



Synthesis and Characterization of Polydentate macrocyclic Schiff bases (14-membered atoms) and their complexes with Co (II), Ni (II), Cu (II) and Zn (II) ions

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Abstract

The condensation reactions of [2+2] carbohydrazone or thiocarbohydrazone with 3,4-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 (L₁): 2,3,9,10-Tetraethyl-6,13-dione-1,4,5,7,8,11,12,14-octaaza-cyclotetradeca-1,3,8,10-tetraene and (L₂):2,3,9,10-Tetraethyl-6,13-dithione-1,4,5,7,8,11,12,14-octaaza-cyclotetradeca-1,3,8,10-tetraene. Mononuclear complexes with the compositions [Co(L₁)Cl₂]. 3H₂O; [M(L₁)] Cl₂.nH₂O (M = Ni (II), Cu (II) or Zn (II); n = 0 when M = Zn (II) and n = 3 when M = Ni (II) or Cu(II)); [M(L₂)Cl₂]. nH₂O; (M=Co (II), Ni (II) or Cu (II); n=0 when M=Ni (II) and n=2 when M= Co (II) or Cu (II)); and also [Zn(L₂)] Cl₂.H₂O were obtained by reacting metal (II) chlorides with the ligand (L₁) or (L₂) in (1:1) molar ratio in ethanol. Mass and infrared spectral techniques suggest the structural features of 14-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 conductivity and magnetic susceptibility measurements, IR, MS and electronic spectral studies. The magnetic moments and electronic spectral data suggested a coordination number six (octahedral geometry) for the [Co(L₁)Cl₂]. 3H₂O; [M(L₁)] Cl₂.nH₂O and [Zn(L₂)] Cl₂.H₂O complexes while the [M(L₂)Cl₂]. nH₂O; are of four coordinated geometry (tetrahedral).

Keywords: Macrocyclic Schiff base, Octaazamacrocyclic, mononuclear complexes, octahedral and tetrahedral geometries.

Introduction

The coordination chemistry of macrocyclic complexes is a fascinating area which has attracted the attention of inorganic chemists¹. The chemistry of metal macrocycles is extensive because of their close relationship to molecules of biological significance². The importance of these complexes also is due to the role they play as models for protein metal binding sites in biological systems³, electrocatalysts in fuel cells⁴, MRI contrast agents⁵, luminescent sensors⁶, and anticancer activity⁷. These extensive applications have been worth investigating for the design of new macrocyclic ligands⁸ for biological and industrial applications^{2,9}.

Over the past decades, great attention has been devoted to the design and synthesis of Schiff bases with enhanced ability to selectively encapsulate the metal ion^{10,11}. A large number of Schiff bases macrocycles and their complexes with metal ions have been synthesized and characterized¹². Also octaazamacrocyclic [N₈] has long been an extremely useful and versatile macrocyclic ligand in coordination, bioinorganic chemistry, and they are known to give several mononuclear complexes, in spite of the large size of the cavity formed by the macrocyclic backbones, as well as to stabilize various anions in their protonated forms.

Because of the wide range of medicinal applications of carbohydrazone¹³ (CH) and thiocarbohydrazone¹⁴ (TCH) and their ability to coordinate with metal ions, therefore it is highly desirable to synthesize and characterize macrocyclic complexes with (CH) and (TCH).

In this paper, we report the synthesis and characterization of macrocyclic Schiff bases complexes [Co(L₁)Cl₂]. 3H₂O; [M(L₁)] Cl₂.nH₂O; [M(L₂)Cl₂].nH₂O and [Zn(L₂)] Cl₂.H₂O obtained from the reaction of the macrocyclic Schiff bases ligands (L₁) or (L₂) with the metals chlorides (figures 2-5).

Material and Methods

Chemicals: All chemicals in this present work were purchased from Sigma-Aldrich, Alfa Aesar, used without further purification except thiocarbohydrazone was prepared according to the reported procedure¹⁵.

Analytical and physical measurements: Metal contents have been determined by using: Inductivity 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) solution at 25C¹. 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 an hp8453UV-Vis. spectrophotometer in DMF at 25C⁰. 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 spectroscopy used to obtain mass spectra for the ligands and the complexes.

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 (400ml) and 3,4-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).

Synthesis of the macrocyclic complexes: The complexes were synthesized by the same general method as follows: A hot ethanolic solution (100 ml) of ligand (L₁) (0.337 g, 0.001 mol.) or ligand (L₂) (0.369 g, 0.001 mol.) and hot ethanolic solution (25 ml) of CoCl₂.6H₂O or NiCl₂.6H₂O (0.238 g, 0.001 mol.), CuCl₂.2H₂O (0.171 g, 0.001 mol.) or ZnCl₂ (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 suggest the thermal stability of the complexes.

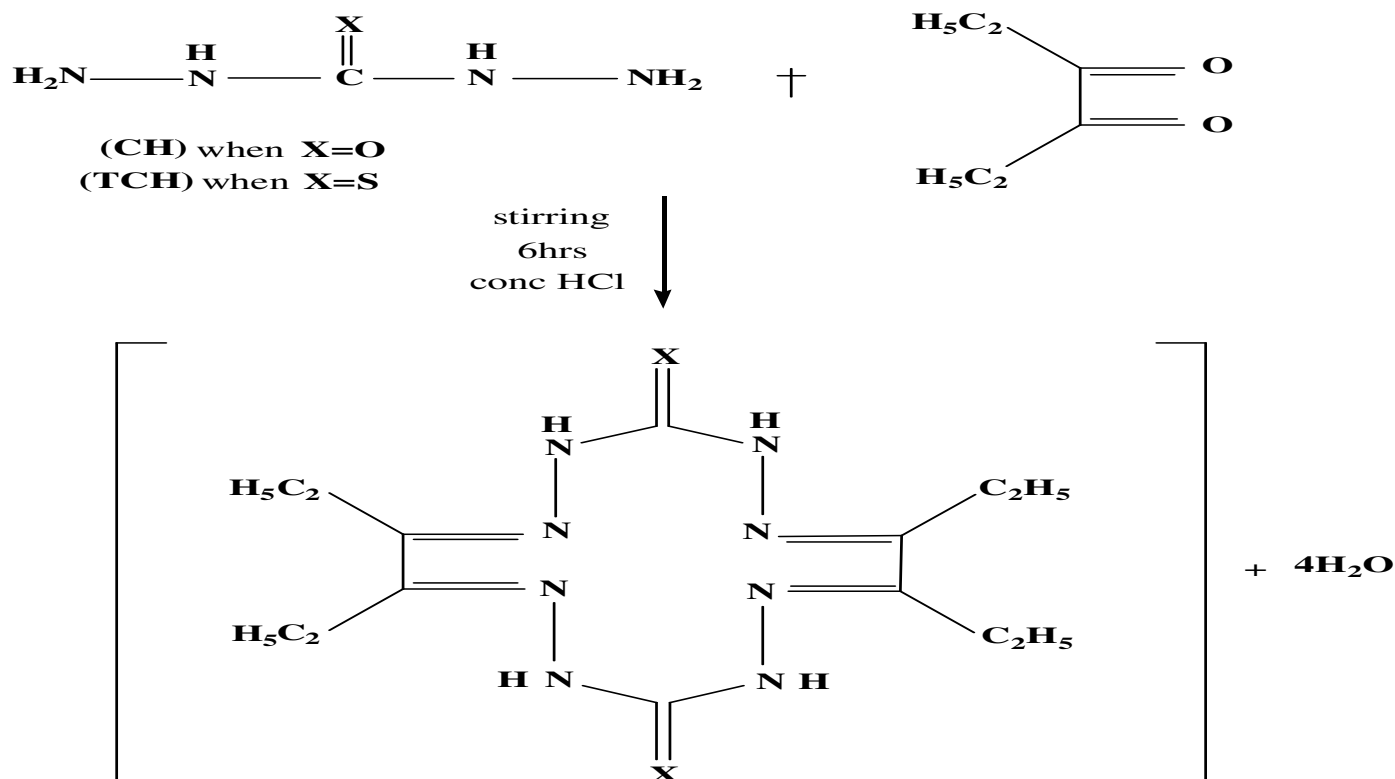


Figure-1
 The structure of the prepared ligands

The reaction of metal chlorides with (L₁) or (L₂) in ethanol (molar ratio 1:1) yields complexes of the general compositions [Co(L₁)Cl₂].3H₂O; [M(L₁)Cl₂].nH₂O (M = Ni (II), Cu (II) or Zn (II) n = 0 when M = Zn (II); and n = 3 when M = Ni (II) or Cu (II)); [M(L₂)Cl₂].nH₂O; (M=Co (II), Ni (II) or Cu (II); n=0 when M= Ni (II) and n=2 when M= Co (II) or Cu (II)); and also [Zn(L₂)Cl₂].nH₂O.

Based on the metal contents measurements and the mass spectra have been supported the above composition, 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 [Co(L₁)Cl₂].3H₂O; [Co(L₂)Cl₂].3H₂O; [Ni(L₂)Cl₂] and [Cu(L₂)Cl₂].2H₂O complexes in DMF solvent 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 coordination¹⁶. The non-conducting character reveals the presence of (Cl⁻) and metals ions in the coordination sphere. Molar conductance of the [Ni(L₁)Cl₂].3H₂O; [Cu(L₁)Cl₂].3H₂O; [Zn(L₁)Cl₂] and [Zn(L₂)Cl₂].H₂O in DMF are in the range (129-146) ohm⁻¹ cm² mol⁻¹ (table-1) indicating a (1:2) electrolytic nature of these complexes¹⁶.

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(NH₂) appeared at (3326) and (3283) cm⁻¹ in the spectrum of carbohydrazide and at (3307) and (3275) cm⁻¹ in the spectrum of thiocarbohydrazide but are absent in IR spectra of the free ligands. Further, no strong absorption band was observed near (1725) cm⁻¹ in the spectra of

the free ligands, indicating the absence of Ketonic group of 3,4-hexanedione, confirming condensation of carbonyl group of 3,4-hexanedione and amino groups of carbohydrazide or thiocarbohydrazide¹⁷ and also elimination of water molecules and as a result, cyclization takes place through the formation of macrocyclic ligands (tetraaminemacrocyclic).

In the IR spectra of the free ligands, the bands appear at (1647) and (1617) cm⁻¹ corresponding to the imine group (C=N) for (L₁) and (L₂) respectively. The IR spectra of these complexes show an absorption in the (1559-1610) cm⁻¹ range attributed to the imine. This absorption band is showing a shift to the lower side in the complexes, suggesting coordination through the nitrogen of the (C=N) group¹⁷. 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 (516-415) cm⁻¹ (table 2)¹⁷.

The presence of carbonyl amide (C=O) is confirmed by the appearance of a sharp band at (1687)cm⁻¹ in the spectrum of (L₁)¹⁸. This band is shifted to lower frequencies in the spectra of the complexes (2), (3) and (4), indicating its involvement of oxygen atoms of the carbonyl amide group in the coordination sphere¹⁹. Further evidence of the bonding is giving by the appearance of new bands of medium or weak intensity between (493-498)cm⁻¹ in the spectra of the complexes (2), (3) and (4), these bands can be assigned to V(M-O)¹⁹ (table 2). However, the spectrum of the complex (1) 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 (L₁), indicating that the oxygen atom is not involved in bonding in this complex. The ligand (L₁) and its complexes have not been found to exhibit Keto-enol tautomerism, which is evidenced by the absence of absorption bands in (2600-2700) cm⁻¹ region²⁰.

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

Compound	Color	Yield %	m.pc ⁰	% Metal		Λ _M Ohm ⁻¹ cm ² mol ⁻¹	Atomic mass g/mole	Mass spectra M/Z
				#cal.	found			
L ₁	white	68	227-229	----	----	----	336	337
L ₂	creamy	63	145*	----	----	----	368	369
[Co(L ₁)Cl ₂].3H ₂ O	dark olive	54	285*	11.33	11.71	27	519.9	520
[Ni(L ₁)Cl ₂].3H ₂ O	green	52	277*	11.29	10.72	139	519.9	519
[Cu(L ₁)Cl ₂].3H ₂ O	light green	62	269-272*	12.11	12.98	136	524.5	525
[Zn(L ₁)Cl ₂]	white	66	301*	13.77	13.28	146	472	472
[Co(L ₂)Cl ₂].2H ₂ O	black	71	225*	11.03	11.87	15	533.9	534
[Ni(L ₂)Cl ₂]	brown	49	243-245*	11.79	12.33	35	497.7	498
[Cu(L ₂)Cl ₂].2H ₂ O	pale green	51	311*	11.79	11.16	19	538.5	539
[Zn(L ₂)Cl ₂].H ₂ O	white	59	282-284	12.45	11.31	129	522	523

#calculated, * decomposition temperature

The presence of thiocarbonyl amide (C=S) is confirmed by the appearance of a band at $(792)\text{cm}^{-1}$ in the spectrum of $(L_1)^{21}$. Since the $\nu(\text{C}=\text{S})$ of the complexes (5), (6) and (7) remains unaltered, it is ascertained that it does not bind to the metal ion²⁰, 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 tautomerism²², which is evidenced by the absence of absorption bands in $(2500-2600)\text{cm}^{-1}$ region. The broad band corresponding to the $\nu(\text{H}_2\text{O})$ at the range $(3459-3355)\text{cm}^{-1}$ (table-2), shows that the complexes (1-3,5,7,8) contain water molecule²³. The (M-Cl) and (M-S) bands do not appear in the IR spectra of the complexes due to instrument limitation.

Electronic spectra and the magnetic moments: The electronic spectra of the macrocyclic ligands and their complexes were recorded in DMF at 25C^0 for 0.001M, (table-3). The bands were observed at (33222) and $(32051)\text{cm}^{-1}$ in the spectra of the ligands (L_1) and (L_2), respectively, which are attributed to $\pi \rightarrow \pi^*$ transition in the (C=N) chromophore⁷. The electronic spectrum of Co (II) complex (1) shows Spain allowed bands at (14858) and $(19960)\text{cm}^{-1}$. The two bands may be assigned as probably the transitions ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})(\nu_2)$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$ respectively, (table 3). The position of the above bands indicates that this complex has distorted octahedral geometry¹². Also the complex (1) spectrum shows a strong absorption at $(29325)\text{cm}^{-1}$, may be charge transfer band due to the azomethine group²⁴(C=N). Unfortunately, the expected weak d-d transition in the visible region(ν_1) for the Co (II) complex (1) cannot be detected even with concentrated solution, may be due to its very low intensity.

At room temperature, the magnetic moment of the cobalt (II) complex (1) lies at (4.92) B.M. corresponding to the three unpaired electrons and is larger than the spin-only value (3.87 B.M.) for six coordinate geometry (figure-2). This value is indicative of an appreciable orbital contribution to the magnetic moment of high-spin Co (II) in octahedral surrounding¹². On the

basis of the above observation, it appears that the symmetry of this complex is not idealized octahedral (Oh), but is(D_4h)¹².

The electronic spectrum of the Ni (II) complex (2) is consistent with the formation of an octahedral geometry with the appearance of two bands at (19417) and $(27624)\text{cm}^{-1}$. These bands refer to the: ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})(\nu_3)$ transitions, respectively (table 3) (figure 3). However, the band (ν_1) for the complex (2) was obscured in the electronic spectrum of this complex due to the lack of the instrument for measurements in the near IR region²⁵. The nickel (II) complex (2) shows μ_{eff} value of (3.10) B.M. This value in tune with a high spin configuration and shows the presence of an octahedral environment around the Ni (II)¹. Also, the observed value for the complex (2) is higher than that of the spin-only value (2.83 B.M.) for octahedral complex. This indicates spin-orbit coupling contribution in magnetic moment value²⁸.

The electronic spectrum of the copper (II) complex (3) shows a band at $(15234)\text{cm}^{-1}$ due to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition, suggesting a distorted octahedral structure²⁶ (table 3) (figure 3). Also, the complex (3) exhibits the high energy band at $(28985)\text{cm}^{-1}$, which is attributed to the charge transfer band. The complex (3) shows magnetic moment at (1.97) B.M., corresponding to one unpaired electron which is higher than spin-only value of (1.73) B.M. for one unpaired electron. This reveals that the complex (3) is monomeric in nature, the absence of metal-metal interaction²⁷ and confirming an octahedral geometry¹⁹.

The absorption spectrum of Zn (II) complex (4) shows 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 spectrum of the complex (4) shows a band at $(30864)\text{cm}^{-1}$ (table 3), which is attributed to the $\pi \rightarrow \pi^*$ transition. The Zn (II) complex (4) is diamagnetic as expected for d^{10} configuration and on the basis of all the data belonging to the complex (4), it appears that the most probable structure for this complex is an octahedral geometry (figure-3).

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

NO.	$\nu(\text{C} = \text{N})$	$\nu(\text{O} = \text{C} \rightarrow \text{NH})$	$\nu(\text{C} = \text{S})$	$\nu(\text{M} - \text{O})$	$\nu(\text{M} - \text{N})$	$\nu(\text{H}_2\text{O})$
L_1	1647(s)	1687(s)	----	----	----	----
L_2	1617(s)	----	792(m)	----	----	----
1	1604(s)	1690(s)	----	----	470(w)	3355(b)
2	1583(s)	1652(s)	----	493(m)	415(w)	3447(b)
3	1599(s)	1660(s)	----	496(m)	434(w)	3400(b)
4	1597(s)	1662(s)	----	498(w)	433(w)	----
5	1609(s)	----	790(w)	----	474(m)	3450(b)
6	1610(s)	----	794(s)	----	516(m)	----
7	1559(s)	----	787(m)	----	436(w)	3459(b)
8	1565(s)	----	765(s)	----	474(s)	3450(b)

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

The Co (II) complex (5) exhibits intense band in the high energy region at $(26178)\text{cm}^{-1}$, which can be assigned to charge transfer band. The (d-d) transition was observed in the $(15797-16750)\text{cm}^{-1}$ range. This band usually corresponds to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition and the splitting of this band into two components (table 3) is expected as a result of spin-orbit coupling suggesting a tetrahedral environment around the (Co^{+2}) ion¹. At room temperature this corresponds to an effective magnetic moment equals to (4.32) B.M. for the complex (3), which lies in the range (4.1-4.8)B.M., known for most of the mononuclear Co (II) complexes in tetrahedral environment¹, and this value reveals that the complex (5) possess tetrahedral geometry and indicating monomeric nature of the complex (5).

In the spectrum of the Ni (II) complex (6), a band appears at $(15873)\text{cm}^{-1}$ which can be assigned to the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition in a high spin tetrahedral geometry¹ (ν_2) (table 3) (figure-4). The other bands (ν_3) and (ν_1) could not be identified because of their lower intensities²⁹. Also, a strong high energy band appears at $(21551)\text{cm}^{-1}$. This band, in turn, may be assigned to a charge transfer band (table-3). The observed magnetic moment for the nickel (II) complex (6) is at (3.59) B.M., corresponding a high spin tetrahedral environment around the Ni (II) ion¹.

The electronic spectrum of the copper (II) complex (7) shows a low energy band at $(12195)\text{cm}^{-1}$ is typically expected for its tetrahedral configuration and may be assigned to the ${}^2T_2 \rightarrow {}^2E$ transition^{1,30} (table-3) (figure-4). The magnetic moment value of the Cu (II) complex (7) is (2.28) B.M. and in

tune with a high spin configuration and shows the presence of a tetrahedral environment around the Cu (II) ion³⁰.

The electronic absorption spectrum of Zn (II) complex (8) shows intraligand transition and no (d-d) transition is expected for a (d^{10}) configuration due to diamagnetic properties of the complex. The band at $(32467)\text{cm}^{-1}$ is due to the $n \rightarrow \pi^*$ transition.

On the basis of all the data belonging to the complex (8), it appears that the most probable structure for this complex is an octahedral geometry (figure-5).

Conclusion

Based on the reported results, it is concluded that the macrocyclic Schiff base ligands (L_1) acts as a hexadentate coordinated donor through the nitrogen atoms of (C=N) groups and the oxygen atoms of the carbonyl amides (N_4O_2) with complexes (2-4). The same ligands (L_1) acts as a tetradentate donor via the nitrogen atoms of (C=N) groups with complex (1). The macrocyclic Schiff base ligand (L_2) acts as a bidentate donor through the two nitrogen atoms of (C=N) groups with the complexes (5-7) and acts as a hexadentate via the nitrogen atoms of (C=N) groups and the sulphur atoms of the thiocarbonyl amide (N_4S_2) with complex (8). Thus, and based on all these data, octahedral molecular geometries are suggested for the complexes (1-4, 8) and tetrahedral geometries for the complexes (5-7). All the complexes are found to be mononuclear. The tentative structures suggested for the complexes are shown in figures 2-5.

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	14858	${}^4T_1g \rightarrow {}^4A_2g(F)$	4.92	octahedral
	19960	${}^4T_1g \rightarrow {}^4T_1g(p)$		
	29325	Charge transfer		
2	19417	${}^3A_2g(F) \rightarrow {}^3T_1g(F)$	3.10	octahedral
	27624	${}^3A_2g(F) \rightarrow {}^3T_1g(P)$		
3	15243	${}^2Eg \rightarrow {}^2T_2g$	1.97	octahedral
	28985	Charge transfer		
4	30864	$n \rightarrow \pi^*$	diamagnetic	octahedral
5	15797	${}^4A_2(F) \rightarrow {}^4T_1(P)$	4.32	tetrahedral
	16750			
	26178			
6	15873	${}^3T_1(F) \rightarrow {}^3T_1(P)$	3.59	tetrahedral
	21551	Charge transfer		
7	12195	${}^2T_2 \rightarrow {}^2E$	2.28	tetrahedral
8	32467	$n \rightarrow \pi^*$	diamagnetic	octahedral

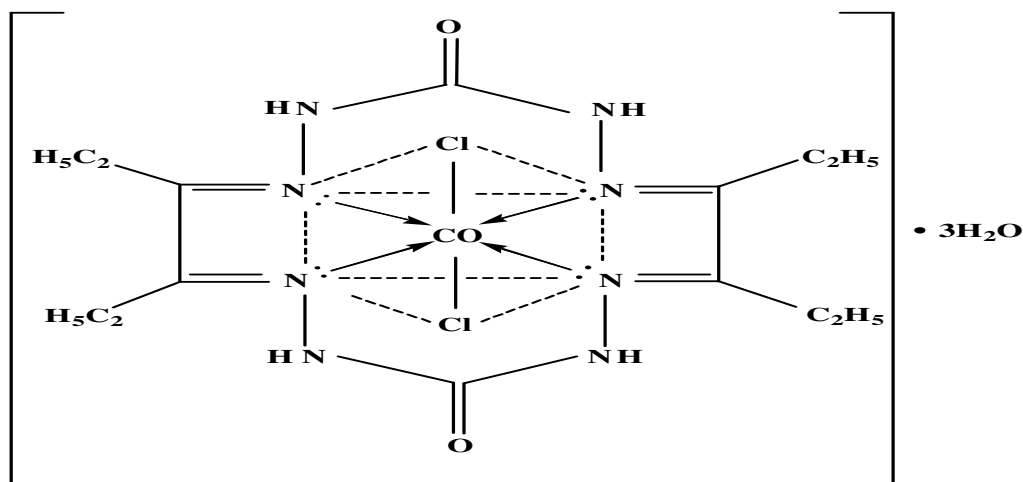


Figure-2
 The proposed structure of the complex (1) $[Co(L_1)Cl_2].3H_2O$

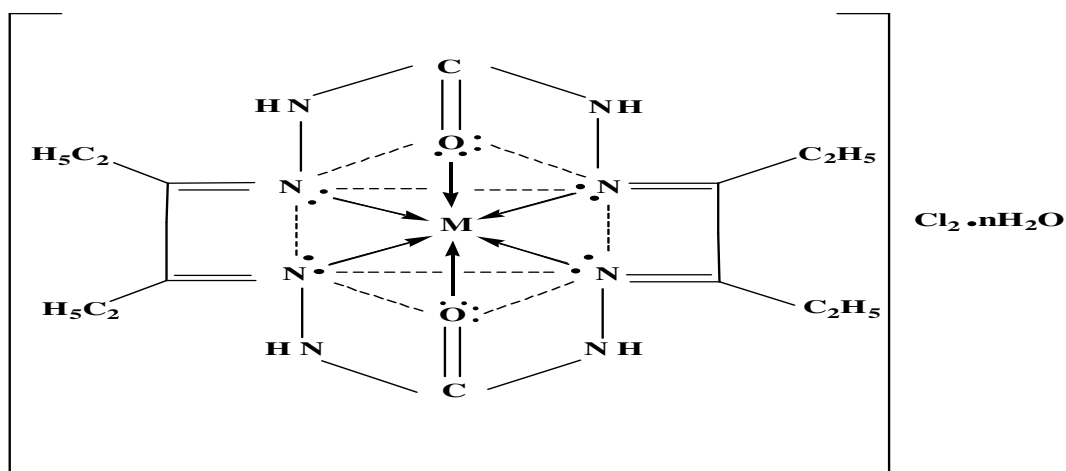


Figure-3
 The proposed structure of the complexes (2-4) $[M(L_1)Cl_2.nH_2O]$, $M = Ni(II), Cu(II)$ and $Zn(II)$, $n = 0$ when $M = Zn(II)$, $n = 3$ when $M = Ni(II)$ or $Cu(II)$

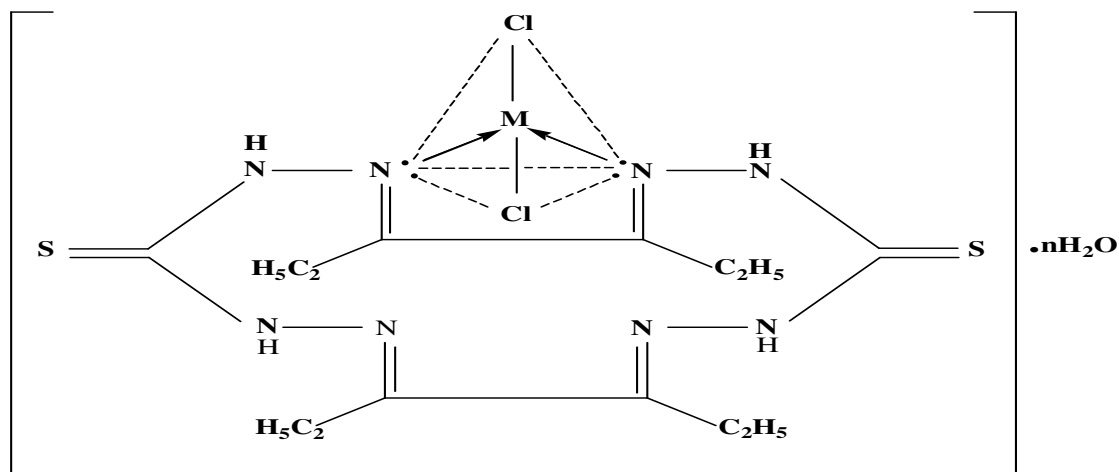


Figure-4
 The proposed structure of the complexes (5-7), $[M(L_2)Cl_2].nH_2O$, $M = Co(II), Ni(II)$ and $Cu(II)$, $n = 0$ when $M = Ni(II)$, $n = 2$ when $M = Co(II)$ or $Cu(II)$

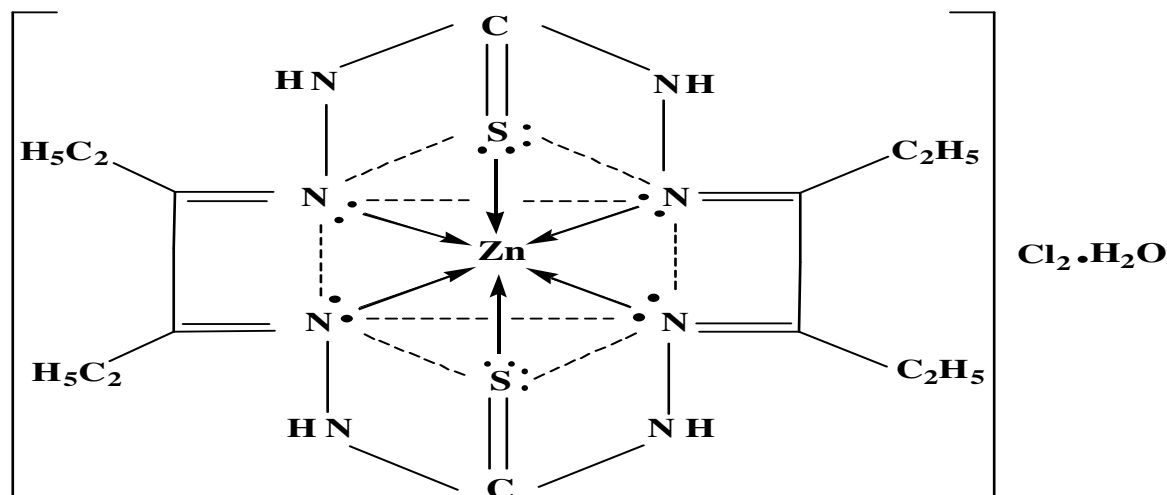


Figure-5
The proposed structure of the complex (8) $[Zn(L_2)] Cl_2 \cdot H_2O$

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