Synthesis and characterization of mixed ligand complexes of some metal chlorides with 8-hydroxyquinoline and amino acid (L- lysine)

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Receiving Date: 13-02-2010 **- Accept Date:** 01-02-2011

Abstract

The mixed ligand complexes of Co (II), Ni (II), Cu(II), Zn(II) and Cd(II) with (L- lysine)and 8-hydroxyqinoline (Oxine) were synthesized and characterized by : (FT-IR, UV-Vis, AAs) spectra, melting point, molar conductivity measurements. Chloride ion content were also evolution by (Mohr method) .Magnetic susceptibility measurements.

From the above data the proposed molecular structure for Co (II), Ni (II), Cu(II), Zn(II) and Cd(II) were forming tetrahedral geometry

Introduction

The amino acid L- lysine and various transition metals are important in the biological functions of humans, animals, and plants. L- lysine is one of the twenty major amino acids and is considered an essential amino acid [1]. Inorganic elements like transition metals are vital to the proper functioning of the body's processes. Metal ions have the ability to form strong bonds and be stable in more than one oxidation state. Iron has a major role in biological reactions. Iron in the blood chelates with protoporphyrin to form heme, a prosthetic group of proteins such as myoglobin, hemoglobin, catalyses, peroxides, and cytochrome c. It also plays a role in enzyme activity. Enzymes called oxygenases catalyze the cleavage or degradation of aromatic amino acid rings in biological systems. For example the degradation of phenylalanine begins with its hydroxylation to tyrosine, a reaction catalyzed by phenylalanine hydroxyls. The active site of this enzyme contains iron that is not part of heme or an iron-sulfur cluster [1,2]. Zinc is found only in the 2+ state in biological systems. It is known to form complexes with amino acids such as L-serine, L-aspartic acid, L-lysine, and L-phenylalanine [3]. In a previous study, a zinc-tyrosine complex was synthesized in the core of encapsulated dendrimers [4]. Copper ions form a complex with tyrosine that inhibits demethlyation and stimulates oxidation of micro small pigments in hepatic cells [5]. The complex acts as an electron acceptor which stimulates the oxidation process. Copper ions have also been found to be required in the metabolic transformation of tyrosine [6].

Report shows that various scientists investigated the quinazolone derivatives as biological and pharmaceutical agents [7-10]. Most of quinazolone containing phenyl group at 3 positions. The area in which the quinazolones containing metal chelating moiety (i.e. ligand) say 8-hydroxy quinoline has not been developed in spite of the 8-hydroxy quinoline is well known metal precipitant [10].

8-hydroxyqinoline or 8-qinoline is the name most commonly used, while its trivial name is (oxine), which is conventionally used for the description of chelate compounds Oxinates, as out of seven possible hydroxyqinoles, only 8-hydroxyqinoline forms chelate with metal ions [11].

8-Hydroxyquinoline is an organic compound with the formula C_9H_7NOH. It is a derivative of the heterocycle by placement of an OH group on carbon number 8. This colorless compound is widely used commercially [11].

The present paper deals with the synthesis, spectral and magneto chemical studies of metal(II) complexes with 8-hydroxyquinoline as a primary ligand and L- lysine as secondary ligand .

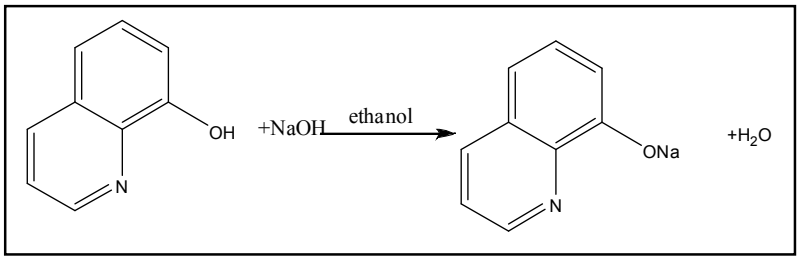
Experimental

a- chemicals and instruments: L- lysine and 8-hydroyqinoline were purchased from (Merck) solvents and all the metal ions Co(II),Ni(II),Cu(II) , Zn(II) and Cd (II) were of Analar grade (BDH). They were used in the form of chlorides without further purification. The reagents were used without further purification.

b- Instruments: FT-I.R spectra were recorded as KBr discs using Fourier transform Infrared Spectrophotometer Shimadzu 24 FT-I.R 8400s. Electronic spectra of the prepared complexes were measured in the region (200- 1100) nm for 10^{-3} M solutions in DMF at 25ºC using shimadzu-U.V-160. A Ultra Violet Visible- Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. While metal contents of the complexes were determined by Atomic Absorption (A.A) Technique using Japan A.A-67G Shimadzu. Electrical conductivity measurements of the complexes were recorded at 25ºC for 10^{-3} M solutions of the samples in DMF using pw9527 Digital conductivity meter (Philips). Magnetic susceptibility measurements were measured using Bruker magnet BM6. Melting points were recorded by using Stuart melting point apparatus. The proposed molecular structures of the complexes were determinated by using chem. office prog, 3DX (2004).

General Method for the Synthesis

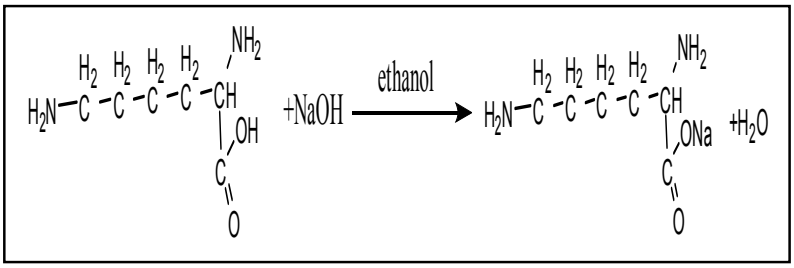
a- Sodium-8-oxyqinolinate:[0.145gm,1mmol] 8- hydroxyquinoline (8-QH) with [0.04 gm (1mmol)] sodium hydroxide in ethanol was deprotonated according to the following reaction scheme (1)



Scheme (1): Preparation of sodium-8-oxyqinolinate

ISSN: 2222-8373

b- Sodium lycinate: [0.146 gm(1mmol)] with [0.04 gm (1mmol)] sodium hydroxide in ethanol was deprotonated according to the following reaction scheme (2)



Scheme (2): Preparation of sodium lycinate

c- Synthesis of complexes: An aqueous solution of the metal salt was added to the solution of the ligand in ethanol respectively using stoichiometric amounts [(1:1:1) (metal):lys:8-HQ] molar ratio, the mixture was stirred for (30 mint) at room temperature, crystalline precipitates observed. The resulting precipitates were filtered off, recrystallized from ethanol and dried at room temperature. The product found to be decomposed at >350^{o} C

Results and Discussion

The complexes are air-stable, non-hygroscopic, insoluble in water, partly soluble in ethanol and methanol, and soluble in DMSO and DMF .The observed molar conductance, (Table-1) values measured in DMF in 10^{-3}M solution fall in the range (7.3- 9.6μS.cm^{2}.Mol^{-1}). These observed values of the molar conductance are well within the expected range for non-electrolytic nature [12].

The atomic absorption measurements and chloride content (Table-1) for all complexes gave approximated values for theoretical values.

The infrared spectra of various mixed ligand complexes synthesized are compiled in (Table-2).The infrared spectra of these complexes in comparison with free oxine (8-HQ) and the respective free amino acids show characteristic band positions, shifts and intensities which can be correlated to bi dentate amino acid (L-lysine) and oxine (8-HQ) chelation Figure (1).

As regards chelation through amino acids, the IR spectra exhibit significant features in the υNH_2 and υCOO^-) regions. It is worth while to mention here that free amino acids exist as zwitterions ($NH_3AA.COO^-$) and the IR spectra of these cannot be compared entirely with those of metal complexes as amino acids in metal complexes do not exist as zwitterions. Some new bands of weak intensity observed in the regions around (450-516)) $cm^{-1}$and (632-644) cm^{-1} may be ascribed to M-O and M-N vibrations, respectively [13, 14].

It may be noted that, these vibrational bands are absent in the spectra of the ligands.

The electronic spectral data of various complexes are presented in table (3) The (UV- Vis) spectrum of the ligand (8-HQ) in DMF solvent Figure.(2)shows signal at 317nm(31545 cm^{-1}) ε_{max} (200 $l.mol^{-1}.cm^{-1}$) assigned to the ($n\rightarrow \pi^*$) electronic transition, the longer wave length and the spectrum of the free ligand (L-lysine),Figure(3)exhibits a high intense absorption peak at (280 nm)(35714.28 cm^{-1})(ε_{max} 946 $molar^{-1}.cm^{-1}$),and an intense peak at 320 nm (31250.0 cm^{-1})(ε_{max}411 $mol^{-1}.cm^{-1}$), which assigned to ($\pi\rightarrow\pi^*$) electronic transition, the shorter wave length, and ($n\rightarrow\pi^*$) the longer wave length this forms (charge transfer) which had very high intenseness allow by selection rules[16,15,17].

[Co ($C_{15}H_{19}N_3O_3$)] (d^7) :The spectrum of brown complex exhibited the following absorptions at(37174) cm^{-1} ,(28571)cm^{-1} and(24038) cm^{-1} wave numbers these bands are characteristic of tetrahedral cobalt (II) complex and were assigned to the transitions Ligand Field, Ligand Field and $^4A_2\rightarrow {}^4T_1(P)$ (d-d) electronic transition type which forms (charge transfer) allow by selection rules happening metallization between metal and ligand .This result is a good Evidence for Co (II) tetrahedral geometry [18].

[Ni($C_{15}H_{19}N_3O_3$)] (d^8): The green complex spectrum revealed the following absorption band at (1587 3) cm^{-1} attributed to the charge transfer (C.T), two absorptions at (23809) cm^{-1} were due to the electronic transition type $^3T_{1(f)} \rightarrow {}^1T_{1(p)}$ and $^3T_{1(f)} \rightarrow {}^3T_{1(p)}$ the green colour of complex proves absorption of spectral at part of red area that longer wave length (red shift) and occurrence metallization between metal and ligand , in fact this result is a good agreement with previous work of tetrahedral geometry [18].

In the [Cu ($C_{15}H_{19}N_3O_3$)] complex the band at (35842) cm^{-1} are assigned to Charge-transfer (C.T), and band at (23809) cm^{-1}, which had been attributed to (d-d) electronic transition type [$^2B_1 \rightarrow {}^2E_1$] exciting state according to (Yan - Tyler) effect, apposition of this peak is a good agreement with reported for Cu (II) distorted tetrahedral geometry [18].

The complexes [Zn($C_{15}H_{19}N_3O_3$)], and [Cd($C_{15}H_{19}N_3O_3$)]:(d^{10}) (white complexes) : because of filled d- shell of these complexes, no ligand field absorptions band was observed, therefore the band appeared at (30769& 25445) cm^{-1} in the spectrum of Zn (II)complex, and (35714& 25062) cm^{-1} in the spectrum of Cd (II) complex Figure. (4) Could be attributed to charge transfer. [18-19] in fact this result is a good

The μeff of values for the following high spin tetrahedral complexes were found as complexes for Co (II) (d^7) complex is 4.32 B.M , for Ni(II) (d^8) complex is 4.39 B.M , for Cu (II) complex is 1.45 B.M .While magnetic susceptibility measurements for Cd (II) and Zn(II) (d^{10})(white complexes) showed diamagnetic as expected from their electronic configuration [19].

Proposed molecular structure:

Studying complexes on bases of the above analysis, the existence of tetra coordinated [M(Lys)(Q)],a proposed models of the species were built with chem3D shows in Figure ***(5)*** .

Nomenclature of prepared complexes:

Table (4) shows empirical formula and nomenclature (IUPAC) with abbreviated.

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Table (1) the physical properties of the compounds

Compounds	M.wt	Color	M .p (de) °c	Λm μS.cm^2.Mol^{-1}	Cl%	%Metal Theory	% Metal Experiment
Lys	146.19	White	> 350	1.0	-	-	-
8-hydroxyquinoline(8-HQ)	145.16	Pale- yellow	77	13.27	-	-	-
Co($C_{15}H_{19}N_3O_3$)	348.26	brown	> 350**(de)**	8.3	Nil	16.92	18.04
Ni ($C_{15}H_{19}N_3O_3$)	348.26	green	> 350**(de)**	7.3	Nil	16.86	17.17
Cu($C_{15}H_{19}N_3O_3$)	352.88	blue	> 350**(de)**	7.6	Nil	18.01	17.27
Zn($C_{15}H_{19}N_3O_3$)	354.74	White	>350**(de)**	9. 6	Nil	18.44	17.68
Cd($C_{15}H_{19}N_3O_3$)	401.74	white	>350**(de)**	8.4	Nil	27.98	26.96

Decomposed = **de**

Table (2) FT-IR spectral data of the Ligands and there complexes (cm^{-1})

Compound	NH $_{sym}$ str	CH$_{(py)}$ str	(CH)$_{cyclic}$	υ (C=N)	υ (C=C)	υ(C–O)	υ∂ (C-O)	υ(-COO$^-$) asym	sym	M-O	M-N
ؚL-Lys								1618 vs	1411 s		-
8-HQ	3240-3047br	-	-	1577	1508	-	-				-
Co($C_{15}H_{19}N_3O_3$)	3168w-	3136s 2854w	2974m	160w	1573vs	1283m	457m	1465s	1323s	450m	640m
Ni($C_{15}H_{19}N_3O_3$)	3194br-s	3136m 2854w	2924w	1590s	1570s	1269m	505m	1465vs	1377vs	450w	648m
Cu($C_{15}H_{19}N_3O_3$)	3356 br s	3240 br-s	2989w	1620s	1520w	1284m	497m	1497vs 1423 s	1373s	503w	644m
Zn($C_{15}H_{19}N_3O_3$)	3384 br	3058m	2925w	1581vs	1504m	1284m	588s	1469vs	1377vs	516m	632m
Cd($C_{15}H_{19}N_3O_3$)	3315s	3085m	2927w	1577vs	1500 vs	1282s	583w	1467vs-1423 s	1371vs-1328vs	503m	640m

Sym: symmetric, asy: asymmetric, py: pyridine, str: stretching,

vs.: very strong, s: strong, m: medium, w: week

Table (3) Electronic data for the ligand and there complexes

Compounds	λ(nm)	$\overline{\upsilon}$ (cm^{-1})	$\varepsilon_{(max)}$ $L.mol^{-1}.cm^{-1}$	Assignment	coordination
8-Hydroxyqinoline	317	31545	200 l	n→π*	-
L-lysine	280 320	35714 31250	946 411	π→π n→π*	-
$Co(C_{16}H_{22}N_3O_3)$	269 350 416	37174 28571 24038	861 247 243	Ligand Field Charge-transfer $^4A \rightarrow {}^4T_1(P)$	Tetrahedral
Ni $(C_{16}H_{22}N_3O_3)$	280 445 630	35842 23809 15873	2195 250 135	Charge transfer $^3T_{1(f)} \rightarrow {}^1T_1$ $^3T_{1(f)} \rightarrow {}^3T_{1(p)}$	Tetrahedral
$Cu(C_{16}H_{22}N_3O_3)$	279 420	35842 23809	2159 238	Charge-transfer $^2B_1 \rightarrow {}^2E$	distorted tetrahedral
$Zn(C_{16}H_{22}N_3O_3)$	277 325 339	36101 30769 25445	2143 1454 1007	Charge -transfer Ligand Field	Tetrahedral
$Cd(C_{16}H_{22}N_3O_3)$	280 399	35714 25062	2175 1407	Charge transfer Ligand Field	Tetrahedral

Table (4) Nomenclature of prepared complexes

Empirical formula	Nomenclature	Abbreviation
$Co(C_{15}H_{19}N_3O_3)$	(8-oxyquinolinato)lysinatocobalt II)	[Co(Q)(lys)]
Ni $(C_{15}H_{19}N_3O_3)$	(8-oxyquinolinato)lysinatonickel (II)	[Ni (Q)(lys)]
$Cu(C_{15}H_{19}N_3O_3)$	(8-oxyquinolinato)lysinatocopper (II)	[Cu(Q)(lys)]
$Zn(C_{15}H_{19}N_3O_3)$	(8-oxyquinolinato)lysinatozinc(II)	[Zn(Q)(lys)]
$Cd(C_{15}H_{19}N_3O_3)$	(8-oxyquinolinato)lysinatocadmium(II)	[Cd (Q)(lys)]

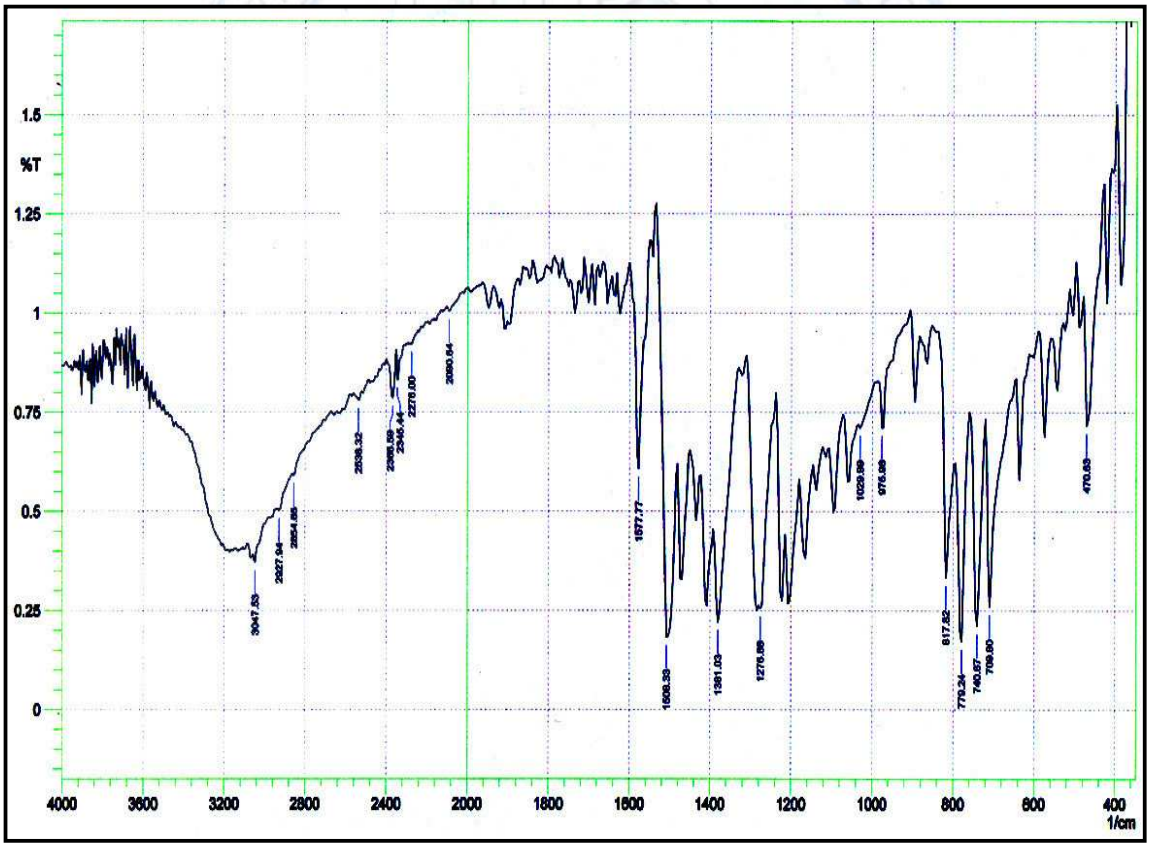

Figure (1): FT-IR spectrum of (8-Hydroxyqinoline)

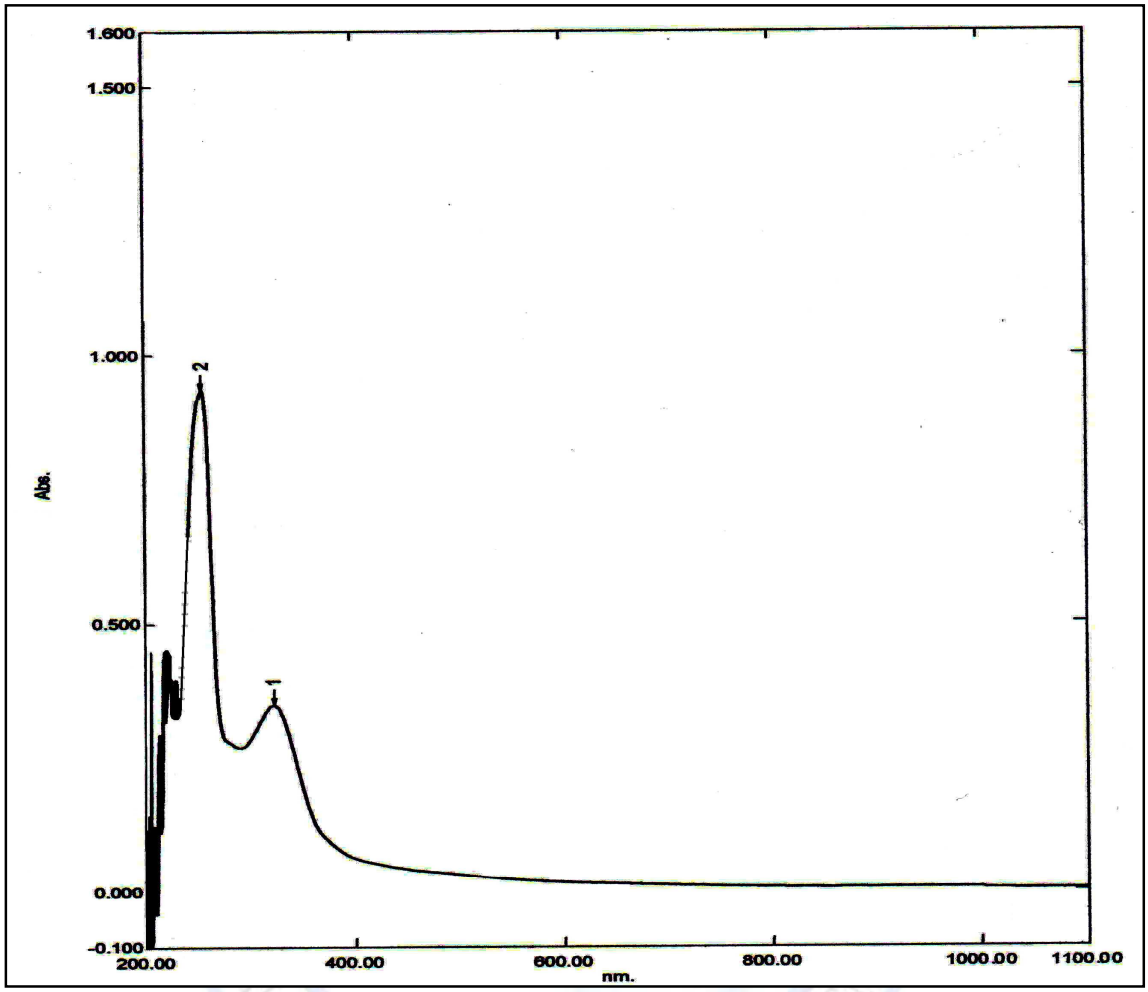

Figure (2): Electronic spectrum of the ligand (L-lysine)

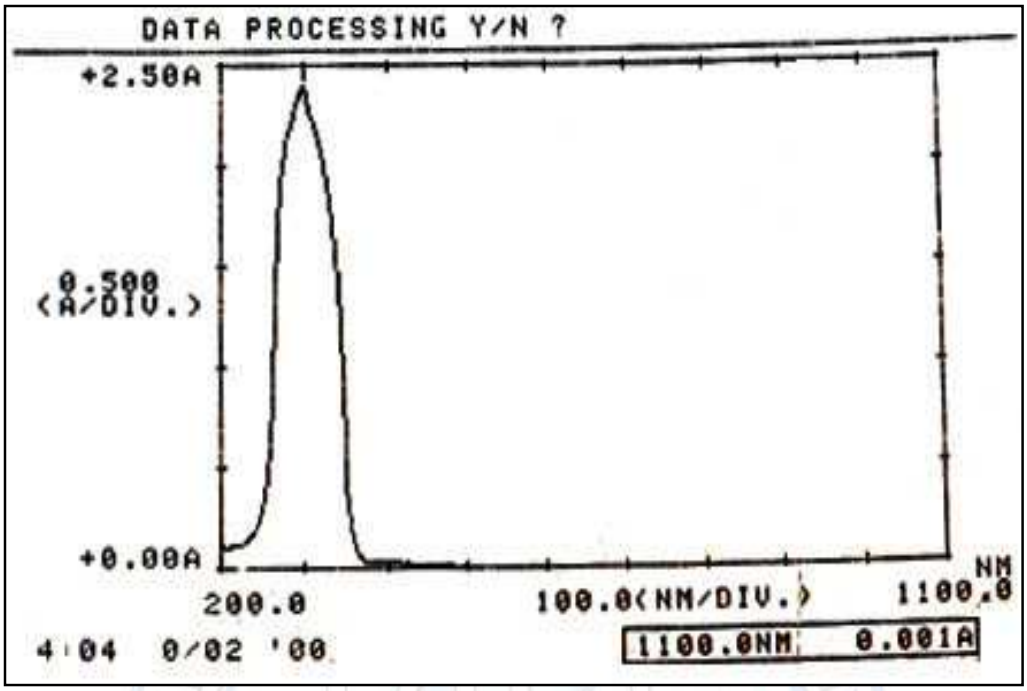

Figure (3): Electronic Spectrum of (8-hydroxyqinoline)

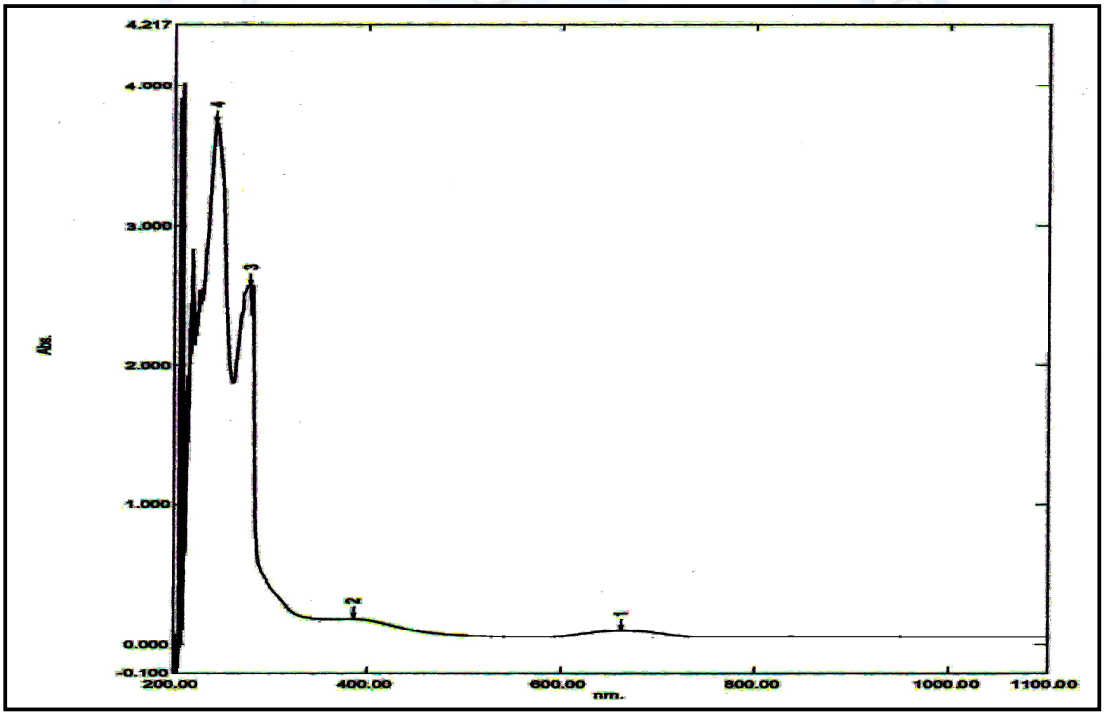

Figure (4): The electronic structure of Cd ($C_{13}H_{19}N_3O_3$)

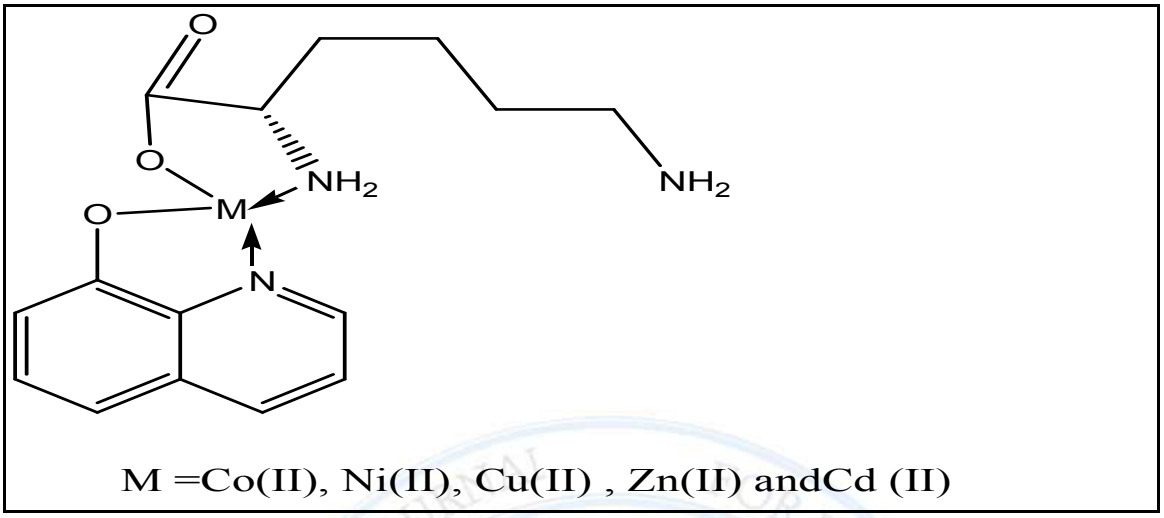

Figure (5): The proposed structure of the complexes