Synthesis, Characterization And Theoretical Study Of Zn(Ii) Complex With New Schiff Base

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Abstract

New Schiff base2-(5-Chloro-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-3-(2-hydroxy-phenylimino)-propionaldehydecontaining indole ring as ligand has been synthesized. Metal complex of this ligand with divalent zinc ion was prepared. Prepared compounds were characterized basd on FTIR, ^{1}H and ^{13}C-NMR spectra, atomic absorption and chlorine determination to identify the final geometry of the complex. Experimental and computational study using Hartree-Fockmethod was carried out to confirm the most probable geometry.

Key word: metal- complex, Schiff base, hartree-fock

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تحضير وتشخيص ودراسة نظرية لمعقد الخارصين الثنائي مع قاعدة شف جديدة

فاضل لفتة فرج ، صلاح الدين جاسم ، وسن باقر علي و تحسين رضا علي

جامعة ديالى – كلية العلوم – قسم الكيمياء

الخلاصة

تم في هذا البحث تحضير مركب جديد من قواعد شف والموصوف ادناه

2-(5-Chloro-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-3-(2-hydroxy-phenylimino)-propionaldehyde

والحاوي غلى حلقة اندول ومن ثم تم اجراء عملية تحضير معقد من هذا المركب مع ايون الخارصين الثنائي. اجريت عمليات التشخيص لهذه المركبات باستخدام تقنيات FTIR و ^{1}H - ^{13}C-NMR والامتصاص الذري اضافة الى تحليل الكلور وذلك لتحديد الشكل الهندسي النهائي للمعقد وقد تم الاستدلال بالطرق العملية والبرامجية التي تستند على نظرية الهارتري فوك Hartree-Fock للوصول الى الشكل الاكثر ترجيحا من بين الاشكال المحتملة

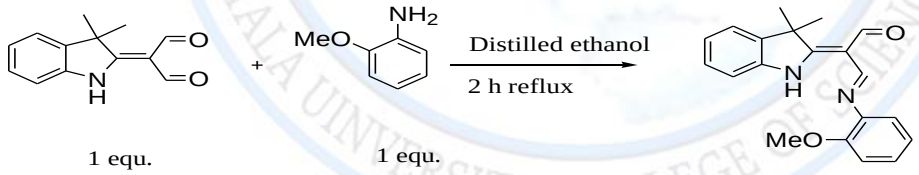
الكلمات المفتاحية: ايون فلز ، معقد ، قاعدة شف ، اندول و هارتري- فوك.

Introduction

Due to the wide applications of Schiff bases derivatives in biology field such as antifungal, antibacterial, anticancer and antioxidant, it can be considered important organic compounds. The flexibility of this type of material can be used as a potent ligand for coordination with several metal ions [1-3]. Ligands containing indole ring which has bicyclic structure consist of benzene ring fused to pyrrole ring is also have pharmacological activities [4-7], so the presence of both groups in some compound should be definitely improve such activity. The coordination modes of metal complexes are closely control by several considerations such as: the nature of the metal ions, the identity of the ligand, type of the anions, organic co-ligands, and the presence of stacking interactions, hydrogen bonding and the type of solvent [8].Although, both six and five membered chelate rings complexes are the most stable compared with the others chelate

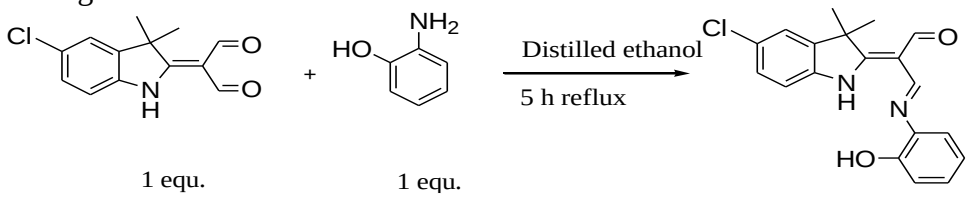
rings. there are some requirements for the stability for each one, small metal ions prefer six-membered chelate rings, but large metal ions favor five-membered chelate rings [9&10], as well, six-membered chelate rings with aromatic ligands or conjugated pi bonds being more stable than five membered chelate because of the release in the strain consideration by resonance and wider angles between bonds. Owing to preferable changes in entropy, aliphatic rings complexes give more stable five membered chelate rings [11].Computational chemistry is commonly used to estimate some useful parameters to understand the coordination between polydentate ligands and metal ions. The Hartree-Fock(HF) method is an Abinitio approach used to treat many electron systems, the Hartree-Fock method describes electronic motion in a mean field of the other electrons [12]. Geometry optimizations of metal complexes of several metal ion complexes were carried out at HF method [13&14], such optimization provides useful information about the coordination modes of a ligand to metal ions. In this work, synthesis and characterization of new polydentate ligand were established and then its coordination properties were studied using HF method.

The preparation method of the new ligand is similar to synthetic pathway of old ligand from indole derivative as described by [15] in scheme below.



1 equ. 1 equ.

In the present work, we used substituted indole derivative to synthesize the new Schiff base containing substituted indole as shown in follow scheme



1 equ. 1 equ.

Experimental Section

1. Materials

All chemicals and solvents used in this work were obtained from Aldrich, Sigma and Merck, and CHD companies (2-(5-chloro-3,3-dimethylindolin-2-ylidene)malonaldehyde,2-hydroxyaniline, zinc chloride, ethanol, potassium hydroxide, hexane, ethyl acetate). The purity of the ligand and zinc complex were checked using pre-coated thin layer chromatography (TLC) plates MERCK, 60F254 with a mixture of hexane: ethyl acetate (4:1) as an eluent. The developed chromatographic plates were visualized under UV.

2.Instruments

^{1}H and ^{13}C-NMR spectra of ligand was recorded on an AVN Bruker 400 MHz FT-NMR spectrometer and the elemental analysis (CHN) was performed on an elemental analyzer Perkin Elmer CHNS/O 2400 series IIin Malaya University/ Malaysia, while IR spectra of ligand and zinc complex was recorded on a FT-IR spectrometer(PERKIN ELMER SPEACTUM-65) in Diyala University. The ^{1}H-NMR spectra of zinc complex was recorded on (NMR burker 400mhz) in (Sharif university of technology) in Iran. Tetramethylsilane TMS was used as an internal standard, and deuterated DMSO was used as a solvent. The melting points of the synthesized compounds were determined by open capillary melting point apparatus. Determination of metal concentration in metal complex solution were recorded on a (Atomic Absorption Spectrophotometry -Aurora) in department of chemistry/college of science /Diyala University.

Synthetic methods

1. Synthesis of 2-(5-Chloro-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-3-(2-hydroxy-phenylimino)-propionaldehyde (ligand) (Fig.1)

(0.655 g, 6.0 mmol) of 2-hydoxy aniline dissolved in 25 ml distilled ethanol was added to (1.5 g, 6.0 mmol) of 2-(5-chloro-3,3-dimethylindolin-2-ylidene) malonaldehyde which dissolved in 50 ml distilled ethanol, then, 1ml of glacial acetic acid was added into the mixture. The

mixture was refluxed in a water bath at 79°C; the progress of the reaction was monitored by TLC. After 5 hours, the reaction was completed and the mixture was left stirring overnight at room temperature; Yellow precipitate was formed in the next day, filtrated off, washed with ethanol and dried over the silica-gel. Yield (1.6 g, 80%), m.p 160-162°C, Anal. Calc .For $C_{19}H_{17}ClN_2O_2$ (340.80), C 66.96, H 5.03, N 8.22. Found C 67.16, H 5.33, N 8.40. IR data in (cm^{-1}) : 3171υ(N-H), 1773υ(C=O), 1652υ(CH=N), 1619 υ(C=C), 1237 υ(C-N) and 1171 υ(C-O).^{1}H NMR (400MHz, DMSO-d_6)δ (ppm): 14.01 (d, J = 12.82Hz, 1H, N*H*), 10.46 (s, 1H, O*H*), 9.41 (s, 1H, C*H*O), 8.66 (d, J = 12.82 Hz, 1H, C*H*=N), 7.67(d, 1H, Ar-*H*), 7.52(s, 1H, Ar-*H*), 7.34 (d, 2H, Ar-*H*), 7.06(t, 1H, Ar-*H*), 7.00 (d, 1H, Ar-*H*), 6.92 (t, 1H, Ar-*H*), 1.60(s, 6H, 2xCH_3).

(Attached Proton Test) (APT) ^{13}C-NMR (100 MHz, DMSO-d_6) δ (ppm): 188.63 (O=*C*H), 184.12 ppm (Ar-NH*C*=C), 155.50 ppm (*C*H=N), 150.59ppm 148.34, 147.79, 129.74, 127.93, 127.72, 126.23, 122.28, 120.31, 119.76, 116.33 and 116.13 (*Ar*-*H*), 108.76ppm (*C*-C=O), 54.98ppm (CH_3*C*-CH_3), 21.93 ppm (2x *C*H_3).

2. Synthesis of zinc complex

Zinc complex was synthesized by a reaction of one equivalent of (0.681 gm , 0.002 mmol) solution of 2-(5-Chloro-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)-3-(2-hydroxy-phenylimino)-propionaldehyde was dissolved in 25 mL of absolute ethanol with one equivalent of (0.272 g , 0.002 mmol) solution of zinc chloride was dissolved in 25 mL of absolute ethanol. The mixture was placed in a 100 mL flat round bottom flask; a few drops of 5% KOH solution were added to make (PH=8.5). Then, the mixture was refluxed in a water bath at 78°C, the color changed to yellow and the precipitate was formed after 30min. The mixture was left refluxing for 4h; yellow precipitate was filtrated off, washed with ethanol and dried in oven.Yield: (0.150g, 85%), m.p.$>$ 280 °C ,IR data of zinc complex in (cm^{-1}): 1701υ(C=O), 1607υ(CH=N), 1540 υ(C=C),1222υ(C-N) and 1108 υ(C-O) .^{1}H-NMR (DMSO-d_6)δ (ppm): 9.00 (s, 1H, C*H*O), 8.30 (s, 1H, C*H*=N), 6.5-8.00(8H, *Ar*-*H*) and 1.60(s, 6H, 2x CH_3)

Computational study

Hartree Fock (HF) calculations were performed in this work. The chembio3D ultra program package and correlation functional (B3LYP) at base set 6-31G was used. HOMO LUMO energy gap were calculated through several cases to investigate the chelation sites of zinc complex

Results and discussions

1. IR Study

IR absorption bands of the ligand and zinc complex illustrated in Figures 2&3 respectively, shown significant differences between them. The appearance of absorption band at 3171 $cm^{-1}$of the ligand spectrum which was attributed to the NH stretching[16]and disappearance this band on zinc complex spectrum, as well as occurrence shifting to lower frequency in the IR complex spectrum of carbonyl group C=O from 1773 cm^{-1} to 1701 cm^{-1}[17,18] and azomethine group CH=N from 1652 cm^{-1} to 1607 cm^{-1}[19,20] give a good evidence of the coordination of the metal ion to the nitrogen atom of indole ring and carbonyl group C=O as well as to the nitrogen atom of azomethine group.

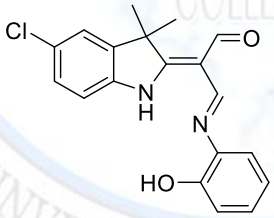


Fig. 1: The chemical structure of ligand

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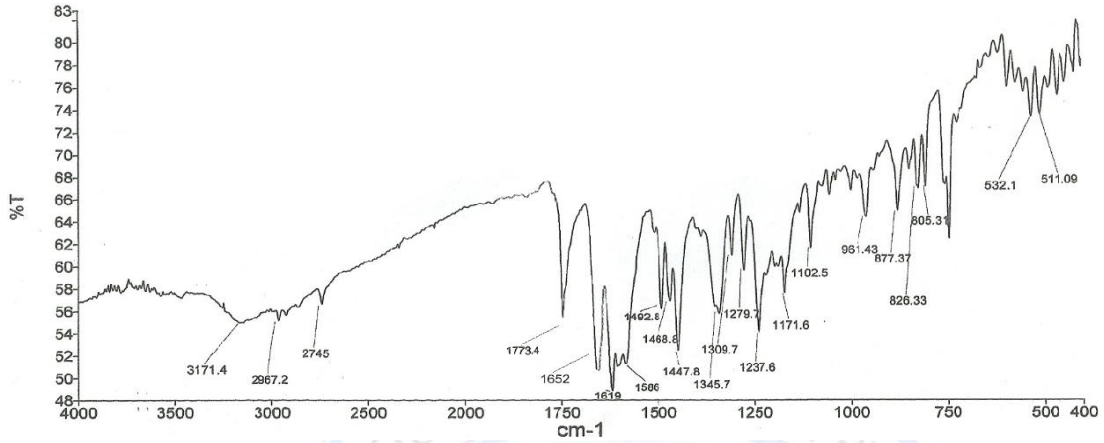

Fig. 2: IR spectrum of ligand

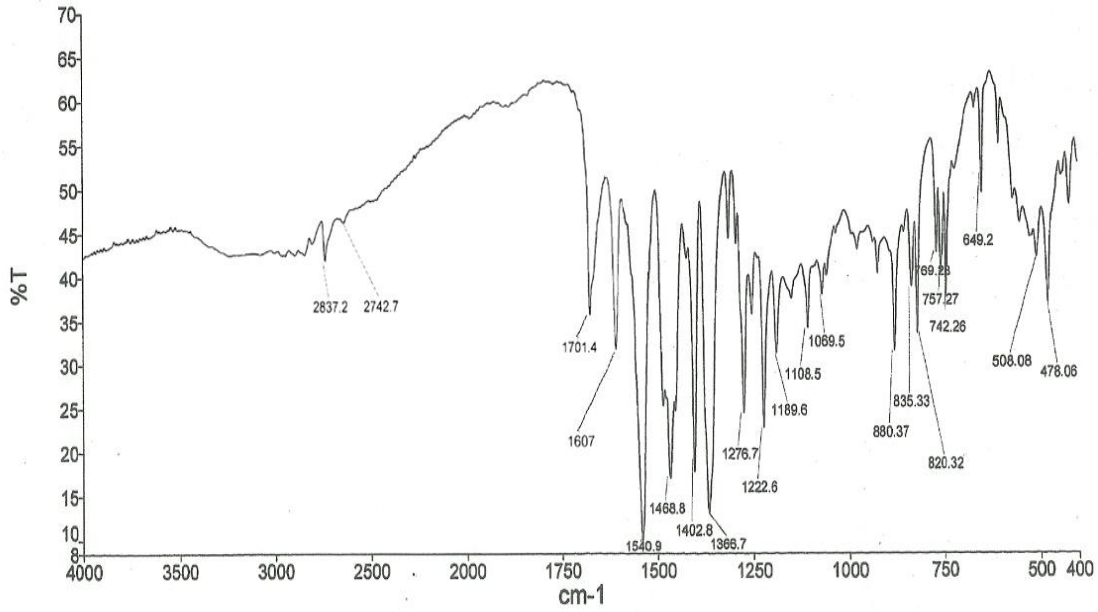

Fig. 3: IR spectrum in of zinc complex

2. NMR study

^{1}H-NMR of zinc complex (Figure-6) showed disappearance of two singlet signals from zinc complex spectrum compared to ^{1}H-NMR spectrum of ligand (Figure 4) at 14.01 ppm and 10.46 ppm belonged to proton atom of NH in indole ring and hydroxyl group of ligand respectively [21, 22] this is evidence the coordination between the zinc ion to nitrogen atom by deportation of hydrogen atom of NH indole ring. Disappearance of hydrogen of hydroxyl group may be attributed to the deprotonation or some other reasons like hydrogen bonding. As well as occurrence shifting of hydrogen of carbonyl group C=O from 9.5ppm on the ligand spectrum to 9.0ppm on zinc complex spectrum and another shifting of hydrogen of azomethine group (-N=CH-) from 8.56ppm on ligand spectrum to 8.20ppm on zinc complex spectrum, this is another evidence to form the complex. Also eight signals appeared in region between 7.50-6.50 ppm were assigned to proton atoms of aromatic rings on both structures (ligand and zinc complex) spectrums [23]. In addition, six proton atoms which attributed to protons of two groups of methyl on both spectrums of ligand and complex are shown [24]. All these signals confirm the formation of the ligand and zinc complex.^{13}C-APT NMR results (Figure 5) as well as ^{1}H results were confirmed accuracy of formation the ligand. Signals for CH and CH_3 appeared at negative side (below of the spectrum), however quaternary carbons and deuterated DMSO solvent were observed at positive side (above of the spectrum).

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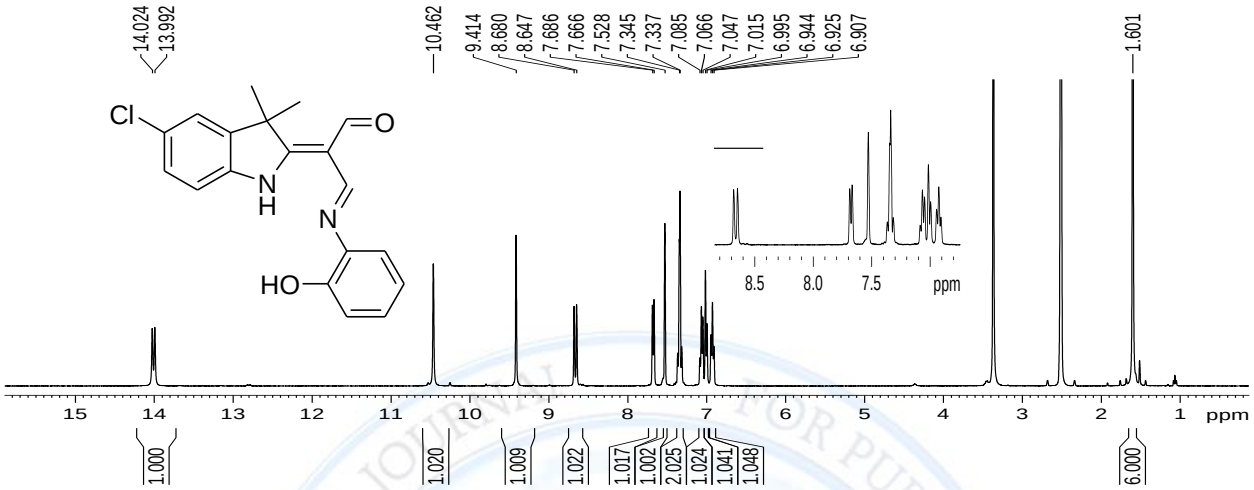

Fig. 4: ^{1}H NMR spectrum of ligand

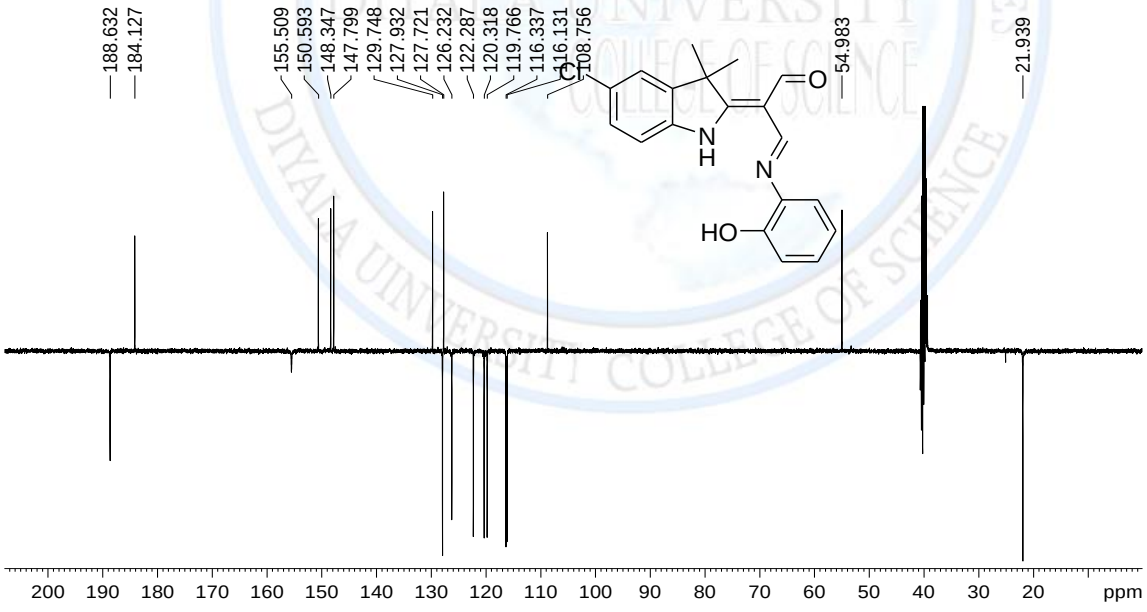

Fig. 5: APT ^{13}C NMR spectrum of ligand

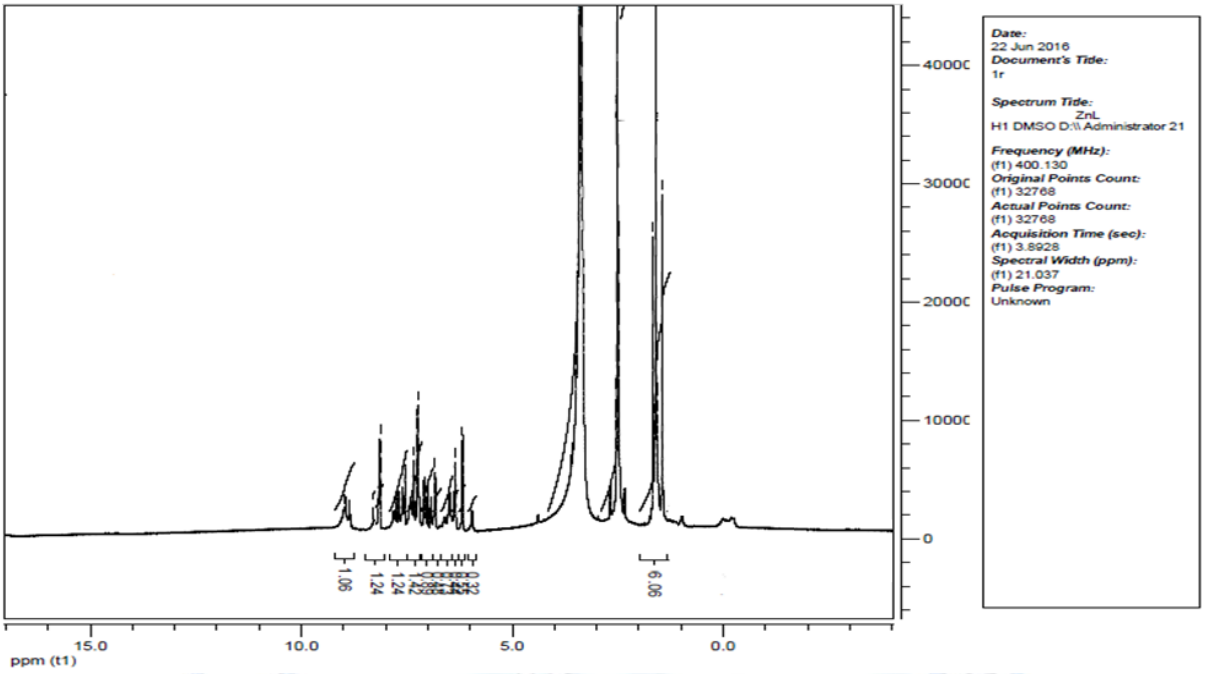

Fig.-6: ^{1}H NMR spectrum in cm^{-1} of zinc complex

3. Computational study

According to HF–B3LYP/ 6-31Gcalculations, it can be concluded the real geometry of zinc complex depending on the rule that: the large HOMO-LUMO energy gap, the most stable compound [25-27]. As shown in Table-1, multiple chelation possibilities of zinc complex were study, the E-gap of tridentate chelating modes within the cases (1-4) (see Table 1) were determined and it seemed that the cases no. 3&4 have the highly energy gap which reflect the stability of these complexes compared to 1&2. Started from this point, it is possible to identify the final geometry of complex, if it is octahedral or tetrahedral (the common geometries for zinc complex). Through the results obtained in table -1, all cases no. (5-8) cannot be confirmed the octahedral structure which contain *ligand/metal mole ratio of 2:1, so all the mentioned cases can be exclud*ed and this conclusion can be substantiated by atomic absorption analysis which confirm the ratio of 1:1*(Zn% calc.= 14.8, found=13.67)***.** Also, octahedral geometry *can be excluded due to* the cases no. 7&8 because of the distortion of some bonds. To suggest the

tetrahedral structure, some notices can be extracted which reveal to this structure and the results listed in cases no. 9 to 17 is so interested in the identification of the required steps to determine the real geometry. It can be clearly concluded that the presence of chloride within the coordination sphere mostly raises the value of E-gap compared to the water molecules and the top two values appear in cases no. 10 & 11 can be considered the most stable cases. Analysis of chlorine content is confirmed the presence of this ion in the coordination spheres (calc.=16%, found=17.4). Convergent values of these two cases does not necessarily be the governed result, because of some common documented errors may be happen in theoretical calculations which needed correction factor [28], so the comparison between these two convergent cases must be supported by the experimental results derived from both FTIR and NMR to identify the most likely geometry. As observed in FTIR figures, Vibrational frequencies spectrum of carbonyl oxygen (symbolled O17) which suffers significant shift is definitely confirmed the contribution of this donor atom in the coordination mode, as well as, the coordination of *azomethine* nitrogen (N16) is clearly appear due to the IR shift, while there is no any doubt that the deprotonated nitrogen (N7) which belonged to the indole ring has been confirmed very well due to completely disappeared from the spectrum of FTIR and NMR. On the other hand, FT-IR analysis does not give clear picture about OH group as well as the NMR chart. In FT-IR, the typical broad band between 3500-2500 cm^{-1} refers to the stretching frequency of ν (O-H) in the ligand and this is still observed in the zinc complex spectrum and it can be concluded that (O-H) remain as it is without deprotonation which leads to the doubt of its participation in the chelating mode. In NMR spectrum, in spite of proton absence of hydroxyl group but this is not evidence of its deprotonation in contribution in the coordination, it may be either form hydrogen bonding or proton exchange with deuterated DMSO solvent required for NMR analysis [29]. After all, it can be concluded that the ligand behaves as tridentate and the chlorine is contributed in the coordination sphere to form tetrahedral zinc complex. Two suggested chelation possibilities (cases no. 10&11) can be extracted but the probability of case no 11 is most likely. The ligand and both suggested structures are shown in (Fig:7-9)

Table-1: Chelation modes possibilities of zinc complex optimized by HF–B3LYP/ 6-31G

Chelating mode		
Case no.	Chelation sites	HOMO-LUMO gap (ev)
1	(Zn + O24 + N16 + O17)	0.800
2	(Zn + N7 + N16 + O17)	0.767
3	(Zn + N7 + N16 + O24)	6.860
4	(Zn + N7 + O24 + O17)	7.518
5	(Zn + O24 + N7 + N16) *2	1.127
6	(Zn + N7 + O24 + O17) *2	0.007
7	(Zn + O24 + N7 + O17+N16) + 2Cl	X
8	(Zn + O17 + N7 +O24+ N16) + $2H_2O$	X
9	(Zn + O24 + N7 + O17+N16)	6.703
10	(Zn + O24 + N7 + N16) + Cl	8.123
11	(Zn + O17 + N7 + N16) + Cl	7.906
12	(Zn + O24 + N7 + O17) + Cl	7.667
13	(Zn + O24 + N16 + O17) + Cl	7.148
14	(Zn + O24 + O17 + N16) + H_2O	0.701
15	(Zn + O17 + N7 + N16) + H_2O	0.781
16	(Zn + O24 + N7 + N16) + H_2O	7.181
17	(Zn + N7 + O24 + O17) + H2O	0.07

7-distorted geometry in which abnormal (O17—Zn) and (N7—Zn) bond length that equal to (5.329 ,3.852)nm respectively. 8- distorted geometry in which abnormal (O28—Zn) and (N7—Zn) bond length that equal to (2.952,3.873)nm respectively

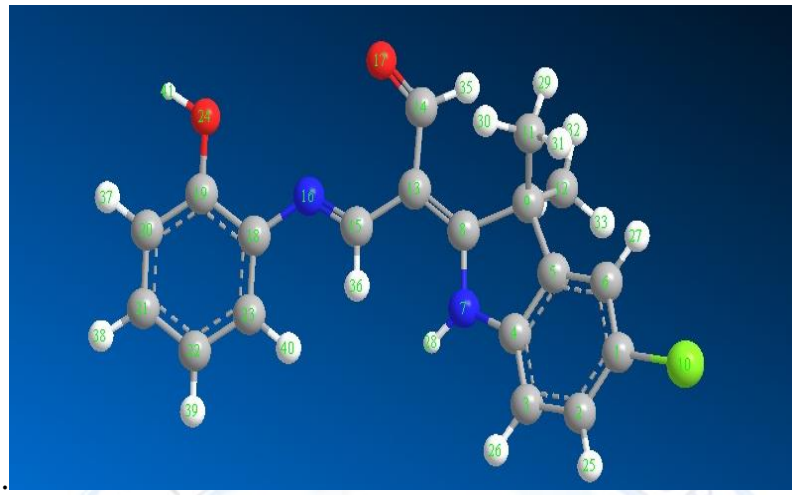

Fig-7: Optimized structure of ligand calculated by HF–B3LYP/ 6-31G

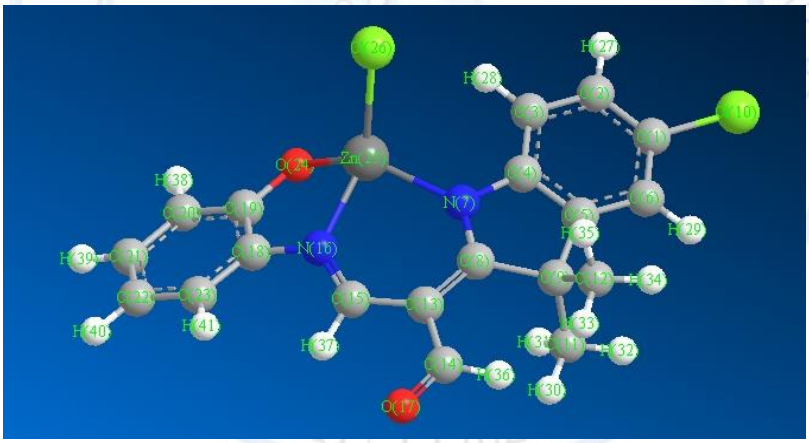

Fig-8 : Optimized structure of zinc complex (case no.11) calculated by HF–B3LYP/ 6-31G

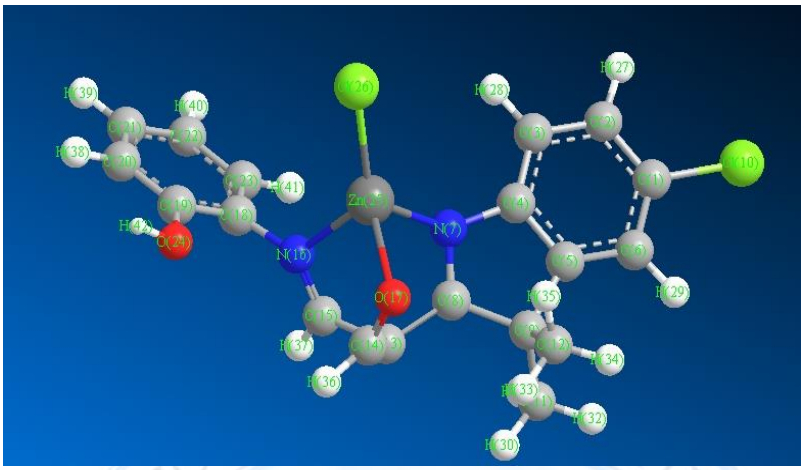

Fig-9 : Optimized structure of zinc complex (case no.11)calculated by HF–B3LYP/ 6-31G

Conclusion

In present study , the new Schiff base [2-(5-Chloro-3,3-dimethyl-1, 3-dihydro – indol - 2-ylidene) -3 - (2-hydroxy - phenylimino)-propionaldehyde] containing indole ring, and its complex with Zn(II) was prepared and characterized by spectroscopic technique such as Atomic absorption, FT-IR,^{1}H-NMR spectroscopy and chlorine analysis. The geometry of the ligand and its zinc complex were optimized with HF–B3LYP/ 6-31Gmethod. Both experimental and computational results confirmed that the complex is tetrahedral containing chloride ion.

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