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تحضير وتشخيص Cu(II),Ni(II),Co(II) و Zn(II) مع قواعد شيف رباعية السن الغير متماثلة معقدات

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الخلاصة

معقدات Co(II)، Ni(II)، Cu(II) و Zn(II) مع ليكاندات قواعد شيف رباعية السن الغير متماثلة (H_2L^1)=2-((1Z)-(8-(2-hyderoxy benzylidene amino)naphthalen-1-ylimino) methyl) - 6- methoxy phenol, (H_2L^2)= 2-((E)-1-(8-(Z) -2-hydroxy benzylidene amino) naphthalen-1-ylimino) ethyl phenol, (H_2L^3)= Synthesis of (1-((8-((Z)-2-hydroxy benzylidene amino) naphthalen -1-ylimino) methyl) naphthalene -2-ol.

حضرت بنسبة مولية (1:1)(فلز–ليكاند) شخصت بتحليل العناصر، التوصيلية المولارية، الطرق الطيفية (طيف الاشعة تحت الحمراء، الاطياف الالكترونية، طيف الرنين النووي المغناطيسي للبروتون) والقياسات المغناطيسية وتعيين المحتوى الفلزي. اوضحت القياسات الطيفية بان الليكاندات تسلك سلوك رباعية السن ثنائية القاعدة مع مانح ONNO وتتناسق مع الايون الفلزي لتعطي معقدات احادية النوى من خلال ذرات الاوكسجين والنتروجين لمجموعة الفينول والايمين على التوالي. اوضحت قياسات التوصيلية في محلول المعقدات غير موصلة. ومن خلال قياسات العزم المغناطيسي والطيف الالكتروني تم اقتراح ترتيب انDMF المربع المستوي لجميع المعقدات.

الكلمات المفتاحية: Schiff Base, Tetradentate ,Unsymmetrical

Preparation and Characterization of Co(II), Ni(II),Cu(II) and Zn(II) Complexes with Unsymmetrical Tetradentate Schiff Bases Ligands

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Abstract

Complexes of Co(II), Ni(II),Cu(II) and Zn(II) with unsymmetrical tetradentate schiff bases ligands H_2L^1 =2-(1Z)- (8-(2-hydroxy benzylidene amino)naphthalen-1-ylimino) methyl) -6- methoxy phenol, H_2L^2 =2-((E) -1-(8-(Z)-2- hydroxyl benzylidene amino) naphthalen -1- ylimino) ethyl) phenol and H_2L^3 = 1-((8-((Z) -2-hydroxy benzylidene amino) naphthalen -1-ylimino) methyl) naphthalene-2-ol, have been prepared in (1:1) (L: M) molar ratio and characterized by elemental analysis, molar conductance, spectral method (I.R, electronic, ^{1}H-NMR), magnetic measurements and metal content analysis. The spectral data suggest that the ligands behave as a dibasic tetradentate ligands with ONNO donor, and coordinate with the metal ion to form mononuclear complexes via the oxygen and nitrogen atoms of the phenolic group and azomethine group respectively. Conductivity data in DMF solution showed that all complexes are non-electrolyte. Magnetic moment and electronic spectra data suggested square planar geometry for all complexes .

Key word: Schiff Base, Tetradentate ,Unsymmetrical

Introduction:

Tetradentate Schiff bases are well known to coordinate with various metal ions; they have attracted a great deal of interest in recent years due to their novel structural features, interesting spectral and magnetic properties, thermal stabilities biological and industrial importance [1-3]. Schiff bases provides potential sites for biochemically active compounds. Metal complexes make the compounds effective as stereospecific catalyst towards oxidation, reduction, hydrolysis, biological activity and other transformations of organic and inorganic chemistry[4]. In biological systems, transition metal ions are usually bound to macrocycle such as a heme ring, or to donor atoms of peptide chains in a distorted environment[5].This unsymmetrical coordination of ligands around central metal ions had led to a growing interest in the design and synthesis of transition metal complexes of unsymmetrically Schiff base ligands as synthetic models[6]. In

addition, this class of compounds presents also a wide range of interesting properties, including biological[7],magnetic[8], nonlinear optical(NLO)[9],and the most commonly explored catalytic activity[10] among others, therefore unsymmetrical tetradentate Schiff base ligands are of significant importance .Since many symmetrical tetra dentate bis- types Schiff bases of diamines with o-hydroxy aldehyde / ketone have been prepared and studied intensively, [11-13] however much less attention has been focused on unsymmetrical tetra dentate Schiff bases derived from diamines and different o-hydroxy aldehyde /ketones[14,15].Therefore in this research it was thought of interest to synthesize unsymmetrical Schiff bases from 2-hydroxy-3-methoxy benzaldehyde, 2-hydroxyacetophenone,2-hydroxy-1-naphthaldehyde, salicylaldehyde and 1,8-diaminonaphthalene.

Experimental :

All chemicals were used as reagent grad from Barco Phrma Lab companies, used as supplied.Melting point and decomposition temperature was determined on Mellting point apparatus, Digital, SMP1O,and SMP2O, IR spectra were recorded on 300 spectrometer (Thermo Mattson) (400-4000 cm^{-1}) using KBr disc .Electronic spectra were recorded in DMF(10^{-3}M) solution on SPECTRO UV-VIS AUTO,11v60 Hz or220v.50Hz at room temperature using 1 cm quartz cell(200-800)nm. Molar conductance was measured for (10^{-3}) M solution in DMF using conductivity meter JENWAY product Manuals 430/PH/cond and Meter JENWAY. Magnetic susceptibility Measurements of the complexes were carried out at 25^0C on the solid state by (Sherwood instruments). Metal content of complexes was determined spectrophotometrically using pg instruments and AA500 Atomic Absorption Spectrophotometer(Flame and graphite analysis) in Scientific Research Center. Elemental analyses of the ligands and complexes were performed on Euro EAE Elemental Analyzer EuroEA 3000Italy . ^{1}H-NMR Spectra were recorded in DMSO-d6 using NMRedy 60 Prrouser and Manual Version 1.0(Nanalysis Crop,c 2015) in college of Education For Pure Sciences/ Ibn Al-Haitham in Baghdad university .

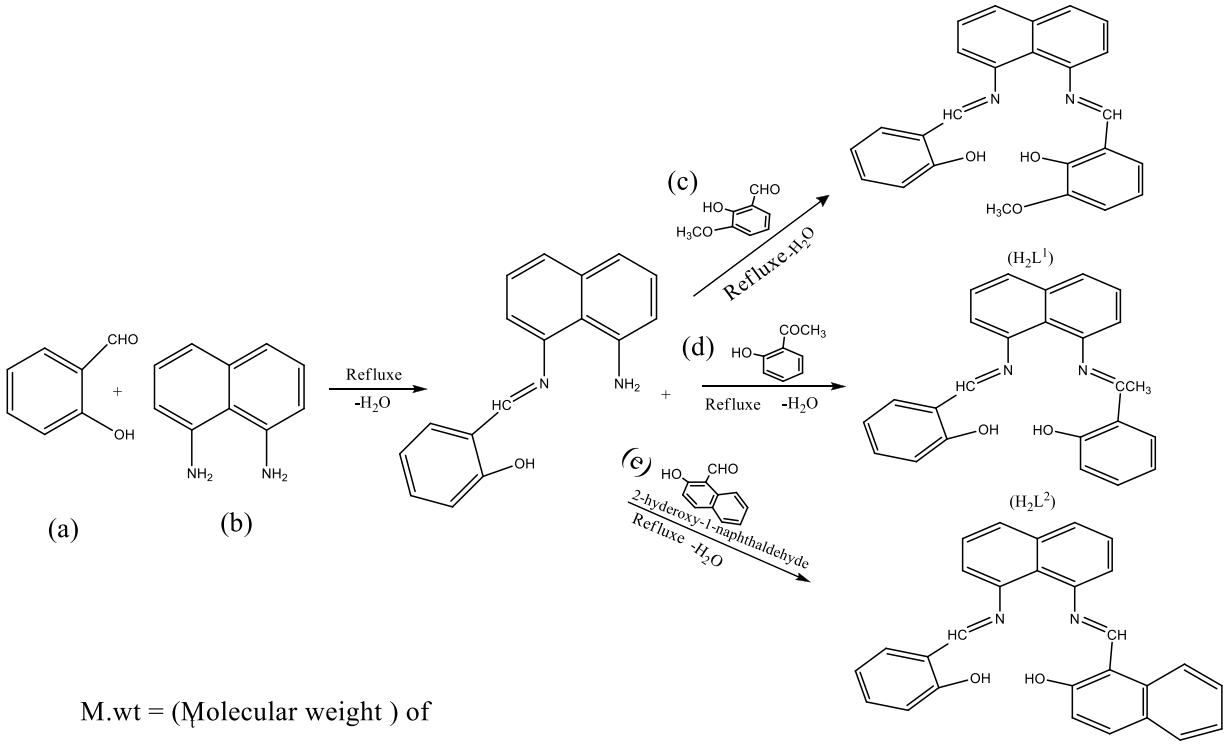
Synthesis of 2-((1Z)-(8-(2-hyderoxy benzylidene amino)naphthalen-1-ylimino) methyl) -6-methoxy phenol (H_2L^1):

The ligands were prepared by a reported method[(12)]. Atypical procedure for the synthesis of unsymmetrical Schiff base was achieved. Accordingly,1,8-diamino naphthalene (0.01 mole,1.58 gm) in (10ml) methanol was slowly added to methanol solution (10 ml)containing salicylaldehyde (0.01 mole, 1.22 gm) and refluxed for 1h,then (0.01mole, 1.52 gm) of 2-hydroxy-3-methoxy benzaldehyde dissolved in (10 ml) methanol was added to the solution .The resulting colored mixture was refluxed with stirring for 4h and cooled; the resulting precipitate was filtered and washed with the methanol, and then dried in vacuum.

Synthesis of 2-((E)-1-(8-(Z) -2-hydroxy benzylidene amino) naphthalen-1-ylimino) ethyl phenol (H_2L^2):was prepared by using (0.01 mole,1.58 gm) of 1,8-diamino naphthalene (0.01 mole, 1.22 gm) of salicylaldehyde and (0.01 mole, 1.36 gm)of 2-hydroxy- acetophenone then applied depending on the procedure mentioned above.

Synthesis of (1-((8-((Z)-2-hydroxy benzylidene amino) naphthalen -1-ylimino) methyl) naphthalene -2-ol (H_2L^3) . This was prepared by using (0.01 mole, 1.58 gm) of 1,8-diamino

naphthalene (0.01mole,1.22 gm) of salicylaldehyde and (0.01 mole, 1.72 gm) 2- hydroxyl-1-naphthaldehyde then applied depending on the procedure mentioned above.



M.wt = (Molecular weight) of

a=122.12 g/mole

b =158.20 g/mole

c=152.15 g/mole

d=136.15 g/mole

e =172.18 g/mole

Fig 1:- Synthesis of Schiff bases ligands (H_2L^1),(H_2L^2)and(H_2L^3)

Preparation of [ML^1] complexes

M= Co(II), Ni(II),Cu(II) and Zn(II).

A solution of (0.01 mole) of metal salt [$CoCl_2.6H_2O$ (2.37gm) $NiCl_2.6H_2O$ (2.37 gm), $CuCl_2.2H_2O$ (1.70 gm) and $ZnCl_2$(1.36 gm)] in 20ml of ethanol was added drop wise for 10-15 min to the solution of ligand H_2L^1 (0.01mole, 3.96 gm) which dissolved in 30 ml of ethanol in 100ml round bottom flask A. The mixture was refluxed for (3-4)h, after cooling the precipitate filtered off and washed with cold ethanol then dried in vacuum.

Preparation of [ML^2] and[ML^3] complexes

M= Co(II), Ni(II),Cu(II) and Zn(II).

They were prepared by using (0.01mole, 3.80 gm) of H_2L^2or (0.01mole, 4.16g) of H_2L^3then applied the procedure mentioned above.

Result and discussion

All the metal complexes are quite stable in dry air and insoluble in common organic solvents, but they are soluble in DMF and DMSO. The elemental analysis shows(1:1) metal to ligand stoichiometry for all complexes.

Some physical properties of ligands and their complexes are listed in(Table1).The molar conductance in 10^{-3} M solution in DMF of complexes is in the range (2.77-27.38) ohm^{-1} cm^2 mol^{-1},indicating a non-electrolytic nature of the complexes[16]. This is consistent with the stoichiometry assumed for complexes on the basis of analytical data.

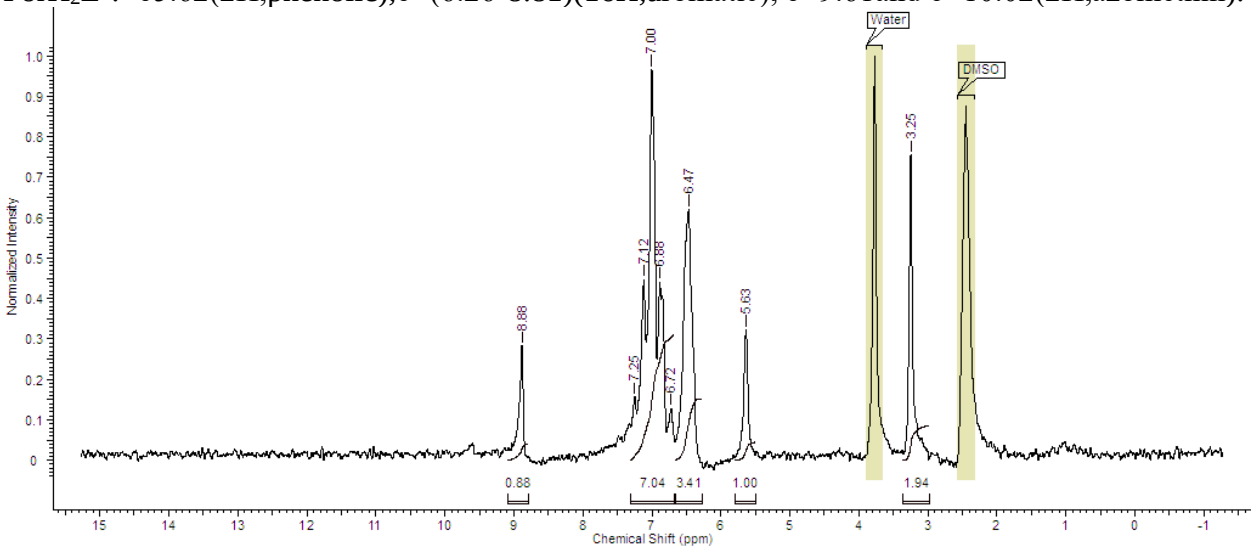
^{1}H-NMR-Spectra of ligands

The^{1}H-NMR.spectra of free ligand at room temperature in DMSO-d^6 show the following singles [1,17].

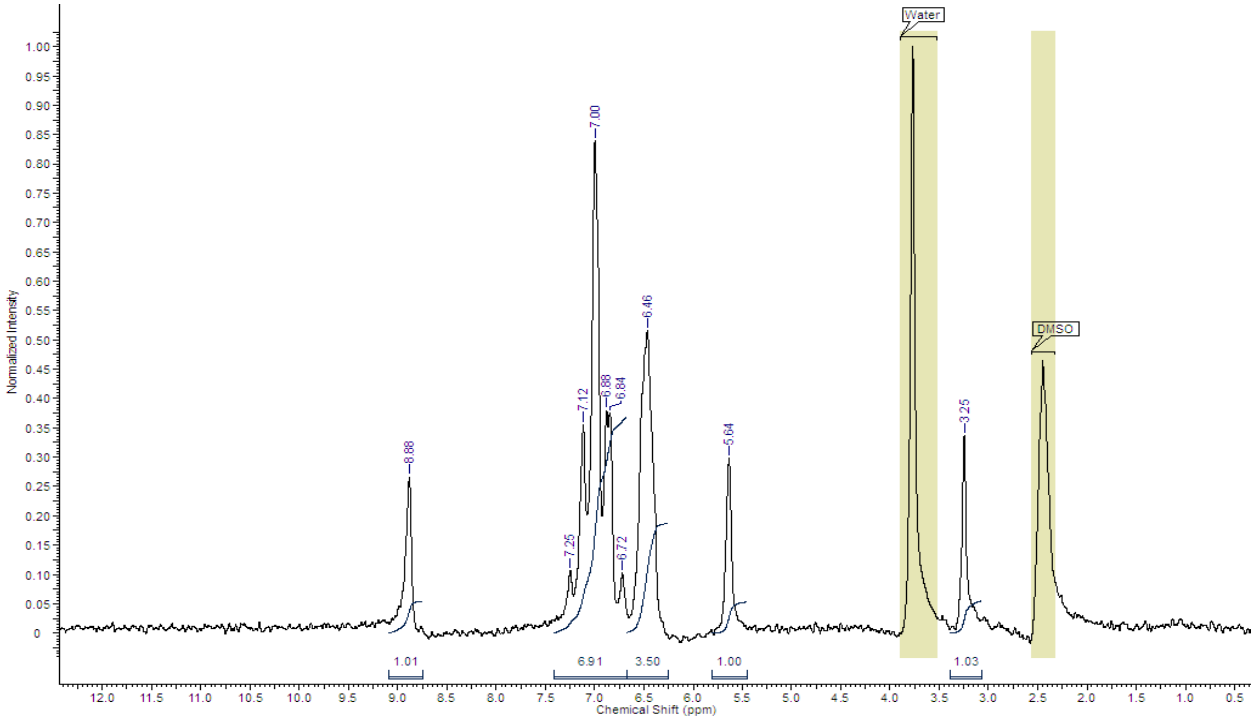
For H_2L^1: δ =3.26(3H,-CH_3), δ=5.63(2H,phenolic), δ= (6.47-7.25) (13 H, aromatic), δ=8.88 (2H, azomethine).

ForH_2L^2: δ=5.61(2H,phenolic), δ=(6.50-7.47)(14 H, Aromatic), δ=3.25 (3H,CH_3), δ=9.61(H, azomethin).

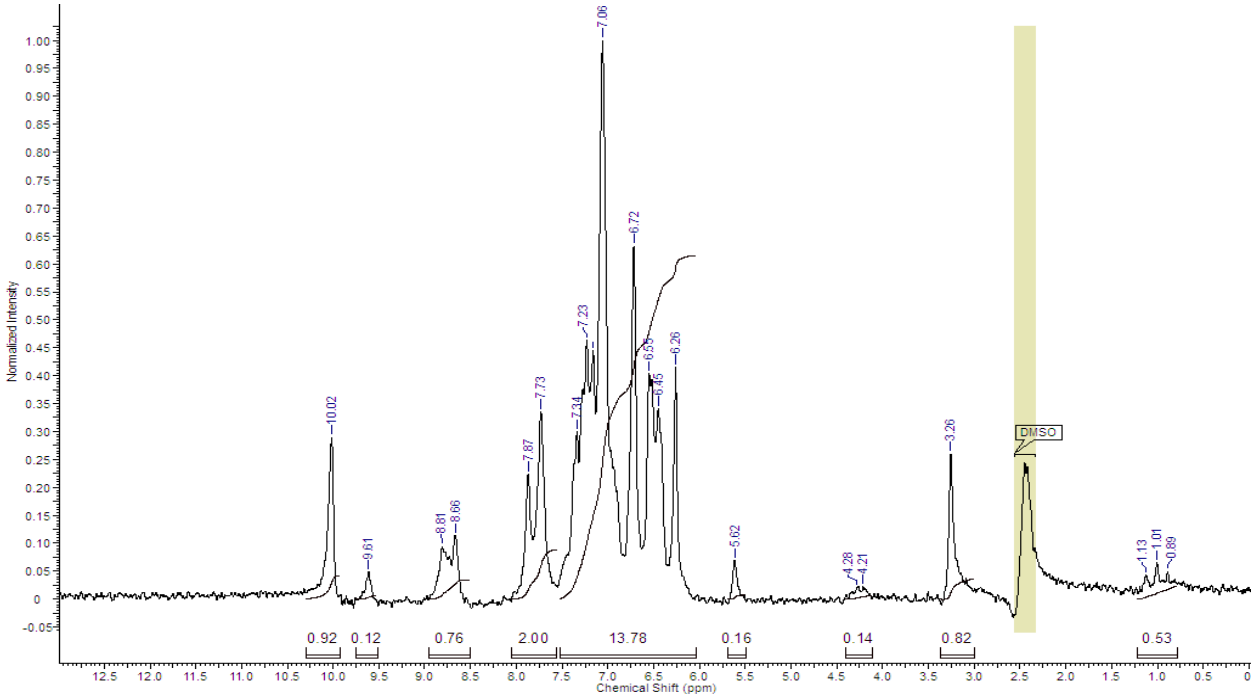
ForH_2L^3:=δ5.62(2H,phenolic),δ=(6.26-8.81)(16H,aromatic), δ=9.61and δ=10.02(2H,azomethin).



(a)



(b)

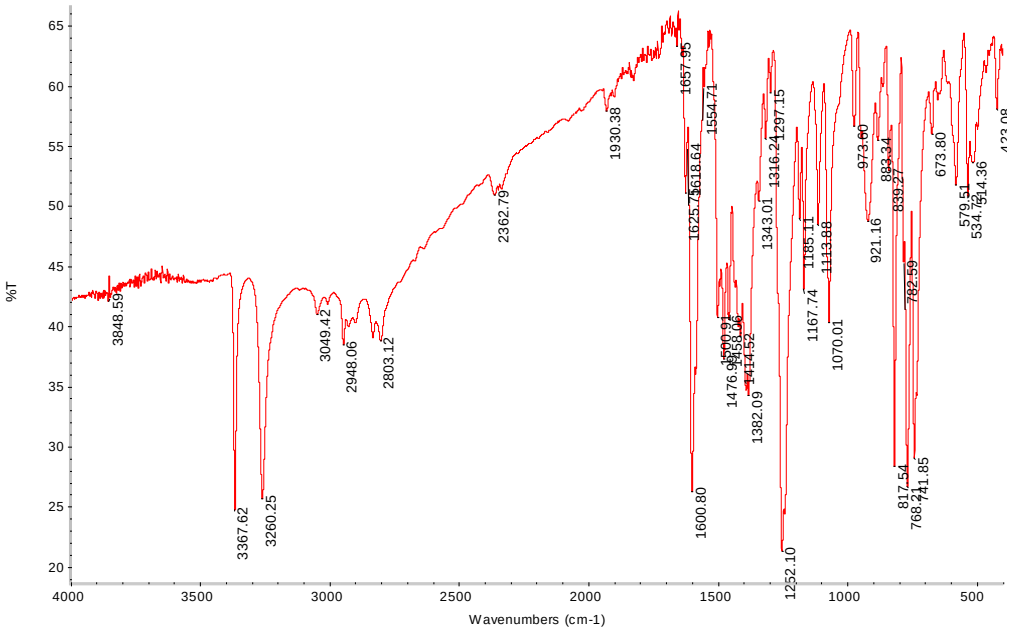


(c)

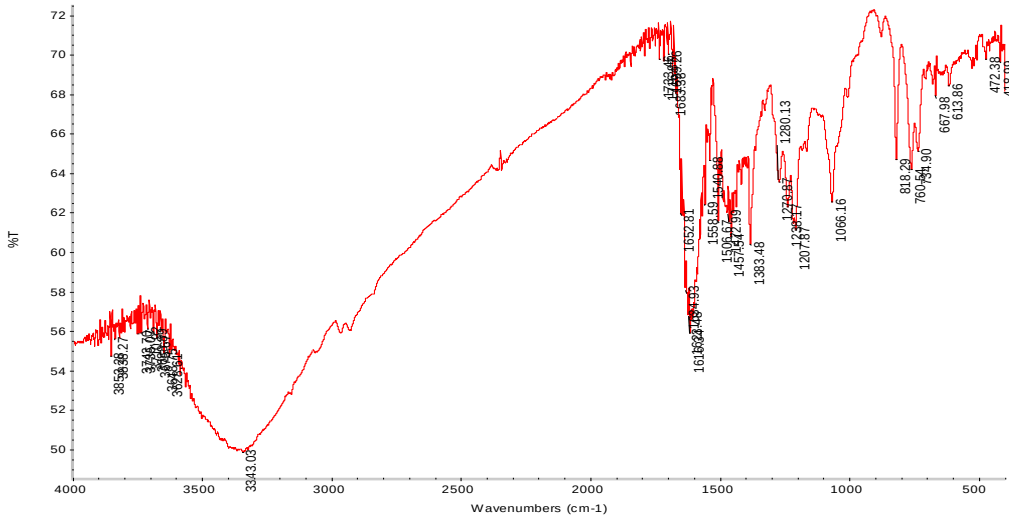
Fig(2):- ^{1}H-NMR for a=(H_2L^1),b=(H_2L^2), and c = (H_2L^3)

IR Spectra

The position of the important bands of the compounds are shown in the (Table2).Tentative assignments of the observed bands for the compounds were made by comparing spectra of the metal complexes with those of the Schiff bases. Due to the unsymmetrical nature of the ligands and the complexes, two bands were observed for each of the following groups. υ (C=N); υ (C-O) and υ (OH) taking their origin from the different aldehyde[18,19].The ligands (H_2L^1, $H_2L^2$and H_2L^3) exhibited characteristic υ(C=N)stretching frequencies at (1618, 1625),(1615,1622) and (1624,1627) cm^{-1}respectively,which shift to higher frequencies, upon complexation[20-22].This indicates participation of azomethine nitrogen in bonding[23] . The IR spectrum of the free ligands shows two bands at (3260, 3367) cm^{-1}, (3322,3359) $cm^{-1}$and (3246,3373) cm^{-1}due to phenolic υ(OH) group[3,24],the absence of these bands in the spectra of complexes indicates the coordination of phenolic oxygen to the metal after deprotonation [25,26], this is further supported by the shifting of υ(C-O)phenolic band to higher wave numbers in the complexes[27]. Which occurs at(1185,1252) cm^{-1},(1234,1247) cm^{-1} and (1165,1235) $cm^{-1}$for(H_2L^1, $H_2L^2$and H_2L^3) respectively. Thus, it can be concluded that the Schiff bases are tetradentate coordinating via the azomethine N and the phenolic O[28].Assignment of the proposed coordination sites is further supported by the appearance of new band at (432-472) cm^{-1} and(501-570) cm^{-1} which could be attributed to υ (M-N) and υ(M-O) respectively[29,30].

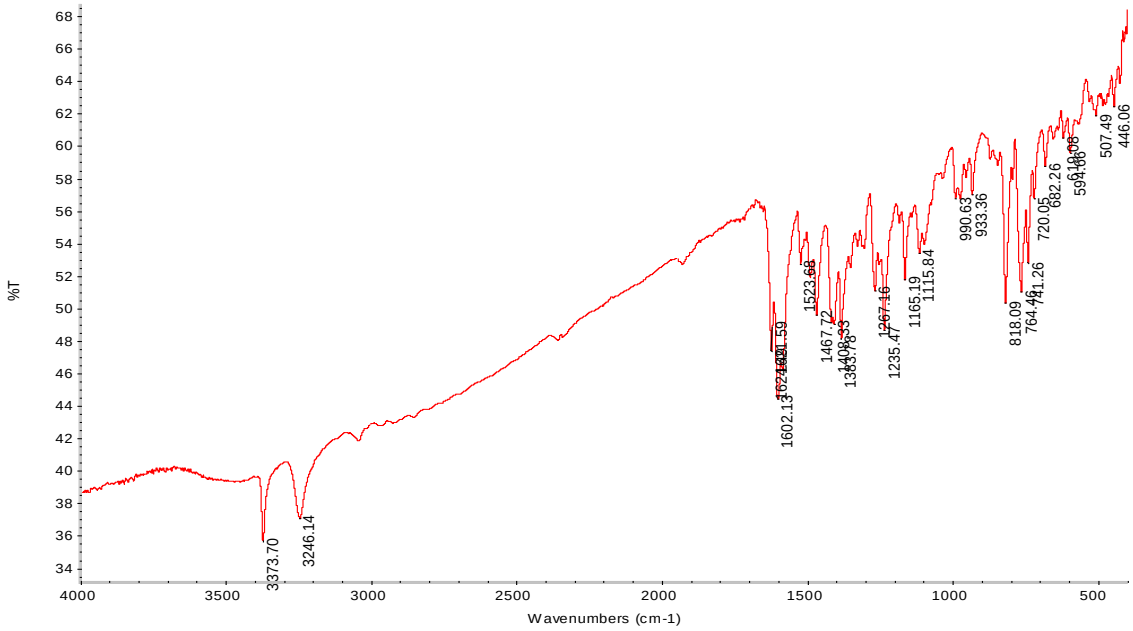


(a)

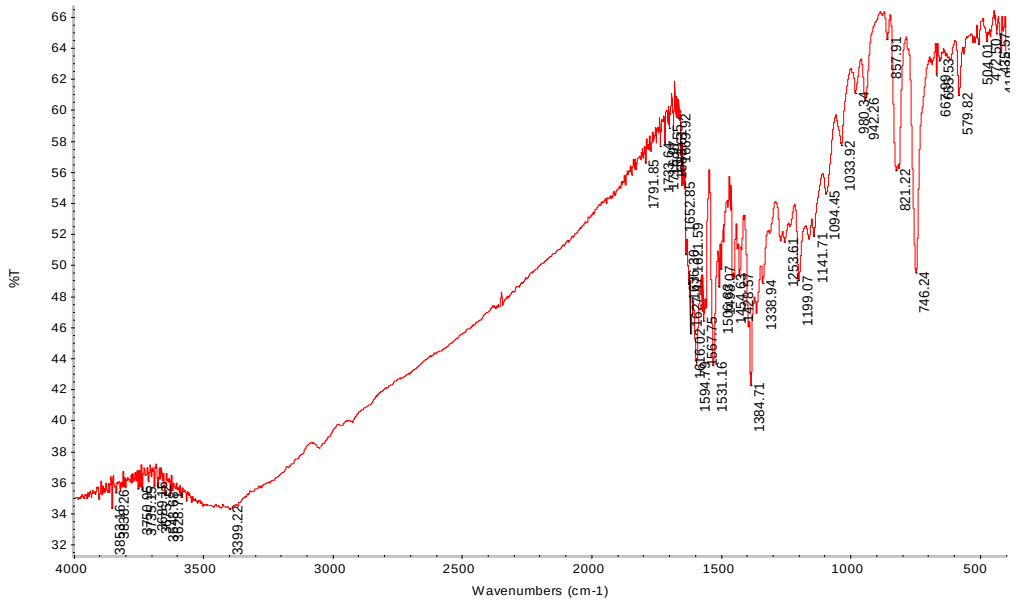


(b)

Fig(3):-I.R -Spectra of H_2L^1(a) and [NiL^1] (b)complex



(c)



(d)

Fig(4):-I.R –Spectra of H_2L^3(c) and[NiL^3] (d)complex

Electronic Spectra and Magnetism

The magnetic moments and electronic spectra data at25^{0}C of the ligands and their complexes are listed in table(3).The electronic spectra of the ligands H_2L^1,H_2L^2andH_2L^3 in DMF solution show the aromatic intense bands in the range of (35714-37735)cm^{-1} attributed to π→π* transition and the range (32258-32786) cm^{-1} due to the n→π* transition of non-bonding electrons present on the nitrogen of the azomethine group, these transition are also found in spectra of complexes but they are shifted, comfirming the coordination of ligands to metal ions[31]. The new bands in spectra of all complexes at range (26315-29411) cm^{-1}may be associated with the charge transfer transition[32].The magnetic moment values of Co(II) complexes (1,5,9) were in the range(2.58-2.73 B.M),indicating square-planar system[33];their electronic spectra showed absorption band at (15625-16666) cm^{-1}, attributed to the $^2A_1g\rightarrow {}^2E'g$,which indicates a square-planer geometry for Co(II) complexes[34]. The Ni(II) complexes (2,6,10) are diamagnetic moiety, because their magnetic moment is almost zero. Therefore the Schiff bases ligands coordinate to Ni(II)ion as four- dentate chelating agent with a square-planar environment[35]. The electronic spectra of those complexes show an absorption bands at (17094-17672) and (23198-23255) cm^{-1} attributed to the$^1A_1g\rightarrow {}^1A_2g$ and$^1A_1g \rightarrow {}^1B_1g$ transition. This shows that Ni(II) complexes have a square–planer geometry [36].The obtained magnetic moment values for Cu(II) complexes (3,7,11) at range(1.81-1.90B.M) indicated square-planar system[37].The electronic spectra of Cu(II) complexes showed a weak bands at (17857-17989) and (24814-24937)cm^{-1} attributed to the $^2B_1g\rightarrow {}^2A_2g$ and $^2B_1g\rightarrow {}^2Eg$ transition which is comparable with complexes having square-planar structure[38].The electronic spectrum of Zn(II) complexes (4,8,12) showed only a band at (27027- 27641) cm^{-1}attributed to the ligands charge transfer transition .The Zn (II) complexes are diamagnetic expected and there geometry are most probably similar to the Co(II),Ni(II) and Cu(II) complexes, depending on the data of other measurements namely metal content and I.R spectra[39].

Conclusion

Unsymmetrical Schiff bases and their complexes were prepared and characterized by spectral and analytical data. The synthesized Schiff bases act as dibasic tetradentate, coordinating via phenolic oxygen and azomethine nitrogen atoms as illustration Fig(5).Magnetic and electronic spectral studies reveal square- planar structure for all complexes.

Table 1: Some physical properties and analytical of the ligands and their complexes

NO.	Complexes	Color	m.p(C^0)	Analysis calc.(found)%			M% Calc.(found)	Λm(ohm^{-1} cm^2 mol^{-1})
				%C	%H	%N		
H_2 L^1	$C_{25}H_{20}N_2O_3$	White yellow	177-181	75.74(75.23)	5.08(5.01)	7.06 (6.56)	----	-----
1	[COL^1]	Brown	› 300	----	-----	-----	12.99(12.56)	21.88
2	[NiL^1]	Green	142 d	66.26(66.10)	4.00 (3.98)	6.18 (6.01)	12.95(12.85)	13.01
3	[CuL^1]	Black	›300	-----	----	----	13.87(13.58)	6.48
4	[Zn L^1]	Pale yellow	141 d	----	----	----	14.21(14.10)	5.66
H_2 L^2	$C_{25}H_{20}N_2O_2$	Pale pink	200-201	78.92(78.79)	5.29 (5.14)	7.36 (7.10)	-----	----
5	[CO L^2]	Dark green	238 d	----	----	----	13.47(13.22)	12.64
6	[NiL^2]	Milky white	173 d	----	----	-----	13.43(13.15)	9.76
7	[Cu L^2]	Black	›300	----	-----	----	14.37(14.50)	13.85
8	[Zn L^2]	yellow	218 d	67.66(67.52)	4.08 (4.01)	6.31(6.10)	14.72(14.53)	2.77
H_2L^3	$C_{28}H_{20}N_2O_2$	Brown	150 d	80.75(80.35)	4.84(4.21)	6.72(6.50)	----	----
9	[CO L^3]	Brown	248 d	71.04(70.95)	3.83(3.21)	5.91(5.40)	12.44(12.15)	9.58
10	[Ni L^3]	Black	›300	----	----	----	12.40(12.20)	3.55
11	[Cu L^3]	Black	›300	----	----	----	13.29(13.10)	27.38
12	[Zn L^3]	Deep brown	243 d	----	----	----	13.62(13.51)	4.29

D= Decomposition temperature

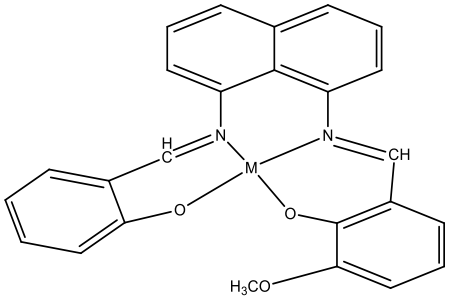
Table 2: Characteristic Infrared spectral data of the ligands and their complexes

NO.	Complexes	IR spectral bands (cm^{-1})				
		V (C=N imin)	**V (C-O) phenol**	**V (O-H)**	**V (M-N)**	**V (M-O)**
H_2L^1	$C_{25}H_{20}N_2O_3$	(1618s, 1625s)	(1185_s, 1252_s)	(3260_s,3367_s)	-----	-----
1	[CO L^1]	(1634_s,1652_s)	(1280_s, 1290_m)	-----	472 m	527_m
2	[Ni L^1]	(1635_s,1652_m)	(1270_m, 1280_m)	----	472_s	529_m
3	[Cu L^1]	(1628_s,1635_s)	(1243_s, 1256_s)	----	465_m	517_m
4	[Zn L^1]	(1628_s, 1630_s)	(1240_m, 1260_m)	----	472_s	503_m
H_2L^2	$C_{25}H_{20}N_2O_2$	(1615_s,1622_m)	(1234_s, 1247_s)	(3322_s, 3359_s)	----	----
5	[CO L^2]	(1620_s,1633_s)	(1242_m, 1255_s)	----	464_m	532_m
6	[Ni L^2]	(1618_s,1630_s)	(1247_m,1268_w)	----	438_m	504_s
7	[Cu L^2]	(1635_s,1648_s)	(1240_m,1271_s)	-----	457_m	503_m
8	[Zn L^2]	(1624_s,1638_s)	(1248_s, 1256_s)	----	456_m	516_m
H_2L^3	$C_{28}H_{20}N_2O_2$	(1624_s, 1627_s)	(1165_m,1235_s)	(3246_s, 3373_s)	-----	-----
9	[COL^3]	(1634_s,1646_s)	(1197_s,1248 m)	----	458 m	570w
10	[Ni L^3]	(1636_s,1652_s)	(1199_m,1253_m)	----	472_m	504_m
11	[Cu L^3]	(1626_s,1636_s)	(1191_s,1239_m)	-----	432_m	501_m
12	[Zn L^3]	(1628_s,1638_s)	(1185_m,1245_w)	-----	432 m	535_w

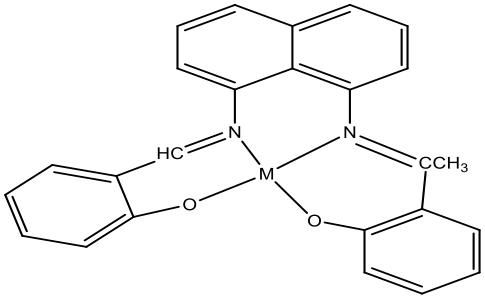
s=strong, m=medium=weak

Table(3):- Magnetic moments and the electronic spectral data of the ligands and their complexes

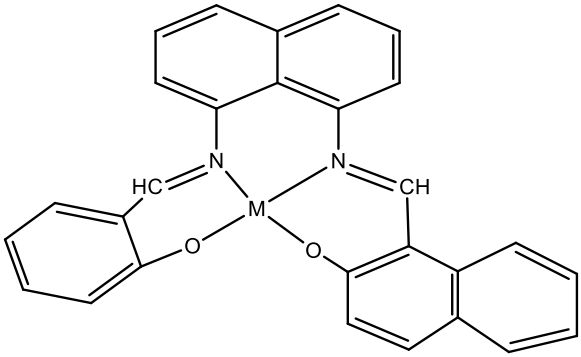
No.	Complexes	μ_{eff} (B.M)	assignment	Band maxima λ(cm^{-1})	Strut.
H_2L^1	$C_{25}H_{20}N_2O_3$	----	n→π*, π → π*	32258, 35714	----
1	$[CoL^1]$	2.73	$^2A_1g \rightarrow ^2E'g$, C.T	16666, 27777	S.q
2	$[Ni\ L^1]$	Diamagnetic	$^1A_1g \rightarrow ^1A_2g, ^1A_1g \rightarrow ^1B_1g$, C.T	17672,23255, 28571	S.q
3	$[CuL^1]$	1.81	$^2B_1g \rightarrow ^2A_1g, ^2B_1g \rightarrow ^2Eg$, C.T	17857,24814, 27397	S.q
4	$[Zn\ L^1]$	Diamagnetic	C.T	27227	S.q
H_2L^2	$C_{25}H_{20}\ N_2O_2$	----	n →π*, π → π*	32258,37735	-----
5	$[CoL^2]$	2.62	$^2A_1g \rightarrow ^2E'g$, C.T	16000,27777	S.q
6	$[NiL^2]$	Diamagnetic	$^1A_1g \rightarrow ^1A_2g, ^1A_1g \rightarrow ^1B_1g$, C.T	17615,23255,29411	S.q
7	$[CuL^2]$	1.90	$^2B_1g \rightarrow ^2A_1g, ^2B_1g \rightarrow ^2Eg$,C.T	17900,24937,28771	S.q
8	$[Zn\ L^2]$	Diamagnetic	C.T	27641	S.q
H_2L^3	$C_{28}H_{20}\ N_2O_2$	-----	n → π*, π → π*	32786, 37037	----
9	$[CoL^3]$	2.58	$^2A_1g \rightarrow ^2E'g$, C.T	16129,28571	S.q
10	$[NiL^3]$	Diamagnetic	$^1A_1g \rightarrow ^1A_2g, ^1A_1g \rightarrow ^1B_1g$, C.T	17094,23198, 26315	S.q
11	$[CuL^3]$	1.90	$^2B_1g \rightarrow ^2A_1g, ^2B_1g \rightarrow ^2Eg$, C.T	17989,24900, 27777	S.q
12	$[ZnL^3]$	Diamagnetic	C.T	27027	S.q



Complexes (1,2,3,4)
M=Co(II),Ni(II),Cu(II),Zn(II)
L=L^1



Complexes (5,6,7,8)
M=Co(II),Ni(II),Cu(II),Zn(II)
L=L^2



Complexes (9,10,11,12)
M=Co(II),Ni(II),Cu(II), Zn(II)
L=L^3

Fig(5) :Suggested structure of complexes [ML]

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