

# Synthesis, Characterization and Theoretical studies of Mixed–Ligand complexes of $[\text{Cu}(\text{bipy})_2(4\text{-methylimidazole-5-carboxaldehyde})(\text{ClO}_4)_2]$ and $\text{Cu}(\text{bipy})_2(\text{indole-3-carboxaldehyde})(\text{ClO}_4)_2$

Oluwafunmilayo F. Adekunle<sup>1,2,\*</sup>, Nelson Obi-Egbedi<sup>3</sup>, Banjo Semire<sup>1</sup> and Olusegun A. Odunola<sup>4</sup>

<sup>1</sup>Ladoke Akintola University of Technology, Department of Pure and Applied Chemistry, P.M.B.4000, Ogbomosho, Nigeria.

<sup>2</sup>Howard University, Department of Chemistry, Washington DC, USA.

<sup>3</sup>University of Ibadan, Department of Chemistry, Ibadan, Nigeria.

<sup>4</sup>Hallmark University, Department of Chemistry, Ijebu-Itele, Nigeria.

## ARTICLE INFO

### Article history:

Received: 6 April 2016;

Received in revised form:

21 May 2016;

Accepted: 26 May 2016;

### Keywords

Mixed- ligand,  
Metal analyses,  
Antiferromagnetic,  
Electrolytes,  
Transitions.

## ABSTRACT

The mixed-ligand complexes,  $[\text{Cu}(\text{bipy})_2(4\text{-methylimidazole-5-carboxaldehyde})(\text{ClO}_4)_2]$  (**1**) and  $\text{Cu}(\text{bipy})_2(\text{indole-3-carboxaldehyde})(\text{ClO}_4)_2$  (**2**) were synthesized and characterized by employing elemental analyses, metal analyses, infrared and UV-Vis spectroscopy, room temperature magnetic susceptibility measurements, conductivity measurements and theoretical studies. The elemental and metal analyses show good agreement which support the formulation for the prepared complexes while the infrared spectroscopy revealed the coordination through both the nitrogen atom of the imidazole ring and the oxygen atom of the aldehyde group for (**1**). In complex (**2**), the coordination was through the oxygen atom only. The electronic transitions observed in the UV-Vis region show the various intraligand transitions and the d-d transitions at  $14,347\text{cm}^{-1}$  with a shoulder at  $11,115\text{cm}^{-1}$  for (**1**) and for (**2**) the bands are  $13,642\text{cm}^{-1}$  and  $11,494\text{cm}^{-1}$ . The magnetic moments 1.44B.M (**1**) and 1.34B.M (**2**) show antiferromagnetic properties of the complexes. From the theoretical studies, the Binding energies (Stabilization Energies) are found to be  $-33.85$  ( $-466.46$ ) kcal/mol and  $-32.73$  ( $-465.17$ ) kcal/mol for (**1**) and (**2**) respectively. Therefore, the theoretical calculations corroborated the formation of a six-coordinate complex in (**1**) and a five-coordinate geometry around the Cu ion in (**2**). The conductivity measurement revealed that the complexes are 1:2 electrolytes.

© 2016 Elixir All rights reserved.

## Introduction

Copper imidazole complexes chemistry has been of considerable interest due to the fact that imidazole as a ligand and the copper ion as the central metal both have biological importance [1, 2]. These biological importance include the roles played by them in a number of metalloproteins, in processes such as electron transfer, oxidation, dioxygen transport, the deactivation of toxic intermediates of  $\text{O}_2$  in reduction and the biological nitrogen cycle [1,3,4]. They also have significant activities in proteins such as azurins, amine oxidase, oxygen binding hemocyanins [3]. The varieties of roles played by copper proteins depend entirely on the interactions between the ligands and or solvent molecules attached to the copper center [4] and also on the redox properties exhibited by that copper center [4]. A number of geometrical arrangements have been reported for these compounds which ranges from three as observed in the plastocyanin and five as in azurin [4]. Heteroleptic copper(II) complexes involving a ligand with imidazole ligand as a co-ligand with their structural properties investigated have been extensively studied due to their structural diversity [3,5-8].

Another important class of nitrogen donor ligand that has received much attention is indole and its derivatives which are widely utilized in making perfumes, dyes, agrochemicals [9]. A number of drug molecules and biologically active

compounds are known to contain the indole ring system [10]. This class of compound has been studied to possess some biological properties such as antibacterial, antitumour, antitubercular and analgesic activities [9,10]. Indole and its derivatives have been studied extensively in the form of their Schiff base complexes with their biological activities investigated [10-15].

Herein, we report the synthesis, characterization and theoretical studies of the mixed ligand complexes of  $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$  with 4-methylimidazole-5-carboxaldehyde (**1**) and indole-3-carboxaldehyde (**2**).

## Experimental

### Materials and method

#### Reagents

2,2'-bipyridine, copper perchlorate hexahydrate, 4-methylimidazole-5-carboxaldehyde, indole-3-carboxaldehyde, and other reagents were purchased from Aldrich Chemical Co., and were used without further purification. Bis-(2,2'-bipyridine) copper perchlorate,  $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$  was synthesized according to Literature [16].

**Synthesis of  $[\text{Cu}(\text{bipy})_2(4\text{-methylimidazole-5-carboxaldehyde})(\text{ClO}_4)_2]$ ,  $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_5\text{H}_6\text{N}_2\text{O})(\text{ClO}_4)_2]$  (**1**)**

176 mg (1.6 mmole) 4-methylimidazole -5-carboxaldehyde was added to a 100 mL acetonitrile solution of

920 mg (1.6mmole)  $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$ . The blue solution obtained immediately was stirred for 24h after which it was filtered by gravity and kept on the bench for crystallization.

After 5days, the blue precipitate obtained was filtered by gravity, washed with acetonitrile and then dried in the dessicator over Calcium chloride. Yield: 983 mg, 87 % Anal. Calcd for  $[\text{Cu}(\text{bipy})_2(\text{C}_5\text{H}_6\text{N}_2\text{O})](\text{ClO}_4)_2$  (%): C, 43.81; H, 3.24; N, 12.27; Cu, 9.28. Found: C, 43.94; H, 3.22; N, 12.20, Cu, 9.26. ATRIR $\nu/\text{cm}^{-1}$ : 1061vs, 768m ( $\text{ClO}_4$ ), 1666 s ( $\text{C}=\text{O}$ ), 1605  $\nu(\text{C}=\text{N})$ , 1251 m  $\nu_{\text{ring}}(\text{C}-\text{N})$ , 3440 br (N-H), 419 m (M-O), 625 m (M-N).  $\mu_{\text{eff}}$ : 1.44 B.M. (at 300 K). UV-Vis ( $\text{CH}_3\text{CN}$ ) $\lambda_{\text{max}}/\text{cm}^{-1}$ : 33,333, 32,362, 27,248, 14,347br, 11,115sh.  $\Lambda_{\text{M}}(\text{CH}_3\text{CN})$ : 171 mho  $\text{cm}^2 \text{mol}^{-1}$  (1:2 electrolyte).

#### Synthesis of $[\text{Cu}(\text{bipy})_2(\text{indole-3-carboxaldehyde})](\text{ClO}_4)_2 \cdot \{[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_9\text{H}_7\text{NO})](\text{ClO}_4)_2\} (2)$

To a solution of 0.69 g (1.2 mmole)  $[\text{Cu}(\text{bipy})_2](\text{ClO}_4)_2$  in 100 mL acetonitrile, 1.2 mmole (0.17 g) indole-3-carboxaldehyde was added and the light - blue colored solution obtained was stirred for 24 h. The resulting clear solution was filtered by gravity and was kept on the bench for crystallization to take place. After five days, the blue precipitates obtained were filtered by suction and dried in the dessicator over calcium chloride. Every attempt to get the single crystals of the compound failed with the formation of the  $[\text{Cu}(\text{bipy})_2](\text{ClO}_4)_2$  starting complex crystals. Yield: 0.66 g (75 %). Elemental analysis: Anal. Calcd for  $[\text{Cu}(\text{bipy})_2(\text{C}_9\text{H}_7\text{NO})](\text{ClO}_4)_2$  (%): C, 48.35; H, 3.22; N, 9.73; Cu, 8.83. Found: C, 50.00; H, 3.48; N, 9.69; Cu, 8.43. ATRIR  $\nu/\text{cm}^{-1}$ : 1634 ( $\text{C}=\text{O}$ ), 1604  $\nu(\text{C}=\text{N})$ , 1244  $\nu_{\text{ring}}(\text{C}-\text{N})$ , 3446 (N-H), 3079 (C-H aromatic), 411 (M-O), 1087 (vs), 772 (m) ( $\text{ClO}_4$ ).  $\mu_{\text{eff}}$ : 1.34 B.M. (at 297 K). UV-Vis ( $\text{CH}_3\text{CN}$ )  $\lambda_{\text{max}}/\text{cm}^{-1}$ : 32,258, 27,247, 13,642, 11,494 sh.  $\Lambda_{\text{M}}(\text{CH}_3\text{CN})$ : 333 mho  $\text{cm}^2 \text{mol}^{-1}$  (1:2 electrolyte).

#### Physical measurements

CHN analyses were carried out by Atlantic Microlab, Atlanta GA. Electronic spectra were recorded on a Genesys 10 UV-Visible Spectrophotometer. Infrared spectra were recorded on a Perkin - Elmer PE 100 spectrometer with an Attenuated Total Reflectance (ATR) window. The room temperature magnetic susceptibility measurements were recorded using Sherwood Scientific magnetic susceptibility balance MSB MK1. The diamagnetic correction evaluated from Pascal's constant. Conductance measurements of ca.  $10^{-3}$  M solutions of the complexes in  $\text{CH}_3\text{CN}$  were measured using a Jenway 4310 Conductivity meter. The percentage metal was determined by the employment of complexometric titration using EDTA [17].

#### Quantum Chemical Calculations

The optimized structures of  $[\text{Cu}(\text{bipy})_2(\text{C}_5\text{H}_6\text{N}_2\text{O})]^{2+}$  (1) and  $[\text{Cu}(\text{bipy})_2(\text{C}_9\text{H}_7\text{NO})]^{2+}$  (2) complexes were modeled using Spartan program (Spartan 10) implemented on an Intel core i3-2350M computer. The two complexes (1) and (2) were modeled based on the spectroscopic interpretations. Therefore in the case of (2), other possibilities involving O and N atoms of indole-3-carboxaldehyde in ligand-metal bonds were considered; hence the three possible coordination modes of 2 (i.e. (2a), (2b) and (2c)) were modeled to determine their thermodynamic stabilities as shown in Fig. 1. The optimization and frequency calculations for the complexes were performed using Density Functional theory (DFT) level based on the preliminary conformational search on all the molecules with MMFF method with Monte Carlo search algorithm [18]. Density functional theory (DFT) calculations were performed with the hybrid B3LYP exchange and correlation functional [19,20] and 6-31G (d) basis set but all

attempt to optimize complex (2c) failed; thus it is not discussed. All calculations were carried out without symmetry restriction.

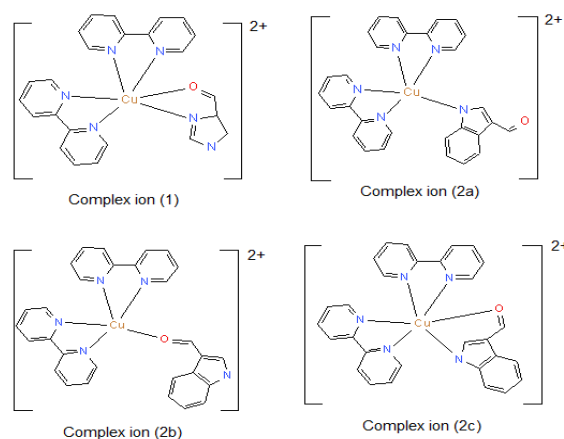


Figure 1. Schematic structures of the studied complexes.

#### Results and Discussion

The copper(II) mixed-ligand complexes were obtained by constant stirring (24 h) of a mixture of the starting complex  $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$  with 4-methylimidazole-5-carboxaldehyde to give (1) and with indole-3-carboxaldehyde to obtain (2). The blue compounds obtained at high yields gave satisfactory results from both the microanalyses and metal analyses data. The infrared spectra of complex (1) show characteristic absorption band of the imidazole  $\nu(\text{N}-\text{H})$  at  $3440 \text{ cm}^{-1}$  [ 2, 21, 22] and the calculated value was found to be  $3602 \text{ cm}^{-1}$ , the  $\nu(\text{C}=\text{N})$  imidazole was at  $1605 \text{ cm}^{-1}$  [21,22-24] and  $1570 \text{ cm}^{-1}$  respectively for the experimental and theoretical values which indicate the coordination to the metal center through the imine nitrogen of imidazole. The  $\nu(\text{C}=\text{O})$  observed at  $1666 \text{ cm}^{-1}$  for the experimental value [ 9,25-27] and at  $1746 \text{ cm}^{-1}$  from the theoretical studies is an indication of the participation of the carbonyl in the formation of the mixed-ligand complex. The  $\nu_{\text{ring}}(\text{C}-\text{N})$  stretching frequency of this complex was at  $1251 \text{ cm}^{-1}$  which is in agreement with similar compounds reported [ 9,26,27] while the calculated value is  $1275 \text{ cm}^{-1}$ . The absorption bands at  $2923 \text{ cm}^{-1}$  and  $2858 \text{ cm}^{-1}$  were attributed to  $\nu(\text{C}-\text{H})$  stretching frequencies [25] of the methyl group in the spectrum of the complex but was calculated to be  $3063 \text{ cm}^{-1}$  while that of the imidazole ring is in the region  $3290-3209 \text{ cm}^{-1}$ . The  $\nu(\text{Cu}-\text{O})$  and  $\nu(\text{Cu}-\text{N})$  were observed at  $419 \text{ cm}^{-1}$  and  $625 \text{ cm}^{-1}$  respectively [9,26,27] these were calculated to be 423 and  $649 \text{ cm}^{-1}$  respectively. For complex (2),  $\nu(\text{N}-\text{H})$  was observed at  $3446 \text{ cm}^{-1}$  [2,22] and was calculated to be  $3615 \text{ cm}^{-1}$  (2b). The  $\nu(\text{C}=\text{N})$  of the indole-3-carboxaldehyde appeared at  $1604 \text{ cm}^{-1}$  while the  $\nu(\text{C}=\text{O})$  of this complex is at  $1634 \text{ cm}^{-1}$  which indicate the use of the oxygen atom of the carbonyl group in the formation of the mixed-ligand complex [9,25-27]. As mentioned in the computational methodology, three complexes were modeled for compound (2) in which only (2a) and (2b) were optimized. The  $\nu(\text{C}=\text{N})$  calculated are  $1618 \text{ cm}^{-1}$  and  $1621 \text{ cm}^{-1}$  for (2a) and  $1519$  and  $1623 \text{ cm}^{-1}$  for (2b) (Table 1). Also,  $\nu(\text{C}=\text{O})$  stretching frequencies calculated are found to be  $1762 \text{ cm}^{-1}$  and  $1657 \text{ cm}^{-1}$  for (2a) and (2b) respectively which indicate that the  $\nu(\text{C}=\text{O})$  of the complex (2b) agrees with the experimental value suggesting (2b) to be the synthesized complex; thus coordination is through the carbonyl oxygen of the indole-3-carboxaldehyde. The absorption band at  $1244 \text{ cm}^{-1}$  which was assignable to the  $\nu_{\text{ring}}(\text{C}-\text{N})$  of the five-membered ring of the indole-3-carboxaldehyde [9,26, 27] was calculated to be  $1287 \text{ cm}^{-1}$  and  $1251 \text{ cm}^{-1}$  for (2a) and (2b) respectively.

Table 1. Selected vibration frequencies for the complexes (1) and (2).

Complex	Experimental							Calculated							
	-NH	C=N	C=O	C-N	C-H	Cu-N	Cu-O		NH	C=N	C=O	C-N	C-H	Cu-N	Cu-O
(1)	3440	1605	1666	1251	2923, 2858	625	419		3602	1570	1746	1275	3290-3209 (C-H) 3167- 3063 (CH <sub>3</sub> )	649	423
(2)	3446	1604	1634	1244	3079	-	411	2a)	-	1618, 1621	1762	1287, 1304	3284-3198 (C-H) 2997 (CH of Carbonyl)	652, 675	-
								(2b)	3615	1519, 1623	1657	1251, 1307	3291-3196 (C-H) 3039 (CH of Carbonyl)	645, 648	424

The visible region of the electronic spectra for complex (1) displayed two bands at 14,347cm<sup>-1</sup> and 11,115cm<sup>-1</sup> these are attributed to the d-d transitions of tetragonally distorted octahedral geometry around the Cu<sup>2+</sup> ion [28,29]. The high energy transitions observed 33,333cm<sup>-1</sup> with a shoulder at 32,365cm<sup>-1</sup> are assignable to the  $\pi^2_{\text{imidazole}} \rightarrow \text{Cu(II)}$  transition [2,29, 30]. In complex (2), the visible region displayed a high-energy, high-intensity peak at 13,643cm<sup>-1</sup> attributed to  $d_{xz} \approx d_{yz} \rightarrow d_{x^2-y^2}$  transition and the shoulder at 11,494cm<sup>-1</sup> assigned to the low-energy transition  $d_z^2 \rightarrow d_{x^2-y^2}$  of the five-coordinate copper(II) geometry [5, 31,32].

The magnetic moments of the two complexes were observed at 1.44 B.M. for (1) and 1.34 B.M for (2). These low values for the magnetic moments are attributed to antiferromagnetic properties present in the complexes [5]. The calculated molecular parameters such as total energy, HOMO, LUMO, dipole moment, binding energy and stabilization energy for the complexes are displayed in Table 2. Total energies for complexes (1), (2a) and (2b) are -3009.60(au), -3107.18(au) and -3107.88 (au) respectively, these show that complex (2b) is thermodynamically more stable by 437.44 kcal/mol than complex (2a). To evaluate the effect of 4-methylimidazole-5-carboxaldehyde and indole-3-carboxaldehyde on complexes (1) and (2) respectively, the binding energy (BE) and the stabilization energy (Stab.E) are calculated from the energy involved in the dissociation processes as shown in equations (1) and (2) [33,34]:  
Binding energy (B.E) = E[CuX<sub>2</sub>L]<sup>2+</sup> - E[CuX<sub>2</sub>]<sup>2+</sup> - E L -----(1)  
Stabilization energy (Stab.E) = E[CuX<sub>2</sub>L]<sup>2+</sup> - E(Cu<sup>2+</sup> + 2X + L)----- (2)

where X = 2,2'-bipyridine and L = 4-methylimidazole-5-carboxaldehyde or indole-3-carboxaldehyde and E = energy of each species.

The calculations of the binding energies as well the stabilization energies are carried out on the complex ions only for the ground states. The B.E and Stab.E for compound (1) are -33.85 kcal/mol and -466.46 kcal/mol respectively. For the compound (2), the B.E and Stab.E are 404.94 kcal/mol and -27.73 kcal/mol for (2a), and -32.73 kcal/mol and -465.17 kcal/mol for (2b) respectively.

The results of the thermodynamic stability, binding and stabilization energies suggest that compound (2b) would be more probable/favorable to exist when compared to (2a)

which agrees with the experimentally proposed coordinated atom for the complex (2).

The HOMO, LUMO and HOMO-LUMO band gap energies calculated at DFT are -12.33 eV, -7.59 eV and 4.74 eV for compound (1); -11.45 eV, -10.06 eV and 1.39 eV for complex (2a) and -10.68 eV, -7.68 eV and 3.00 eV for (2b).

Table 2. Molecular parameters calculated for the complexes at DFT level.

Parameters	(1)	(2a)	(2b)
Total Energy (au)	-3009.59995	-3107.17919	-3107.87630
Rel Energy (kcal/mol)	-	437.44	0.00
HOMO (eV)	-12.33	-11.45	-10.68
LUMO (eV)	-7.59	-10.06	-7.68
Band gap (eV)	4.74	1.39	3.00
Dipole Moment (Debye)	4.59	7.36	4.19
Stab.E (kcal/mol)	-466.46	-27.73	-465.17
B.E (kcal/mol)	-33.85	404.94	-32.51
Mullikan charge (e)			
N1	-0.641	-0.634	-0.655
N2	-0.595	-0.591	-0.617
N3	-0.621	-0.626	-0.649
N4	-0.642	-0.632	-0.639
N5	-0.597	-0.656	-0.651
N6	-0.576	-	-
O1	-0.430	-0.364	-0.548
Cu1	1.000	0.930	0.971

The band gap energy of complex is related to the thermodynamic stability, compounds with higher values of HOMO-LUMO band gap energies are more thermodynamically stable and hence compound (2b) will be thermodynamically feasible compared to (2a). The HOMOs revealed that the  $\pi$ -electrons of the system dwell mainly on one unit of 2,2'-bipyridine ligands for (1) and on indole-3-carboxaldehyde for (2) (Fig.2). The LUMOs are spread over the 2,2'-bipyridines in the two complexes.

This shows that in these Cu(II) complexes, the unoccupied molecular orbitals are located on 2,2'-bipyridine moiety.

The dipole moment (D.M) and solvation energy (S.E) are some important parameters to be considered in solute-solvent interactions, therefore D.M and S.E calculated show that compounds (1) and (2b) may exhibit more complex-solvent

interactions. The electronic charges on nitrogen atoms involved in the coordination and Cu(II) show transfer of charges (electrons) from nitrogen atoms to the Cu(II) ion. The electronic charges on O1, N5 and Cu(II) ion are  $-0.364e$ ,  $-0.656e$  and  $0.930e$  for compound (2a);  $-0.548e$ ,  $-0.651e$  and  $0.971e$  for compound (2b) respectively as shown in Table 2, suggesting that O1 not N5 was involved in the coordination in compound (2), thus complex (2b) is actually synthesized complex.

#### Geometries of the Cu(II) complexes

The selected calculated geometries for the modeled complexes at B3LYP/6-31G\* are displayed in Table 3.

#### Conclusion

$[\text{Cu}(\text{bipy})_2(\text{C}_5\text{H}_6\text{N}_2\text{O})](\text{ClO}_4)_2$  (1) and  $[\text{Cu}(\text{bipy})_2(\text{C}_9\text{H}_7\text{NO})](\text{ClO}_4)_2$  (2) complexes were synthesized and successfully characterized. Complex (1), a six-coordinate octahedral complex obtained by the participation of both the nitrogen atom and the oxygen atom of the 4-methylimidazole-5-carboxaldehyde to form a bond to the central  $\text{Cu}^{2+}$  ion. The data from the theoretical studies was in support of the involvement of both the nitrogen atom and the oxygen of the carbonyl group in the formation of the six-coordinate

geometry. On the other hand, complex (2) which was obtained by the reaction of  $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$  with indole-3-carboxaldehyde is a five-coordinate copper(II) complex from the data obtained from the UV-Visible spectrum. The theoretical studies supported this coordination number for the complex. The calculated thermodynamic stability, binding and stabilization energies reveal that carbonyl oxygen atom (not nitrogen atom) of the indole-3-carboxaldehyde was involved in coordination to the copper ion in the complex (2). Furthermore, The CHN analyses coupled with copper(II) ion content determination were used in formulating the molecular formula of the complexes. The infrared, electronic spectra in conjunction with room temperature magnetic susceptibility measurements corroborated the molecular formula.

#### Conflict of Interests

The authors declare that there is no conflict of interests.

#### Acknowledgment

O. F. A is grateful to Department of Chemistry Howard University, Washington DC for the use of their laboratory to carry out research as a visiting Research Scientist and to Ladoké Akintola University of Technology, Ogbomoso, Nigeria for the leave of absence.

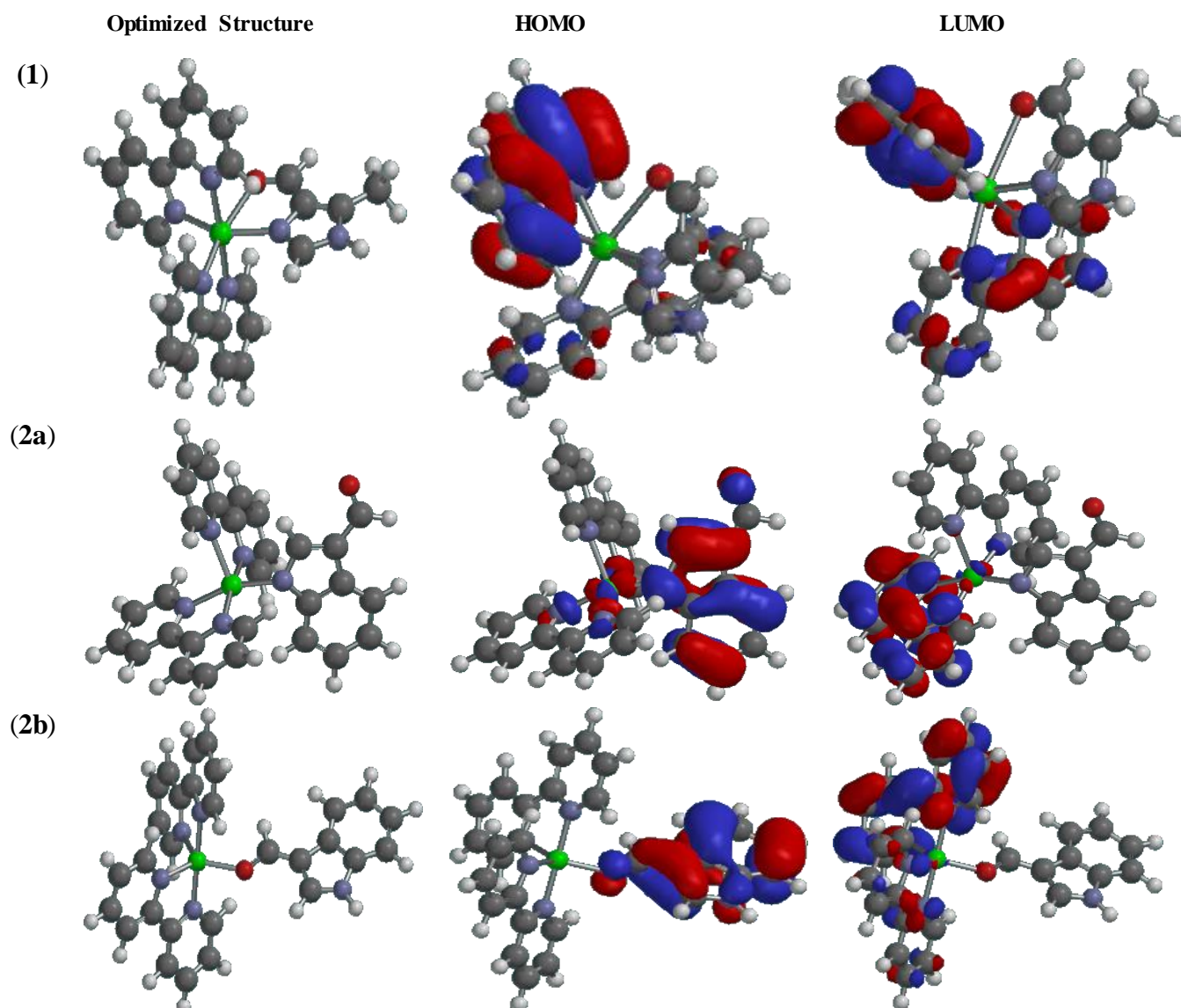


Fig 2. The optimized structures, HOMO and LUMO overlays of the complexes.

## References

- [1] C.T. Brewer, G. Brewer, M. Shang, W.R. Scheidt and I. Muller, "synthesis and characterization of neutral, low spin iron(III) complexes of a hexadentate tripodal ligand containing 3-imidazole arms-use as a dinucleating agent," *Inorg. Chim. Acta* 278, pp.197 – 201, 1998.
- [2] S. Mukherjee, T. Weyhermuller, E. Bill and P. Chaudhuri, "Tetranuclear copper(II) and nickel(II) complexes incorporating a new imidazole containing ligand," *Eur. J. Inorg. Chem.* pp. 4209 – 4215, 2004.
- [3] S. Godlewska, J. Jezier, K. Baranowska, E. Augustin and A. Dolega, "Copper(II) complexes with substituted imidazole and chloride ligands: X-ray, uv-vis, magnetic and EPR studies and chemotherapeutic potential," *Polyhedron* 65, pp. 288 – 297 2013.
- [4] E. K. Beloglazkina, A. G. Majouga, A.V. Mironov, A.V. Yudina, A.A. Moiseeva, M.A. Lebedeva, A.N. Khlobystov and N.V. Zyk, synthesis, X-ray crystallographical and electrochemistry of three novel copper complexes with imidazole-containing hydantoin and thiohydantoins," *Polyhedron* 63, pp15 – 20, 2013.
- [5] L-S. Long, J-W. Cai, Y-P. Y-X. Ji L-N., R-B. Huang and L-S. Zheng, "Hydrogen bond induced change of geometry and crystallized form of copper(II) complexes: syntheses and crystal structure of complexes with Schiff-base ligands containing two imidazolyl groups," *J. Chem. Soc., Dalton Trans.*, pp. 845 – 849, 2001.
- [6] R.N. Patel, N. Singh, K.K. Shukla and V.L.N. Gundla, "E.s.r, magnetic, electronic and superoxide dismutase studies of imidazole –bridged  $\text{Cu}^{\text{II}}$  – $\text{Cu}^{\text{II}}$  complexes with ethylenediammine as capping ligand." *Spectrochimica Acta Part A* 61, pp.1893 – 1897, 2005 .
- [7] P. K. Coughlin and S.J. Lippard, "Magnetic, ESR, electrochemical and potentiometric titration studies of the imidazolate –bridge dicopper(II) ion in a binucleating macrocycle," *Inorg.Chem.*23, pp.1446 – 1451 1984.
- [8] M.F. Iskander, T.E. Khalil, R. Werner, W. Haase, I. Svoboda and H. Fuess " Synthesis, characterization and magnetochemical studies of some imidazole and imidazolate copper(II) ternary complexes derived from N-salicylidenearylhidrazines. X-ray crystal and molecular structures of [N-salicylidene-p-chlorobenzoylhidrazine)ONO(-2)imidazole] copper(II) monohydrate and dimeric [N-salicyliden-p-methylbenzoylhidrazine)ONO(-2)imidazole]copper(II)hemihydrate," *Polyhedron* 19, pp.1181 – 1191, 2000.
- [9] R. S. Joseyphus and M.S. Nair, " Synthesis , characterization and biological studies of some Co(II),Ni(II), and Cu(II) complexes derived from indole-3-carboxaldehyde and glycyglycine as Schiff base ligand,"*Arabian Journal of Chemistry* 3, pp.195 – 204, 2010.
- [10] N. Sari, S. Arslan, E. Logoglu and I. Sakiyan, " Antibacterial activities of some new amino acid Schiff base" *G.U.Journal of Science* 16, pp.283 – 288, 2003.
- [11] B.K. Rai, Ranjana, P. Prakash and P. Lata" Synthesis, spectral and biocidal screening of Schiff base complexes of Co(II), Ni(II) and Cu(II) containing nitrogen and sulphur donor atoms," *Orient. J. Chem.*, 28, pp.1803 – 1808, 2012.
- [12] T. Rosu, E. Pahontu, D-C. Ilies, R. Georgesu, M. Mocanu, M. Leabu, S. Shova, A. Gulea, " Synthesis and characterization of some new complexes of Cu(II), Ni(II), V(IV) with Schiff base derived from indole-3-carboxaldehyde. Biological activity on prokaryotes and eukaryotes," *European Journal of Medicinal Chemistry* 53, pp.380 – 389, 2012.
- [13] R.S. Joseyphus and M. S. Nair," Antibacterial and antifungal studies of some Schiff base complexes of zinc(II)," *Mycobiology* 36,pp. 93 – 98, 2008.
- [14] M. S. Nair, D. Arish and R.S. Joseyphus, " Synthesis, characterization, antifungal, antibacterial and DNA cleavage studies of some heterocyclic schiff base metal complexes," *Journal of Saudi Chemical Society* 16, pp. 83 – 88, 2012.
- [15] J. Kaur, A. Bhardwaj, Z. Huang, and E. E. Knaus, "N-1 and C-3 substituted indole schiff bases as selective COX-2 inhibitors: synthesis and biological evaluation" *Bioorganic and Medicinal Chemistry letters* 22, pp.2154 – 2159, 2012.
- [16] H. Nakai, "The crystal structure of perchlorate-bis(2,2'-bipyridine)copper(II)perchlorate, $[\text{Cu}(\text{ClO}_4)(\text{bipy})_2]\text{ClO}_4$ ," *Bull. Chem.Soc. Jpn.* 44, pp.2412 -2415, 1971.
- [17] J. Basset, R. C. Denney, G.H. Jeffery, Mendham J. Vogel's Textbook of Quantitative Inorganic Analysis: Longman Scientific and Technical: London, 1986, pp.316 – 322.
- [18] Spartan user's guide, Wave function, Inc, Irvine, CA 92612 USA
- [19] P.J. Stephens, F.J. Devlin, C.F. Chabalowski and M. J. Frisch, " Ab Initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields" *J. Phys. Chem.*, 98, p. 11623, 1994.
- [20] Becke A.D., "Density –functional thermochemistry.III. The role of exact exchange" *J. Chem. Phys.*, 98, p. 5648, 1993.
- [21] C. Brewer, G. Brewer, R. J. Butcher, E. E. Carpenter, L. Cuenca, B. C. Noll, W.R. Scheidt., C. Viragh, P.Y. Zavalij and D. Zielaski, " Synthesis and characterization of manganese (II) and iron(II)  $d^5$  tripodal imidazole complexes. Effect of oxidation, protonation state and ligand conformation on coordination number and spin state," *Dalton Trans* pp. 1009 – 1019, 2006.
- [22] R.S. Joseyphus, C. Shiju, J. Joseph, C. J. Dhanaraj, and K.C. Bright, "Synthesis and characterization of Schiff base metal complexes derived from imidazole-2-carboxaldehyde with L-phenylalanine," *Der Pharma Chemica* 7, pp. 265 – 270, 2015.
- [23] R.K. Gupta, A.K. Singh, M. Yadav, P. Kumar, S. K. Singh, P. Li, Q. Xu and D. S. Pandey, " Synthesis and characterization of Ru(IV) and Rh(I) complexes containing phenylimidazole ligands," *Journal of Organometallic Chemistry* 695, pp. 1924 – 1931, 2010.
- [24] G. Brewer, C. Brewer, R. J. Butcher, E. E. Carpenter, L. May and G. White, *Inorg. Chim. Acta* 360, pp. 2153 – 2161, 2007.
- [25] G. Brewer, C. Brewer, G. White, R. J. Butcher, C. Viragh, E.E. Carpenter and A. Schmiedekamp, " Synthesis and characterization of iron(II) and iron(III) complexes - a tripodal ligand derived from tris (2-aminoethyl)methane, *Inorg. Chim. Acta* 362, pp. 4158 – 4166, 2009.
- [26] M.S. Nair, D. Arish and J. Johnson, "Synthesis, characterization and biological studies on some metal complexes with Schiff base ligand containing pyrazolone moiety," *Journal of Saudi Chemical Society* xxx, pp. xxx – xxx, 2013.
- [27] M. Sonmez, " Synthesis and characterization of copper(II), nickel(II). Cadmium(II), cobalt(II) and zinc(II) complexes with 2-benzoyl-3-hydroxy-1-naphthylamino-3-phenyl-2-prpen-1-on, *Turk. J. Chem.* 25, pp. 181 – 185, 2001.

- [28] T. E. Olalekan, D.R. Beukes, B. V. Brecht and G.M. Watkins, "Copper(II) complexes of 2-(methylthiomethyl) anilines: spectral and structural properties and in vitro antimicrobial activity," *Journal of Inorganic Chemistry* 2014, pp. 1 – 10, 2014.
- [29] S. Supriya and S. K. Das., " A simple Cu(II) complex, CuII{C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>}(NO<sub>3</sub>)<sub>2</sub> with an unprecedented hydrogen bonding supramolecular network in the solid state and its solution emission at room temperature in the visible region" *Inorganic Chemistry Communication* 6, pp. 10 – 14, 2003.
- [30] I. Ali, W.A. Wani, K. Saleem and M-F. Hseih, "Design and synthesis of thalidomide based dithiocarbamate Cu(II), Ni(II) and Ru(III) complexes as anticancer agents," *Polyhedron* 56, pp. 134 – 143, 2013.
- [31] F.A. Adekunle, J.A.O. Woods, O.O.E. Onawumi and O.A.Odunola, "Synthesis and characterization of nickel(II) complexes of various substituted acid hydrazides," *Asian Journal Of Chemistry* 22, pp. 5543 – 5550, 2010.
- [32] F.A.O. Adekunle and O.A.Odunola, " Synthesis and characterization of mixed ligand complexes of Cu(phen)<sub>2</sub> (ClO<sub>4</sub>)<sub>2</sub> with some aromatic ligands," *Chem. Sci. Trans.* 2, pp. 491 – 496, 2013.
- [33] F.A.O. Adekunle, B. Semire and O.A. Odunola "Mixed ligand complexes of Ru(II) complexes with 5,6-dimethyl-3pyridin-2-yl-[1,2,4] triazine: Synthesis, characterization and quantum chemical study using semi-empirical PM3 and Abinitio methods," *Elixir Comp. Chem.* 61, pp. 17019-17023, 2013.
- [34] F.A.O. Adekunle, B. Semire and O.A. Odunola "Synthesis, characterization and quantum chemical studies of Ru(phen)<sub>2</sub> Cl<sub>2</sub>.2H<sub>2</sub>O and Ru(bipy)<sub>2</sub> Cl<sub>2</sub>.2H<sub>2</sub>O with 2,6-diacetylpyridinedihydrazone," *Synth.React. Inorg. Met.-Org.Chem.* 45, (8) pp. 1102 -1107, 2015.