

Synthesis And Characterization Of Schiff-Base Ligand Derivative From 4-Aminoantipyrine And Its Transition Metal Complexes

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الخلاصة

تضمن هذا البحث تحضير احد قواعد شيف وهو الليكاند الجديد (٤- (٤- ثنائي مثيل -امينو بنزليدين) امينو- [١،٥- ثنائي مثيل -٢- فنيل ١، ٢- ثنائي هايدرو -بيروزول -٣-ون) حيث تم تحضيره من خلال التفاعل بين المركب ٤-امينو انتبايرن مع ٤-ثنائي مثيل امينو بنزالديهيد في محلول الايثانول النقي كما حضرت اربع معقدات مع الليكاند الجديد وهي معقدات (Co(II)، Zn(II)، Cd(II)، Hg(II) إذ أجرى تشخيص هذه المعقدات بواسطة أطيف FTIR و UV-visible والتحليل الطيفي للعناصر وتم تعيين النسب المولية (M:L) والنسبة المئوية للعنصر بالمطيافية الذرية اللهيبي وقياس الحساسيه المغناطيسيه لهذه المعقدات.

Abstract

A new ligand 4-[(4-Dimethylamino-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one (L) was synthesized by the reaction of 4-aminoantipyrine with 4-Dimethylamino benzaldehyde in absolute ethanol . the complexes of Co(II), Zn(II) Cd(II) and Hg(II) with this ligand have been prepared. The characterization of ligand complexes are verify by elemental analysis, FT-IR, and UV/visible spectra. Beside, the determination of mole ratio M:L for complexe, determination of metal content M% by flame atomic absorption spectroscopy, molar conductance in absolute ethanol and magnetic moments (μ_{eff}) are presented.

Key Words: 4-[(4-Dimethylamino-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one, 4-Dimethylamino benzaldehyde, magnetic moments.

Introduction

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864 [1]. Schiff bases which are condensation products of primary amines and aldehydes or ketones ($RCH=NR/$), where R and R/ represent alkyl or aryl cycloalkyl or heterocyclic substituents [2]. They are represent valuable intermediates in organic synthesis and at the same time these compounds are used as fine chemicals and medical substrates [3].

Schiff bases play a central role as a chelating ligands in transition metal coordination to give complexes [4,5]. Schiff bases and their complexes have many applications in biological field [6,7], catalyst, complexion ability towards some toxic metals [8], and in medicine as antibiotics and anti-inflammatory agents [9].

An interesting application of Schiff bases is their use as an effective corrosion inhibition, it is based on their ability to spontaneously from a monolayer on the surface to be protected.

Experimental

Materials and Measurements

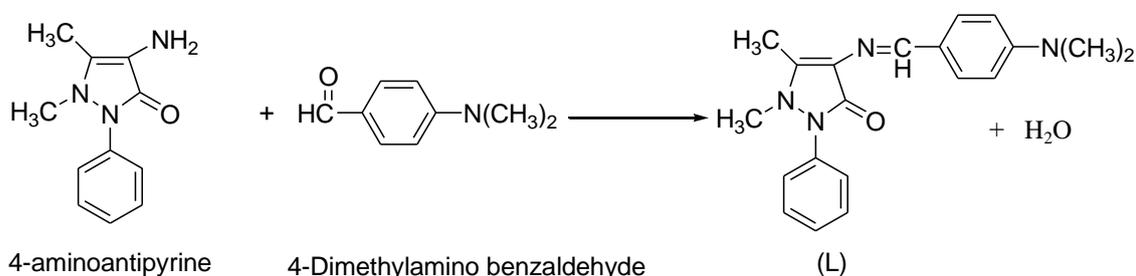
All chemical and solvents used in the present work were supplied by Merck, BDH, Fluka with high purity without more purification.

The FTIR spectra in the range (400 –4000) cm^{-1} were recorded as potassium bromide disc on FTIR 8400S Shimadzu Spectrophotometer (Japan). The UV-Visible spectra were measured in ethanol by using Shimadzu UV-Vis. (Japan). model 1650PC in the range (200 -1000) nm at room temperature . Magnetic susceptibility measurement for complexes were obtained at room temperature using Balances-Magnetic Susceptibility, Model MSB-Mk-1 . Melting point were used to measure the melting point of all the prepared compounds by stuart melting point. Elemental analysis (C.H.N) was obtained by using Elemental Microanalyzer, CHNS-analyzer, EA3000A . The molar conductance measurements were carried out in DMF solvent ($1 \times 10^{-3} \text{M}$) at room temperature by using conductivity meter ER 214. The metal percentage in the complexes was measured by using flam atomic absorption spectrophotometer, Shimadzu. AA-6300 .

Preparation Of The Ligand

A new the Schiff base ligand (L), was synthesized from the reaction of 4-aminoantipyrine with 4-Dimethylamino benzaldehyde in absolute ethanol (**Scheme 1**).

To a solution of (2 g, 10mmol) 4-aminoantipyrine dissolved in 25ml of absolute ethanol was added dropwise 4-Dimethylamino benzaldehyde (1.5 g , 10 mmol) dissolved in 25 ml of absolute ethanol with continuous stirring with adding a few drops of glacial acetic acid. This mixture was refluxed for (4hrs) .The precipitate was filtered and then cooled to room temp. The solid product was filtered off and recrystallized from ethanol. The physical properties and the spectral data were shown in **Table 1** and **2** respectively.



Scheme 1: Preparation Of Ligand(L)

Preparation Of The Metal Complexes

The metal complexes were prepared by adding a hot absolute ethanol solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and HgCl_2 (2mmol) to ethanolic solution of ligand (L) (2mmol) with Zn(II) Cd(II) and Hg(II) and (4mmol) with Co(II), then heating under reflux for 1 h. The reaction mixtures were concentrated to a small volume by evaporation. Precipitation complexes at coolies, after filtered and, washed with ethanol dried over CaCl_2 in a desiccators.

Results and Discussion

The structure of ligand preparer and its complexes were limited by different studies such as elemental analysis, IR spectra, electronic spectra, magnetic susceptibility measurements and molar conductivity. The ligand and its complexes are soluble in polar organic solvents, such as DMSO, THF and DMF.

The physical properties and elemental analysis are in agreement with the formula of the ligand and its complexes are given in **Table 1**. The analytical data show that the metal to ligand ratio in complexes is (1:2) with Co(II) and (1:1) with Zn(II) Cd(II) and Hg(II).

Table 1: Elemental Analysis And Some Physical Properties Of The Ligand And Its Complexes

No	Compounds	Color	M.P (Co)	Yield %	Molecular Formula	Found (Calc.)%				
						C	H	N	O	M
1	L	Brown	174	74	$\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}$	71.61 (71.83)*	6.51 (6.63)*	16.59 (16.75)*	4.63 (4.78)*	-
2	$[\text{Co}(\text{L})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$	Green	192	73	$\text{C}_{40}\text{H}_{46}\text{Cl}_2\text{N}_8\text{O}_3\text{Co}$	58.59 (58.83)*	5.54 (5.68)*	13.55 (13.72)*	5.45 (5.88)*	7.02 (7.22)*
3	$[\text{Zn}(\text{L})\text{Cl}_2] \cdot \text{H}_2\text{O}$	White- Yellow	197	75	$\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_2$ Zn	49.02 (49.15)*	4.79 (4.95)*	11.31 (11.46)*	6.42 (6.55)*	13.22 (13.38)*
4	$[\text{Cd}(\text{L})\text{Cl}_2] \cdot \text{H}_2\text{O}$	White- Yellow	202	64	$\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_2\text{Cd}$	44.67 (44.84)*	4.39 (4.52)*	10.38 (10.46)*	5.63 (5.97)*	20.79 (20.98)*
5	$[\text{Hg}(\text{L})\text{Cl}_2]$	White- Yellow	223	82	$\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{N}_4\text{O}_2\text{Hg}$	38.37 (38.52)*	3.74 (3.88)*	8.86 (8.98)*	2.43 (2.64)*	-

* Theoretical

The Infrared Spectra

The important infrared spectral bands for the synthesized ligand and its complexes are given in **Table 2** and **Figures 1, 2, 3, 4 and 5**. The spectrum of free ligand showed a two bands at (1650 and 1616) cm^{-1} assigned for $\nu(\text{C}=\text{O})$ of the carbonyl group and $\nu(\text{C}=\text{N})$ of the

azomethine group respectively. The bands at (1526 , 1498 , 1433), (3086 , 3027) and (2866, 2901) cm^{-1} were assigned to $\nu(\text{C}=\text{C})$, $\nu(\text{C}-\text{H})$ aromatic and $\nu(\text{C}-\text{H})$ aliphatic respectively.

The azomethine vibration of the ligand at 1616 cm^{-1} was shifted to lower frequencies after complexation, i.e.1581 , 1602, 1598 and 1597 cm^{-1} for Co(II) , Zn(II) Cd(II) and Hg(II) complexes, respectively. The $\nu(\text{C}=\text{O})$ band at 1650 cm^{-1} in the free ligand was moved to a lower frequency after complexation, this band exhibits at 1620 , 1632 , 1629 and 1632 cm^{-1} for Co(II), Zn(II), Cd(II) and Hg(II) complexes, respectively, which means that the shifts are due to coordination of ligand to metal atom by the azomethine nitrogen and carbonyl oxygen. The broad bands observed for complexes Co(II), Zn(II), Cd(II), and Hg(II) in the region $(3274 - 3353)\text{cm}^{-1}$ are due to the $\nu(\text{O}-\text{H})$ stretching of water [14-17].

The new bands at $(523 , 502 , 514 , 545)\text{cm}^{-1}$ and $(467 , 461 , 419 , 484)\text{ cm}^{-1}$ are due to the $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ for complexes Co(II), Zn(II) Cd(II) and Hg(II) respectively[15,18].

Table 2: The Important Infrared Spectral Bands For The Synthesized Complexes And Ligand

Compounds	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$ aromatic	$\nu(\text{C}-\text{H})$ aromatic	$\nu(\text{C}-\text{H})$ aliphatic	$\nu(\text{O}-\text{H})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
L	1650	1616	1526 1498 1433	3086 3027	2901 2866	-	-	-
[Co(L) ₂ Cl ₂].H ₂ O	1620	1581	1533 1466 1428	3066 3024	2900 2801	3353	467	523
[Zn(L)Cl ₂].H ₂ O	1631	1602	1533 1452 1402	3062 3000	2932 2803	3274	461	502
[Cd(L)Cl ₂].H ₂ O	1629	1598	1563 1491 1452	3076	2916 2802	3278	419	514
[Hg (L) Cl ₂]	1632	1597	1541 1465 1418	3071 3018	2909 2836	-	484	545

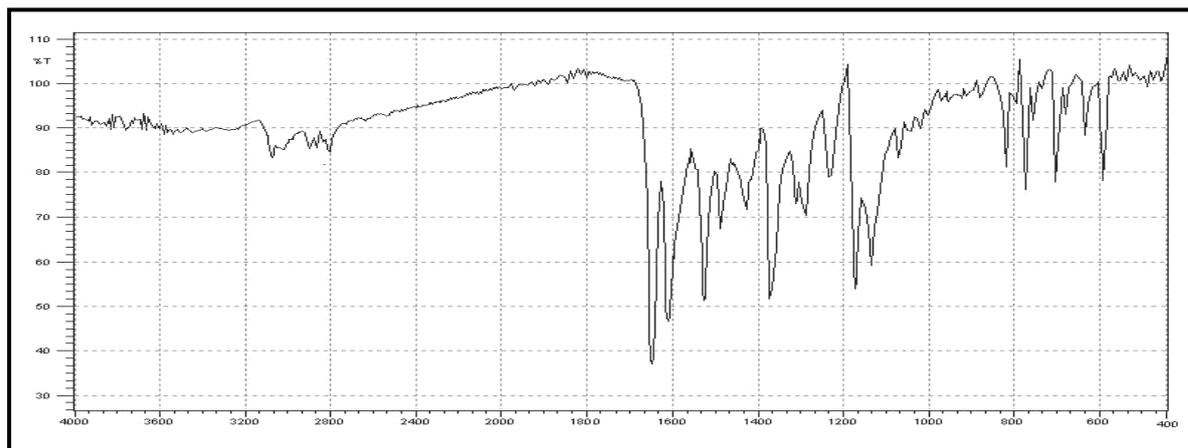


Fig. 1: Infrared Spectrum Of The Free Ligand (L)

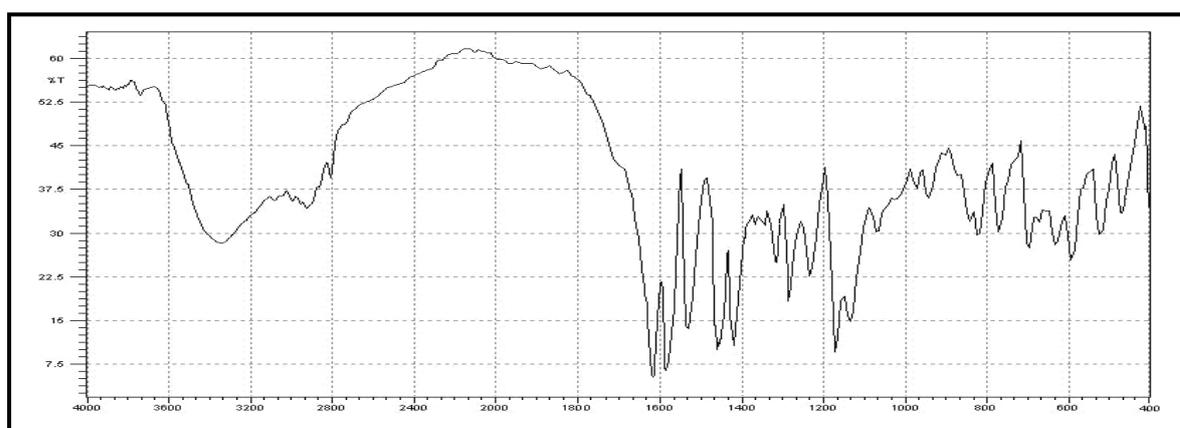


Fig. 2: Infrared Spectrum Of The Complex $[\text{Co}(\text{L})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$

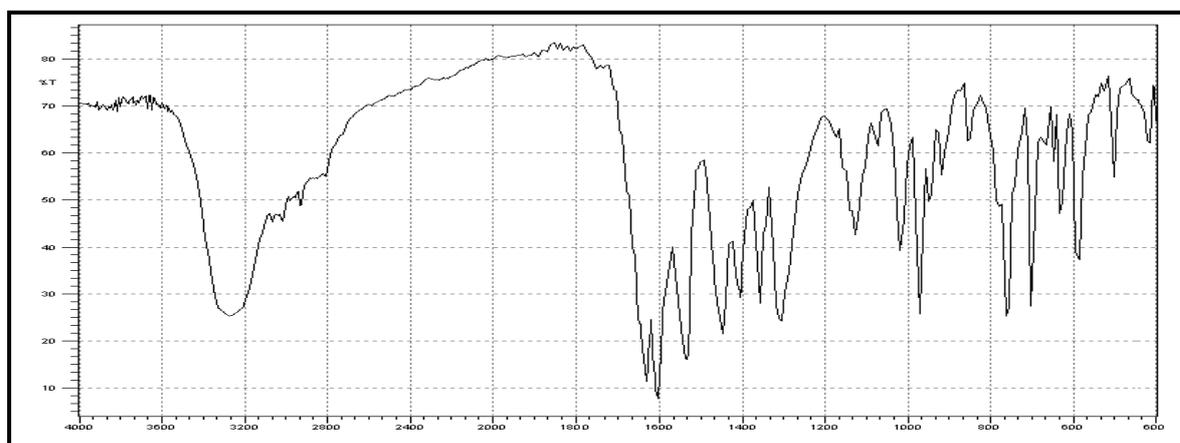


Fig. 3: Infrared Spectrum Of The Complex $[\text{Zn}(\text{L})\text{Cl}_2]\cdot\text{H}_2\text{O}$

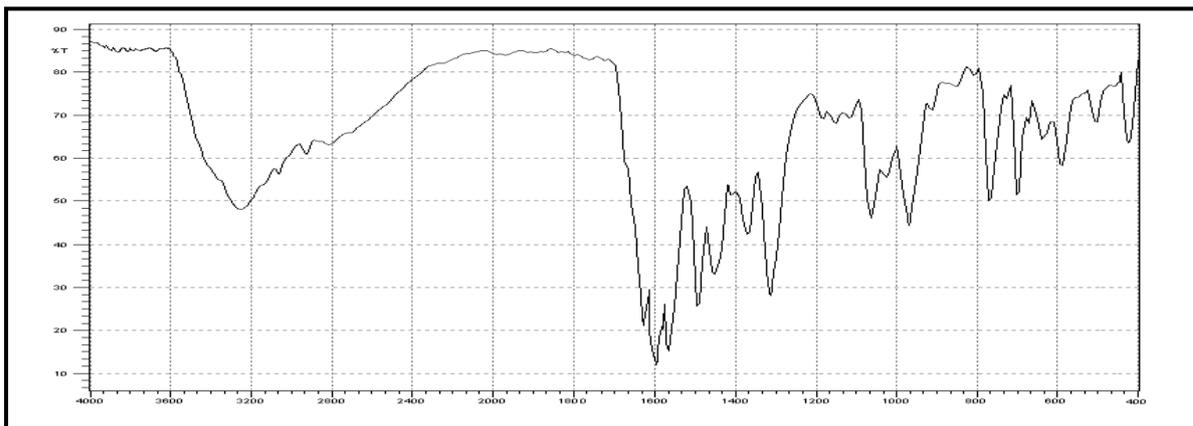


Fig. 4: Infrared Spectrum Of The Complex $[\text{Cd}(\text{L})\text{Cl}_2] \cdot \text{H}_2\text{O}$

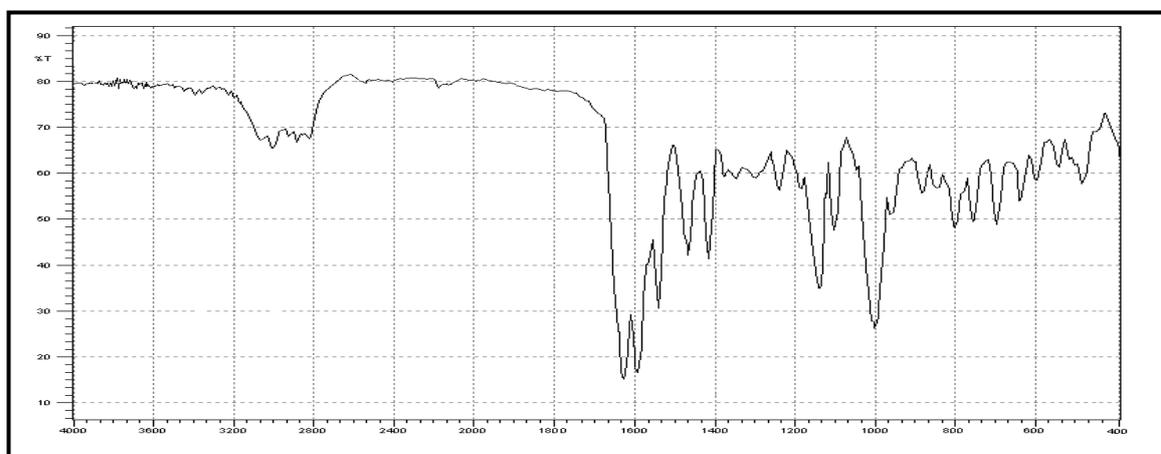


Fig. 5: Infrared Spectrum Of The Complex $[\text{Hg}(\text{L})\text{Cl}_2]$

Molar Conductivity Measurements

The molar conductance values of the synthesized Co(II), Zn(II), Cd(II) and Hg(II) complexes are in range from $(11.4\text{--}18.2 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1})$ in DMF solutions, indicating the non-electrolyte nature of these compounds. (8,18) Table 3 shows the molar conductance values of the complexes.

Magnetic Susceptibility And Electronic Spectra Measurements

The Magnetic moments and electronic spectra of the ligand and its complexes are showed in Table 3. The absorption spectra for of L in absolute ethanol, Figure 6 gives two bands at 244 and 345 nm. These bands can be attributed to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions [16,19]. The (Uv-Vis.) spectrum of Co(II) complex, Figure 7 exhibits three bands at 436, 605 and 658 nm, which may be assigned to the $4\text{T}_{1g} \rightarrow 4\text{T}_{1g} (\text{P})$, $4\text{T}_{1g} \rightarrow 4\text{A}_{2g} (\text{F})$ and $4\text{T}_{1g} \rightarrow 4\text{T}_{2g} (\text{F})$. The magnetic susceptibility measurement ($\mu_{\text{eff}} = 4.92 \text{ B.M.}$) This results with conductivity

measurements, molar ratio, atomic absorption and Elemental analysis measurements , which suggest octahedral geometry [20,21].

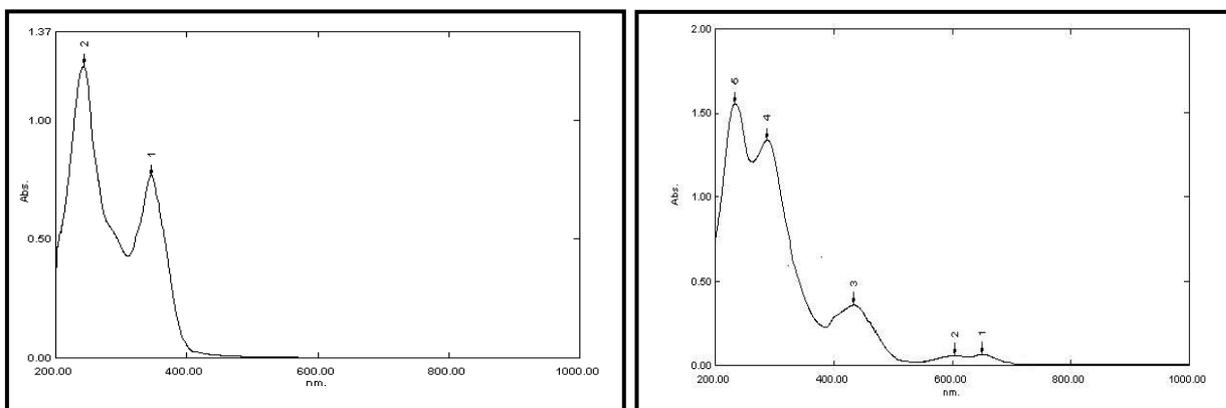


Fig. 6: Electronic Spectrum Of The Free Ligand **Fig.7:** Electronic Spectrum Of The Complex $[\text{Co}(\text{L})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$

The complexes of Zn(II) Cd(II) and Hg(II) are diamagnetic. The (Uv-Vis.) spectra for these complexes , **Figures 8, 9 and 10** show bands at 376, 386 and 368 nm, which may be attributed to charge transfer . This results with conductivity measurements, molar ratio, atomic absorption and Elemental analysis measurements which suggest tetrahedral geometry [8].

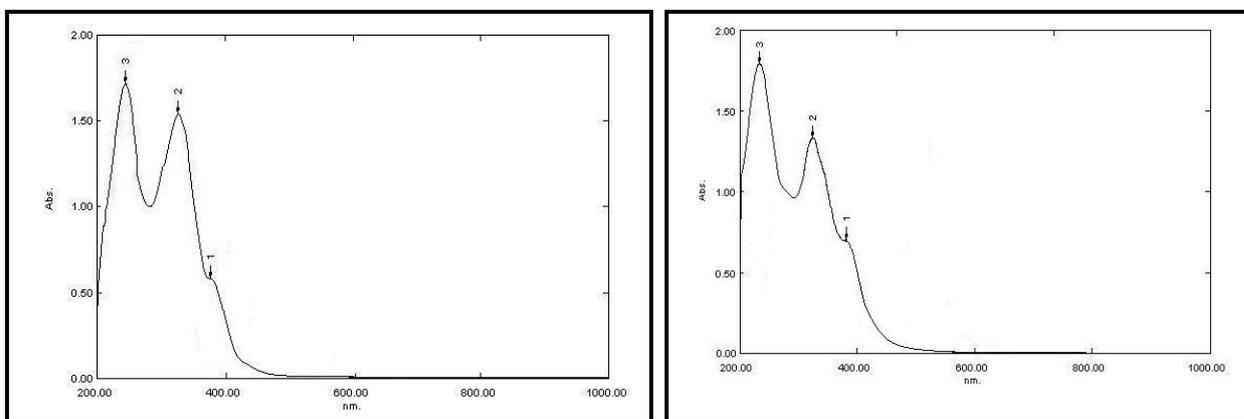


Fig. 8: Electronic Spectrum Of The Complex $[\text{Zn}(\text{L})\text{Cl}_2]\cdot\text{H}_2\text{O}$ **Fig. 9:** Electronic Spectrum Of The Complex $[\text{Cd}(\text{L})\text{Cl}_2]\cdot\text{H}_2\text{O}$

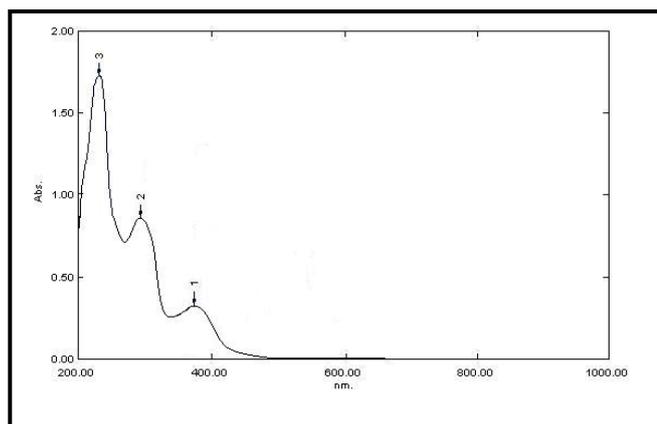


Fig.10: Electronic Spectrum Of The Complex $[\text{Hg}(\text{L})\text{Cl}_2]$

Table 3: Electronic Spectra , Magnetic Moments And Molar Conductivity Of The Complexes

No	Compounds	$\lambda(\text{nm})$	Transitions	μ_{eff} (B.M)	Conductivity $\text{Ohm}^{-1}.\text{cm}^2.\text{mole}^{-1}$	Geometry
1	L	244	$\pi-\pi^*$	-	-	-
		345	$n-\pi^*$			
2	$[\text{Co}(\text{L})_2\text{Cl}_2].\text{H}_2\text{O}$	436	$4\text{T}1\text{g} \rightarrow 4\text{T}1\text{g} (\text{P})$	4.92	17.7	octahedral
		605	$4\text{T}1\text{g} \rightarrow 4\text{A}2\text{g} (\text{F})$			
		658	$4\text{T}1\text{g} \rightarrow 4\text{T}2\text{g} (\text{F})$			
3	$[\text{Zn}(\text{L})\text{Cl}_2].\text{H}_2\text{O}$	376	Charge transfer	dia.	11.4	tetrahedral
4	$[\text{Cd}(\text{L})\text{Cl}_2].\text{H}_2\text{O}$	386	Charge transfer	dia.	15.6	tetrahedral
5	$[\text{Hg}(\text{L})\text{Cl}_2]$	368	Charge transfer	dia.	18.2	tetrahedral

Conclusions

The Schiff-base ligand coordinates to the Co(II) , Zn(II) Cd(II) and Hg(II) ions in bidentate manner using the azomethine nitrogen and carbonyl oxygen atoms. From the elemental analysis , Infrared and electronic spectra , magnetic susceptibility measurements flame atomic absorption spectroscopy and molar conductivity which suggest tetrahedral geometry to complexes Zn(II) Cd(II) and Hg(II) and octahedral to complex Co(II) (**Figure 11**) .

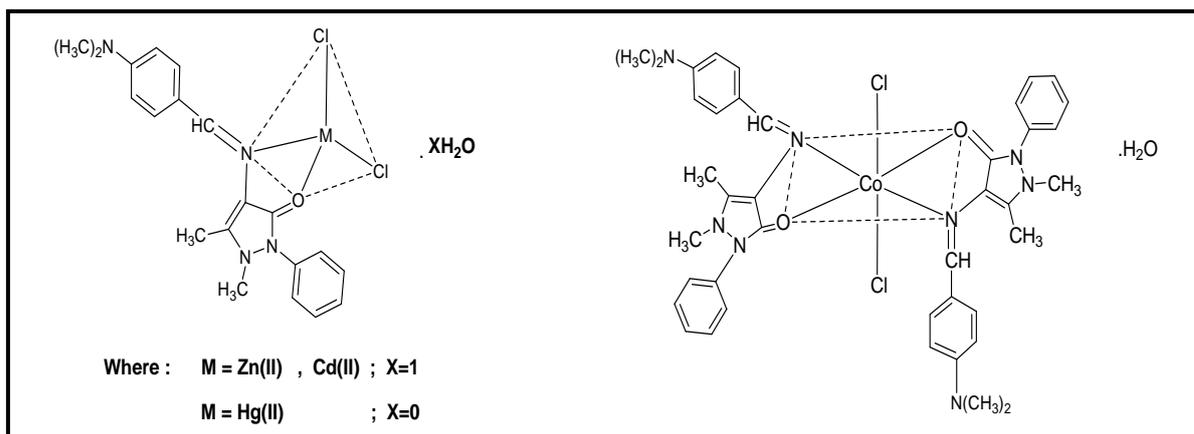


Fig. 11: The Proposed Chemical Structure Formula Of The Complexes

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