexes. DFT/B3LYP theoretical analysis, respectively.

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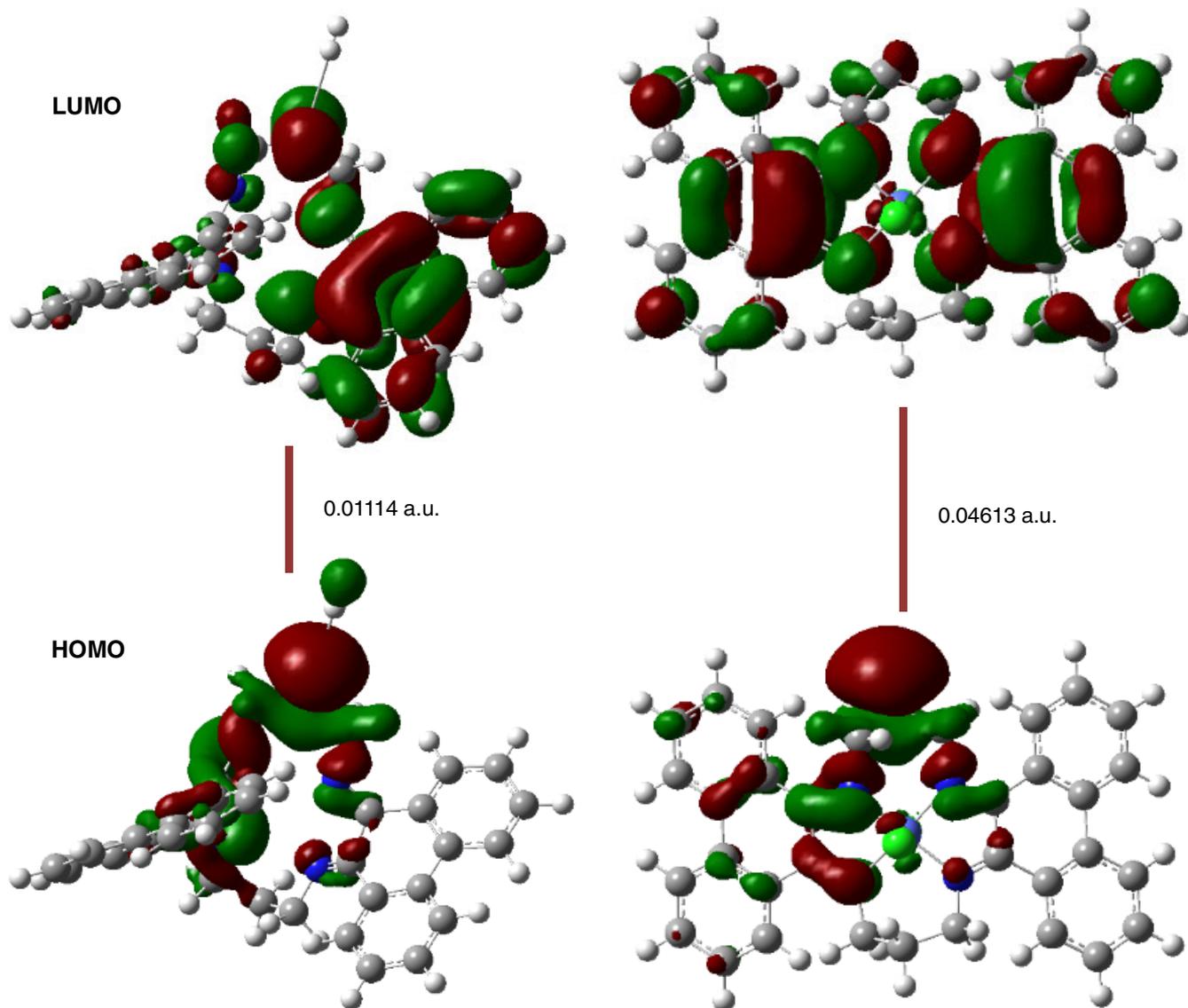


Fig. 11. Frontier molecular orbitals of Schiff base ligand L₂ and its cobalt complex (from left to right)

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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