

Synthesis and Characterization of Two Schiff Base Tetradentate Ligands and their Related Complexes of Cu(II) and Pd(II)

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ABSTRACT

The compound [H₂L¹] (2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo-9-2-amino ethylimine) was used to prepare two novel Schiff base ligands 2,4-bis [2,6-di(phenyl-4-methyl)[3.3.1] azabicyclo-9- 2-imine ethylimine] butane [L₂] and 2,5-bis [2,6-di(phenyl-4-methyl)[3.3.1] azabicyclo- 9-2-imine ethylimine] pentane [L₃], by the reaction of [2,3-butandione] and [2,4-pentandione] with 2,6-di (phenyl-4-methyl) [3.3.1] azabicyclo -9-2-amino ethylimine [H₂L¹] in [1:2] ratio in presence of concentrated HCl acid. The mixture was refluxed in ethanol for eight hours. The new ligands were used to prepare new complexes with Cu(II) and Pd(II). The prepared compounds were identified by IR, U.V-Vis, ¹H, ¹³C NMR spectra, elemental microanalysis (C.H.N). In addition the complexes were characterized by IR, U.V-Vis, conductivity, magnetic susceptibility and melting point. Results showed that all complexes have an octahedral structure.

Introduction:

The compound (2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo-9-one) was prepared recently(1) and used as starting material to prepare 2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo -9-2-amino ethylimine [H₂L¹]. This ligand contains NN donor atoms derived from ethylene diamine, and used to prepare octahedral structure around CoII and NiII and a square planar structure around CuII ion(2).

The attention of Inorganic chemistry had been caught by the extraordinary of the coordination chemistry of metals in biological system(3). The challenge of synthesizing model ligands which will be proved to those in the binding of the copper proteins has been taken up and many ligands have been produced for this purpose(4).

Coordination chemistry of the transition metal complexes contains nitrogen donor atoms have received a great deal of importance. This may be attributed to their stability, biological activity(5), potential catalysis(6) and electrochemistry(7).

The metal complexes of ligands contain N,N donor groups have many applications(8) in medicine, pharmacology and industry(9). Copper(II) complexes of those types of ligands are believed to have a great biological importance for their participation in biological transport reaction(10).

While copper radio nuclides have attracted considerable attention in nuclear medicine because they include isotopes with both diagnostic and therapeutic(11). The Pd(II) complexes of ligands contain N,N donor group show a dynamic behavior by exchange the position of bonding with different groups (12).

The goal of this paper is to prepare two macrocyclic ligands (N₂,N₂) and the characterization study of the complexes Cu(II) and Pd(II) with (L₂, L₃).

Experimental:

Synthesis:

preparation of precursor and 2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo-9-2-aminoethylimine [H₂L¹]:

2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo-9-one was prepared by mix of 4-methyl benzaldehyde (4.02ml, 38.0mmol), ammonium acetate (1gm, 12.9mmol) and cyclohexanone (2ml, 19.15mmol) in methanol in [2:1:1] ratio respectively(1). The reaction mixture was refluxed for 1hr, and orange crystals were formed where collected by filtration, washed with cold methanol (4ml), dried under vacuum. Yielded 2.5gm (89%), m.p(122°C).

2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo-9-one (0.4gm, 1.24mmol) dissolved in methanol (40ml)

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was added to solution of ethylene diamine (0.082gm, 1.36mmol). The resulted mixture was treated with concentrated hydrochloric acid (2ml) and refluxed for 6hrs(12). The resulted yellow crystals upon slow evaporation of solvent were collected by filtration, washed by diethyl ether (5ml), dried under vacuum to give 0.315gm of 2,6-di(phenyl-4-methyl)[3.3.1] azabicyclo-9-2-amino ethylimine [H2L1](2). Yield(70%), m.p(166°C), soluble in methanol, ethanol and DMSO.

preparation of 2,4-bis [2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo-9- 2-imine ethylimine] butane [L2]

A solution of [H2L1] (0.2gm, 0.55mmol) in methanol (40ml), was added slowly to a solution of 2,3 butandione (0.023gm, 0.26mmol) in methanol (20ml), in [2:1] ratio respectively. The resulted mixture was treated with 2ml of concentrated hydrochloric acid, and refluxed for 8hrs. The final mixture was evaporated and cooled to give pale-yellow crystals, filtered, washed with cold methanol (4ml), dried under vacuum. Yield (0.32gm) (76.7%), m.p(172°C).

preparation of 2,5-bis [2,6-di(phenyl-4-methyl)[3.3.1] azabicyclo- 9-2-imine ethylimine] pentane [L3] :

40ml of methanolic solution of [H2L1] (0.2gm, 0.55mmol), was added slowly to 20ml methanolic solution of (2,4-pentandione) (0.027gm, 0.27 mmol) in [2:1] ratio respectively. The resulted mixture was treated with 2ml of concentrated hydrochloric acid, and refluxed for 8hrs. The final mixture was evaporated and cool to give pale- yellow crystal, filtered, washed with cold methanol (4ml), dried under vacuum. Yield (0.36gm), (83.8%), m.p (188°C).

Preparation of [Cu(L2)Cl2] complex:

To an ethanolic solution of [L2] (0.2gm, 0.26mmol) was added slowly to a stirred ethanolic solution of copper(II) chloride dihydrate (0.044gm, 0.25mmol). The pH of the mixture was adjusted to ca. (10) by an ethanolic solution of potassium hydroxide. Refluxed on water bath for 3hrs, under nitrogen atmosphere, during this time the solution become yellowish-green, it was filtered, washed by diethyl ether (5ml) and dried under vacuum to give a pale green crystals of the title compound, (0.22gm), (94%), m.p(195°C).

Preparation of [Pd(L3)Cl2] complex:

A (0.045gm, 0.25mmol) of palladium chloride (PdCl2) was dissolve in (5ml) of ethanol, then added slowly to (0.2gm, 0.25mmol) of ethanolic solution of [L3] with stirring. The pH of the mixture was adjusted to ca. (10) by an ethanolic solution of potassium hydroxide. The resulted mixture was refluxed under nitrogen atmosphere for 3hrs, it was filtered, washed by diethyl ether (5ml) and dried under vacuum to give red brown sold of the title compound, (0.22gm), (89.7%), m.p (240°C).

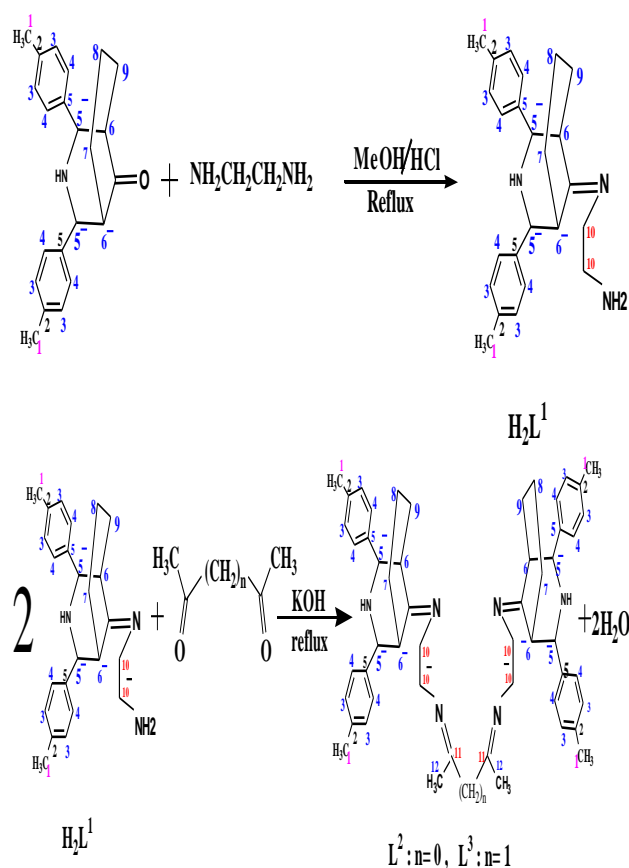
Preparation of [Cu(L3)Cl2] and [Pd(L2)Cl2] complexes:

The method used to prepare both complexes were similar to that used for [Cu(L2)Cl2] and [Pd(L3)Cl2] complexes.

Results and discussion:

Synthesis and characterization of [H2L1], [L2] and [L3] :

The three ligands were synthesized according to scheme (1) :



Scheme (1)

These two macro schiff base ligands contained four donor atoms of nitrogen were characterization such as pale yellow crystals which they are stable in a wide range of temperatures and soluble in some organic solvents methanol, ethanol, DMSO, and C6H6.

Microanalysis of the prepared ligands are in good agreement with the calculated values, Table (1).

Table (1) Micro analysis and some physical properties of the prepared compounds

Compound	M.Wt	Yield%	color	(M.P) ^o	Micro analysis found (calculate)%		
					C	H	N
[H ₂ L ¹]	361	70	yellow	166	80.12 (79.7)	8.654 (8.58)	11.57 (11.6)
L ²	772	76.7	Pale yellow	172	79.93 (80.8)	7.88 (8.29)	10.36 (10.8)
L ³	786	83.8	Pale yellow	188	81.55 (80.9)	8.87 (8.39)	10.29 (10.6)
[Cu(L ²)Cl ₂]	906	94	Yellowish-green	195	—	—	—
[Pd(L ²)Cl ₂]	949.4	91.6	Red brown	220 (dec)	65.88 (65.7)	7.77 (6.7)	9.77 (8.84)
[Cu(L ³)Cl ₂]	920	80	Yellowish-green	211	—	—	—
[Pd(L ³)Cl ₂]	963.3	89.7	Red brown	240 (dec)	—	—	—

IR spectra :

Fig (1) showed the IR spectra of the free ligands (L2, L3) and some their complexes, while the assignment of the characteristic bands are summarised in Table (2).

The IR spectrum of the ligand [H₂L¹], showed

several bsnds at (3311, 3250, 3065, 2877, and 1527) cm⁻¹ which have been assigned to $\nu(\text{N-H})_{\text{asy}}$, $\nu(\text{N-H})_{\text{sym}}$, $\nu(\text{C-H})_{\text{arom}}$, $\nu(\text{C-H})_{\text{aliph}}$ and $\delta(\text{N-H})$ respectively(10). The band at (1665)cm⁻¹ can be attributed to imine group $\nu(\text{C=N})$ stretching(11).

The IR spectrum of the ligands [L₂] and [L₃] exhibited the bands with some shifting to the lower frequency at (1660, 1658)cm⁻¹ respectively, due to $\nu(\text{C=N})$ in comparison with $\nu(\text{C=N})$ of [H₂L¹], while disappearance of the bands at (1730, 1640)cm⁻¹ related to the $\nu(\text{C=O})$ of the starting material 2,3-butandione and 2,4-pentandione respectively. Also the IR spectrum of [L₂] and [L₃] exhibited bands at (3230-3135), (3057-3055), (2844-2820) and (1590)cm⁻¹ which attributed to the $\nu(\text{N-H})$, $\nu(\text{C-H})_{\text{arom}}$, $\nu(\text{C-H})_{\text{aliph}}$ and $\nu(\text{C=C})$ stretching respectively(10). Other bands are summerised in Table (2).

The comparison of IR spectra of the free ligands [L₂] and [L₃] with that in complex [M(L_{2,3}) Cl₂], (where M=CuII, PdII), showed the shifting of the bands of (C=N) to the lower wave number and appearance as strong bands at (1650)cm⁻¹ due to reduced bond order. This can be attributed to the delocalisation of metal electrons density into the ligand π -system, indicated to coordination of the imine nitrogen with the copper and palladium ions(12). The band around 500cm⁻¹ may be due to $\nu(\text{Cu-N})$, the far IR spectrum showed a band at 350cm⁻¹ which due to $\nu(\text{Cu-Cl})$ (13).

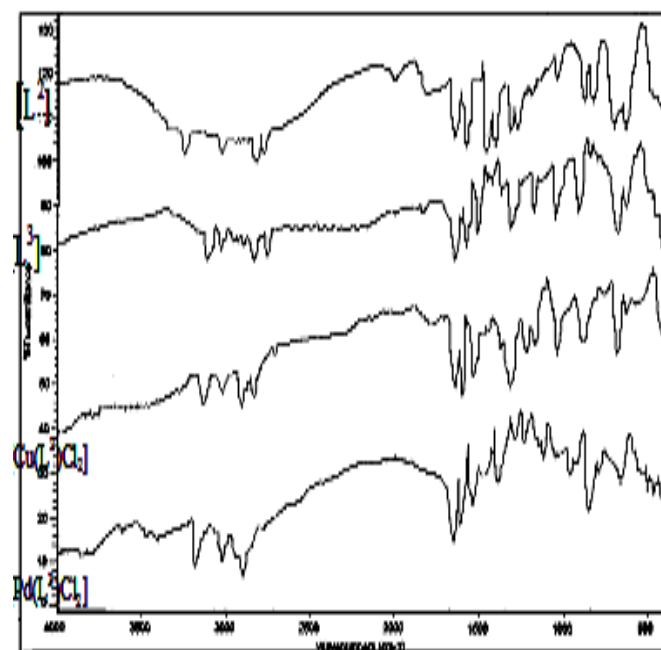


Fig (1) I.R spectrum of (L₂), (L₃) and their complexes with Cu^{II} and Pd^{II} ions.

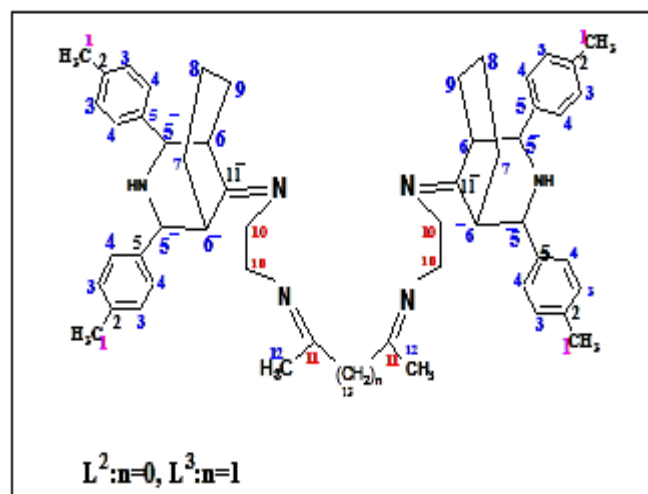
Table (2) Infrared spectra data (wave number ν) of prepared ligands and their complexes

Compound	$\nu(\text{N-H})$	$\nu(\text{C-H})_{\text{arom}}$	$\nu(\text{C-H})_{\text{aliph}}$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C=C})$	$\delta(\text{N-H})$	$\nu(\text{C-N})$
2,3-butandione	-	-	2915(w)	1730(s)	-	-	-	-
2,4-pentandione	-	-	2940(s)	1640(s)	-	-	-	-
$[\text{H}_2\text{L}^1]$	3311(w) 3250(w)	3065(w)	2877(m)	-	1665(m)	1585(w)	1527(w)	1477(m)
L^2	3230(w)	3057(w)	2844(w) 2833(w)	-	1660(s)	1590(m)	1540(w)	1480(m)
L^3	3135(w)	3055(w)	2820(w) 2845(w)	-	1658(s)	1590(m)	1540(w)	1485(m)
$[\text{Cu}(\text{L}^2)\text{Cl}_2]$	3150(w)	3022(w)	2910(w)	-	1650(s)	1605(m)	1530(w)	1485(m)
$[\text{Pd}(\text{L}^2)\text{Cl}_2]$	3163(w)	3015(w)	2890(w)	-	1650(s)	1605(m)	1535(w)	1486(m)
$[\text{Cu}(\text{L}^3)\text{Cl}_2]$	3130(w)	3000(w)	2885(w)	-	1650(s)	1605(m)	1530(w)	1495(m)
$[\text{Pd}(\text{L}^3)\text{Cl}_2]$	3145(w)	3021(w)	2905(w)	-	1650(s)	1605(m)	1535(w)	1500(m)

(w= weak, m= medium, s= strong)

$^1\text{H},^{13}\text{C}$ NMR Spectra of the ligands:

The $^1\text{H},^{13}\text{C}$ NMR recorder at 400 MHz by used DMSO solvent to characterise the ligands [L2] and [L3], were $^1\text{H},^{13}\text{C}$ NMR spectrum Fig. (2) and Fig (3) displayed signals corresponding to the various proton and carbon nuclei consistent with the proposed structural formula scheme (2). The results are summarised in Table (3) and (4).



Scheme (2): The proposed structure of ligands [L2] and [L3]

^1H NMR Spectrum of [L2] and [L3] :

The ^1H NMR Spectra of two ligands are shown in Fig (2), Table (3). The chemical shifts of the phenyl groups appeared as two signals resonance at 7.25ppm (8H, m, $8 \times \text{C}3\text{-H}$) and 7.1ppm(8H, m, $8 \times \text{C}4\text{-H}$)(14). The signals at [(3.11); (2.51); (2.33-2.2); (1.71); (1.31); (0,91)]ppm, may be assigned to [(4H, br, $\text{C}5\text{-H}$); (12H, s, $\text{C}1\text{-H}$); (4H, d, ($\text{C}6,\text{N}$)-H); (12H, d, $\text{C}7,8,9\text{-H}$); (8H, d, $\text{C}10\text{-H}$) and (6H, s, $\text{C}12\text{-H}$)] respectively(15), whilst the chemical shift of the ($\text{C}13$)H of [L3] ligand is appeared signal at (3.32)ppm equivalent to two protons, in contrast this signal disappeared in [L2] spectra.

^{13}C NMR Spectrum of [L2] and [L3] :

The ^{13}C NMR Spectra for ligands [L2] and [L3] Fig (3) Table (4), show the chemical shifts of ($\text{C}11=\text{N}$, $\text{C}11=\text{N}$) in L2 are equivalent and appear at (154.2)ppm. While the chemical shifts in L3 are nonequivalent at 154.2 and (154)ppm, this very important evidence of the appearance of ($\text{C}=\text{N}$) in the two synthesized ligands [L2] and [L3](16).

The ^{13}C NMR Spectra showed a set of signals at [(136.3); (130.2, 129.6); (55); (47.9) and (20.7)]ppm can be assigned to ($\text{C}5$); ($\text{C}3$, $\text{C}4$); ($\text{C}5\text{-}$); ($\text{C}10$) and ($\text{C}12$)] carbon atoms respectively.

The signals at the regions (30.88-30.81)ppm and (28.3-26.4)ppm assigned to carbon atoms of ($\text{C}6,6\text{-}$) and ($\text{C}7,8,9$)of macro cycle respectively, while the signal at ($\delta=35.1$)ppm of [L3] may be due to $\delta(\text{C}13)$ atom(10,17).



Fig (2) 1H-NMR spectrum of the ligand [L2]

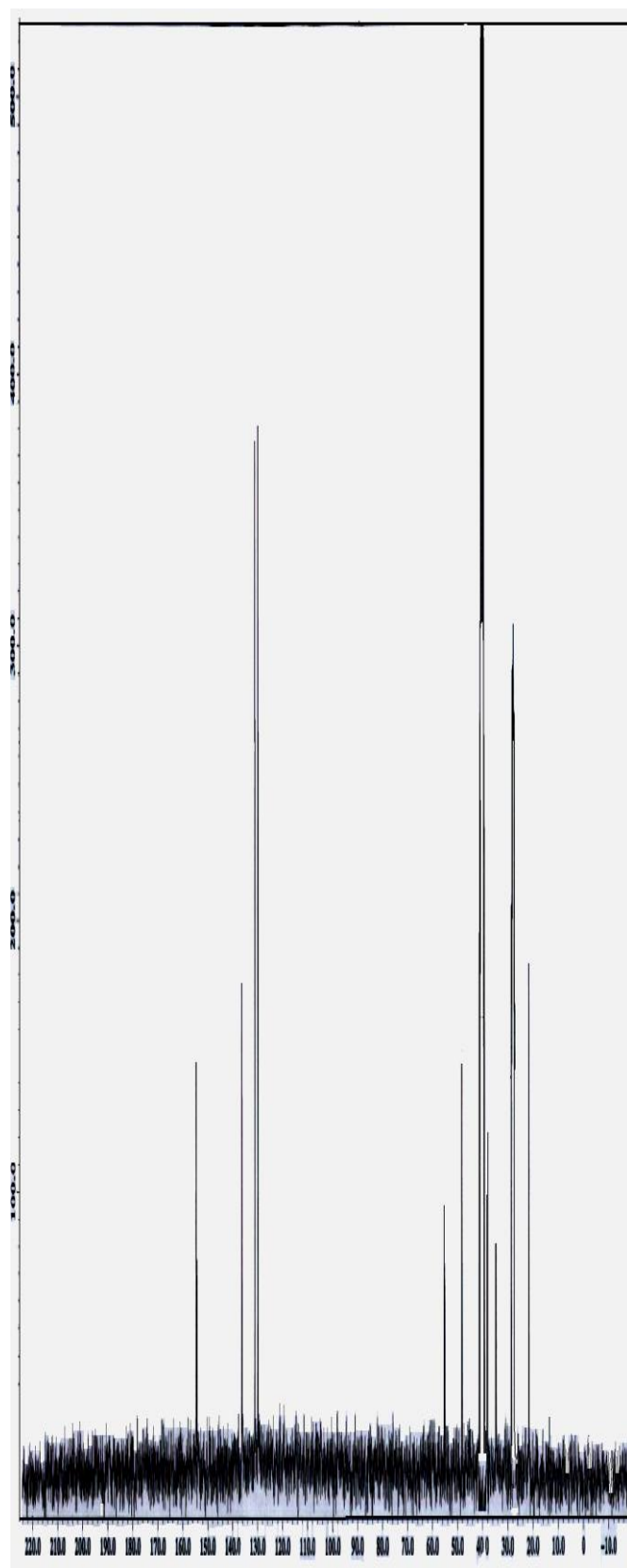


Fig (3) 13C-NMR spectrum of the ligand [L3]

Table (3) ¹H NMR data of [L2] and [L3] compounds measured the chemical shift in ppm (δ)

Comp.	L ²	L ³
δ (-C _{3,4})H	7.25-7.1	7.25-7.1
δ (C ₅ -)H	3.11	3.11
δ (C ₁₃)H	-	3.32
δ (C ₁)H	2.51	2.51
δ (d ₁ C _{6,6} ,NH)	2.33-2.2	2.33-2.2
δ (C _{7,8,9})H	1.71	1.71
δ (C ₁₀)H	1.31	1.31
δ (C ₁₂)H	0.91	0.91

Table (4) ¹³C NMR data of [L2] and [L3] compounds measured the chemical shift in ppm (δ)

Comp.	L ²	L ³
δ (C=N)	154.2	154.2, 154.0
δ (C ₅)	136	136.3
δ (C _{3,4})	130, 129.6	130, 129.6
δ (C ₅ ')	55	55
δ (C ₁₀)	47.9	47.9
δ (C _{6,6'})	30.88-30.81	30.88-30.81
δ (C ₁₃)	-	35.1
δ (C _{7,8,9})	28.3-26.4	26.4-28.3
δ (C ₁₂)	20.7	20.7

(UV-Vis) Spectra :

The UV-Vis spectra data of (L2) and (L3) complexes are listed in Table (5). The spectra of (L2) and (L3) showed two absorption peaks at (266, 295)nm and (340, 345)nm, which were assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively(18).

The spectra of [Cu(L2)Cl₂], [Pd(L2)Cl₂], [Cu(L3)Cl₂] and [Pd(L3)Cl₂] complexes displayed two intense peaks in the (UV) region, at (270, 277, 262, 267)nm and (334, 348, 320, 354)nm respectively. These peaks were assigned to ligand field and Charge transfer transition respectively.

The UV-Vis spectra of copper and palladium complexes showed absorption peaks in (Vis) region at (622)nm and (598, 590)nm respectively, can be assigned to (d-d) transitions type ($2E_g \rightarrow 2T_2g$) and ($3A_{2g}(f) \rightarrow 3T_2g(f)$) in an octahedral structure around CuII and PdII ions(19) respectively. Table (3).

Molar conductivity for the complexes:

The conductivity of the copper and palladium

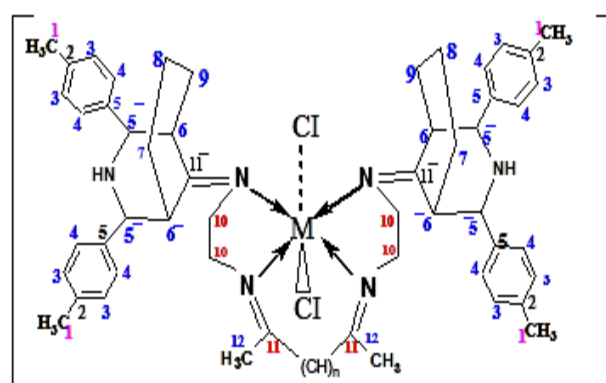
complexes were estimated by their molar conductivity, in DMSO (10-3M) at room temperature Table (5), indicate non-electrolyte nature(20).

Magnetic moment measurements:

The magnetic susceptibilities measured showed that the complexes have paramagnetic properties(21), Table(5), suggesting octahedral geometry around the copper and palladium ions Scheme (3).

Table (5) U.V-Vis Spectra, molar conductivity and magnetic moments data of prepared compounds

Compound	λ_{nm}	Transition	Molar Conductivity S. cm ² . mol ⁻¹	Magnetic Susceptibility B.M
L ²	266 340	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
L ³	295 345	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
[Cu(L ²)Cl ₂]	270 334 622	Ligand field Charge transfer $^2E_g \rightarrow ^2T_2g(F)$	14	1.743
[Pd(L ²)Cl ₂]	277 348 598	Ligand field Charge transfer $^3A_{2g}(F) \rightarrow ^3T_2g(F)$	8.2	3.44
[Cu(L ³)Cl ₂]	262 320	Ligand field Charge transfer	10	2.71
[Pd(L ³)Cl ₂]	267 354 590	Ligand field Charge transfer $^3A_{2g}(F) \rightarrow ^3T_2g(F)$	4.8	2.88



M=Cu, pd where: n=0,1

Scheme (3): proposed structures of metal complexes.

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تحضير وتشخيص ليكاندين جديدين لقواعد شف رباعيه السن ومعداتها مع (PdII, CuII)

محمود صالح مطر

الخلاصه:

تم تحضير ليكاندين جديدين لقواعد شف [L2] 2,4-bis [2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo-9-2-imine ethylimine] butane و [L3] و [2,3- 2,5-bis [2,6-di(phenyl-4-methyl) [3.3.1] azabicyclo- 9-2-imine ethylimine] pentane من مفاعلة كل من المادة [2,3- 2,6-di(phenyl-4 -methyl) [3.3.1] azabicyclo -9-2-amino على انفراد مع الليكاند [2,4-pentandione] والمادة butandione] [2,4-pentandione] بنسبة [2:1] على التوالي، بوجود حامض الهيدروكلوريك المركز، تم تسخين محتويات التفاعل بواسطة التصعيد باستخدام الايثانول كمذيب لمدة 8 ساعات. استخدمت الليكاندات الجديده لتحضير معقدات مع ايوني (PdII , CuII) . شخضت الليكاندات المحضره باستخدام اطياف الاشعه تحت الحمراء وفوق البنفسجيه، اطياف الرنين النووي المغناطيسي 1H, 13C والتحليل الدقيق للعناصر. كما تم تشخيص المعقدات المحضره باستخدام اطياف الاشعه تحت الحمراء وفوق البنفسجيه والمرئيه، التحليل الدقيق للعناصر لمعقد البليديوم مع [L2] بالاضافه الى الحساسيه المغناطيسيه والتوصيليه الكهربائيه مع درجة الانصهار، واطهرت النتائج بان للمعقدات شكل ثماني السطوح.