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SYNTHESIS, CHARACTERIZATION AND THEORETICAL ASPECTS OF COPPER AND ZINC DIVALENT ION COMPLEXES WITH AZO DYE DERIVED FROM 4,5-DIPHENYLIMIDAZOLE

Suad Taha Saad*

Department of Chemistry, College of Science for Women, University of Babylon-Hilla, Iraq

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ABSTRACT. Azo dye ligand derived from 4,5-diphenyl imidazole and 4,4-diaminodiphenylmethane was synthesized by diazomium coupling reaction. In this reaction an amine (4,4-diaminodiphenylmethane was converted to the diazonium salt and coupled with 4,5-diphenyl imidazole. The bright coloured Cu(II) and Zn(II) complexes with this ligand were synthesized by refluxing the latest with both metals chloride salts. The prepared compounds were characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR, UV-Visible, molar conductivity and atomic absorption. By the infrared data, the coordination between copper and zinc ions and the azo ligand achieved through the nitrogen of the azo group and one of the nitrogen atoms in the imidazole ring. By the molar conductivity test, the non-electrolytic nature of both complexes was also confirmed. The suggested structure for these complexes is octahedral. Using density functional theory (DFT) some theoretical data was obtained for the synthesized complexes. The obtained data include the highest occupied and the lowest unoccupied molecular orbitals energy (HOMO and LUMO), electron density, thermodynamic functions (ΔG°, ΔS°, ΔH°, ΔE°), ionization potential (IP), electron affinity (EA), electrophilicity($\dot{\omega}$), electronegativity (En), chemical hardness (η) and dipole moment (μ). According to these studied parameters some properties of the two complexes were explained and discussed.

KEY WORDS: Cu(II) and Zn(II) complexes, Azo ligand, 4,5-Diphenylimidazole, 4,4-Diaminodiphenylmethane, Theoretical study

INTRODUCTION

Azo dyes containing heterocyclic molecules in their structure are considered as an important class of dyes. Thanks to their attractive properties, such as the bright colour and the ease of synthesis [1, 2]. Therefore, such compounds have been exploited in different fields, such as in medicine, as they have been used for cancer, virus and fungi treatment [3-5]. While in industry they have been used as colorants for fibres, papers and cosmetics [6-8]. The wide varieties of these applications are due to the presence of the significant azo group (-N=N-) in these compounds structure [9-11]. Where this group bridges aromatic or alkyl units and gives the final azo compound structure [12]. In addition to this group, the presence of the heterocyclic units in the backbone of these dyes increases the conjugation in their chemical structure and leads to more intensive colours [13].

One of the most important heterocyclic units is the imidazole ring which has the properties of five and six membered rings molecules with one or two nitrogen atoms in their structure and that gives imidazole containing compounds more stability and a wide range of applications [1, 14-16]. Beyond these applications, in coordination chemistry, imidazole forms complexes with metal ions as this type of complexes is very common and interesting [13, 17]. Azo-imidazole containing complexes are formed through the two coordination sites namely, the azo group and one of the nitrogen atoms in the imidazole ring [18]. In some cases the presence of an adjacent coordinated atom also helps forming more stable complexes. The resulted complex is stable due to the formation of the five or six membered chelate ring [19]. In this paper azo ligand containing one imidazole derivative was synthesized and two of its complexes with Cu(II) and Zn(II) were also synthesized and characterized.

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*Corresponding author. E-mail: wsci.suaad.taha@uobabylon.edu.iq

EXPERIMENTAL

Materials

All the used materials are commercially available and used without further purification. 4,5-Diphenylimidazole and 4,4-diaminodiphenylmethane were supplied from Macklin, hydrochloric acid was supplied from Thomas Baker . Sodium nitrite and $ZnCl_2$ were purchased from CDH. Sodium hydroxide was supplied by BDH and $CuCl_2.2H_2O$ from Merck. Ethanol and methanol were purchased from Scharlau and Biosolvechimie SARL, respectively.

Instrumentation

The infrared spectra were measured using Fourier transform infrared spectrophotometer (FT-IR – 8400S) (4000-400 cm^{-1}) from Shimadzu. The electronic transitions were detected by UV-Visible spectrophotometer (CECIT CE 7200, 7000 series) from Aquaris. Bruker spectrometer instrument operating at (400 MHz) was used to measure ^1H NMR spectra. While the conductivity was measured by WTW SERIES, cond 722. Melting points were measured by using melting point/SMP30 Stuart apparatus.

Synthesis of azo dye ligand (A)

4,4-Diaminodiphenylmethane (1.5 g, 7.57 mmol) was dissolved in an aqueous solution of hydrochloric acid (4 mL, 16 mL DW). To this acidic solution sodium nitrite (1.044 g, 15.130 mmol) was added drop wise after dissolving it in 10 mL of DW. The temperature of this reaction was kept at 0-5 °C and the reaction left for 15 min. to complete the diazonium salt formation. On the other hand 4,5-diphenylimidazole (3.333 g, 15.130 mmol) was dissolved in methanol (100 mL) and an aqueous solution of sodium hydroxide (10 mL, 10%) was added. The diazonium salt solution was added to the basic solution of 4,5-diphenyl imidazole drop wise. An immediate orange azo dye was formed and left overnight, then was filtered, washed with water and ethanol.

Synthesis of copper and zinc divalent ions complexes

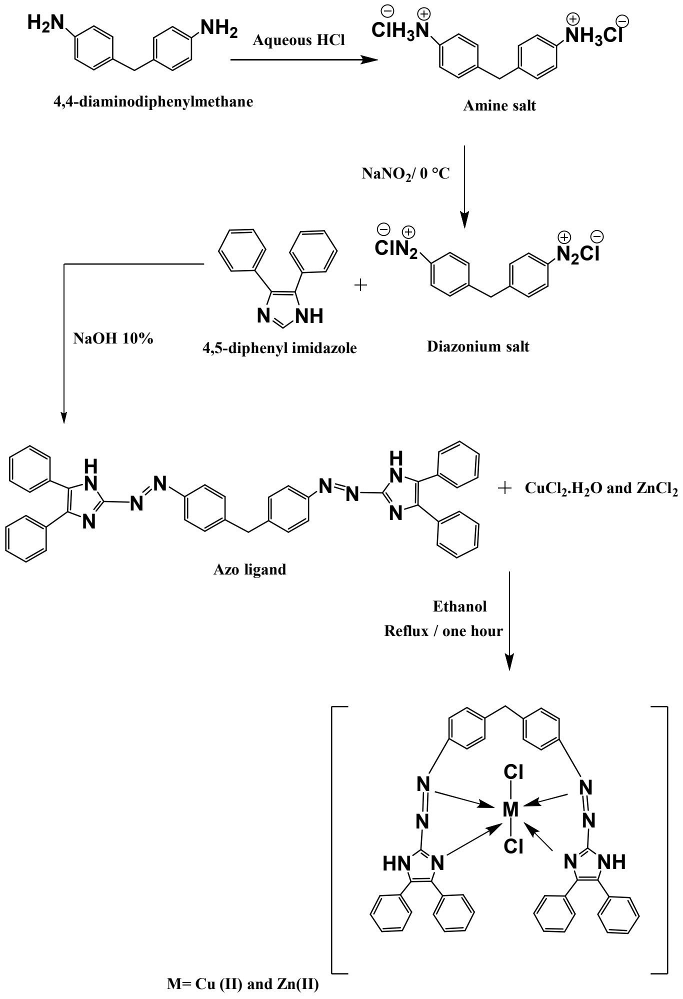
Both copper(II) and zinc(II) complexes with the synthesized azo ligand were synthesized by mixing the alcoholic ligand solution (0.5 g, 0.757 mmol) with an aqueous solution of $CuCl_2.2H_2O$ and $ZnCl_2$ (0.129 g, 0.757 mmol) and (0.103 g, 0.757 mmol) respectively in 5mL distilled water in 1:1 ligand:metal ratio. To complete this reaction, the reaction mixtures were refluxed for one hour. After cooling the red metallic complexes were separated and filtered. This filtration followed by washing step with water and ethanol.

RESULTS AND DISCUSSION

Ligand and metal complexes synthesis

The azo ligand was synthesized by the common and the simple method of diazonium coupling reaction. Firstly the diazonium salt was formed by adding an aqueous solutions of HCl followed by $NaNO_2$ solution to the used amine in this reaction (4,4-diaminodiphenylmethane). The formed salt was added to the basic alcoholic solution of the coupling compound which is 4,5-diphenyl imidazole. An immediate orange azo dye was precipitated.

By the reflux reaction between the synthesized dye with two metal ions, namely copper(II) and zinc(II) complexes were obtained. Their synthesis relies on the reflux reaction between the azo ligand with the two metal chloride salts in 1:1 (ligand:metal) molar ratio for one hour. The synthesis steps of the azo ligand and its complexes are given in Schemes 1 while, Table 1 shows some of their properties.



Scheme 1. Azo dye ligand (A), copper(II) and zinc(II) complexes synthesis.

Table 1. Features of the synthesized compounds.

Compound	Colour	m.p. °C	MWt g/mol	Yield %
Azo dye ligand (A)	Orange	143-145	660.79	90
$[Cu(A)Cl_2]$	Purple	233-235	795.23	53
$[Zn(A)Cl_2]$	Red	274-276	797.07	50

FT-IR spectroscopy

The infrared data of the azo ligand show some significant bands that related to the building blocks in the ligand structure. Such blocks include the imidazole ring, azo group, aliphatic –CH_2– group and the –CH– group in the phenyl rings. For example, the band at 3394 cm^{-1} refers to –NH– group in the imidazole ring. While the υ(C=N) in the imidazole moiety frequency vibration appears at 1597 cm^{-1}. The ligand spectra data also show the significant (–N=N–) band frequency vibration at 1435 cm^{-1}. While the aliphatic –CH_2– group and the –CH– group in the phenyl rings appear at 2980 $cm^{-1}$and 3059, 3026 cm^{-1}, respectively.

When the metal complexes formed these bands are shifted and changed in intensity which indicates the coordination through the related groups. In copper(II) and zinc(II) complexes, the –NH– group is affected slightly however, that doesn't indicates the chelation with the azo ligand doesn't occur through the –NH group [9]. While other groups such as, the (C=N) have been changed in its intensity in both complexes. Which refers to the coordination between the two metals and the ligand through the nitrogen atom of the (C=N) group in the imidazole ring. The (N=N) band frequency vibration is also shifted to 1442 and 1444 cm^{-1} in both complexes, respectively. Which indicates the coordination between the metals and the ligand occurs through one of the nitrogen atoms of the azo group [17]. Other new bands in the range (400-600) cm^{-1} refers to the formation of M-N bond type [20]. Table 2 gives a summary of FT-IR data.

Table 2. FT-IR data in cm^{-1} of azo ligand and the two complexes.

Compound	υ(-NH-)	υ(C-H) (aromatic)	υ(C-H) (aliphatic)	υ(N=N)	υ(C=N)	υ(M-N)
Azo dye ligand (A)	3394	3059, 3026	2980	1435	1597	---
[Cu(A)Cl_2]	3416	3059, 3026	2902	1444	1597	516
[Zn(A)Cl_2]	3392	3059, 3028	2920	1442	1597	617

^{1}H-NMR ligand spectra

The ^{1}H-NMR spectrum of the ligand was detected in DMSO-d_6 which appears at 2.5 ppm as a single signal. The spectrum also shows three important signals in the ligand structure namely, –CH_2–, –NH– and the aromatic protons. The first group appears as a single peak between 2-3 ppm, while the –NH– appears at 8 ppm and the aromatic protons appear in the region 6-7 ppm.

^{13}C-NMR ligand spectra

The ^{13}C spectrum of the ligand was also detected in DMSO-d_6. The spectra shows the three important signals which are related to the carbon atom of the methylene group, the carbon atoms of the aromatic rings and (C=N) carbon atom respectively. The –CH_2– group appears at 40 ppm, the carbon atoms of the aromatic rings appear in the region 120-150 ppm and the carbon atom of (C=N) in the aromatic rings appears at 152 ppm.

Electronic spectra

The electronic transitions of the ligand and the complexes are measured in ethanol and illustrated in Figure 1. The ligand spectra shows four peaks at 208, 220, 283, 407, 448 nm which refer to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$, respectively [21-22]. Both complexes these transitions are red shifted which suggest the coordination between the metals and the ligand. Metal-ligand charge transfer is the suggested as an electronic transition in these complexes. Table 3 gives these electronic transitions with their wavelengths.

Table 3. Suggested electronic transitions for all the synthesized compounds.

Compound	λmax	Type of Transition
Azo dye ligand (A)	208, 220, 283, 407, 448	π→π* and n→π*
[$Cu(A)Cl_2$]	238, 245, 318, 497	MLCT
[$Zn(A)Cl_2$]	240, 312, 397, 465	MLCT

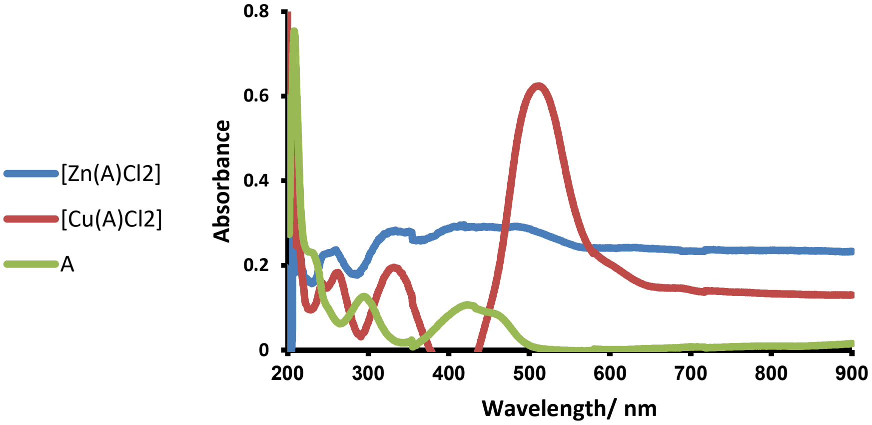


Figure 1. UV-Visible spectra of ligand (A), copper(II) and zinc(II) complexes.

Conductivity and atomic absorption

The conductivity measurements of the complexes (concentration 10^{-3} M) were carried out in ethanol and given in Table 4. These measurements for the two complexes show the non-electrolytic nature of them and suggest the direct bonding of chloride ions with the metal center. [23].

Table 4. Molar conductivity measurements data and the proposed complexes structure for the complexes.

Type of compound	Molar conductivity ($Ohm^{-1}.mol^{-1}.cm^{-1}$)	Metal content%		Suggested structure for the complex
		(Theoretical value)	(Practical value)	
[$Cu(A)Cl_2$]	2.2	7.99	7.794	Octahedral
[$Zn(A)Cl_2$]	1.4	8.2	8.177	Octahedral

Theoretical study

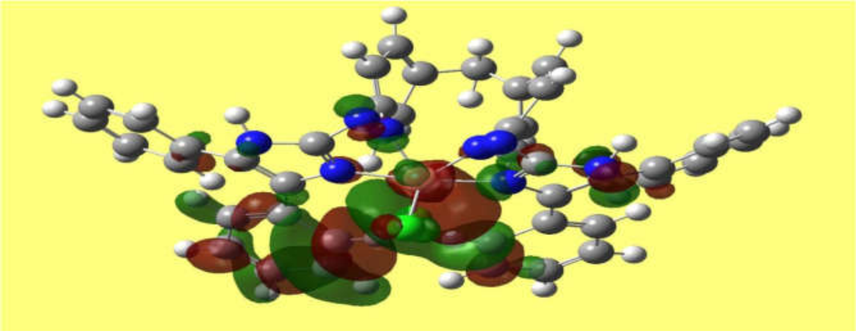
The theoretical investigation involved the quantum mechanics calculations using density functional theory (DFT), Gaussian 09 and Gaussian view 5 programs. A summary of these calculations is given in Table 5.

These calculations include The highest occupied and the lowest unoccupied molecular orbitals energy calculations(HOMO and LUMO), electron density, thermodynamic functions (ΔG°, ΔS°, ΔH°, ΔE°), ionization potential (IP), electron affinity (EA), electrophilicity(ώ), electronegativity (En), chemical hardness (η) and dipole moment (μ) [24], which can be explained in details as below.

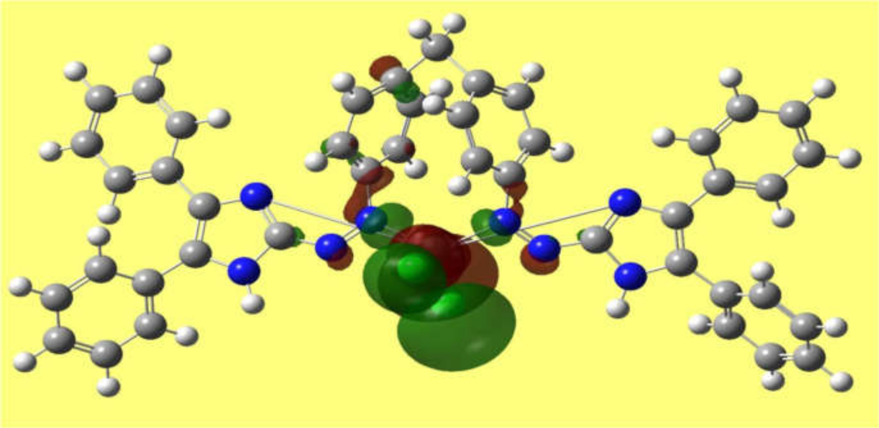
Table 5. A summary of some quantum mechanics calculations.

Parameter	[Cu(A)Cl$_2$]	[Zn(A)Cl$_2$]
E (kcal/mol)	412.597	444.449
H (Hartree/Particle)	0.658459	0.709218
S Cal/mol.Kelvin	196.194	278.539
G (Hartree/Particle)	0.565241	0.576876
(μ in Debye)	12.9502	12.0414
HOMO	-0.14598	-0.15087
LUMO	-0.11482	-0.12313
HOMO- LUMO	0.03116	0.02774
IP (eV)	0.14598	0.15087
EA (eV)	0.11482	0.12313
En (eV)	0.13040	0.13700
η *(eV)*	0.01558	0.01387
2 η	0.03116	0.67660
Ꞷ *(eV)*	0.54570	0.67660

While the energy deference between HOMO-LUMO in Cu(II) complex has the highest which suggests the high stability of its complex in comparison with Zn(II) complex as this agrees with Erving-Williams series of complexes stability [25].



A



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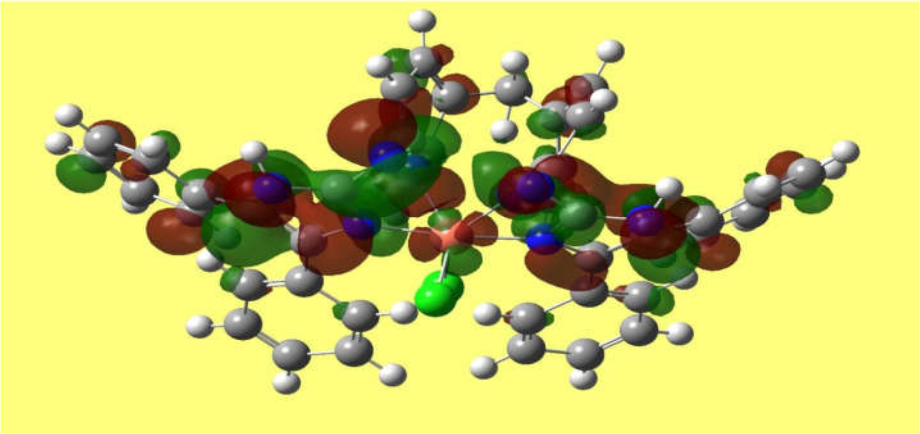

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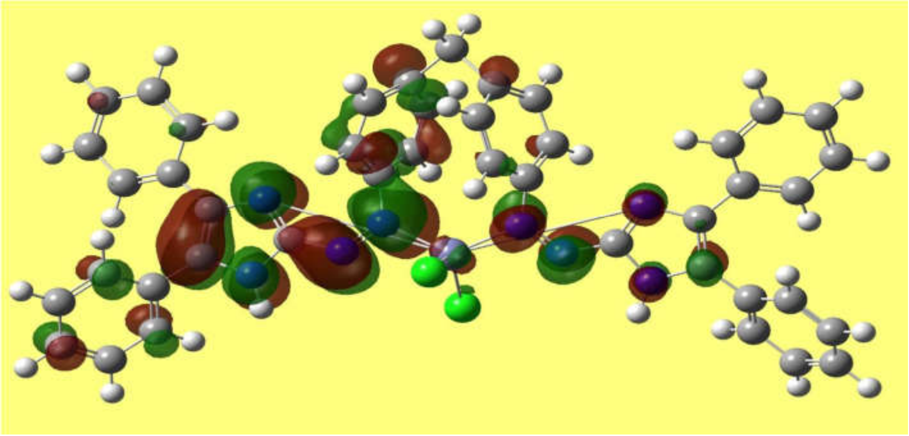


D

Figure 2. Highest occupied molecular orbitals of both complexes (A: Cu(II) complex, B: Zn(II) complex) and the lowest unoccupied molecular orbitals of both complexes (C: Cu(II) complex, and D: Zn(II) complex).

The highest occupied and the lowest unoccupied molecular orbitals (E_{HOMO} and E_{LUMO}): The energy of the highest occupied molecular orbitals is larger in Zn(II) complex in comparison with that of Cu(II) complex, which suggests the difficulty to loss electrons and the movement of electrons between the t_{2g} and e_g levels. On the other hand, Cu(II) complex has a low value of the LUMO energy, which means its ability to accept electrons. Figure 2 shows the HOMO-LUMO for both complexes, while Figure 3 gives the electron density for them.

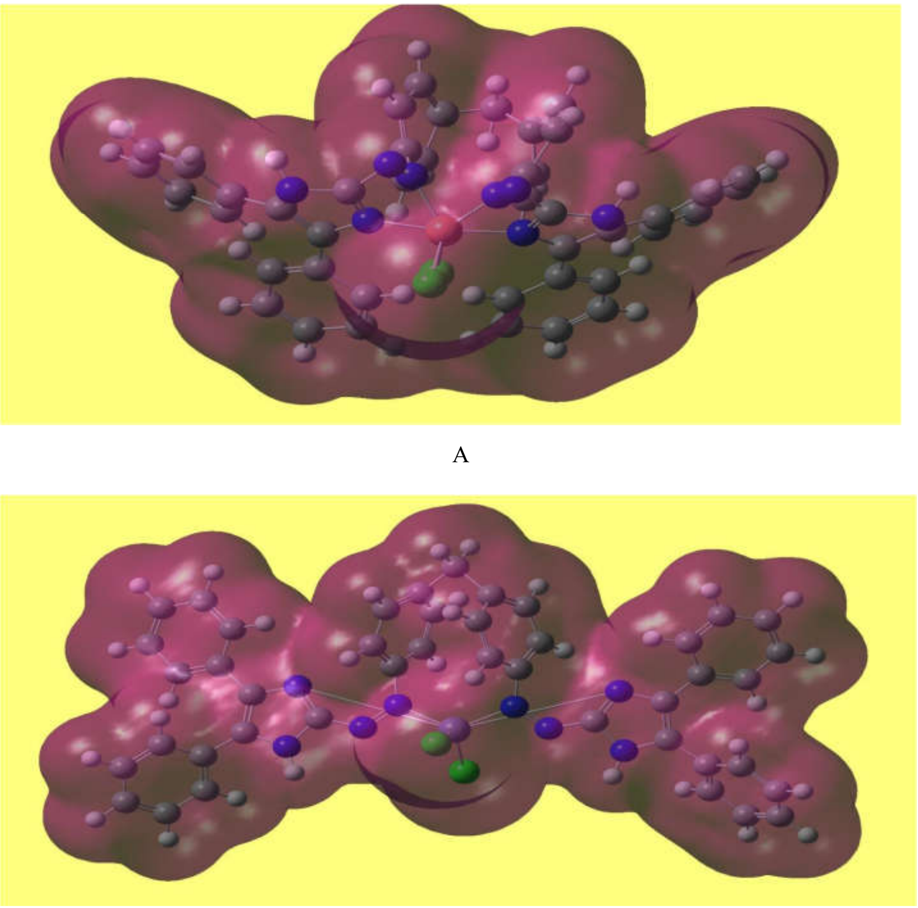
The thermodynamic functions ΔG°, ΔS°, ΔH°, ΔE°: These functions for Zn(II) is higher than those of Cu(II) complex because of its stable crystal field stabilization energy.

The ionization potential (IP): values for the two complexes show that Zn(II) complex has the highest ionization potential. In other word, this complex is hard to loss more than two electrons from the valence orbitals. This is due to the stability of the fully occupied d-orbital in Zn(II) .

The electronegativity (En), electron affinity (EA) and the electrophilic property of both complexes (ὠ): Zn(II) has the highest En, EA and ὠ values, which means the high ability of electrons attraction by this complex.

The chemical hardness (η): This property is very useful to reflect the firm structure of the complexes and its stability against disfigurement. From Table 5, Cu(II) complex is more rigid than Zn(II) complex.

Dipole moment (μ): Cu(II) complex has the highest μ value means the high reactivity of the metal complex. Figure 4 shows the charge distribution and the dipole moment for both complexes.



A

B

Figure 3. Electron density in both complexes (A: Cu(II) complex and B: Zn(II) complex).

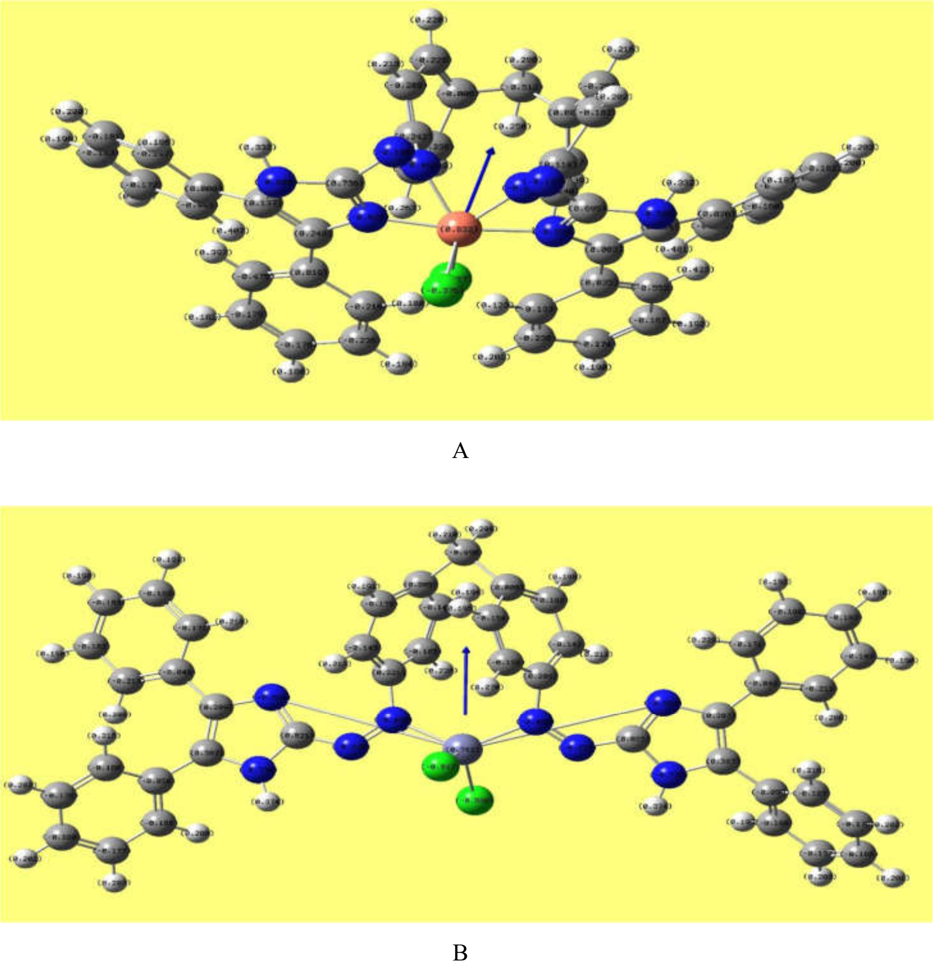


Figure 4. The charge distribution and the dipole moment for both complexes (A: Cu(II) complex, B: Zn(II) complex).

CONCLUSION

Azo ligand was obtained from the well-known diazonium coupling reaction between 4,5-diphenyl imidazole, 4,4-diaminodiphenylmethane. Two metal complexes, Cu(II) and Zn(II) complexes were synthesized from this ligand. These synthesized compounds were characterized by the known and available characteristic techniques. According to these techniques the shape of these complexes is suggested to be octahedral. Some properties of the two synthesized complexes were studied theoretically and interpreted.

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