Synthesis and characterization of Fe(II),Co(II),Ni(II),Cu(II) and Zn(II) complexes with Hexaaza macromolecule Ligands Derived from Semicarbazide

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الخلاصة

في هذا البحث تم تحضير ليكاندين من نوع : (L$_1$) (3,4,6,14,15,17,23,24-Octaazatricyclo [17.3.1.1^8,12] tetracosa-1(23),8(24),9,11,19,21- hexaene - 2,5,7,13,16,18– hexaone)L$_1$, من تفاعل بيريدين- 6,2 ثنائي الحامض الكاربوكسلي وحامض الكلوتاريك مع السيميكاربازايد اما الليكاند الثاني : (L$_2$): 2-(5-hydroxypentanoyl) hydrazinecarboxamide حضر بنفس طريقة الواردة في (L$_1$) باستثناءاستخدام ثنائي حامض البيكولين (pyridine-2,6-dicarboxylicacid) باستخدام تقانة الاشعه القصيره في الحاله الصلبه لليكندين ثم مفاعلة كلااليكاندين مع بعض ايونات العناصر الانتقاليه لتكوين معقدات من نوع : [M(L$_1$)Cl$_2$, [M(L$_1$)]Cl$_2$, [M(L$_2$)$_2$Cl]Cl, [M(L$_2$)$_2$Cl$_2$ where M = Fe(II) , (Co(II) , Ni(II) , Cu(II) , and Zn(II).

كما تم تحضير معقدات اضافة من نوع :

[M(L$_1$)(PPh$_3$)Cl]Cl , [M(L$_2$)$_2$(PPh$_3$)]Cl$_2$ and [M(L$_2$)$_2$(PPh$_3$)Cl]Cl

باستخدام نفس المعقدات المذكوره اعلاه مع ثلاثي فنيل فوسفين وبنسبة موليه 1:1 , 2:1 شخصت جميع المعقدات باستخدام التحليل الدقيق والمحتوى الفلزي والتوصيلية الكهربائيه والقياسات المغناطيسيه والطيفية وطيف الاشعة تحت الحمراء كما شخص الليكندين L$_1$, L$_2$ بطيف ^{1}H-NMR وطيف ^{13}C-NMR دلت قياسات الطيف الالكتروني والقياسات المغناطيسيه على ان المعقدات تمتلك بنية ثماني السطوح.

ABSTRACT

A new ligands(3,4,6,14,15,17,23,24-Octaazatricyclo [17.3.1.18,12] tetracosa-1(23),8(24),9,11, 19 ,21- hexaene - 2,5,7,13,16,18 – hexaone), (L$_1$) and 2-(5-hydroxypentanoyl) hydrazinecarboxamide,(L$_2$)was prepared from the reaction of pyridine-2,6-dicarboxylic acid and glutaric acid with semicarbazide by microwave irradiation in solid state ,then was reacted with some transition metal(II) ions to form complexes of the type

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$[M(L_1)Cl_2]$, $[M(L_1)]Cl_2$ and $[M(L_2)_2\,Cl]Cl$, $[M(L_2)_2Cl_2]$ where M= Fe(II) ,Co(II),Ni(II),Cu(II) and Zn(II). Adducts of the type $[M(L_1)(PPh_3)Cl]Cl$, $[M(L_2)_2(PPh_3)]Cl_2$ and $[M(L_2)_2(PPh_3)Cl]Cl$ were prepared by the reaction of the above complexes with triphenylphosphine in a 2:1 and 1:1 molar ratio . The prepared complexes and adducts were characterized by (C,H,N) analysis , metal content analysis , molar conductance, magnetic moment measurements ,electronic and IR spectroscopy, the ligand was characterized by ^{1}H ,^{13}C -NMR . The electronic spectra and magnetic measurements indicated that the complexes have octahedral environment around the metal ions.

Keywords Microwave - assisted synthesis .macrocyclic molecules

INTRODUCTION

Metal-template synthetic for the preparation of poly-aza macrocyclic compounds are known since the early 2010(1) .Owing to their metal coordinating properties , metal ions are able in several favorable cases , to organize reacting molecular fragments according to specific geometry and to drive the reaction toward the formation of cyclic compound .Transition metal macrocyclic compound have an active part of metalloenzymes as bionomic model compounds due to their resemblance with natural proteins like hemerythrin and enzymes(2).

Poly aza macrocyclic modified with tetraamide and hexaamide function a cyclic tetra peptide moieties in capsulate bind metal ions without under going any deprotonating process of the amide group and are capable to stabilize even the low oxidation states of the metal ions(3).On other hand not only the above macro molecules ligands form complexes with transition metals but also they were mixed with the phosphine . Macrocyclic phosphine hold promise as incredibly stable ligands for applications requiring robust complexes such as radio active transition metal complexes for use as radiopharmaceuticals .because of this possibility , these ligand and their complexes have been synthetic targets since soon after the macrocyclic effect was discovered .

Microwave techniques for preparation of organic substances have received a great deal of attention due to it's various advantages such as selectivity , rapid and direct controllable internal reactions….etc(4).This technique has been used to prepare an eighteen member ring ligand and it's reaction with transition metal ion's to form a new complexes of different geometries(5).

In view of these interesting results and as continuation of our studies on transition metal complexes with macrocyclic ligand(6,7,8,9),we have prepared new types of complexes containing different donor atoms using microwave technique .

EXPERIMENTAL

General

All chemicals used were either analytical grade or chemically pure . IR spectra were recorded on a Fourier-Transform (FT.IR) Spectrophotometer Tensor 27 Co.Brucker in the range (4000-400cm^{-1}) using KBr discs.The CHN analysis carried out by(Euro Vactor Model E A 3000 in AL-Albeit University (Jordan) . The metal content analyses were carried out by (PYE UNICAM SP9-atomic absorption Spectrophotometer). Conductivity measurements were carried out on 10^{-3} M solution of all complexes in DMSO using (Conductivity Meter Model PCM3-JENWAY),at ambient temperature .the electronic spectra were recorded on Shimadzu-UV-Visible recording ,UV–1650PC-spectrophotometer , using 10^{-3} M of the complexes in DMSO. The magnetic measurement was measured at 25 C° on the solids by Farady's method using Bruker BM6 instrument .^{1}H-NMR &^{13}C-NMR carried out by(BRUKER 300 MHz Switzerland) and shimadzu QP 5050 A(JAPAN) at Al–Albeit University – Jordan . The ligand prepared in solid state using microwave oven type morph Richards EM 820 CPT .

1.Prepararation of the Ligands:

3,4,6,14,15,17,23,24-octaazatricyclo[17.3.1.1^{8},12]tetracosa-1(23),8(24),9,11, 19 ,21- hexaene - 2,5, 7 ,13 ,16 , 18 – hex aone(L_1) has been synthesized acoording to the following procedure$^{(5,10,11)}$. A solid state pyridine-2,6-dicarboxylic acid (0.33 g , 0.002 mol) was mixed with solid semicarbazide (0.15 g , 0.002 mol) and (0.005 g , 0.0001mol) of cerium ammonium nitrate (CAN)as a catalyst ,the solid mixture was irradiated using a microwave 800 W for 10 minutes .A gray solid was formed cooled at room temperature,then ethyl acetate (20 ml) was added and the mixture stirred for about 1hr to dissolve the CAN which was separated from the mixture by filtration , then a gray precipitate was washed with n- hexane , ethanol and dried under vacuum for several hours. L_2 ligand was prepared by the similar procedure except using (o.30gm,0.001mole) glutaric acid and semicarbazide (0.75gm,0.001 mol)to get yellow precipitate.

2.Preparation of [M(L)Cl$_2$] , [M (L)]Cl$_2$]and [M(L)Cl]Cl :

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

L= L_1 and $2L_2$.

The solution of the ligand ($L_{1)}$ (0.42 g ,0.001 mole) in (10 ml) DMF and ethanolic solution of the hydrated metal chloride salts (0.001 mole) were mixed together with stirring. The mixture was refluxed for 2 hr , on cooling a colored precipitate were obtained , the product was filtered off , washed with cold ethanol and dried under vacuum .The same procedure was carried out to prepare other complexes.

3.Preparation of the adducts[M(L)(PPh_3)Cl]Cl and [M(L)(PPh3)]Cl_2: M= Fe(II) , Co(II) , Ni(II) , Cu(II) , and Zn(II)

The metal complexes[Fe(L_1)Cl]Cl (0.54 g ,.0001 mol) was dissolved in (10 ml) DMF and added to a solution of triphenylphosphine (0.26 gm , 0.001 mol) in (10 ml) ethanol , the mixture was refluxed for 1h then a pale brown precipitate formed , filtered off , washed with diethylether and dried . The same procedure was carried out to prepare the other adducts L=L_1 , 2L_2

RESULTS AND DISCUSSION

Microwave irradiation of a mixture of the semicarbazide , dicarboxylic acid and CAN catalyst afforded the ligands(L_1&L_2) in 90% and85% Yield respectively , which is stable in air , non-hydroscopic at room temperature .

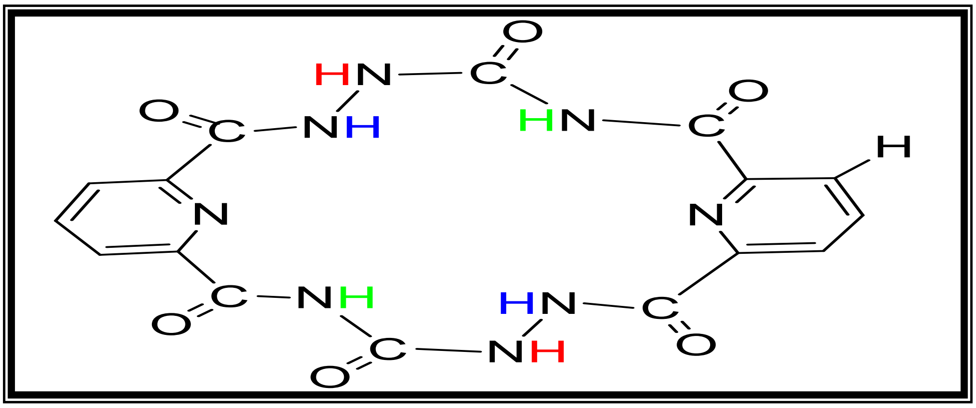
The ligand(L_1) characterized(12) by ^1H NMR and the chemical shift's data are listed in Table(1) the band at δ(8.6 ppm) attributed to 6 H (H-pyr ring) assisted by the integration. The band at δ(7.2ppm) attributed to 2H for the NH-NH-CO-pyr group ,the band at (δ 8.1ppm)attributed to 2H for the(NH-NH-CO-pyr) group , and δ(11.2 ppm) attributed to 2H for the (N-H) group. Table (2) contains ^{13}C–NMR chemical shift's data ,the bands at (160 ppm) for (N-CO-N), (165 ppm) for (-CO-pyr) , (140 ppm) for (C-pyr meta),(148.9 ppm) for(C-pyr ortho) and (128 ppm) for (C-pyr Para) . The band for the solvent (DMSO) appear at(40 ppm) figure(1), all these data assist the expecting structure for L_1 ligand.

Table(1) Chemical shift for ^1H-NMR

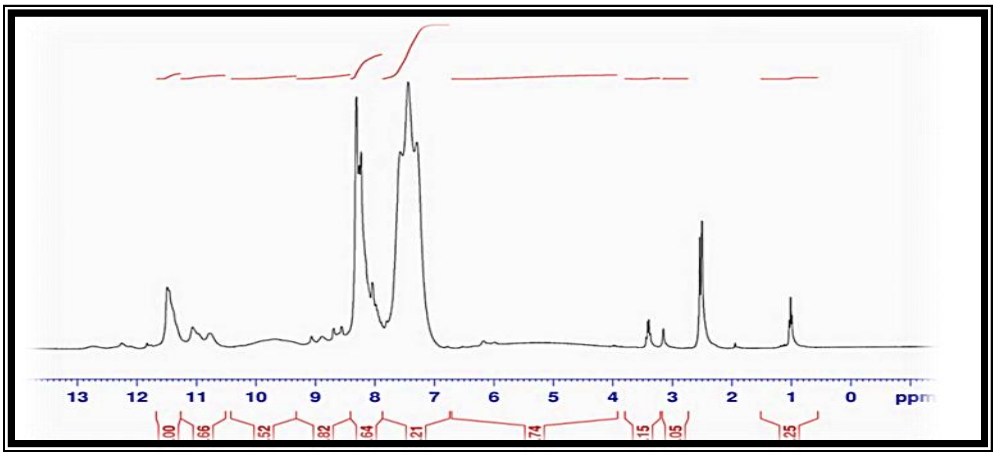
compound	NH-NH-CO-pyr	NH-NH-CO-pyr	N-H	H- pyr
L_1	7.2	8.1	11.2	8.6

Table(2) Chemical shift for ^{13}C –NMR

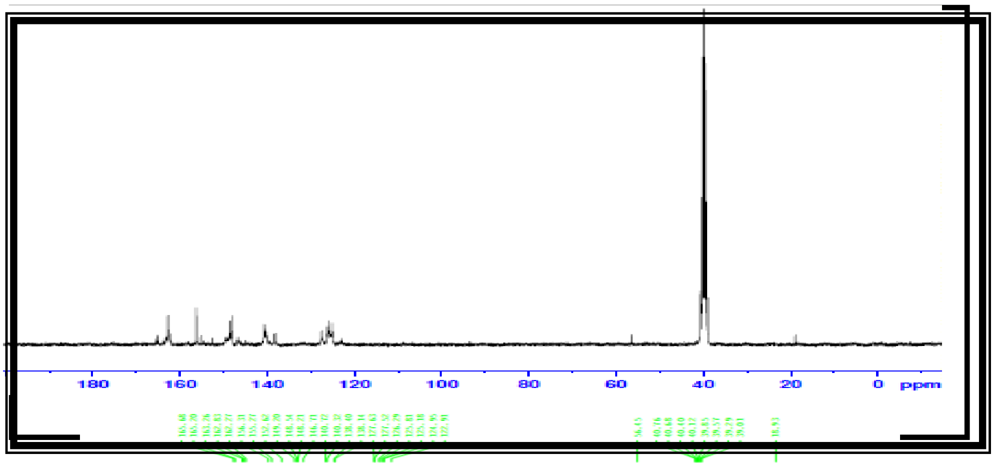
compound	N-CO-N	-CO-pyr	C-pyr meta	C-pyr ortho	C-pyr Para
L_1	160	165	140	148.9	128

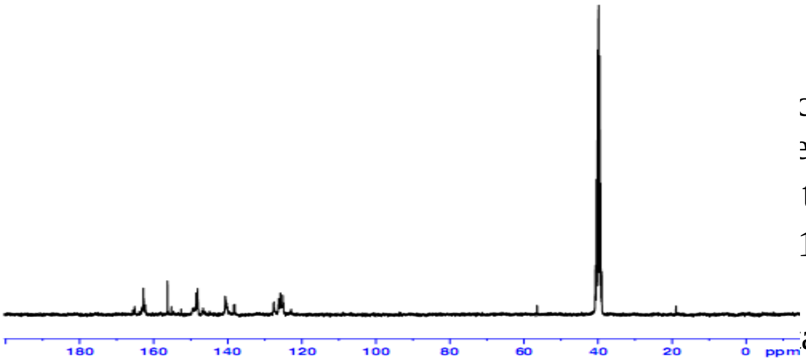


(A)structure of the ligand L_1



(B):^{1}H **NMR for L_1 ligand**





liga cal shift's
data are l ed to 3H
(HO-CH to (CH-
CH-CH= 1.2 ppm)
attributed ($N-H_2$) ,
(7.7 ppm) ains ^{13}C–

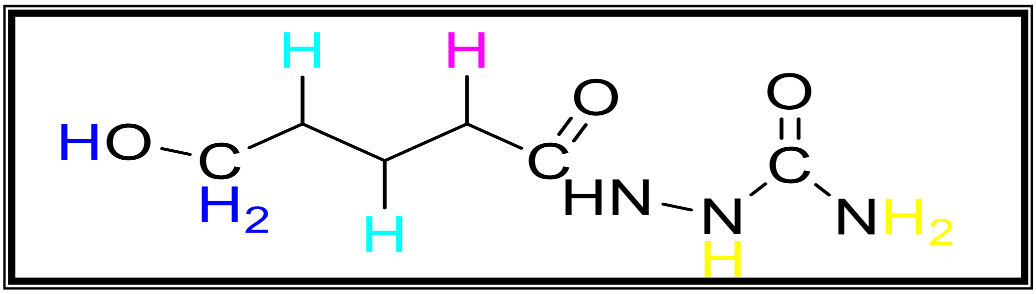
NMR chemical shift's the band at(35-20 ppm) attributed to (C-C-C-) , (58 ppm) for (HO-C-R) , (175 ppm) for (R-CO-N-N) , (156.3 ppm) for (C=O)-NH) and the solvent (DMSO) shows a band at(40 ppm) , figure (1) .All these bands assist the expecting ligand L$_2$ structure.

Table(3) Chemical shift for L$_2$ ^{1}H-NMR

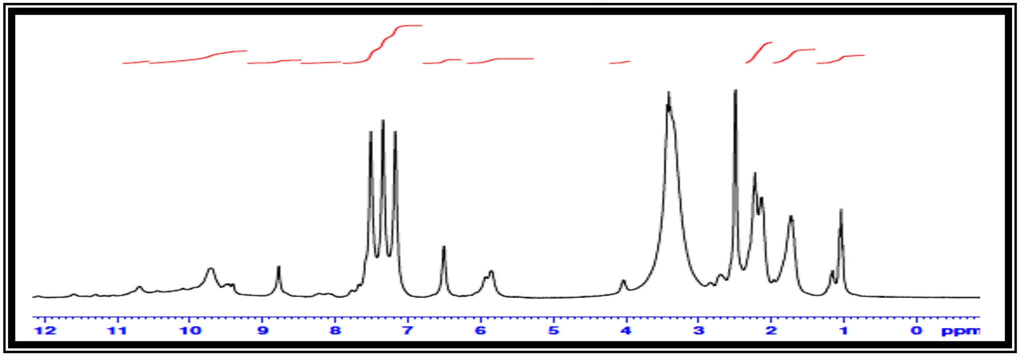
compound	HO-CH$_2$-δ	CH-CH-CH=Oδ	CH-CH-CH=O	N-H$_2$δ	C-NH-Nδ
L$_2$	3.4-3.6 3H	2.3 2H	1.2 4H	6.5 3H	7.7 1H

Table(4) Chemical shift for L$_2$ ^{13}C –NMR

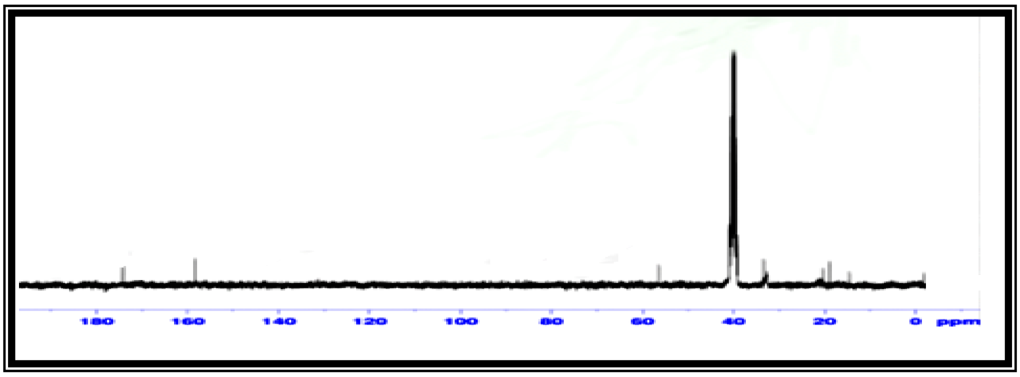
compound	C-C-C-	HO-C-R	R-CO-N-N	C(=O)-NH
L$_2$	35-20	58	175	156.3



(A)structure of the ligand L$_2$



(B):^{1}H **NMR for L$_2$ ligand**



(C): ^{13}C NMR for L$_2$ ligand
Fig(2): A,B,C

The IR spectrum data of (L_1 , L_2) Table (6) exhibited absorption frequencies assignable to **υ**(N – H) stretching as a strong band at(3225 cm^{-1}) , δ((N-H) appears at (1236 cm^{-1}) , υ(N – N) stretching vibration appears at (1018 cm^{-1}) , and the frequency assignable to υ**(**C=O) band at (1709 cm^{-1}) as medium intensity(13) . The IR spectrum characteristic to **υ**(N–N) , **υ**(CO –NH-CO) and **υ**(C = O) stretching frequencies confirm the condensation reaction between the carboxylic acid and semicarbazide , to form a 20 membered hexa amide macrocycle L_1&L_2 , as shown in figure (1) ,on Complexsation , the stretching frequencies of υ(N–H), δ(CO –NH-CO) and υ(N–N) shifted to lower frequency ,which may indicate the coordination of two (NH) from the semicarbazide group figure (2) , other support of this coordination comes from the appearance of new bands attributed to υ (M-N) stretching at(418-460 cm^{-1}) . However , the position of υ**(**C=O) stretching vibration has been shifted to lower frequencies in complexes number (7) , where as the other complexes and adducts number (1,2,3,4,5,6,8,9), the υ**(**C=O) are not shifted(14,15) . A new band attributed to the stretching of υ(M-O) group in complexes number(7) at (509 cm^{-1}) may prove this coordination.

ELECTRONIC SPECTRA & MAGNETIC MEASUREMENTS

The spectrum of the L_1 , L_2 ligands has a bands in the U.V spectra at(36760 and 45871 cm^{-1}), assigned to n $\longrightarrow \pi^*$ and π π^* transition , respectively.

The electronic spectra data and the magnetic moments for all complexes are given in Table(5).

The magnetic moment values for the Fe(II) complexes (1,3) have a magnetic moment values (4.87 – 5.12 B.M) while the electronic band at 10224–10526 cm^{-1} are attributed to $^5T_2g \longrightarrow {}^5Eg$ transition , indicating octahedral structure(5) .

The cobalt complex number 4 has a magnetic moment value (4.80 B.M) corresponding to three unpaired electrons[Table 5].The U.V–visible spectra show three bands at 10245 –15625 cm^{-1},16889 cm^{-1} and 32051 cm^{-1}due to the transitions ^4T_1g (F) $\longrightarrow$ ^4T_2g(F) υ_1, ^4T_1g (F) $\longrightarrow {}^4A_2g$(F) υ_2 and ^4T_1g (F)$\longrightarrow$ ^4T_1g(P) υ_3 , respectively .These data may attribute to octahedral structure(16) .

The UV – visible spectra of the Ni (II) complexes number(5,6) shows three bands at (10111 ,9469 cm^{-1}),(15337 ,14534 cm^{-1}) and (22676, 21233 cm^{-1}) corresponding to three spin allowed transition ^3A2g(F)$\longrightarrow$ ^3T2g(F)(υ_1), ^3A2g (F) $\longrightarrow$ ^3T_1g (F) (υ_2) , and ^2A2g (F)$\longrightarrow$ ^3T_1g (P) (υ_3) , respectively. The magnetic moment values (2.99 , 3.31 B.M) agree with high spin configuration indicating an octahedral environment around the Ni(II)ions(10).

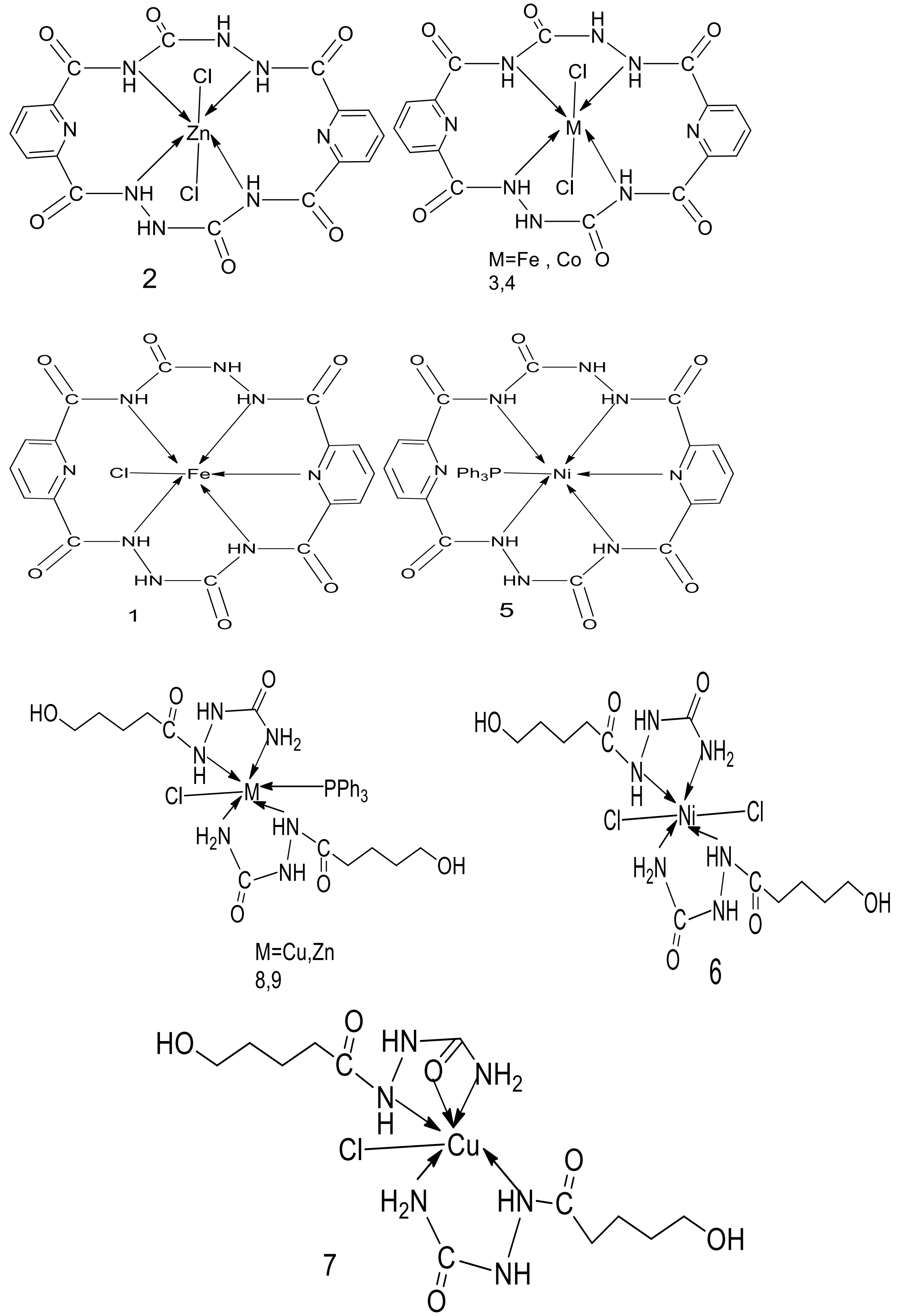
The magnetic moment of the Cu(II) complexes number(7,8) lie in the range (2.11 , 2.03 B . M) , corresponding to one unpaired electron and electronic spectra have a band in the range (20832 , 22935 cm^{-1}) assigned to the $^2E_2g(F) \longrightarrow {}^2T_2g$ transition in distorted octahedral environment(17). The µeff values of the two Zn(II) complexes were diamagnetic as expected .

Table(5):Some physical properties including molar conductance and elemental analysis data of the complexes

No	Compound	Color	M.P, C°	CHN Elemental analysis data found (Calculated %)				Molar conductance Ω-1 cm2.mol	μ_{eff} B.M
				%C	%H	%N	Metal %		
L_1	$C_{16}H_{12}N_8O_6$	Gray	158	51.18(51.58)	6.16(6.47)	19.90(20.34)	—	—	—
L_2	$C_6H_{13}N_3O_3$	Pale brown	—	39.43(39.01)	4.74(4.30)	15.33(15.06)	—	—	—
1	$[Fe(L_1)Cl]Cl$	Gray	80	---------	----------	-----------	10.19(10.02)	48	4.87
2	$[Zn(L_1)]Cl_2$	Dark blue	175	35.03(34.21)	2.20(2.10)	20.43(19.85)	10.68(10.58)	5.6	Dia
3	$[Fe(L_1)(PPh_3)Cl]Cl$	Dark blue	110	---------	------------ -	------------	10.64(10.13)	34	5.12
4	$[Co(L_1)(PPh_3)Cl]Cl$	Pale green	60	-----------	----------	-----------	11.42(11.01)	35.5	4.80
5	$[Ni(L_1)(PPh_3)]Cl_2$	Pale yellow	80	----------	----------	----------	11.71(11.32)	70.5	2.99
6	$[Ni(L_2)_2Cl_2]$	Pale brown	170	----------	---------	-----------	5.98(5.75)	18	3.31
7	$[Cu(L_2)_2Cl]Cl$	Pale brown	120	29.73(29.63)	5.41(5.40)	17.33(17.30)	6.08(5.95)	40	2.11
8	$[Cu(L_2)_2(PPh_3)l]Cl$	Deep blue	100	----------	---------	---------	6.39(6.09)	36	2.03
9	$[Zn(L_2)_2(PPh_3)Cl]Cl$	Brilliant green	90	-----------	---------	----------	5.87(5.53)	36	Dia

COUNCLUSION

On the basis of the above results , we proposed the following structures for the Fe(II),Co(II),Ni(II),Cu(II) , and Zn(II) complexes , and adducts.



Fig(2):Proposed structures of the complexes and the adducts

Table(6):Selected I.R bands and their assignment in cm^{-1}

No	Band maxima (λ_{Max}) nm	I.R spectra								
		N-υ(H)	**N-δ(H)**	**δ (N-H_2)**	**N-υ(N)**	**υ(C=O)**	**M-υ(O)**	**υ(OH)**	**N-Pyr**	**(M-υN)**
L$_1$	——	3250	1306	——	1001	1708	——	——	1520	——
L$_2$	——	3265	1257	1640	1011	1709	——	3477	——	——
1	10526 , 32679 , 34482	3124$_{(w)}$	1267	——	999	1705	——	——	1481	453
2	30121 , 37962	3211	1277	——	951	1705	——	——	1522	430
3	10224 , 29230 , 36762	3170	1290	——	941	1706	——	——	1522	453
4	10245,15625, 16889,32051	3190	1279	——	997	1704	——	——	1523	547
5	10111,15337, 22676,36496	3201	1280	——	951	1697	——	——	14882	465
6	9469 ,14534 , 21233 ,36761	3215	1201	1655	979	1701	——	3473	——	428
7	20833 ,32679	3232	1205	1655	991	1685	509	3479	——	498
8	22935 , 32055	3165	1203	1651	991	1701	——	3466	——	498
9	31278 , 35421	3197	1203	1652	983	1701	——	3465	——	451

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