

Synthesis and characterization of polydentate macrocyclic Schiff bases (18-membered atoms) and their complexes with cobalt (II), nickel (II), copper (II) and zinc (II) ions

Akram A. Mohammed¹, Abdul Ghany M. Al-daher², Hikmat A. Mohamad³ and Roger G. Harrison⁴

^{1,2}Department of Chemistry, College of Science, University of Mosul, Mosul, IRAQ

³Department of Chemistry, College of Education, University of Salahaddin, Erbil, IRAQ

⁴Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, USA

Abstract: The condensation reactions of [2+2] carbohydrazide or thiocarbohydrazide with 2, 5-hexanedione in a (1:1) molar ratio in aqueous solution at room temperature resulted in the formation of the novel Schiff bases tetraimine, macrocyclic ligands (L_1): 2,5,11,14-Tetramethyl-8, 17-dione-1,6,7,9,10,15,16,18-octaaza-cyclo octadeca-1,5,10,14 - Tetraene and (L_2): 2,5,11,14-tetramethyl- 8,17 -dithione-1,6,7,9,10,15,16,18 -octaaza-cyclo octadeca-1,5,10,14 tetraene. Mononuclear, complexes with the compositions $[Co(L_1)Cl]Cl \cdot H_2O$; $[M(L_1)]Cl_2 \cdot nH_2O$ ($M = Ni(II), Cu(II)$ or $Zn(II)$; $n = 0$ when $M = Zn(II)$ and $n = 1$ when $M = Cu(II)$ and $n = 2$ when $M = Ni(II)$); $[M(L_2)Cl_2]$; ($M = Co(II), Ni(II)$ or $Cu(II)$); and $[Zn(L_2)]Cl_2$ were obtained by reacting metal (II) chlorides with the ligand (L_1) or (L_2) in (1:1) molar ratio in ethanol. Mass, ¹HNMR and infrared spectral techniques suggest the structural features of 18-membered [2+2] Schiff base macrocyclic ligands while the nature of bonding and the stereochemistry of the complexes have been deduced by elemental contents analyses, molar conductance and magnetic susceptibility measurements, IR, MS, ¹HNMR and electronic spectral studies. The magnetic moments and electronic spectral data suggested tetrahedral geometries for the $[Co(L_1)Cl]Cl \cdot H_2O$ and $[Co(L_2)Cl_2]$ complexes; octahedral geometries with coordination number six for the complexes $[Ni(L_1)]Cl_2 \cdot 2H_2O$, $[Zn(L_1)]Cl_2$, $[Ni(L_2)Cl_2]$, $[Cu(L_2)Cl_2]$ and $[Zn(L_2)]Cl_2$ while a square planar suggested for the $[Cu(L_1)]Cl_2 \cdot H_2O$ complex.

Keywords: Macrocyclic Schiff base, azamacrocyclic, mononuclear complexes.

Introduction

The complexes of transition metal ions with macrocyclic ligands are significant because of their resemblance with many natural systems such as porphyrins and cobalamines^(1,2). The main interest in new macrocyclic bifunctional chelating agents arises due to their use in labeling monoclonal antibodies with radioactive metals⁽³⁻⁵⁾ and for cancer diagnosis^(6,7,15). Macrocyclic Schiff base ligands have received special attention because of their mixed soft-hard donor character, versatile coordination behavior^(8,9) and their pharmacological properties i.e. toxicity against bacterial fungal growth⁽¹⁰⁾, anticancerous⁽¹¹⁾, antitumor⁽¹²⁾ and also their capacity for anions and environmental importance^(13,17).

The synthesis and characterization of coordination compounds with azamacrocyclic ligands have evolved as a main research area during recent years^(14,15). Aza-type ligands appear to be very promising for catalysis and have been discussed as chelating systems in the literatures^(16,17). The complexation capabilities of polyaza macrocycles are mainly governed by the macrocyclic ring size⁽¹⁸⁾. Aza-macrocyclic ligands, as well as their coordination and organometallic compounds, play important roles in catalytically activating small molecules in electrochemically assisted reactions with several substrates⁽¹⁹⁾.

Because of the wide range of medicinal applications of carbohydrazide⁽²⁰⁾ (CH) and thiocarbohydrazide⁽²¹⁾ (TCH) and their ability to coordinate with metal ions, therefore it is highly desirable to synthesize and characterize macrocyclic complexes⁽²²⁾ with (CH) and (TCH).

In this paper, we report the synthesis and characterization of macrocyclic Schiff bases complexes $[Co(L_1)Cl]Cl \cdot H_2O$; $[M(L_1)]Cl_2 \cdot nH_2O$; ($M = Ni(II), Cu(II)$ or $Zn(II)$; $n = 0$ when $M = Zn(II)$ and $n = 1$ when $M = Cu(II)$ and $n = 2$ when $M = Ni(II)$); $[M(L_2)Cl_2]$; ($M = Co(II), Ni(II)$ or $Cu(II)$); and $[Zn(L_2)]Cl_2$ were obtained from the reaction of the macrocyclic Schiff bases ligands (L_1) or (L_2) with the metals chlorides (Figures 2-7).

Experimental

1. Chemicals

All chemicals in the present work were purchased from Sigma-Aldrich and Alfa Aesar used without further purification except thiocarbohydrazide was prepared according to the reported procedure (ref. 23).

2. Analytical and physical measurements:

Metal contents have been determined by using: Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) after the decomposition of the complexes by acid digestion with nitric acid. Melting points were determined by using MEL-TEMP LAB. Devices apparatus. Molar conductivities of the complexes have been measured on a digital conductivity meter (VWR International model 2052-B-EC meter) using 0.001M of the complexes in dimethylformamide (DMF) solutions at 25°C. The IR spectra were recorded on a FTIR spectrophotometer (Avatar 370) in the range (400-4000) cm⁻¹ using KBr disc. Electronic spectra were recorded on a hp 8453UV-Vis. spectrophotometer in DMF at 25°C. For 0.001 M solution of the compounds using a 1 cm quartz cell in the range (200-1100) nm. Gouy balance calibrated with $Hg[Co(NCS)_4]$ was used for the determination of magnetic susceptibilities of complexes in solid state at room temperature (Magnetic Susceptibility balance, Johnson Matthey Fabricated Equipment). Agilent 6210 TOF LC/Mass spectra spectroscopy used to obtain mass spectra for the ligands and the complexes.

A varian NMR INOVA 300 MHZ spectra spectroscopy used to obtain ¹HNMR spectra for the ligands.

3. Synthesis of the macrocyclic ligands

Aqueous solution of carbohydrazide (1.80 gm, 0.02 mol.) or thiocarbohydrazide (2.12 gm, 0.02 mol.) in distilled water (400 ml) and 2,5-hexanedione (2.28 gm, 0.02 mol.) were mixed slowly with constant stirring for (6) hrs. at room temperature and in presence of (6) drops of concentrated HCl. On cooling in the ice bath for (24) hrs., a solid precipitate was formed, which was filtered, washed with cold distilled water, and dried under vacuum (Figure 1).

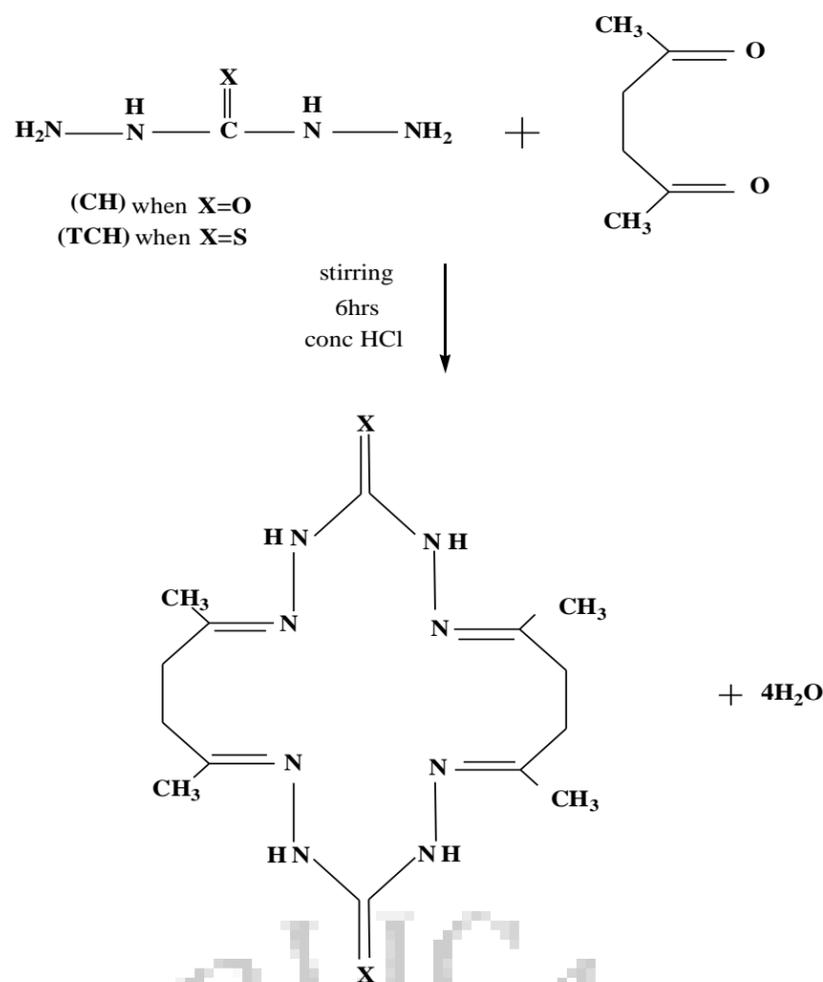


Figure (1) : The structure of the prepared ligands

4. Synthesis of the macrocyclic complexes

A. Synthesis of complexes with macrocyclic ligand (L_1):

A warm methanolic suspension (100 ml) of ligand (L_1) (0.336 g, 0.001 mol.) , a hot methanolic solution (25 ml) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 0.001 mol.) , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.171 g, 0.001 mol.) or ZnCl_2 (0.136 g , 0.001 mol) were mixed together with constant stirring . The mixture was refluxed for (5) hrs. A precipitate was formed. It was filtered, washed with cold MeOH and then diethyl ether and dried under vacuum.

B. Synthesis of complexes with macrocyclic ligand (L_2):

A hot ethanolic solution (100 ml) of ligand (L_2) (0.368 g, 0.001 mol.) and hot ethanolic solution (25 ml) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.238 g, 0.001 mol.) , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.171 g, 0.001 mol.) or ZnCl_2 (0.136 g , 0.001 mol) were mixed together with constant stirring . The mixture was refluxed for (5) hrs. a precipitate was formed. It was filtered, washed several times with EtOH and then diethyl ether and dried under vacuum.

Results and Discussion

The formation of the ligands and the complexes, also the coordination of the two ligands to cobalt (II), nickel (II), copper (II) and zinc (II) ions, in neutral medium, indicated from various chemical and spectral properties (Table 1-3).

The prepared ligands and complexes are powders. Crystals of these compounds could not be grown therefore X-ray crystal determination is not possible. The two ligands and the complexes are moisture stable solids (stable in air at room temperature). The higher melting and the decomposition points of these complexes than the metal free ligands suggests the thermal stability of the complexes⁽²⁴⁾.

The reaction of metal chlorides with (L_1) or (L_2) in alcohol (molar ratio 1:1) yields complexes of the compositions $[\text{Co}(L_1)\text{Cl}_2] \cdot \text{H}_2\text{O}$; $[\text{M}(L_1)]\text{Cl}_2 \cdot n\text{H}_2\text{O}$ (M = Ni (II), Cu (II) or Zn (II)) n = 0 when M = Zn (II) ; n = 1 when M = Cu (II) and n=2 when M = Ni(II) ; $[\text{M}(L_2)\text{Cl}_2]$; (M=Co (II), Ni (II) or Cu (II)) ; and $[\text{Zn}(L_2)]\text{Cl}_2$.

Based on the metal contents measurements and the mass spectra, have been supported the above composition (Table 1), which shows that in each complex the ratio of metal: ligand is (1:1), and that means all the complexes act as mononuclear complexes (monomer). The monomeric nature of the complexes was also evidenced from their magnetic susceptibility values (Table 3).

The molar conductance values of the $[\text{Ni}(L_1)]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$; $[\text{Cu}(L_1)]\text{Cl}_2 \cdot \text{H}_2\text{O}$; $[\text{Zn}(L_1)]\text{Cl}_2$ and $[\text{Zn}(L_2)]\text{Cl}_2$ complexes in DMF solvent are in the range (128-153) $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ (Table 1) indicating that they are (1:2) electrolytic nature of these complexes⁽²⁵⁾. The molar conductance values of the $[\text{M}(L_2)\text{Cl}_2]$ (M=Co (II), Ni (II) or Cu (II)) complexes in DMF have lower values (Table 1) indicating that they are non-electrolytic in nature and that no inorganic anions such as Cl^- ions are present in outer sphere coordination⁽²⁵⁾. The non-conducting character reveals the presence of (Cl^-) and metals ions in the coordination sphere,

while the molar conductance value of the complex $[Co(L_1)Cl] \cdot Cl \cdot H_2O$ is $(63) \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating a (1:1) electrolytic nature of these complex⁽²⁵⁾.

Table (1): The physical, mass spectral and analytical properties of the macrocyclic ligands and their complexes

| NO | Compound | color | Yield % | m. p C° | % Metal | | Λ_M $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ | Atomic mass g/mole | Mass spectra M/Z |
|----|-----------------------------------|---------------|---------|------------|---------|-------|--|-----------------------|---------------------|
| | | | | | #cal. | found | | | |
| | L_1 | creamy | 72 | 214-216 | ---- | ---- | ---- | 336 | 337 |
| | L_2 | creamy | 65 | 196* | ---- | ---- | ---- | 368 | 369 |
| 1 | $[Co(L_1)Cl] \cdot Cl \cdot H_2O$ | dark green | 72 | 314* | 12.17 | 12.74 | 63 | 483.933 | 483.98 |
| 2 | $[Ni(L_1)Cl_2] \cdot 2H_2O$ | green | 62 | 304* | 11.70 | 12.12 | 128 | 501.71 | 502 |
| 3 | $[Cu(L_1)Cl_2] \cdot H_2O$ | brown | 79 | 324* | 13.00 | 13.66 | 153 | 488.54 | 489 |
| 4 | $[Zn(L_1)Cl_2]$ | dark yellow | 77 | 291-294 | 13.77 | 14.65 | 140 | 472 | 472 |
| 5 | $[Co(L_2)Cl_2]$ | greenish blue | 66 | 261-263 | 11.83 | 12.71 | 30 | 497.933 | 497.95 |
| 6 | $[Ni(L_2)Cl_2]$ | bright brown | 78 | 233-235 | 11.79 | 12.44 | 20 | 497 | 497 |
| 7 | $[Cu(L_2)Cl_2]$ | pale pink | 64 | 298-302 | 12.64 | 12.77 | 23 | 502.54 | 503 |
| 8 | $[Zn(L_2)Cl_2]$ | yellow | 63 | 245-247 | 12.89 | 13.42 | 132 | 504 | 505 |

#calculated, * decomposition temperature

IR Spectra

The IR absorption bands, which provide information about the formation of macrocyclic ligands and the mode of coordination in their complexes are given in Table (2). A pair of bands corresponding to $V(NH_2)$ appeared at (3326) and $(3283) \text{ cm}^{-1}$ in the spectrum of carbonyl hydrazide (CH) and at (3307) and $(3275) \text{ cm}^{-1}$ in the spectrum of thiocarbonyl hydrazide (TCH) but are absent in IR spectra of the free ligands. Further, no strong absorption band was observed near $(1722) \text{ cm}^{-1}$ in the spectra of the free ligands, indicating the absence of Ketonic group of 2,5-hexanedione, confirming condensation of carbonyl group of 2,5-hexanedione and amino groups of carbonyl hydrazide or thiocarbonyl hydrazide⁽¹⁰⁾ and also elimination of water molecules and as a result, cyclization takes part through the formation of macrocyclic ligands (tetraaminemacrocyclic).

In the IR spectra of the free ligands, the bands appear at (1663) and $(1631) \text{ cm}^{-1}$ corresponding to the imine group (C=N) for (L_1) and (L_2) , respectively. The IR spectra of all the complexes show an absorption in the range $(1522-1654) \text{ cm}^{-1}$ attributed to the imine. This absorption band shows a shift to the lower frequencies in these complexes, suggesting coordination through the nitrogen of the (C=N) group⁽¹⁰⁾. This mode of coordination of ligands is also supported by appearance of band corresponding to the stretching vibration of $V(M-N)$ in the range $(413-490) \text{ cm}^{-1}$ ⁽¹⁰⁾(Table 2).

The presence of carbonyl amide ($\begin{matrix} O \\ || \\ C-N-H \end{matrix}$) is confirmed by the appearance of a sharp band at $(1703) \text{ cm}^{-1}$ in the spectrum of (L_1) ⁽²⁶⁾. This band is shifted to lower frequencies in the spectra of the complexes (1), (2) and (4), indicating its involvement of oxygen atoms of the carbonyl amide group in the coordination sphere⁽²⁷⁾. Further evidence of the bonding is given by the appearance of new bands of medium or weak intensity between $(433-531) \text{ cm}^{-1}$ in the spectra of the complexes (1), (2) and (4), these bands can be assigned to $V(M-O)$ ⁽²⁷⁾ (Table 2). However, the spectrum of the complex (3) shows the band due to the carbonyl amide group (C=O) is not affected in position too much compared to the corresponding band in the ligand (L_1) , indicating that the oxygen atom is not involved in bonding in this complex⁽²⁶⁾. The ligand (L_1) and its complexes have not been found to exhibit keto-enol tautomerism, which is evidenced by the absence of absorption bands in $(2600-2700) \text{ cm}^{-1}$ ⁽²⁸⁾ region.

The broad band corresponding to the $V(H_2O)$ at the range $(3451-3480) \text{ cm}^{-1}$ (Table 2) shows that the complexes (1-3) contain water molecule⁽²⁹⁾.

The presence of thiocarbonyl amide (C=S) is confirmed by the appearance of a very strong band at $(758) \text{ cm}^{-1}$ in the spectrum of (L_2) ⁽³⁰⁾. Since the $V(C=S)$ of the complexes (5), (6) and (7) remains unaltered, it is ascertained that it does not bind to the metal ion⁽³⁰⁾, while it is shifted to lower frequency in the spectrum of the complex (8), indicating its involvement of sulphur atom of the thiocarbonyl amide in the coordination sphere towards zinc (II) ion (Table 2). The free ligand (L_2) and its complexes have not been found to exhibit thioketo-enol tautomerism⁽³¹⁾, which is evidenced by the absence of absorption bands in $(2500-2600) \text{ cm}^{-1}$ region.

The (M-Cl) and (M-S) bands do not appear in the IR spectra of the complexes due to instrument limitation.

Table (2): Important IR spectral bands (cm^{-1})

| NO. | $\nu(C=N)$ | $\begin{array}{c} O \\ \\ \nu(C-N) \end{array}$ | $\nu(C=S)$ | $\nu(M-O)$ | $\nu(M-N)$ | $\nu(H_2O)$ |
|-------|------------|--|------------|------------|------------|-------------|
| L_1 | 1663(s) | 1703(s) | ---- | ---- | ---- | ---- |
| L_2 | 1631(s) | ---- | 758(vs) | ---- | ---- | ---- |
| 1 | 1615(s) | 1653(s) | ---- | 531(w) | 418(w) | 3472(b) |
| 2 | 1616(s) | 1654(s) | ---- | 433(w) | 413(w) | 3451(b) |
| 3 | 1654(m) | 1710(s) | ---- | ---- | 433(w) | 3480(b) |
| 4 | 1614(s) | 1653(s) | ---- | 506(m) | 421(w) | ---- |
| 5 | 1621(s) | ---- | 754(m) | ---- | 490(w) | ---- |
| 6 | 1612(s) | ---- | 754(m) | ---- | 425(w) | ---- |
| 7 | 1522(s) | ---- | 756(s) | ---- | 433(w) | ---- |
| 8 | 1619(s) | ---- | 735(m) | ---- | 439(w) | ---- |

v: very, b: broad, w: weak, m: medium, s: strong

Electronic spectra and the magnetic moments:

The electronic spectra of the macrocyclic ligands and their complexes were recorded in DMF at solvent $25^\circ C$ for 0.001 M (Table 3). The bands were observed at (29585) and (29239) cm^{-1} in the spectra of the ligands (L_1) and (L_2), respectively, which are attributed to $\pi \rightarrow \pi^*$ transition in the (C=N) chromophore⁽³²⁾.

The electronic spectra of Co (II) complexes (1) and (5) show the d-d transition in the range (14792-16420) cm^{-1} . This band usually corresponds to the $^4A_2(F) \rightarrow ^4T_1(P)$ transition and the splitting of this band into two components is expected as a result of spin-orbit coupling⁽³³⁾ suggesting a tetrahedral environment around the (Co^{2+}) ion. Also, the Co (II) complex (5) exhibits intense band in the high energy region at (32051) cm^{-1} , which can be assigned to the charge transfer band. At room temperature, the observed magnetic moments for the cobalt (II) complexes (1) and (5) lie at (4.13-4.39)⁽³⁴⁾ B.M., corresponding a high spin tetrahedral environment around the Co (II) ion (Table 3) (Figure 2 and 5).

The electronic spectra of the Ni (II) complexes (2) and (6) show bands at (16051) and (24691) cm^{-1} corresponding to the: $^3A_2g(F) \rightarrow ^3T_1g(F)(v_2)$, and $^3A_2g(F) \rightarrow ^3T_1g(P)(v_3)$ Transitions, respectively for the complex (2) and at (10101) and (16666) cm^{-1} corresponding to the $^3A_2g(F) \rightarrow ^3T_2g(F)(v_1)$ and $^3A_2g(F) \rightarrow ^3T_1g(F)(v_2)$ transitions, respectively for the complex (6) (Table 3). These transitions support the formation of an octahedral geometry around the (Ni^{2+}) ion⁽³⁵⁾. However, the band (v_1) for the complex (2) was obscured in the electronic spectrum of this complex due to the lack of instrument for measurements in the near IR region⁽³⁵⁾. Also the expected third band (v_3) for the complex (6) being hidden by the absorbance of the ligand (L_2)⁽³⁶⁾. The complex (6) exhibits the high energy band at (28011) cm^{-1} , which is attributed to the charge transfer band. The complexes (2) and (6) show magnetic moments lie at (2.98-3.03) B.M.. These values in tune with a high spin configuration and show the presence of an octahedral environment around Ni (II) ion⁽³⁵⁾. Also, these observed value of complexes (2) and (6) are higher than that of the spin-only value (2.83 B.M.) for octahedral complexes. This indicates spin-orbit coupling contribution in magnetic moment value⁽³⁷⁾ (Figures 3 and 6).

The Cu (II) complex (3) shows a d-d band at (21834) cm^{-1} due to $^2B_{1g} \rightarrow ^2A_{1g}$ transition which supports square- planar geometry⁽³⁸⁾. In addition, the μ_{eff} value for this complex at (1.81) B.M, indicative of one unpaired electron of Cu (II) ion and suggesting that the square-planar geometry⁽³⁹⁾ (Table 3) (Figure 4).

The electronic spectrum of the copper (II) complex (7) shows a band at (16863) cm^{-1} due to the $^2Eg \rightarrow ^2T_{2g}$ transition, suggesting a distorted octahedral structure⁽⁴⁰⁾ (Table 3) (Figure 6). Also, the complex (7) exhibits the high energy band at (24154) cm^{-1} , which is attributed to the charge transfer band. It has been further confirmed by the observed magnetic moment at (2.00) B.M., suggesting a distorted octahedral geometry around the Cu (II) complex (7)⁽²⁷⁾ (Figure 6).

The absorption spectra of Zn (II) complexes (4) and (8) show no bands due to (d-d) transitions. This phenomenon is natural as there is no possibility of transition due to non-availability of empty d-orbital. The electronic spectra of the complexes (4) and (8) show a band at the range (33003-33333) cm^{-1} (Table 3), which is attributed to the $\pi \rightarrow \pi^*$ transition. Also, these spectra show the high energy band at the range (25773-27397) cm^{-1} , which is attributed to the charge transfer. On the basis of all the data belonging to the complexes (4) and (8), (Tables 1,2 and 3), it appears that the most probable structure for these complexes are octahedral geometries (Figures 3 and 7).

Table (3): The electronic spectral data (cm^{-1}) and magnetic moments (B.M.) of the complexes

| No. | Absorption Region (cm^{-1}) | Possible assignments | μ_{eff} (B.M.) | Geometry |
|-----|---------------------------------|-----------------------------------|--------------------|---------------|
| 1 | 14792, 16420 | $^4A_2(F) \rightarrow ^4T_1(P)$ | 4.39 | tetrahedral |
| 2 | 16051 | $^3A_2g(F) \rightarrow ^3T_1g(F)$ | 3.03 | octahedral |
| | 24691 | $^3A_2g(F) \rightarrow ^3T_1g(P)$ | | |
| 3 | 21834 | $^2B_1g \rightarrow ^2A_1g$ | 1.81 | Square planar |
| 4 | 27397 | Charge transfer | diamagnetic | octahedral |
| | 33333 | $n \rightarrow \pi^*$ | | |
| 5 | 14814, 16420 | $^4A_2(F) \rightarrow ^4T_1(P)$ | 4.13 | tetrahedral |
| | 32051 | Charge transfer | | |
| 6 | 10101 | $^3A_2g(F) \rightarrow ^3T_2g(F)$ | 2.98 | octahedral |
| | 16666 | $^3A_2g(F) \rightarrow ^3T_1g(F)$ | | |
| | 28011 | Charge transfer | | |
| 7 | 16863 | $^2Eg \rightarrow ^2T_2g$ | 2.00 | octahedral |
| | 24154 | Charge transfer | | |
| 8 | 25773 | Charge transfer | diamagnetic | octahedral |
| | 33003 | $n \rightarrow \pi^*$ | | |

1H NMR Spectra of the ligands

1H NMR Spectra of the free ligands (L_1) and (L_2) have been recorded in DMSO- d_6 with tetramethylsilane ($SiMe_4$) as internal reference and are summarized in (Table 4) with proposed assignments. 1H NMR Spectral data for these ligands show the signals corresponding to primary amines of (CH) and (TCH).

The spectra of the (L_1) and (L_2) exhibit a singlet at (2.745) and (1.104) ppm respectively, equivalent to (12 H) of four methyl groups (CH_3). Also, the (L_1) and (L_2) spectra show a triplet at (3.290) and (1.958) ppm respectively, equivalent to (8H) of four methylene groups (CH_2).

The spectrum of the (L_1) exhibits a singlet at (7.967) ppm equivalent to (4 H) of four amide protons (NH) while the spectrum of the (L_2) shows the singlets at (5.814) and (9.822) ppm which are assigned to the protons of amide (NH) groups in two different environments, where one of them is deshielded to lower chemical shift than the other, this is due to the anisotropic effect⁽⁴¹⁾ of the neighboring thioketo (C=S) group (Table 4).

Table (4): 1H NMR data for the ligands

| Ligand | Formula | Band location (ppm) | Band multiplicity | Protons No. | Group |
|--------|----------------------|---------------------|-------------------|-------------|--------|
| L_1 | $C_{14}H_{24}N_8O_2$ | 2.745 | Singlet | 12H | CH_3 |
| | | 3.290 | triplet | 8H | CH_2 |
| | | 7.967 | singlet | 4H | NH |
| L_2 | $C_{14}H_{24}N_8S_2$ | 1.104 | singlet | 12H | CH_3 |
| | | 1.958 | triplet | 8H | CH_2 |
| | | 5.814 | singlet | 2H | NH |
| | | 9.822 | singlet | 2H | NH |

Conclusion

Based on the reported results, it is concluded that the macrocyclic Schiff base ligands (L_1) and (L_2) act as a hexadentate coordinated donor through the nitrogen atoms of the (C=N) groups and the oxygen atoms of the carbonyl amide (N_4O_2) for (L_1), resulting complexes (2) and (4) with an octahedral configuration or the nitrogen atoms of the (C=N) groups and the sulphur atoms of thiocarbonyl amide (N_4S_2) for (L_2), resulting the complex (8) with an octahedral configuration.

Also, (L_1) and (L_2) acts as tetradentate donors via the nitrogen atoms of (C=N) groups (N_4), resulting a square planar complex (3) by (L_1) and octahedral complexes (6) and (7) by (L_2).

Finally, (L_1) acts as tridentate donor via the two nitrogen atoms of (C=N) groups and one of oxygen atom of (C=O) group resulting the complex (1) with a tetrahedral geometry while (L_2) acts as a bidentate donor through the two nitrogen atoms of (C=N) groups resulting the complex (5) with a tetrahedral geometry.

All the complexes are found to be mononuclear.

The tentative structures suggested for the complexes are shown in Figures (2-7).

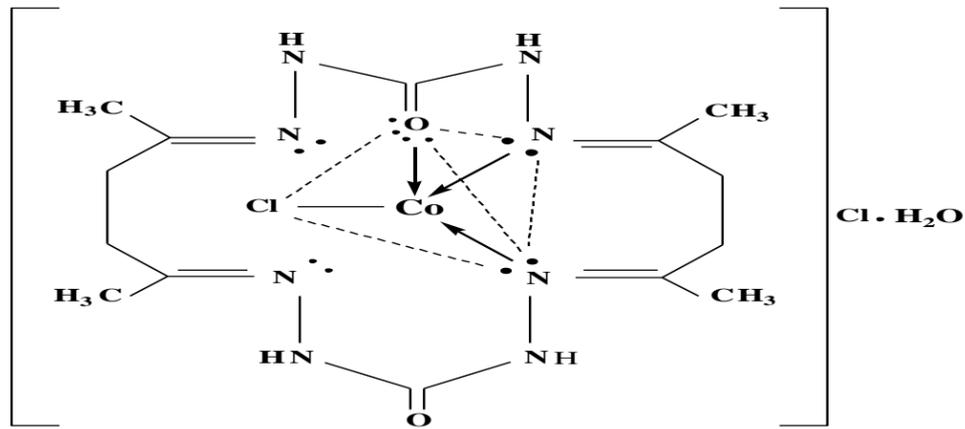


Figure (2): The proposed structure of the tetrahedral complex (1)
 $[\text{Co}(\text{L}_1)\text{Cl}] \text{Cl} \cdot \text{H}_2\text{O}$

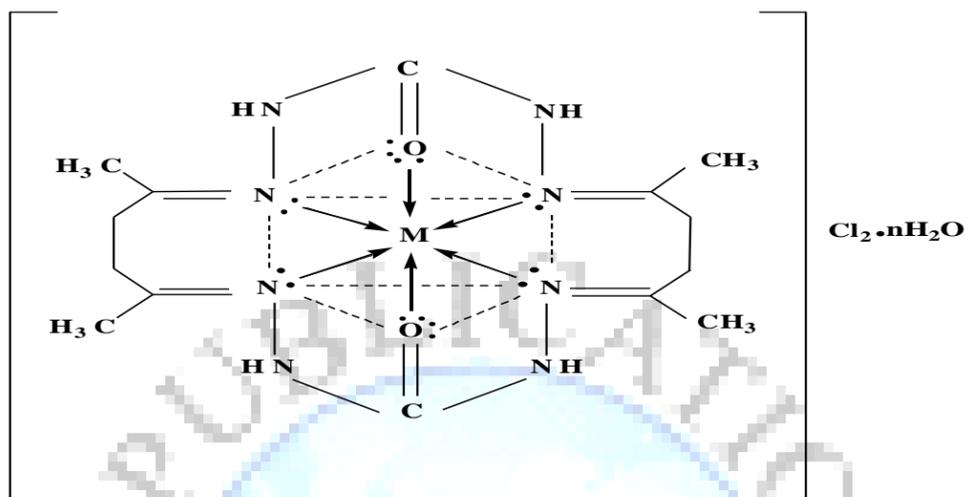


Figure (3): The proposed structure of the octahedral complexes (2) and (4)
 $[\text{M}(\text{L}_1)]\text{Cl}_2 \cdot n\text{H}_2\text{O}$
 M = Ni (II) and Zn (II)
 n = 0 when M = Zn (II)
 n = 2 when M = Ni (II)

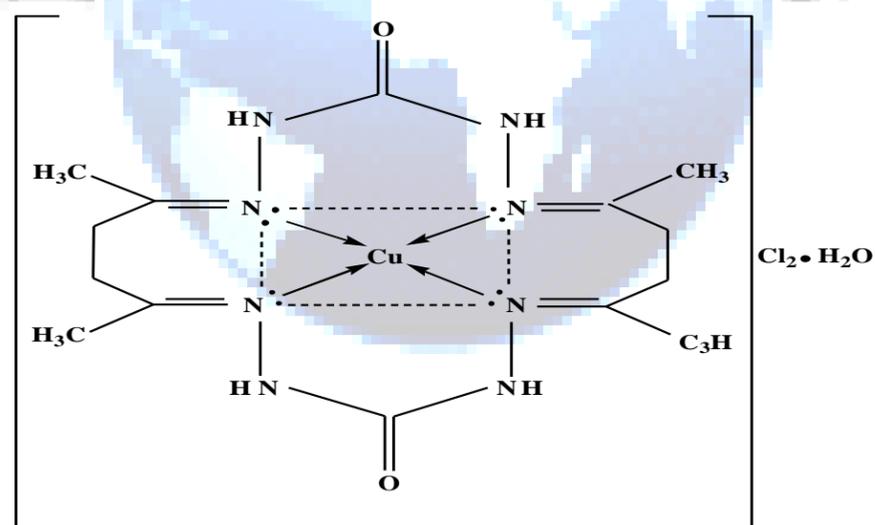


Figure (4): The proposed structure of the square planar complex (3)
 $[\text{Cu}(\text{L}_1)]\text{Cl}_2 \cdot \text{H}_2\text{O}$

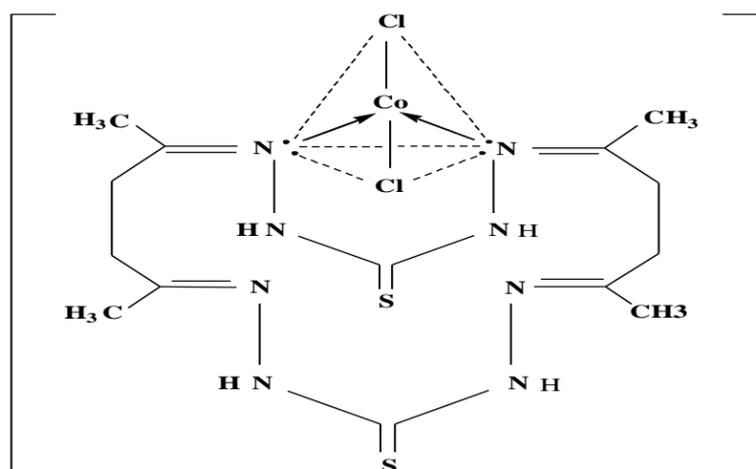


Figure (5): The proposed structure of the tetrahedral complex (5)

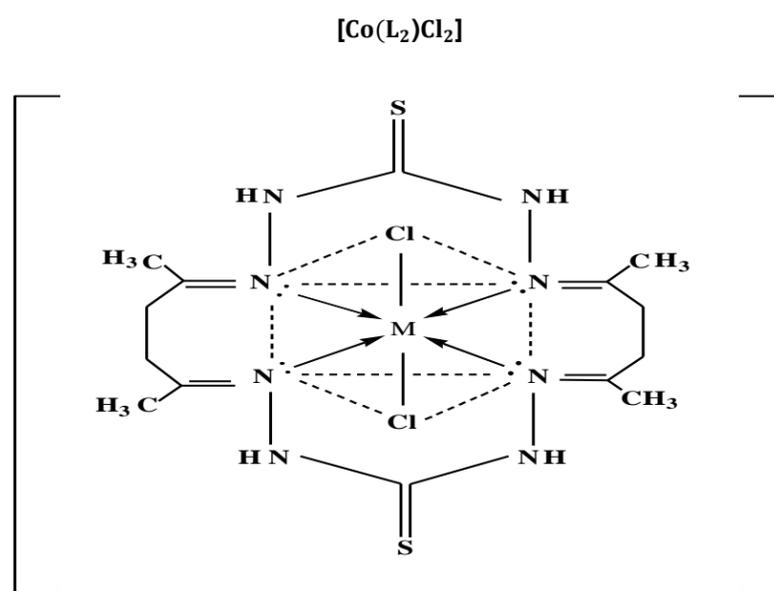


Figure (6): The proposed structure of the octahedral complexes (6) and (7)
 $[\text{M}(\text{L}_2)\text{Cl}_2]$
 M=Ni (II) and Cu (II)

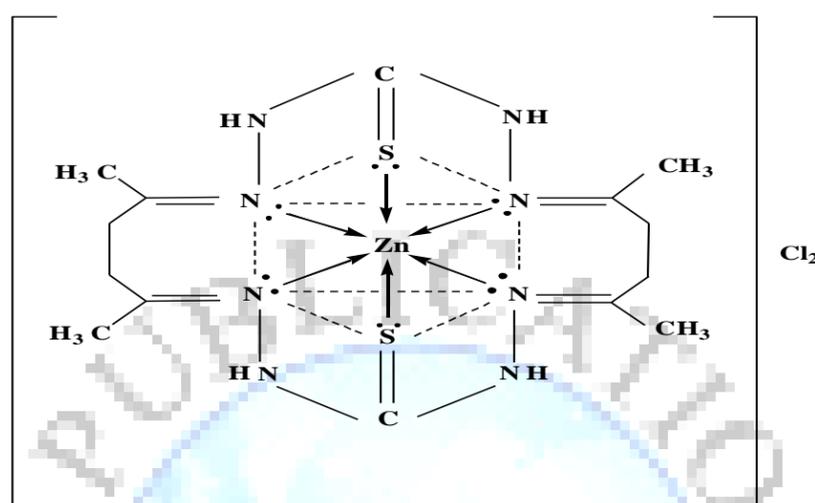


Figure (7): The proposed structure of the octahedral complex (8)
 $[\text{Zn}(\text{L}_2)\text{Cl}_2]$

References

- [1]. Fry F. H, Graham B. , Spiccia L. , Hockless D.C.R. and Tiekink E.R.T. , Binuclear copper complexes of bis(1,4,7-triazacyclonon-1-yl) ligands incorporating acetate pendant arms, *J.Chem. Soc. , Dalton Trans.* 827-831, (1997).
- [2]. Rossignoli M. , Bernhardt P.V., Lawrance G. A. and Maeder M. , Gold(III) template synthesis of a pendant-arm macrocycle, *J. Chem. Soc. , Dalton Trans.* , 323-327 , (1997).
- [3]. Brandes S. , Denat F. , Lacour S. , Rabiet F. , Barbette F. , Pulumbi P. and Guillard R. , Synthesis of macropolycyclic ligands based on tetraazacycloalkanes , *Eur. J. Org. Chem.* , 2349, (1998).
- [4]. Mewis R. E. and Archibald S. J. , Biomedical applications of macrocyclic ligand complexes, *Coord. Chem. Rev.* , **254**, 1686-1712, (2010).
- [5]. Marques F. , Gano L. , Campello M. P. , Lacerda S. , Santos I. , Lima L.M.P. , Costa J. , Antunes P. and Delgado R. , 13- and 14- membered macrocyclic ligands containing methylcarboxylate or methylphosphonate pendant arms: Chemical and biological evaluation of their ^{153}Sm and ^{166}Ho complexes as potential agents for therapy or bone pain palliation, *J. Inorg. Biochem.* , **100** , 270 – 280 , (2006).
- [6]. Maldonado C. R. , Salassa L. , Blanco N. G. and Rivas J. C. M. , Nanofunctionalization of metal complexes for molecular imaging and anticancer therapy , *Coord. Chem. Rev.* , **257** , 2668- 2688, (2013).
- [7]. Pilip A. M and Bilewicz A. , Macrocyclic complexes of scandium radionuclides as precursors for diagnostic and therapeutic radiopharmaceuticals , *J. Inorg. Biochem.* , **105** , 313-320 , (2011).
- [8]. Verma S. , Chandra S. , Dev U and Joshi N. , Synthesis , spectral and biological studies of nitrogen-sulphur donor macrocyclic ligands and their transition metals complexes, *Spectrochim. Acta A.* , **74** , 370 – 374 , (2009).
- [9]. Chandra S. , Gupta L. K. and Sangeetika , Spectroscopic , cyclic voltammetric and biological studies of transition metal complexes with mixed nitrogen-sulphur (NS) donor macrocyclic ligand derived from thiosemicarbazide , *Spectrochim Acta A.* , **62** , 453-460 , (2005).
- [10]. Tyagi M. , Chandra S. , Akhtar J. and Chand D. Modern spectroscopic technique in the characterization of biosensitive macrocyclic Schiff base ligands and its complexes: Inhibitory activity against plantpathogenic fungi , *Spectrochim. Acta A.* , **118** , 1056 -1061 , (2014).
- [11]. El-Boraey H.A. and El-Gammal O.A., New 15-membered tetraaza (N_4) macrocyclic ligand and its transition metal complexes: Spectral, magnetic, thermal and anticancer activity, *Spectrochim. Acta A*, **138**, 553 - 562, (2015).
- [12]. Chaudhary A. and Singh R. V. , Antitumour, antimicrobial and antifertility effects of potentially biodynamic sixteen to twenty four membered tetraazamacrocyclic ligands and their tin (II) complexes, Phosphorus, sulfur, and the related elements , **182**, 2647-2665, (2007).
- [13]. Choi K. , Chun K. M. and Suh I. , Synthesis and characterization of one dimensional nickel (II) macrocyclic complexes with bridging organic ligands, *Polyhedron* , **20** , 57-65, (2001).
- [14]. Ambrosi G. , Borgogelli E. , Formica M. , Fusi V. , Giorgi L. , Micheloni M. , Rampazzo E. , Sgarzi M. , Zaccheroni N. and Prodi L. , Plus nanoparticles as a tool to control the metal complex stoichiometry of a new thioazamacrocyclic chemosensor for Ag(I) and Hg (II) in water, *Sensors and Actuators B : Chemical* , **207** , 1035-1044 , (2015).
- [15]. El-Boraey H. A. and El-Din A. A. S. , Transition metal complexes of a new 15-membered [N_5] Pentaazamacrocyclic ligand with their spectral and anticancer studies, *Spectrochim. Acta A*, **132**, 663-671, (2014).
- [16]. Lu Q. , Martell A. E. and Motekaitis R. J. , Complexation of nucleotides and molecular catalysis of ATP-hydrolysis by a protonated hexaaza macrocyclic ligand, *Inorg. Chim. Acta*, **251** , 365-370 , (1996).
- [17]. Makki M. S. T. , Abdel-Rahman R. M. and El-Shahawi M. S. , Synthesis and voltammetric study of new macrocyclic sulfur compounds for use as chelating agents for separation of arsenic (III) in wastewater and as molluscicidal agents against Biomophalaria Alexandrina Snails, *Comptes Rendus Chimie* , **15** , 617-626 , (2012).
- [18]. Fabbri L. , Some properties of macrocyclic complexes in solution which are related to the ligand ring size, *Adv. Mole. Relax. Inter. Proc.* , **18** , 109-113 , (1980).
- [19]. Canales J. , Ramirez J. , Estiue G. and costamagna J. , Bis-bipyridine hexa-aza-macrocyclic complexes of zinc (II) and nickel (II) and the catalytic reduction of carbon dioxide, *Polyhedron* , **19** , 2373-2381 , (2000).
- [20]. Singh D. P. , Grover V. , Rathi P. and Jain K. , Trivalent transition metal complexes derived from carbohydrazide and dimedone , *Arab. J. Chem.* , in press , (2013).
- [21]. Siddiqi K. S. , Khan S. , Nami S. A. A. and El-ajaily M. M. , Polynuclear transition metal complexes with thiocarbohydrazide and dithiocarbamates , *Spectrochim. Acta A*, **67**, 995 – 1002 , (2007).
- [22]. Chohan Z. H. , Khan K. M. and Supuran C. T. , Synthesis of antibacterial and antifungal cobalt (II) , copper (II) , nickel (II) and zinc(II) complexes with bis – (1,1 – disubstituted ferrocenyl) thiocarbohydrazide and bis-(1,1 – disubstituted ferrocenyl) carbohydrazide , *Appl. Organomet. Chem.* , **18** , 305 – 310 , (2004).

- [23]. Audrieth L. F. , Scott E. S. and Kippur P. S. , Hydrazine derivatives of the carbonic and thiocarbonic acids. The preparation and properties of thiocarbohydrazide, *J. Org. Chem.* , **19** (5) , 733 – 741 , (1954).
- [24]. Chandra S. , Ruchi , Qanungo K. and Sharma S. K. , New hexadentate macrocyclic ligand and their copper (II) and nickel (II) complexes: Spectral , magnetic , electrochemical , thermal , molecular modeling and antimicrobial studies *Spectrochim. Acta A* , **94** , 312 – 317, (2012).
- [25]. Geary W. J. , The use of conductivity measurements in organic solvent for characterization of coordination compounds, *Coord. Chem Rev.* , **7**, 81 – 122, (1971).
- [26]. Raman N. , Jeyamurugan R. , Sakthivel A. and Mitu L. , Novel metal-based pharmacologically agents of transition metal (II) complexes : Designing , synthesis , structural elucidation , DNA binding and photo-induced DNA cleavage activity , *Spectrochim. Acta A.* , **75**, 88-97 , (2010).
- [27]. Halli M. B. and Sumathi R.B. , Synthesis, physico-chemical investigations and biological screening of metal (II) complexes with Schiff base derived from naphthofuran-2-carbohydrazide and citral, *Arab. J. Chem.* 1-12 , (2013).
- [28]. Sloop J. C. , Bumgardner C. L. , Washington G. , Loehle W. D. , Sankar S. S. and Lewis A. B. , Keto – enol and enol - enol tautomerism in trifluoromethyl – β - diketones, *J. Fluor. Chem.* , **127**, 780 -786, (2006).
- [29]. Tai X, Wang H. , Sun X and Tan M. , Synthesis and spectral characterization of methyl -2- pyridyl ketone benzoyl hydrazone and its complexes with rare earth nitrates , *Spect. Lett.* , **38** , 497 – 504 , (2005)
- [30]. Siddiqi K. S. , Khan S. , Nami S. A. A. and El-ajaily M. M. , Polynuclear transition metal complexes with thiocarbohydrazide and dithiocarbamates , *Spectrochim. Acta A*, **67**, 995 – 1002 , (2007).
- [31]. Laly S. and Parameswaran G. , Thermal , spectral , ESR and magnetic studies of some copper (II) thiosemicarbazone complexes , *Thermochim. Acta* , **168** , 43 – 51 , (1990).
- [32]. Eren Tugba, Kose M. Kurtoglu N. , Ceyhan G. , Mckee V. and Kurtoglu M. , An azo-azomethine ligand and its copper (II) complex : Synthesis , X-ray crystal structure, spectral , thermal , electrochemical and photoluminescence properties, *Inorg. Chim. Acta* , **430** , 268-279, (2015).
- [33]. Travnicek Z. , Klanicova A. , Papa I. and Rolcik J. , Synthetic , spectral, magnetic and in vitro cytotoxic activity studies of cobalt (II) complexes with cytokinin derivatives : X- ray structure of 6-(3- methoxybenzylamino) purinium chloride monohydrate, *J. Inorg. Biochem.*, **99** , 776 – 786, (2005).
- [34]. Lechat S. , Khan M. A. , Bouet G. and Vierling F. , Spectrophotometric study of cobalt (II) chloride complexes in ethanol and propan -2—ol , *Inorg. Chim. Acta* , **211** , 33 -36 , (1993).
- [35]. Al-Radadi N. S. , Al-Ashqar S. M. and Mostafa M. M. , Synthesis and characterization of some novel macrocyclic Ni (II) complexes , *J. Incl. phenom. Macrocycl. Chem.* , **69** , 157 – 165 , (2011).
- [36]. El Ghachtouli S. , Cadiou C. , Olivier I. D. , Chuburu F. , Aplincourt M. , Patinec V. , Baccon M. L. , Handel H. and Roisnel T. , Nickel (II) complexes of cyclen-and cyclam-pyridine: topological reorganisations induced by electron transfer, *New J. Chem.* , **30**, 392-398, (2006).
- [37]. Khan T.A. , Naseem S. , Hajra R. , and Shakir M. , Synthesis , physicochemical , and antimicrobial screening studies of complexes of Co (II) , Ni (II) , Cu (II) and Zn (II) with 18 – membered Schiff base Octaazamacrocyclic ligand, *Synth. React. Inorg. Met. – Org. Nano Met. Chem.* , **40** , 861 -868 , (2010).
- [38]. Raman N. , Muthuraj V. , Ravichandran S. and Kulandaisamy A. , Synthesis, characterisation and electrochemical behavior of Cu (II) , Co (II) , Ni (II) and Zn (II) complexes derived from acetylacetonate and p-anisidine and their antimicrobial activity , *Proc. Indian Acad. Sci. (Chem. Sci.)* , **115**(3) , 161-167, (2003).
- [39]. Angelusiu M. V. , Almajan G. L. , I lies D. C. , Rosu T. and Negoiu M. , Cu (II) complexes with nitrogen-oxygen donor ligands : Synthesis and biological activity, *Chem. Bull. "Politehnica" univ. , (Timisoara)* , **53**(67) , 1-2 , (2008).
- [40]. Al – Hazmi G. A. A. , El-Shahawi M. S. , Gabr I. M. and El –Asmy A. A. , Spectral , magnetic, thermal and electrochemical studies on new copper (II) thiosemicarbazone complexes , *J. Coord. Chem* , **58** (8) , 713 – 733 , (2005).
- [41]. Martin N. H. , Allen N. W. , Brown J. D. , Kmiec D. M. , L. VO, An NMR shielding model for protons above the plane of carbonyl group , *J. Mole. Graph. Model.* , **22**, 127-131 , (2003).