Synthesis and Characterization of New Bidentale Ligand type (NO) [2-hydroxy -4- butoxy aniline] and its Complexes with Metal ion Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}.

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Abstract

The aim of this work is the synthesis and characterization of the new ligand (HL) containing (N and O) as donar atoms where :

HL = 2-hydroxy -4-n-butoxyanilin

The preparation of ligand includes two steps. Reaction of para Nitro phenol with n-Bromobutan in 1:1mole Raito. the second step is adding ammonium chloride and Zinc powder.The ligand was reacted with some metal ions in the presence of ethanol as a solvent 2:1 mole ratio to give the complexes in general formula

[M(L)2(H2O)n] where :

M = Mnп , Coп , n=2; M= Niп , Cuп , Znп n=0

All compounds have been characterized by spectroscopic (I.R,U.V.Vis.) metal content, melting point and molar conductivity measurement, which showed that the complexes are non-electrolyte .The proposed geometry for complexes were Mn,Co octahedral while Cu have been square planer . Finally Zn .Ni complexes a tetrahedral geometry.

Introduction

Ligands containing amine and hydroxyl groups have been of interest for along time because of there importance in protein synthesis of living organisms. Regarding bond formation with central metal ion , NH2 is stronger than OH group . In the present work 2-hydroxy 4-n-butoxy aniline is chosen to be studied as aligand which contains NH2 and OH groups in ortho position . As simillir work the studies on the o-phenylenediamine complexes at 1929.In these first studies Hieber and his coworker(1) suggested that unidentate diamine was present in divalent cobalt , nickel and zinc complexes with four or six o-phenylenediamine molecules per metal ion On the other hand , Marks and his coworker (2)suggested bidentate chelate behviour for bis and tris complexes,basing on the observation that NH2 band at 3416 cm-1 which was characteristic of uncomplexed amine was not present in the spectra of its complexes.There are other reports of this compound acts as a bidentate ligand (3,4,5).Mannar and Naida(6)suggest that o-phenylenediamine acts as a bidentate chelate while meta and para phenylenediamines act as a bridging ligands.

Experimental

Reagents were purchased from Fluka and Redial-Dehenge chemical Co. I.R spectra were recorded as (KBr) discsusing a shimadzu 8300 FTIR spectro photometer in the rang (4000-400)cm-1 . Electronic spectra of prepared compounds were measured in the region (200-1100)nm for 10^{-3}M solutions in (DMF) at 25˚C using a shimadz, 160 spectrophotometer with 1.000 ± 0.001cm matehed quartz cell. Electrical conductivity measurements of the complexes were recorded at 25˚C for 10^{-3}M solutions of the samples in (DMF) using a PW 9526 digital conductivity meter .

Synthesis of the ligand (HL)

A (0.8g ,14.2mmol) of KOH was dissolved in (50 ml) Ethanol and added to (2g ,14.1 mmol)of para nitro phenol, then (2ml)n-bromo butane was added .The mixture was refluxed for (4 hrs)with stirring, KBr was removed by filtration .In beaker equipped with

athermometer and magnetic stirrer ,(2g)of ammonium chloride was added to (200ml)of water .Then solution (A) was added to ammonium solution .

The mixture was stirred vigorous mechanically then add (5g, 76.9mmol)of Zinc powder in smollportions during about (15 minutes).

The rate of addition should be such that tempreture rapidly rises to (60 -65˚C) and remains in this range until all the Zinc has been added continually, further (15 minutes) by which time the reduction is complete . The warm reaction mixture was filtered to remove the Zinc oxid the filterate was cooled them (8 ml)of concentrated sulphuric acid was added to solution with keeping. The temprcher less than (10˚C) during the addition . Finaly we neutralize the solution by addition of ammonium hydroxide until the PH of the solution became =8. Then extracted twice with ether, the ether was vaporated to gate the ligand (0.534 g) , yield (21%) ,m.p.(210co) dec.

Synthesis of [(Mn (L)2(H2O)2] complex

(0.2g ,3.5mmol) from KOH was dissolive in (5 ml)of distilled and deoxginated water and part (0.05g ,0.27mmol) from the ligand was mixed and closed to prevent the oxiedation of the phenoxied. The solution of the matel prepared by dissoliving (0.24g,1.42mmol) from the salt (MnSO4.H2 O) in (5ml) distilled and deoxginated water, the resuiting solution was mixed with ligand solution .then cooled until appeating (dark violet) precipitate of the complex crystals (0.0326 g) ,yield (57 %) , m.p. (330 ˚C) dec .

Synthesis of [Co(L)2(H2O)2] ,[Ni(L)2] ,[Cu(L)2] , [Zr(L)2] complexes

The method used to prepare these complexes was similar to that mentioned in preparation of [Mn(L) 2(H2O)2] complex. Table (I) stated weight of starting materials, yield and some physical properties of complexes.

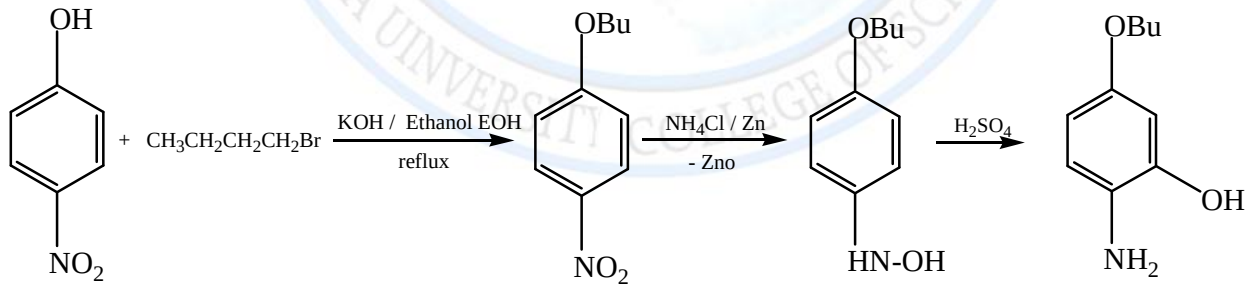
Table (1) some physical properties of the ligand and it's complexes

Compound	m.p.˚C	Color	Weight of metal		Weight of product g	Yield %	M.Wt	Metal Content Found (calc)
			g	mmol				
(HL)	210dec	dark violet	____	___	0.534	21	181	___
$[Mn(L)_2(H_2O)_2]$	330dec	redish brown	0.024	0.138	0.0326	79	451	12.00 (12.30)
$[Co(L)_2(H_2O)_2]$	330dec	dark violet	0.040	0.138	0.0253	63	454	12.70 (12.90)
$[Ni(L)_2]$	340dec	dark violet	0.079	0.27	0.0369	61	470	11.90 (11.72)
$[Cu(L)_2]$	345dec	olive green	0.073	0.28	0.0377	65	423	14.80 (14.96)
$[Zn(L)_2]$	350dec	redish brown	0.079	0.27	0.0739	74	479	13.50 (13.68)

dec: decomposition .

Results and Discussion

The new ligand type (NO) was prepared according to the general method shown in scheme (1).



Bu = $CH_3CH_2CH_2CH_3$ 2-hydroxy-4-n-butoxy annilin

Scheme (1) synthesis of the ligand 2-hydroxy-4-n-butoxy annilin

I.R spectrum of the ligand showes spilited band at (3341 cm-1) and (3279cm-1) assigned to asymmetric and symmetric stereching vibration of NH2 group(7)respectively, this band over laped with (OH)group, appeared as broad band at range (2400 – 3600 cm-1) . The two bands at (1512 cm-1) and (1238cm-1)assigned to υ(C-N) and υ (C-O) respectively.

The reaction of(HL)ligand with metal salts gives complexes of general formula [M(L)2(H2O)2] (M=MnII,CoII); [M(L)2](M=NiII, CuII, ZnII)

The analytical an physical data (table-1) and spectral data (table-2 and table-3) are in good agreement with the suggested structure.

The Spectra of the complexes showed shifting to lower frequencies for υ (C-O) and υ (C-N) bands compared to ligand spectrum and appeared at (1111cm-1) ,(1466cm-1) ; (1096cm-1) , (1460cm-1) ; (1099cm-1) , (1481cm-1) ; (1123cm-1) , (1508cm-1) and (1099cm-1) , (1435cm-1) for complexes1,2,3,4and 5 respectively. This can be attributed to the delocalization of metal electron density to ligand (π system)(8) , this confirms the coordination through (O) and (N) atoms to metal atoms(9) .

Appearance of a new bands at the range (420-480)cm-1 (582-617)cm-1 assigned to the υ M-O and υ M-N respectively 10) . The broad band at (3379),(3410) in the spectra of complexes 1,2 respectively assigned to the (O-H) of the water molecules(11)that coordinate to the metal ion in complexes 1,2.

(U.V-Vis) spectrum for the ligand Fig (2) exhibit a high intense absorption peak at (317) nm (31545cm) (ε max =2054 mol-1.L .cm-1) which assigned to overlap of ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions(12) (table-3).The electronic spectral data of the complexes are summarized in table 3 .The (uv-vis) spectra of the complexes displayed absorption at rang (314-350) nm were assigned to the ligand filed(13) In the [Mn(L)2(H2O)2] complex the two bands at (369,471) nm was attributed to (d-d) electronic transition type ($6A1g \rightarrow 4T2g(p)$)($6A1g \rightarrow 4A1g(G),4Eg(G)$), suggesting octahedral structure about MnII ion(14). The bands at (407 nm) (586 nm) in spectrum of [Co(L)2 (H2O) 2] complex was attributed to (d- d) electronic transition type ($4T1g \rightarrow 4T1g(p)$) ($4T1g \rightarrow 4A2g$), suggesting a octahedral structure about CoII ion(15) , The bands at (364 nm) (588 nm)(654nm) in spectrum of [Ni(L)2] complex . assigned to (d-d) electronic transition type ($3T1(F) \rightarrow 3T1(p)$) ($3T1(F) \rightarrow 1E$), suggesting tetrahedral structure about Ni ion(16). The uv-vis spectra (table-3) of the complex [Cu (L) 2] showed absorption band at (382 nm) refers to charge transfer

transition while the band at (567nm) was assigned to the (2Eg→2T2g) electronic transition characteristics of square planar CuII ion(17). The absences of (d-d) electronic transition in the complex [Zn (L)2] are due to the configuration (d10) structure for the metal ion and sp3 hyperdization of ZnII.

The molar conductance values determined in (DMF) solution (10-3 M) (table-3) lie in the range (2.2 -8 s.cm-1.mol-1), indicated that the complexes are non electrolytes(18) and confirm the suggested formula .

Table (2) I.R spectral of the ligand and its complexes (cm^{-1})

NO	Formulae	υas (N-H) υs (N-H)	υ (OH/H_2O)	υ (C-N)	υ (C-O)	υ (M-N)	υ (M-O)
1	[HL]	(3341) (3279)	(3183)	1512	1238	–	–
2	[Mn$(L)_2(H_2O)_2$]	(3406) (3345)	(3379)	1466	1111	582	484
3	[Co$(L)_2(H_2O)_2$]	(3321) (3252)	(3410)	1460	1096	595	444
4	[Ni$(L)_2$]	(3329) (3189)	–	1481	1099	585	440
5	[Cu$(L)_2$]	(3391) (310)	–	1508	1123	617	447
6	[Zn$(L)_2$]	(3260) (3260)	–	1435	1099	567	420

(1)[Mn(L)2(H2o)2]

(2) [Co(L)2 (H2O)2]

(3) [Ni(L)2]

(4) [Cu(L)2]

(5) [Zn(L)2]

Table(3)Electronic spectral data and conductance measurement in DMF as solvent

Compound	nm λ	ε max molar^{-1} cm^{-1}	Λ_m s.cm^2.mole^{-1}	Assignment
(HL)	317	2054	------	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$[Mn(L)_2 (H_2O)]$	369 471	1771 856	3.0	$^4A_{1g} \rightarrow {}^4T_{2g\,(p)}$ $^4A_{1g} \rightarrow {}^4A_{1g\,(G)}$
$[Co(L)_2 (H_2O)]$	407 586	725 518	5.0	$^4T_{1g} \rightarrow {}^4T_{1g\,(p)}$ $^4T_{1g} \rightarrow {}^4A_{2g}$
$[Ni (L)_2]$	364 588 654	1453 1631 720	8.0	C.T $^3T_{1(F)} \rightarrow {}^3T_{1(p)}$ $^3T_{1(F)} \rightarrow {}^1E$
$[Cu (L)_2]$	382 567	1607 645	2.2	C.T $^2E_g \rightarrow {}^2T_{2g}$
$[Zn (L)_2]$	272 320	1610 394	2.7	Ligand field Ligand field

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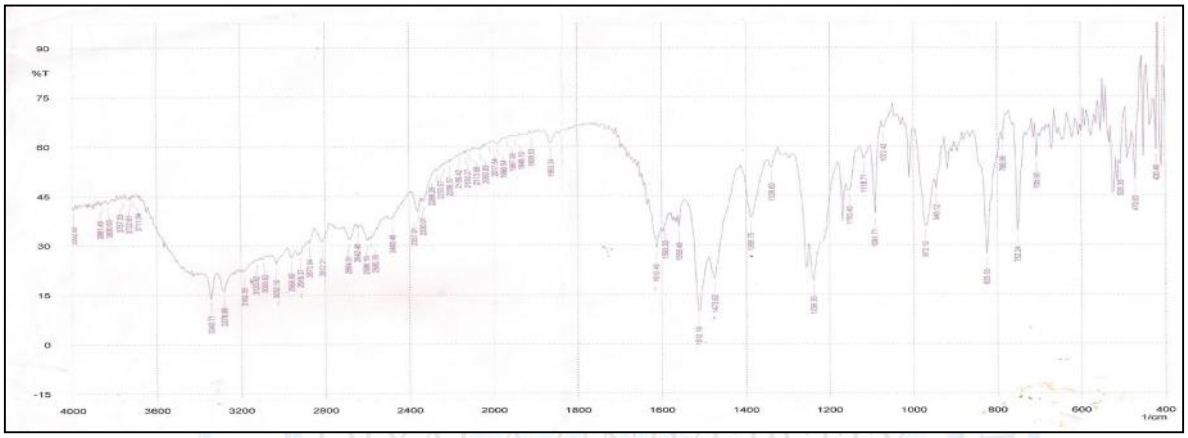

Fig.(1) The (I.R) Spectrum of the ligand (HL).

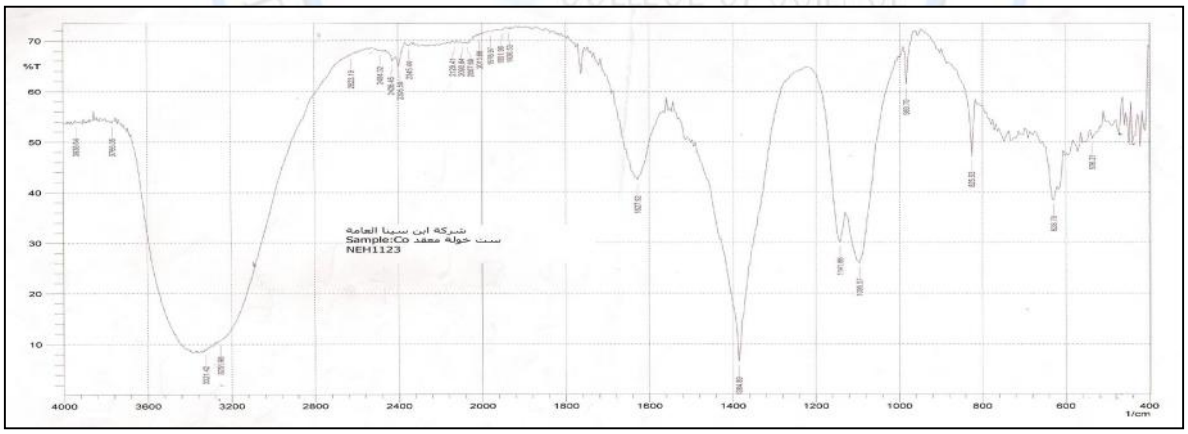

Fig.(1-a) The (I.R) Spectrum of $[Co(L)_2(H_2O)_2]$complex.

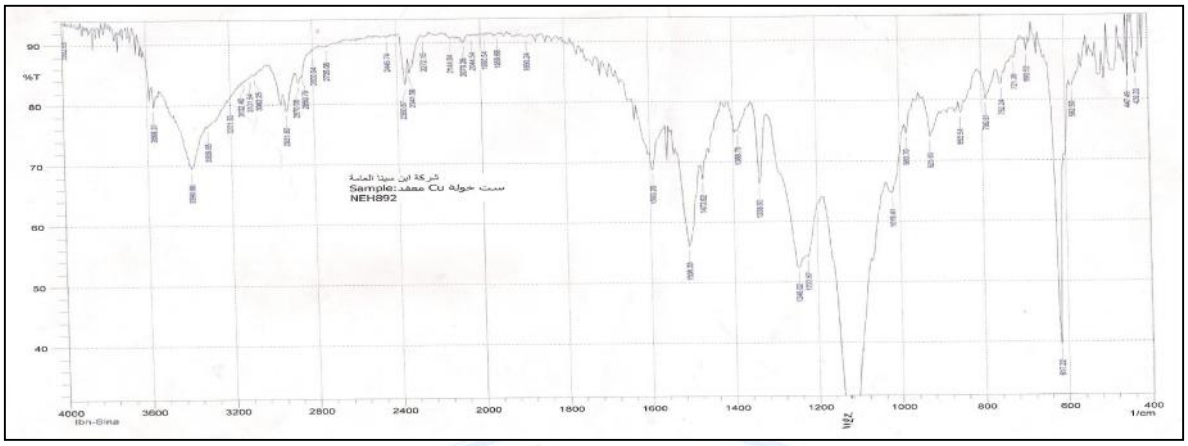

Fig.(1-b) The (I.R) Spectrum of [Cu(L)2]complex.

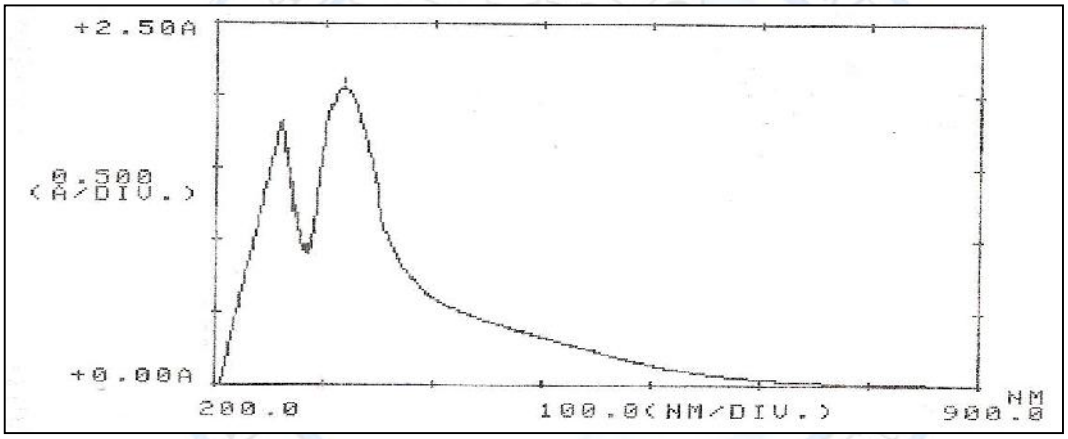

Fig.(2) The (UV-Vis) Spectrum of The ligand (HL) complex.

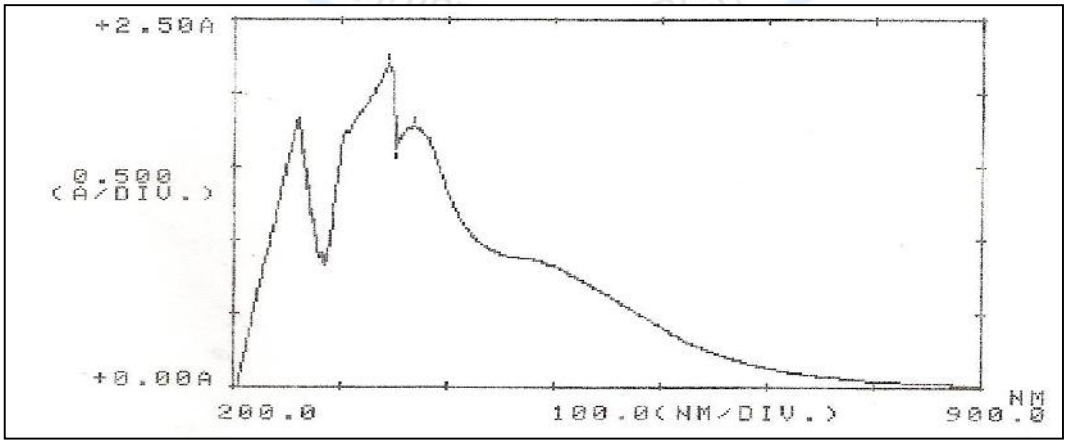

Fig.(2-a) The (UV-Vis) Spectrum of complex $[Mn(L)_2(H_2O)_2]$.

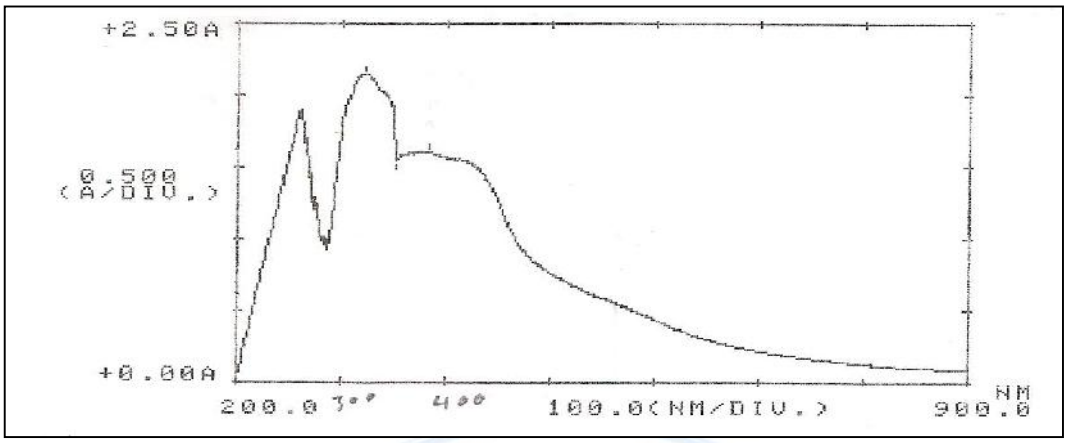

Fig.(2-b) The (UV-Vis) Spectrum of complex $[Cu(L)_2]$.

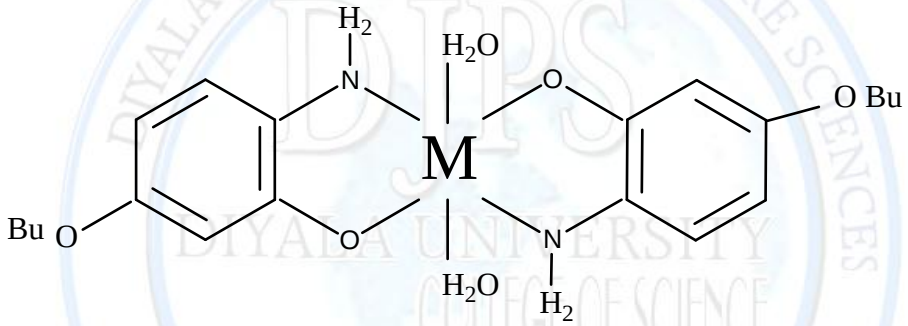

Figure (3): The Suggested structure for the [M(L)2(H2O)2] complexes

M= Mn^{II}, Co^{II}
Bu = $CH_2CH_2CH_2CH_3$

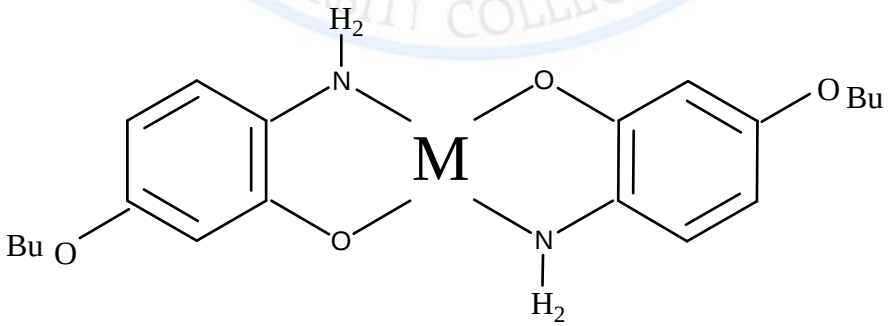

Figure (4): The Suggested structure for the $[M(L)_2]$ complexes.

M= Ni^{II}, Cu^{II} , Zn^{II}