

Synthesis And Characterization Of Fluorescent Schiff Bases And Their Metal Complexes From 9-Anthracenecarboxaldehyde

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ABSTRACT

Synthesis and characterisation two Schiff bases[L1] (N2Z,N6Z)-N2,N6-bis(4-((E)-anthracen-9-ylmethyleneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylidene)pyridine-2,6-diamine Synthesis via reaction of 2,6-diaminopyridine, 4-aminoantipyrine and 9-anthracenecarboxaldehyde with mole ratio (1:2:2) respectively two steps. And[L2] (N1Z,N2Z)-N1,N2-bis(4-((E)-anthracen-9-ylmethyleneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylidene)-4-methylbenzene-1,2-diamine Synthesis from reaction of o-phenylenediamine, 4-aminoantipyrine and 9-anthracenecarboxaldehyde with mole ratio (1:2:2) respectively two steps. A new series of transition metal complexes of Mn(II), Co(II), Ca(II), Cd(II), Zn(II) and Pd(II) were synthesized. The structural features were derived from their elemental analyses, infrared, UV-visible spectroscopy, ¹HNMR, ¹³CNMR spectroscopy, thermal gravimetric analyses spectral, magnetic susceptibility measurement, chloride content and conductivity measurements. The electronic spectral data and magnetic measurements indicate that the complexes exhibit octahedral geometry around Ca(II), Mn(II), Cd(II), Co(II), Zn(II) while Square planer geometry around Pd(II).

Keywords: Schiff base o-phenylenediamine, 2, 6-diaminopyridine, 9-anthracenecarboxaldehyde, fluorescence

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INTRODUCTION

The compounds containing azomethine (-C=N-) group which known as Schiff bases, are formed by the condensation of a primary amines with a carbonyl compounds such as aldehydes or ketones^(1,2). Schiff bases are characterized by Cyclic imides have wide applications in pharmacological and industrial fields. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions in the periodic table^(3, 4). Schiff base ligands are very important in the development of coordination chemistry as they can readily form stable complexes with most metal ions⁽⁵⁾. Schiff base complexes of transition metals have been extensively investigated for many years. Their ready syntheses and excellent properties have contributed greatly to their popularity as well as to the

development of inorganic chemistry⁽⁷⁻¹³⁾. 4-Aminoantipyrine and its derivatives are identified for their variety of applications in the area of catalysis, medicine and pharmacology(). Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, such as biological, inorganic and analytical chemistry⁽¹⁴⁾. The aim of the present study, is to synthesis of Schiff bases which are based on the condensation of 4-aminoantipyrine with some Aromatic diamine, 9-anthracenecarboxaldehyde and then prepare their complexes with Ca (II), Mn(II), Cd(II), Co(II), Zn(II),Pd(II) ion. These Schiff bases and complexes are identified by IR, UV/vis., ¹HNMR, ¹³C-NMR and atomic absorption techniques. This study also includes investigation on conductivity, magnetic properties and fluorescence studies. solution of the samples in DMSO by using (conductivity meter ,model 4070) ,Magnetic measurements of the metal complexes were performed on a Magnetic susceptibility Balance Mode (MSB-MKI), ¹HNMR, acquired using a Bruker-500 MHz and 300 MHz for thermogravimetric analysis (TGA) was carried out using STA PT-100 Linseis company /Germany.

EXPERIMENTAL

Chemicals

2,6diaminopyridine,4-Aminoantipyrine,9-anthracenecarboxaldehyde, o-phenylenediamine, calcium chloride, mangans(II)chloride tetra hydrate, cadmium(II)chloride, cobalt(II) Chloride hexahydrate,Zinc (II) chloride and palladium chloride DMSO acetic acid and ethanol were provide from Aldrich company.

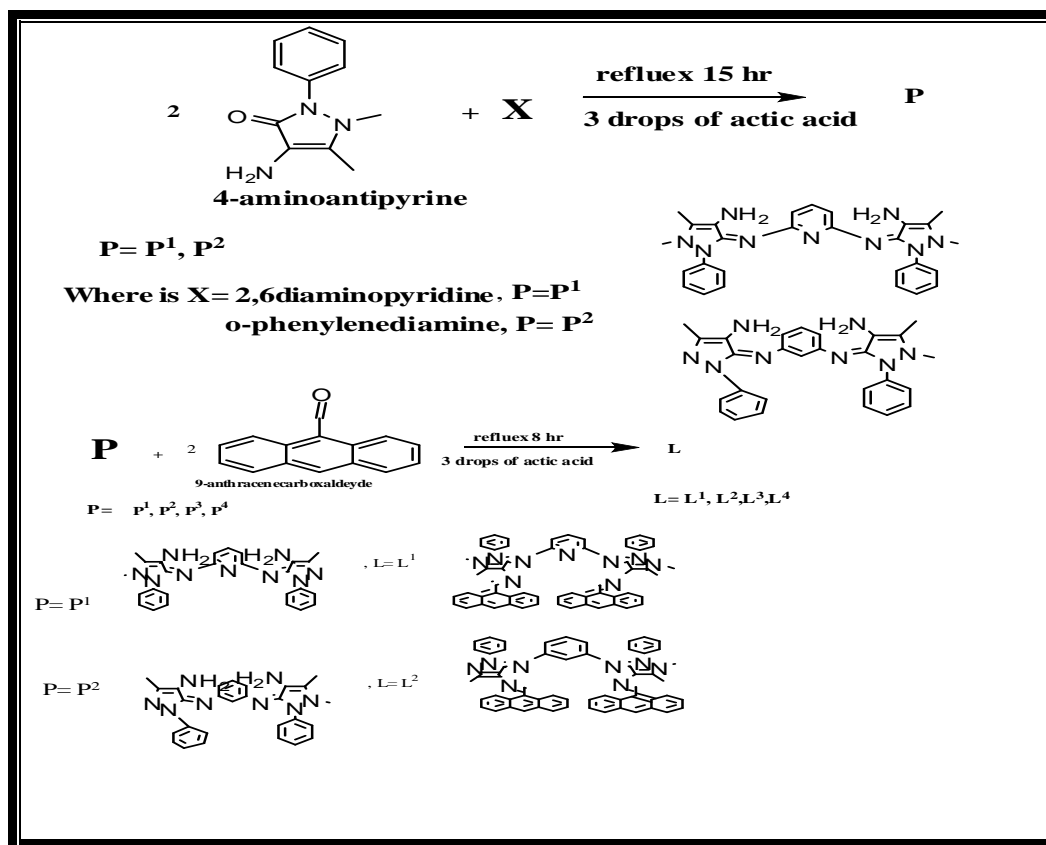
Physical measurements

Melting points for prepared complexes were measured by electro thermal (stuart melting point apparatus). Infrared spectra were performed using a shimadzu (FT-IR)-8300 spectrophotometer in the range (4000-400)cm⁻¹, Electronic spectra of the compounds were recorded by using double-beam (U.V-Vis)spectrophotometer type U.V 160A(Shimadzu) in the region (200-900)nm using 10⁻³ M solution in DMSO at 25°C,Elemental analysis (C.H.N) recorder by using Euro Vector, model EA3000 single V.3,Osinglein, The Chloride contents were determined using (686-Titro processor-665. Dosimat Matron Swiss), Electrical conductivity measurements of the complexes were recorder at (25 °C)for (10-3mol.L⁻¹)

SYNTHESIS

Synthesis of Schiff base ligands

The Schiff base ligands (L¹, L²) were synthesized by mixture of precursor(P¹) of((N2Z,N6Z)-N2,N6-bis(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylidene)pyridine-2,6-diamine) precursor (N1Z,N2Z)-N1,N2-bis(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylidene)-4-methylbenzene-1,2-diamine(P²), and 9-anthracenecarboxaldehyde in absolute ethanol (Scheme 1) in ethanol in the presence of some drops of glacial acetic acid. The mixture was refluxed for (8) hrs. the obtained crystalline precipitates were filtered, washed with ethanol and recrystallized from absolute ethanol and dried. The suggested structure for the prepared ligands was given in (Scheme 1) and some physical properties were listed in tables (1).

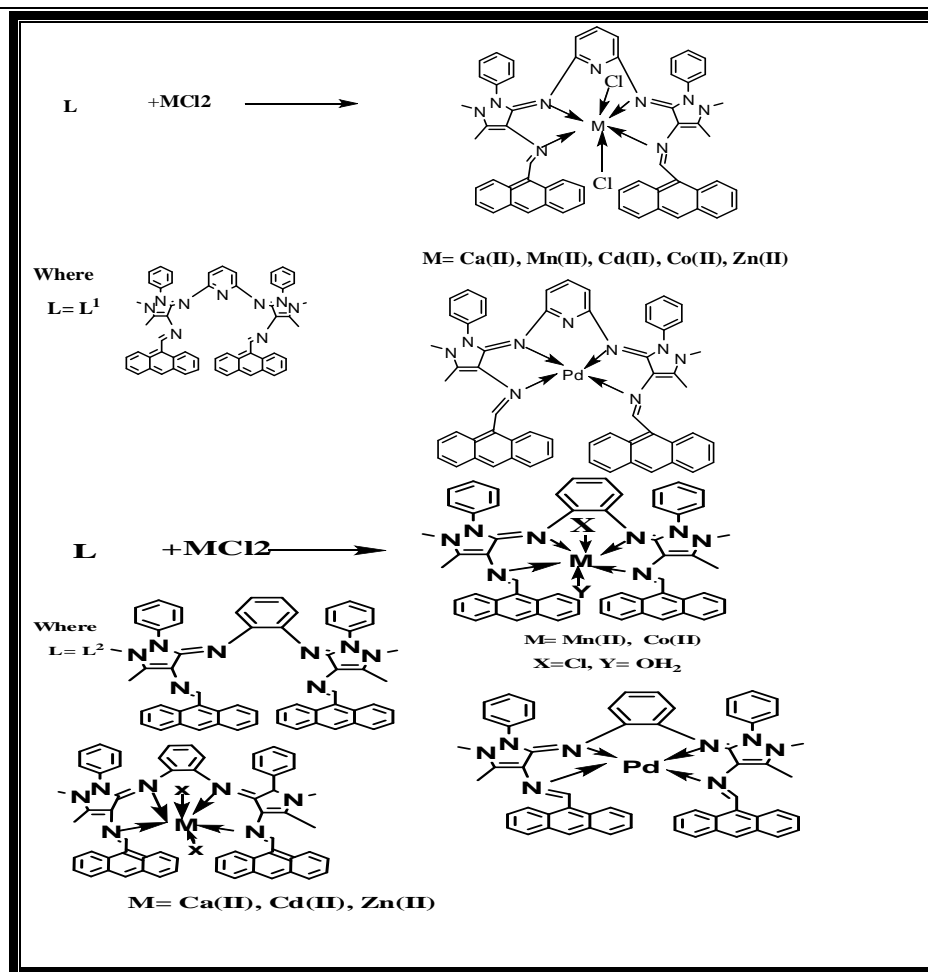


Scheme (1) Synthesis route of schiff base ligands [L¹, L²]

Synthesis of Ca(II), Mn(II), Cd(II), Co(II), Zn(II) and Pd(II) complexes

All the complexes were prepared by mixing ethanolic solution of ligands (L¹, L²) and metal salts in required molar ratio (1:1). The reaction mixture was refluxed on a water bath

for 2-3 hrs. After cooling, desired crystals of the complexes obtained were filtered, recrystallized and washed in the ethanol and dried in vacuum over. The physical properties of the complexes and their reactant quantity displayed in (Table 1).



Scheme (2): Synthesis rout of ligand $[L^1, L^2]$ metal complexes

The Electronic Spectra of the ligand $[L^1, L^2]$ and their complexes

The electronic spectrum of the Schiff base ligands (L^1, L^2) exhibits two peaks around (270 nm and (332 – 388) nm related to intra- ligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and charge transfer (C.T) transition. The electronic spectrum of Co(II) show peak at (412nm) is due to charge transfer transition overlap with d-d electronic transition peak type ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ and show a peak at visible at (674nm), assignable to ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ suggesting octahedral geometry around Co(II) ion^(18,19,20). The electronic spectrum of Mn(II) complex displayed two new absorption peak, the first peak at 424 nm and another peak at 498nm assigned to (d-d) electronic transition type ${}^6A_{1g} \rightarrow {}^4T_{2g(D)}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g(G)}$ respectively, suggesting octahedral geometry about Mn(II)^(21,22). The spectrum of the Pd(II) complex showed peak in the (d-d) region at (419nm) and (889nm) assigned to ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ respectively indicating square planar

geometry around Pd(II) ion. The electronic spectra of Ca (II) Zn (II) and Cd(II) complexes respectively, exhibit no peak in the visible region because of (d^{10} -system) of metal (II) ion^(23,24,25). This means no (d-d) electronic transition happened. All observations were summarized in the Table (4, 5).

${}^1\text{H-NMR}$ Spectrum of ligand $[L^1]$

The ${}^1\text{H}$ NMR spectrum of ligand $[L^1]$ was recorded in DMSO- d_6 solvent shows a signal at ($\delta = 10.86$ ppm) equivalent to two protons assigned to (–H anthracene) group. The multiplet signals obtained in the δ 7.0-8.0 ppm range are due to the aromatic protons of Schiff base ligand. The signal for pyrazolone ring carbon attached methyl protons (–CH₃) appear as a singlet at δ 2.42 ppm while pyrazolone ring nitrogen attached methyl protons (–N-CH₃) appear as a singlet at δ 3.09 ppm. The spectrum displayed chemical shifts at ($\delta_H = 2.51$ ppm and 2.55 ppm) referred to DMSO, and the presence of water molecules in the solvent respectively⁽²⁶⁻²⁷⁾.

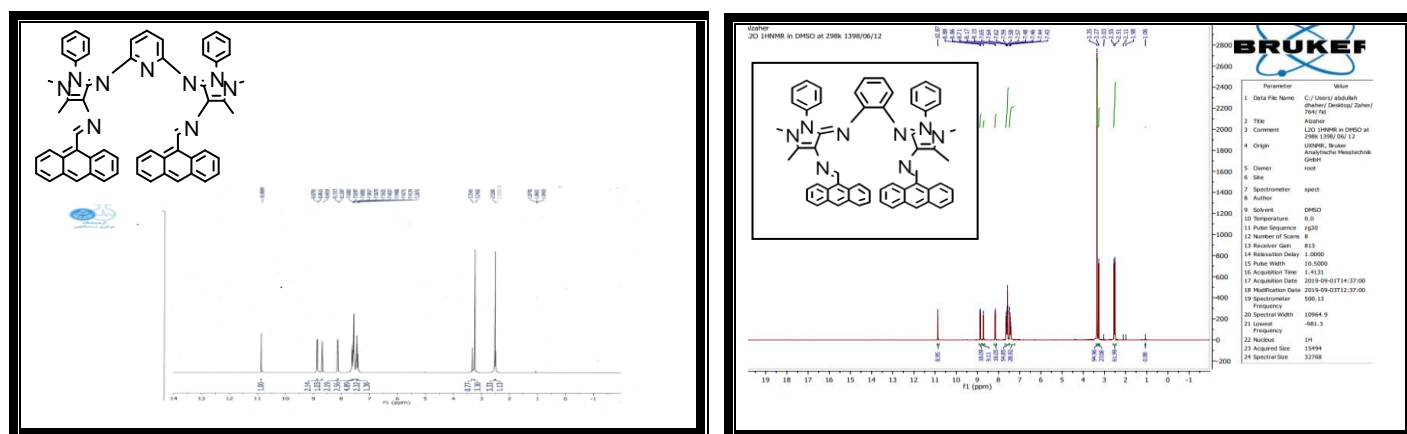


Fig. (1): ^1H -NMR spectrum the free ligands [L^1 and L^2] measured in DMSO-d_6 solvents.

Mass spectral fragmentation of the Schiff base ligands [L^1, L^2]:

The mass spectrum of Schiff bases (Fig.4) shows a base peak m/z at 855.38 and 853.39 which is due to the original

molecular weight of the prepared compounds (Schiff base) respectively. This means that the condensation of the reactant substances gave pure compound.

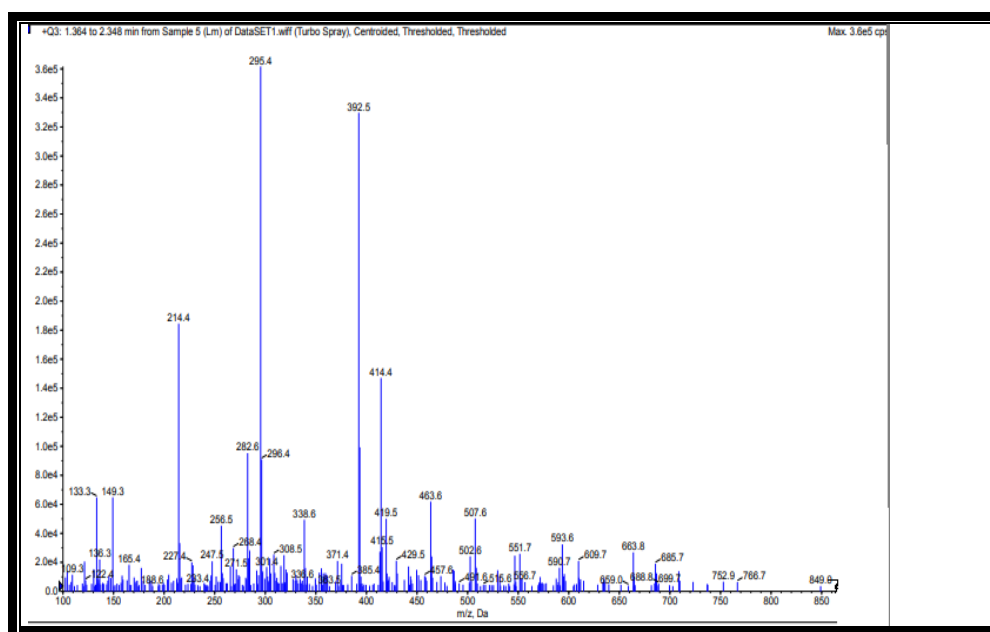


Fig.(2): mass Spectrum of ligand [L^2]

Thermal Decomposition:

The TGA thermal analysis curve for $[\text{Cd}(\text{L}^1)\text{Cl}_2]\text{H}_2\text{O}$ complex that revealed the complex is stable up to 145°C in Argon atmosphere. It is decomposed three steps. In the TGA curve, peak recognized at 263.01°C is related to the loss of $(\text{H}_2\text{O} + \text{H}_2)$ portions, (det. = 1.953 %, calc. = 1.999 %). The second step at 458.848°C that designated the loss of $(\text{C}_{29}\text{H}_{38}\text{N}_9)$ fragment, (obs. = 49.3043, calc. = 49.278). The third step at 595.623°C is related to the loss of $(\text{C}_6\text{H}_6 + \text{C}_6\text{H}_4)$ segments, (obs. = 7.59508 %, calc. = 7.50721%). The DSC analysis curve proved peaks at $(118.1, 222.9, 595.62)^\circ\text{C}$ refer to an endothermic decomposition process. Peaks Observed at 240 and 515°C were related to exothermic decomposition processes. The exothermic and endothermic peaks may demonstrate ignition of the natural ligand in an argon atmosphere. The last endothermic pinnacle may imply the ligand bond breaking.

Fluorescence spectra

The emission properties of the ligands and complexes have been studied by passing UV radiation of appropriate wavelength through these compounds in solution state (10^{-6} M Ethanol solution). Fluorescent colours under UV light are often easier to observe than a weak change in colour in an ordinary colour indicator⁽²⁸⁾. The emission spectra of the Schiff base (L^2) and its metal complexes are recorded in Ethanol at room temperature. L^2 exhibits a strong fluorescence emission at 447 nm with excitation at 224 nm . In contrast with fluorescence spectra of L^2 , partial fluorescence quenching phenomena are observed in its metal complexes with weak fluorescence emission at $440, 448\text{ nm}$ for complexes, respectively revealed that fluorescence emission intensity with transition metal ions. The reason for the weak fluorescence intensity with formation of metal complexes is due to decrease in electron density on Schiff

base⁽²⁹⁻³¹⁾. The decrease in emission maxima was in the order

of $L^2 > Co(II) > Cd(II) > Ca(II)$.

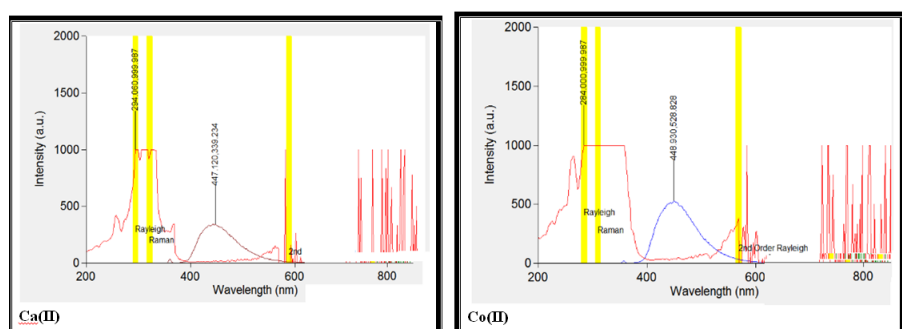


Fig.(3) Fluorescence spectra of Ca(II) and Co(II)

CONCLUSION

The preparation and characterization of Two Schiff base ligands L^1 and L^2 and their metal complexes are described. The preparation of two Schiff base ligands obtained by reaction of the precursor P^1 , P^2 with 9-anthracenecarboxaldehyde. The ligands complexes were by adding the L^1 and L^2 with metal salt in 1:1 mole ratio. physico-chemical and spectroscopic methods were implemented to confirm mode of bonding and over all structure of the complexes. The ligands and their complexes showed interesting fluorescence properties. These results lead to the preparation of six coordinate complexes.

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Table (1) Elemental microanalysis and some physical properties of the ligand prepared [L¹ and L²] complexes.

No.	Empirical formula	Wt. g/mol.	Yield %	colour	M.P °C	Microanalysis found, (Calc.) %				
						metal	Cl	C	H	N
1	[Ca(L ¹)Cl ₂]H ₂ O	967	73	black	275-280	4.14 (4.08)	7.33 (7.40)	70.80 (70.60)	4.69 (4.55)	13.04 (12.00)
2	[Mn(L ¹)Cl ₂]H ₂ O	982	68	Brown	238-240	5.60 (5.42)	7.22 (7.10)	69.72 (69.33)	4.62 (4.40)	12.84 (12.54)
3	[Cd(L ¹)Cl ₂]H ₂ O	1039	68	Yellow	255-260	10.82 (10.65)	6.82 (6.66)	65.87 (65.55)	4.36 (4.23)	12.13 (12.00)
4	[Co(L ¹)Cl ₂]H ₂ O	986	66	Brown	178-180	5.98 (5.66)	7.19 (7.06)	69.44 (69.25)	4.60 (4.40)	12.79 (12.40)
5	[Zn(L ¹)Cl ₂]H ₂ O	992	79	orange	300dec.	6.59 (6.30)	7.15 (7.00)	68.99 (68.70)	4.57 (4.33)	12.70 (12.33)
6	[Pd(L ¹)]H ₂ O	962	69	Brown	198-200	11.06 (11.00)	-	71.13 (71.00)	4.71 (4.55)	13.10 (13.00)

Table (2): FT-IR spectral data (cm⁻¹) of the ligand [L¹] and its metal complexes.

No.	compounds	$\nu(\text{C}=\text{N})$ imine	$\nu(\text{C}=\text{C})$ ar.	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$	Additional peaks
	[L ¹]	1639	1585	-	-	C-H _{ar.} =3068-3041v C-H _{ali.} =2918 v
1.	[Ca(L ¹)Cl ₂].H ₂ O	1641	1589	505		C-H _{ali.} =2922 v v OH=3408-3433
2.	[Mn(L ¹)Cl ₂]	1645	1550	563		C-H _{ali.} =2922 v
3.	[Cd(L ¹)Cl ₂]	1637	1587	515	327	C-H _{ar.} =3049 C-H _{ali.} =2922 v
4.	[Co(L ¹)Cl ₂]	1641	1566	503	325	C-H _{ali.} =2924 v
5.	[Zn(L ¹)Cl ₂].H ₂ O	1630	1514	519		C-H _{ali.} =2924 v vOH=3440
6.	[Pd(L ¹)]H ₂ O	1618	1491	509		C-H _{ali.} =2817 v vOH=3438

Table (3): FT-IR spectral data (cm⁻¹)

NO	compound	C=N imines'	C=O	M-N	M-Cl	Addition peaks
	[L ²]	1637	-	-	-	C-H _{ar.} =3043v (C-H _{ali.} =2918v(C=C) _{ar.} =1587v (
7	[Ca(L ²)Cl ₂].H ₂ O	1641		-		
8	[Mn(L ²)(H ₂ O)Cl]Cl	1641 1622		503		C-H _{ar.} =3051v(C-H _{ali.} =2922v (C=C) _{ar.} =1587v (OH)=3392 v (coordinate
9	[Cd(L ²)Cl ₂].H ₂ O	1939		563		C-H _{ar.} =3045v (C-H _{ali.} =2918v (C=C) _{ar.} =1587v (OH)=3438 v(hydrate
10	[Co(L ²)(H ₂ O)Cl]Cl	1627		536		(C-H) _{ali.} =2962v C=C) _{ar.} =1552v(OH)=3417 v (coordinate
11	[Zn(L ²)Cl ₂].H ₂ O	1639 1620		561		C-H _{ar.} =3047v(C-H _{ali.} =2920v (C=C) _{ar.} =1587v (OH)=3435v (hydrate
12	[Pd(L ²)]H ₂ O	1633		544		C-H _{ar.} =3043v (C-H _{ali.} =2925v(C=C) _{ar.} =1589v (OH)=343 v (hydrate

Table (4) Electronic spectral data of [L¹] and its complexes

NO	compound	λ (nm)	ν – (cm ⁻¹)	ϵ_{max} (molar ¹ cm ⁻¹)	Assignment	Suggested Structure
1	[Ca(L ¹)Cl ₂]H ₂ O	274 352 419	36496 28409 23866	2296 644 2019	Intra-ligand MLCT	Oh
2	[Cd(L ¹)Cl ₂]H ₂ O	274 424 689	36496 23584 14513	2335 2284 6	Intra-ligand 6A ₁ g→4T ₂ g(G) 6A ₁ g→4E _g (D)	Oh
3	[Mn(L ¹)Cl ₂]H ₂ O	274 424 498	37453 23584 20080	1562 443	Intra-ligand 6A ₁ g→4T ₂ g(G) 6A ₁ g→4T ₂ g(G)	Oh
4	[Co(L ¹)Cl ₂]H ₂ O	278 344 412 674	35971 32467 24271 14836	3711 2479 2357 51	Intra-ligand Intra-ligand 4T ₁ g→4T ₁ g(P) 4T ₁ g(F)→4T ₂ g(f)	Oh
5	[Zn(L ¹)Cl ₂]H ₂ O	272 301 404	36764 33222 24752	2443 2011 6	Intra-ligand Intra-ligand MLCT	Oh
6	[Pd(L ¹)]	276 419 889	36231 23866 11248	2443 2011 6	Intra-ligand 1A ₁ g→1E ₁ g 1A ₁ g→1B ₁ g	sq

Table (5) Electronic spectral data of [L²] and its complexes

No	Compound	λ (nm)	ν – (cm ⁻¹)	ϵ_{max} (molar ¹ cm ⁻¹)	Assignment	Suggested Structure
7	[Ca(L ²)Cl ₂]H ₂ O	273 301 419	36360 33222 23866	2274 2071 2165	Intra-ligand Intra-ligand MLC.T	Oh
8	[Mn(L ²)Cl ₂]H ₂ O	268 333 370 388 882	37313 30030 27027 25773 11337	1559 252 507 580 10	Intra-ligand Intra-ligand MLC.T MLC.T (6A ₁ g→4E _g (D))	Oh
9	[Cd(L ²)Cl ₂]H ₂ O	269 348 369 388	37174 28735 27100 25773	583 1664 614 753	Intra-ligand Intra-ligand MLCT	Oh
10	[Co(L ²)Cl ₂]H ₂ O	266 369 389 517 676	37593 27100 25706 19342 14792	1152 206 236 171 4	Intra-ligand MLC.T MLC.T 4T ₁ g(F)→4T ₂ g(F) 4T ₁ g→4T ₁ g(P)	Oh
11	[Zn(L ²)Cl ₂]H ₂ O	269 332 369 388	37174 30120 27100 25773	1625 322 600 704	Intra-ligand Intra-ligand MLCT MLTC	Oh
12	[Pd(L ²)]	273 394 721	36630 25380 13869	2122 1304 16	Intra-ligand MLCT 1A ₁ g→1E ₁ g	SP

Table (6) Fluorescence spectra of ligand [L²] metal complexes

No.	compounds	Excitation wavelength (nm)	Emission wavelength (nm)
1	[Ca(L ²)Cl ₂]	294	447
2	[Cd(L ²)(OH ₂)Cl]Cl	322	440
3	[Co(L ²)Cl ²]	284	448