



## Preparation of New Schiff Base Derived from Cyclohexylamine with Piperonaldehyde and its $\text{Cu}^{+2}$ , $\text{Co}^{+2}$ and $\text{Rh}^{+3}$ Metal Complexes

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### ABSTRACT

A new ligand  $N$ -[( $E$ )-1,3-benzodioxol-5-ylmethylidene]cyclohexylamine ( $L_A$ ) having nitrogen and oxygen atoms was synthesized from cyclohexylamine with piperonaldehyde the yield was 75.8%. Metal complexes were synthesized were prepared by reaction of the new ligand with the copper (II), cobalt (II) as nitrate salts and with rhodium (III) as chloride salt. All the new compounds were characterized using different physico-chemical techniques including NMR spectrometry UV-Visible, magnetic susceptibility, IR spectroscopy, molar conductance, and Metal content. The paramagnetic copper complex and cobalt complex are proposed to adopt square planner and octahedral geometry respectively while diamagnetic rhodium complex shows octahedral geometry ,

**Keywords:** fusion; piperonaldehyde; cyclohexylamine; metal complexes.

### INTRODUCTION

Schiff bases are normally derived by condensation reaction of amine and aldehyde, the importance of these class of ligands is their coordination with metal ions via azomethine nitrogen<sup>1</sup>. The chemistry of the carbon-nitrogen double bond plays a vital role in the progresses of chemistry science<sup>2</sup>. A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., catalytic activity<sup>3</sup> and transfer of the amino group<sup>4</sup>, photochromic properties<sup>5</sup> and complexing ability towards some toxic metals<sup>6</sup>.

Schiff bases are used as ligands in the preparation of a number of industrial and biologically active compounds via ring closure, cycloaddition, and replacement reactions<sup>7</sup>, in addition to their biological activities such as antimicrobial<sup>8-11</sup>, antifungal<sup>12</sup>, antitumor<sup>12-15</sup>, and as herbicides<sup>16</sup>.

New Schiff base  $N$ -[( $E$ )-1,3-benzodioxol-5-ylmethylidene]cyclohexylamine ( $L_A$ ) was synthesized from the condensation reaction of cyclohexylamine with piperonaldehyde also three new transition metal complexes were synthesized by reacting the new Schiff base with  $\text{Cu(II)}$ ,  $\text{Co(II)}$  nitrate and  $\text{Rh(III)}$  chloride salts.

## MATERIAL AND METHODS

### Materials

Chemicals that have been used in this research are: Piperonaldehyde (Heliotropin) (BDH), Cyclohexylamine (BDH), Cupper(II) nitrate trihydrate (BDH), Cobalt (II)nitrate hexahydrate (fluka), Rhodium(III) trichloride hydrate (BDH). All chemicals were of analytical grade and were used as supplied without any further purification. Absolute ethanol (99.99%, BDH), dimethyl sulphoxide (DMSO) (99% BDH), Diethyl ether (fluka), glacial acetic acid (BDH), diethylether (fluka).

### Physical measurements

The infrared spectra of the prepared compounds were recoded using FT-IR-8300-Shimadzu, in the wave length range of (4000-400)  $\text{cm}^{-1}$ . Carbon, hydrogen, nitrogen and sulfur analyses were carried out using a Leco CHNS-932 analyzer. The electronic spectra of the prepared compounds were obtained using (UV-Vis-160A) Shimadzu Spectrophotometer, of wavelength (200-1100 nm) all prepared compounds were dissolved in (DMSO) at ( $10^{-3}$  M). The magnetic susceptibility values were obtained at room temperature using (Magnetic Susceptibility Balance), of Johnson mattey catalytic system division. The metals content of the complexes were measured using atomic absorption technique by Perkin-Elmer-5000. The molar conductivity measurements were carried out using Wissenschaftlich-Technisch Werk-statten 8120

Weilheim I.O.B, Drucker-Printer. Melting points were carried out using Gallen kamp M.F.B 600.01.

### Preparation of *N*-[(*E*)-1,3-benzodioxol -5-ylmethylidene]cyclohexan amine ( $L_A$ )

This ligand was prepared by fusion of a mixture of (1.5 g, 10 mmole) of piperonaldehyde and (1.1 ml, 10 mmole) of cyclohexylamine in crucible and heated on hot plate then few drops of glacial acetic acid were added as catalyst, A solid mass was formed which was washed with diethyl ether and recrystallized from ethanol then dried under vacuum oven at 30°C for two days. (Yield 75.8%, m.p 64 °C).

### Preparation of the metal complexes of [ $L_A$ ]

A Solution of (0.866 mmole) Copper nitrate trihydrate, Cobalt nitrate hexahydrate, Rhodium chloride monohydrate dissolved in (10 ml) of absolute ethanol was added to (1.731 mmole) of [ $L_A$ ] dissolved in (15 ml) of absolute ethanol. The mixture was refluxed with stirring for three hours, the resulting precipitate was filtered and washed with diethyl ether and recrystallized from hot ethanol then dried under vacuum at 40°C for two days. Yields: ca. 70-73.5%.

## RESULTS AND DISCUSSION

The new Schiff base, *N*-[(*E*)-1,3-benzodioxol-5-ylmethylidene]cyclohex- -anamine ( $L_A$ ) has been synthesized and characterized successfully. Different metal complexes were also

Table 1: Physical properties of the synthesized compounds

Compound	Colour	Yield%	Melting point (°C)± 1°C	% Found(calculated)				
				%C	%H	%N	%O	%M
$L_A$	Deep	75.8	64	70.19	7.54	6.16	13.84	-
$C_{14}H_{17}NO_2$	Brown			(73.44)	(7.81)	(5.71)	(13.04)	
$L_A Cu(II) [Cu(L_A)_2(ONO_2)(H_2O)].NO_3 \cdot 2H_2O$	Brownish green	72	139	54.08	5.67	7.47	24.97	9.52
$L_A Co(II) [Co(L_A)_2(ONO_2)_2(H_2O)_2] \cdot 2H_2O$	Gray	70	110	45.18	5.98	7.42	28.88	8.94
$L_A Rh(III) [Rh(L_A)_2(Cl_2)(H_2O)_2] \cdot Cl \cdot 3H_2O$	Reddish brown	73.5	198	46.02	5.96	3.97	12.39	13.85
			Dec.	(48.32)	(6.22)	(7.51)	(30.04)	(7.90)
			Dec.	(47.79)	(5.88)	(3.72)	(14.85)	(13.65)

Dec. = Decompose

prepared successfully by reacting metal ions salts Cu(II), Co(II) and Rh(III) with the new ligand.

All the physical data of the prepared ligand ( $L_A$ ) and its metal complexes and the expected formula of the synthesized complexes are shown in Table 1. The data in this table appeared to be near to the predicted formula and the structure to all the synthesized compounds.

#### Infra-Red spectra

The F.T.IR spectra of the ligand [ $L_A$ ], showed the absence of carbonyl  $\nu(C=O)$  band

at ( $1690\text{ cm}^{-1}$ ) and the absence of two bands at ( $3400\text{ cm}^{-1}$ ) and ( $3340\text{ cm}^{-1}$ ) due to asymmetrical and symmetrical of  $\nu(NH_2)$  stretching vibration<sup>62</sup> of starting material, and a strong new band appeared at ( $1639\text{ cm}^{-1}$ ) assigned to azomethine  $\nu(C=N)$  linkage which is shifted to lower frequencies in the spectra of all the complexes ( $1616-1608\text{ cm}^{-1}$ ) indicating that coordination may took place through nitrogen of azomethine group<sup>75, 82</sup>. For the  $L_A$ Cu metal complex, three bands were absorbed at ( $1379, 1328$  and  $995\text{ cm}^{-1}$ ) refer to coordination of nitrate group ( $NO_3^-$ ) to the metal atoms, and sharp band appeared at ( $1762\text{ cm}^{-1}$ ) indicate the presence

**Table 2: The most significant bands of F.T.IR spectra of [ $L_A$ ] and its metal complexes in ( $\text{cm}^{-1}$ )**

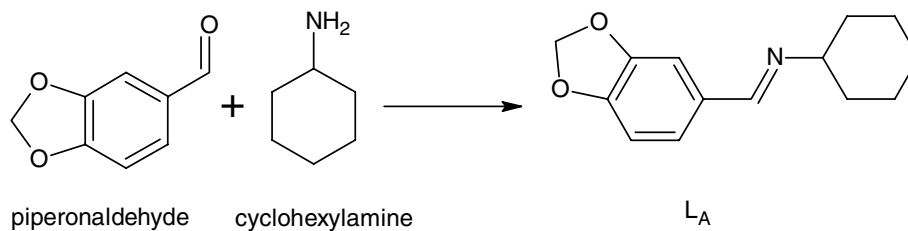
Symbol	$\nu(C=N)$	$\nu(C-O-C)$	$\nu(C-H)$ Alkyl ring	$\nu(C=C)$ Arom.	$\nu(C-H)$ Arom.	$\nu(M-N)$	$\nu(M-O)$
$L_A$	1639	(1035) (1255)	2850	1600	2925	–	–
$L_A$ Cu(II)	1608	(1035) (1259)	2981	1525	3002	453	426
$L_A$ Co(II)	1608	(1035) (1259)	2983	1525	3002	451	406
$L_A$ Rh(III)	1616	(1033) (1253)	3020	1596	3072	547	457

**Table 3: Uv/Vis Data for Schiff Bases and Their Metal Complexes**

Compound	$\lambda_{\text{max}}$ ( $\log \epsilon$ ) (nm)
$L_A$	348(1.5), 322(3.0), 249(0.05)
$L_A$ Cu(II)	622( 0.06), 283(0.45)
$L_A$ Co(II)	725 (0.03), 493( 3.0)
$L_A$ Rh(III)	909( 0.01), 487( 0.4), 361(1.8)

**Table 4: Magnetic moments, Conductivity and Suggested Structures for Complexes of  $L_A$  in ( $10^{-3}\text{ M}$ ) DMSO solvent**

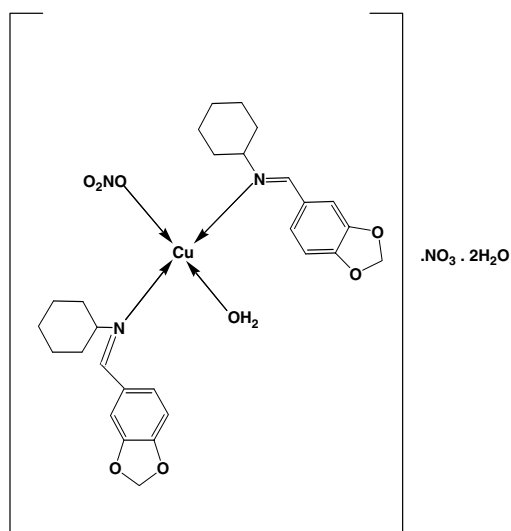
Complex	Magnetic moment $\mu_{\text{eff.}}$ (B.M.)	Conductivity $\mu\text{S.cm}^{-1}$	Suggested structure
$L_A$ Cu(II)	1.21	48.5	Square planar
$L_A$ Co(II)	4.92	20.0	Octahedral
$L_A$ Rh(III)	Diamagnetic	42.9	Octahedral



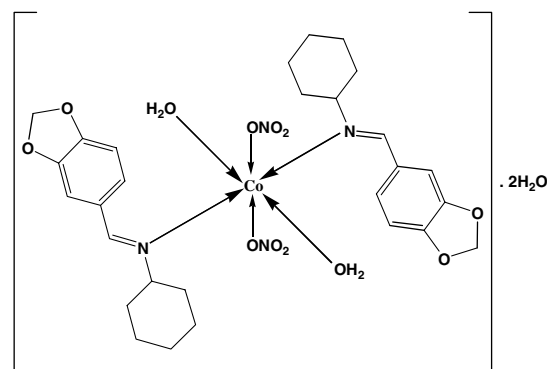
**Scheme 1: Condensation Reaction to Form L<sub>A</sub>**

of nitrate ion ( $\text{NO}_3^-$ ) out of the coordination sphere in the structure<sup>25</sup>, furthermore the appearance of new weak low frequency bands around 511, 451, 547  $\text{cm}^{-1}$  which are due to  $\nu(\text{M-N})$ <sup>19</sup>, And another bands

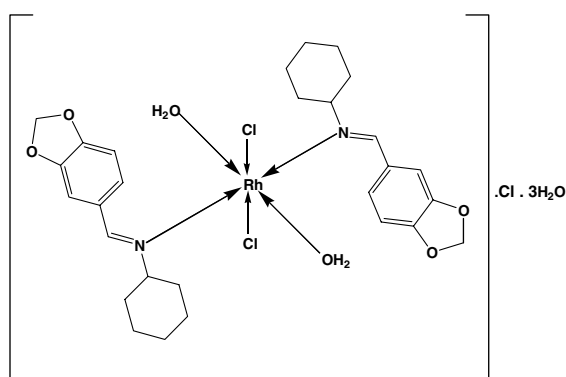
observation at (426, 406  $\text{cm}^{-1}$ , 457  $\text{cm}^{-1}$ ) indicated the participation of oxygen in the complexes ( $\text{M-O}$ )<sup>25,26</sup>. A medium sharp band which appeared at (784  $\text{cm}^{-1}$ , 846  $\text{cm}^{-1}$ , 887  $\text{cm}^{-1}$ ) indicate the presence



**Fig. 1: Sq. planner Cu(II) complex**



**Fig. 2: Octahedral Co(II) complex**



**Fig. 3: Octahedral Rh(II) complex**

of  $\text{H}_2\text{O}$  in the lattice molecules of the structure of prepared complexes<sup>(25)</sup>. Also broad band which appeared at (3539  $\text{cm}^{-1}$ , 3606  $\text{cm}^{-1}$  and 3483  $\text{cm}^{-1}$ ) refer to the presence of water molecules out of the coordination sphere in the structure of prepared complexes<sup>(25, 27)</sup> Table (2) shows the most characteristic bands of [L<sub>A</sub>] and its metal complexes

#### Study of the electronic spectra Magnetic susceptibility and conductivity measurements

Electronic spectral studies of compounds were carried out in DMSO solution ( $1 \times 10^{-3}$  M). The ligand shows three bands in UV and visible region (348, 322 and 249 nm) which can be attributed to

( $\pi-\pi^*$ ) transition for the aromatic system, ( $\pi-\pi^*$ ) transition of imines group and ( $n-\pi^*$ ) transition<sup>28</sup> which was shifted to a longer wavelength (red shift) upon formation of the complexes. This shift attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion ( $N:-M$ )<sup>29</sup>.

The ( $L_A$ Cu) complex show a broad band at (622 nm) which can be assigned to  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions, this band refers to highly distorted octahedral geometry (Jahn-Teller distortion)<sup>30</sup>. The magnetic moment value is (1.21 B.M) lower than 1.73 B.M which is indicated the formation of square planar geometry<sup>31</sup>. Conductivity measurements shows that the complex is ionic. Electronic spectra of cobalt (II) complex shows three transitions and great overlapping of them<sup>30</sup>, three transitions were noticed with octahedral geometry of Co (II) complexes<sup>32</sup>. In the this work two bands appear; one at (725 nm) and the other at (493 nm) which were assigned to the d-d transitions and LMCT respectively.

The magnetic moment of the ( $L_A$ Co(II)) complex was (4.92 B.M), which show the complex to be paramagnetic and have three unpaired electrons indicating a high-spin octahedral configuration<sup>(34)</sup>. The formula was further confirmed to be non-ionic by conductivity measurement. 909( 0.01), 487( 0.4), 361(1.8 )

The electronic spectra of ( $L_A$ Rh(III)) complex, shows a broad band at 909 nm, 487 nm and 361 nm which can be assigned to [ ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ,  $\nu_2 {}^1A_{1g} \rightarrow {}^1T_{2g}$ , and  ${}^1A_{1g} \rightarrow {}^3T_{1g}$ ] transitions which agreed with low spin and octahedral geometry for this complex<sup>34, 35</sup>.

Rhodium(III) complex is diamagnetic and the conductivity measurements shows that the complex is ionic. Table (3) shows electronic spectra of the prepared compounds and Table (4) shows molar conductivity measurements and the suggested structure for each complex. The expected structures for the metal complexes are shown in Figures 1, 2 and 3.

## CONCLUSION

Prepared, isolation, and characterization of a new Schiff base derived from piperonaldehyde, and its metal complexes of Cu(II), Co(II) and Rh(III). It is tentatively proposed that the Schiff base ligand coordinates through the nitrogen of the azomethine group. Based on the above observations of F.T.IR, UV-Vis spectroscopy, metal analysis spectrophotometer, conductivity magnetic susceptibility measurements and solubility in common organic solvents, the propose structures are the square planar geometry structure to Cu(II) and distorted octahedral structures for Co(II) and Rh(III). The novel Schiff base and the new metal complexes expected to show activity against bacteria fungi and cancer cells.

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