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Synthesis, characterization and biological studies of schiff bases derived from piperonal and their complexes with cobalt (II)

Mouayed Yousif Kadhum and Abduljleel Mohammed Abduljleel*

Department of Chemistry, College of Education for pure sciences, University of Basrah, Basrah, Iraq

ABSTRACT

Three new Schiff base ligands derived from piperonal and diamine compounds(ethane-1,2-diamine, propane-1,3diamine, butane-1,4-diamine) have been synthesized. These ligands were treated with Co(II) chloride with a metal : ligand ratio of 1:1 to afford the three new complexes $[CoL^{1}(H_{2}O)_{2}]Cl_{2}$, $[CoL^{2}(H_{2}O)_{2}]Cl_{2}$ and $[CoL^{3}(H_{2}O)_{2}]Cl_{2}$. These ligands and complexes have been characterized by techniques like IR, NMR, UV visible absorption, atomic absorption, molar conductance, molecular weight determination and magnetic measurements. The data shows that the ligands are bidentate and the linked sites are two azomethine nitrogen. The complexes are suggested as electrolytes paramagnetic, compounds and they have coordination number equal four. The ligands and metal complexes were screened for their antimicrobial activities against gram positive bacteria and gram negative bacteria. They were found to biologically active.

Key words : Schiff bases, Transition metal complexes, piperonal, diamine compounds, antibacterial activity.

INTRODUCTION

Schiff bases having the general structure R-CH=N-Ar. Where R and Ar are aliphatic or aromatic groups result from the condensation of primary amines with aldehydes or ketones⁽¹⁾ []. They are characterized by (-N=CH-) groups which have biological activities such as antimicrobial^(2,3), antifungal⁽⁴⁾ and anticancer⁽⁵⁾.

Schiff bases derived from aldehydes and diamines constitute one of the most relevant synthetic ligand systems with importance in asymmetric catalysis. They appear to be of importance for a broad range of transition metal catalyzed reactions including lactide polymerization⁽⁶⁾, epoxidation of olefins⁽⁷⁾, hydroxylation⁽⁸⁾ and asymmetric ring opening of epoxides⁽⁹⁾.

The chelating Schiff base ligands derived from diamines and various carbonyl compounds, encompass a highly remarkable class of compounds having a wide range of applications in catalytic⁽¹⁰⁾, synthetic⁽¹¹⁾, analytical⁽¹²⁾, clinical⁽¹³⁾, and biochemical⁽¹⁴⁾ areas and they possess considerable physiological activities⁽¹³⁾. A perusal of earlier work revealed that the coordinating possibility of diamine compounds such as 1,4 – butanediamine is enhanced by condensing with a variety of carbonyl compounds. But the literature survey show that no work has been done on the transition metal complexes of the Schiff base derived from some diamine and piperonal.

The aim of the present study, is to synthesis of Schiff bases which are based on the condensation of piperonal with some aliphatic diamine and then prepare their complexes with cobalt (II) ion. These Schiff bases and complexes are identified by IR, UV/vis., ¹HNMR, ¹³C.NMR and atomic absorption techniques. This study also include investigation on conductivity, magnetic properties and antibacterial activities.

MATERIALS AND METHODS

Physical measurements

All reagents were used without purification and supplied by Merck. Melting points were determined in a electro thermal fisher apparatus. The IR spectra were recorded in the range $400 - 4000 \text{ cm}^{-1}$ by KBr pellet using FTIR – 8400 S – Shimadzu spectrometer. ¹HNMR spectra in CDCl₃ were recorded on NMR spectrophotometer (Brucker – 400 MHZ). conductance was measured in DMF at room temperature using Jenway Pcmb conductivity meter. The UV visible spectra in THF were recorded on SPV – 725 (Germany) spectrophotometer. The molar ratio of metal – ligands was determined by atomic absorption apparatus (AAnalyst200AtomicAbsorptionSpectrometer). The magnetic measurements were made at room temperature by the Guoy method using Hg[Co(NCS)₄] as calibrant

Synthesis of Schiff base ligands

The Schiff base ligands (L^1, L^2, L^3) were synthesized by mixture of piperonal (3.0028 gm, 20mmol) and diamine (10mmol) in ethanol in the presence of some drops of glacial acetic acid. The mixture was refluxed for 2 –3 hrs. TLC examination suggested the complete conversion of starting materials to the Schiff bases. On cooling, 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 Figure (1) and some physical properties were listed in tables (1).



Figure (1):Chemical structure of the prepared Schiff base ligands

Table (1) : Some physical properties of prepared Schiff base ligands

Symbol	Molecular formula	Physical state	Time of reactoin	Melting poiunt (°C)	yield (%)
L^1	C ₁₈ H ₁₆ N ₂ O ₄	White crystal	2	181-183	88
L^2	C ₁₉ H ₁₈ N ₂ O ₄	White crystal	3	129-131	84
L ³	C ₂₀ H ₂₀ N ₂ O ₄	White crystal	3	147-149	86

Table (2) : Solubility of prepared Schiff base ligands

Symbol	ethanol	methanol	acetone	hexane	chloroform	Petroleum ether	CH ₂ Cl ₂	benzene	butane	acetonitrile	THF	DMF	DMSO	H_2O
L^1	±	Ŧ	±	-	+	-	+	+	+I	±	+	+	+	-
L^2	+	±	+	±	+	-	+	+	+	+	+	+	+	-
L^3	±	±	+	-	+	-	+	+	+	+	+	+	+	-

Where : + soluble , \pm partial soluble , - in soluble

Synthesis of Co(II) Complexes

All cobalt complexes were synthesized by the following method. A hot methanolic solution of the cobalt(II) chloride hexa hydrated was mixed with a hot methanolic solution of Schiff base ligand in the (1:1 molar ratio). The reaction mixture was refluxed on a water bath for limited time. On cooling the reaction mixture at room temperature, the

colored complexes precipitated out. The complexes were filtered and recrystallized, washed with methanol and dried under vacuum .The suggested structure for the prepared complexes was given in Figure (2) and Some physical properties were shown in tables (3,4).





Table (3) : Some physical properties of prepared complexes

Symbol	formula	Physical state and colour	Time of reactoin	Melting poiunt (°C)	yield (%)
L ¹ Co	$[Co(L^1) (H_2O)_2] Cl_2$	Green powder	9	296-294 °C	66
L ² Co	$[Co (L^2) (H_2O)_2] Cl_2$	Blue powder	20	260-258 °C	68
L ³ Co	$[Co (L^3) (H_2O)_2] Cl_2$	Green powder	2	298-296 ℃	66

Table (4) : Solubility of prepared complexes

formula	DMSO	THF	DMF	acetone	chloroform	CH ₂ Cl ₂	ethyl acetate	hexane	acetonitrile	benzene	H ₂ O
$[Co(L^1) (H_2O)_2] Cl_2$	+	-	+	-	-	±	-	-	+	+	-
$[Co (L^2) (H_2O)_2] Cl_2$	+	-	+	-	±	-	-	-	±	-	-
$[Co (L^3) (H_2O)_2] Cl_2$	+	-	+	-	-	±	+	-	+	-	-

RESULTS AND DISCUSSION

IR spectra of the ligands and complexes :

The IR absorptions of the ligands and their complexes are given in table (5) and figures (3-8). The most signification differences in the IR spectra of the ligands (L^1, L^2) and complexes (L^1Co, L^2Co) was the shift of C=N stretching frequencies to lower frequencies due to metal – ligand coordination^(15,16). The azomethine vibration of the ligand (L^3) at 1643 cm⁻¹ was shifted to a higher frequencies in the complex (L^3Co) because of back bonding and decreasing the planar property of after complexation^(17,18). The absorption bands in the spectra of complexes $(L^1Co), (L^2Co)$ and (L^3Co) at 3400cm⁻¹, 3400cm⁻¹ and 3047cm⁻¹ respectively were attributed to OH absorptions which show that they contain water molecules.

Table (5) : Characteristic IR bonds of the ligands and the complexes

Symble	v _{C-H} Alph cm ⁻¹	v _{C-H} Arom cm ⁻¹	v _{HC=N} cm ⁻¹	v_{C-O} cm ⁻¹	$\begin{matrix} \nu_{C==CAr} \\ cm^{-1} \end{matrix}$	ν _{OH} cm ⁻¹	v _{M-H2O} cm ⁻¹
L^1	2837m	3008w	1641s	1255s	1500s		
L^2	2819m	3200w	1651s	1255s	1500s		
L ³	2951m	3072w	1643s	1255s	1500s		
L ¹ Co	2850w	3100w	1625s	1267s	1504m	3400b H ₂ O	1111m
L ² Co	2916vw	3057vw	1633s	1267s	1496m	3047b H ₂ O	1112w
L ³ Co	2883m	3100m	1650s	1253s	1500s	3400b H ₂ O	1097m



Figure (3) : I.R Spectrum of the ligand (L¹)



Figure (4) : I.R Spectrum of the ligand (L^2)



Figure (5) : I.R Spectrum of the ligand (L³)



Figure (6) : I.R Spectrum of the ligand L^1Co



Figure (7) : I.R Spectrum of the complex (L²Co)



Figure (8) : I.R Spectrum of the complex (L³Co)

UV - Visible spectra of the ligands and complexes :

The UV – Visible spectral data of the ligands and their complexes are given in table (6) and figures (7-12). The aromatic band of the ligands L^1 , L^2 and L^3 at 232 nm, 230 nm and 228 nm respectively is attributed to phenyl of piperonal $\pi \rightarrow \pi^*$ transition⁽¹⁹⁾. The azomethine group in these ligands was appeared two bands is due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions^(20,21).

These two bands were shifted to longer wavelengths in the complexes. The spectra of complexes (L^1Co) , (L^2Co) and (L^3Co) show the appearing newer two bands in longer wavelengths (visible region) are assigned to d – d transitions of the metal ion⁽²²⁾. and metal – ligand charge transfer (MLCT) bands^(23,24).

Table (6) :	Electronic s	pectral data	for the	ligands	and their	· complexes
				0		

Compound	(π–π*) (nm) phenyl Cycle	-C==N- (nm) (π—π *)	-C==N- (n—π*) (nm)	(nm) (C—T)	(dd) (nm)
L^1	232	273	300		
L ¹ Co	233	263	318		500
L^2	230	268	304		
L ² Co	231	272	310	500	620
L^3	228	269	305		
L ³ Co	233	285	317	450	610



Figure (7) : UV spectrum of the ligand (L¹)



Figure (8) : UV -Visible spectral of the complex (L¹Co)



Figure (9) : UV spectrum of the ligand (L^2)



Figure (10): UV -Visible spectrum of the complex (L²Co)



Figure (11) : UV spectrum of the ligand (L³)



Figure (12): UV -Visible spectral of the complex (L³Co)

¹H, ¹³C – NMR spectra of the ligands

The H¹ – NMR spectra of the ligands L¹, L² and L³ were recorded in CDCl₃. Using 500 MHZ, and it showed a number of characteristic signals of the ligands as shown in table (7) and figures (13-15). The peaks observed in the range $\delta = 3.8 - 3.6$ ppm and $\delta = 1.95 - 1.8$ ppm were assigned to the methylinic protons of the alkane diamine moiety of the ligand⁽²⁵⁾. The singlet peak at $\delta = 6$ ppm was assigned to the protons of O – CH₂ –O group of the piperonal present in the ligands⁽²⁶⁾. The signals due to the aromatic protons were observed in the range $\delta = 8.2 - 5.9$ ppm. The peak observed in the range $\delta = 8.2 - 8.1$ ppm was assigned to the azomethine protons in the molecule^(27,28). C¹³ – NMR data of ligands were correspondent with H¹ – NMR data indicated above as shown in table (8) and figures (16-18), and that confirm the proposed structure of the ligands.

protons	Chemical shift δ (ppm)							
protons	L^1	L^2	L^3					
C ₁	8.1	8.1	8.2					
C2	7.25	7.25	7.4					
C3	7	7	7.2					
C4	6.7	6.75	6.8					
C ₅	5.9	5.9	6					
C ₆	3.75	3.6	3.6					
C ₇		1.95	1.8					

Table (7): chemical shift of ¹H-NMR for the ligands

Table (8) : chemical shift of ¹³C-NMR for the ligands

Symbol	Chemic	al shift δ	(ppm)
Symbol	L^1	L^2	L^3
C ₁	162.7	160.3	160.8
C ₂	149.7	149.7	149.6
C ₃	148.2	148.2	148.2
C ₄	132.06	131.2	131.1
C5	124.3	124.1	124.1
C ₆	108.3	106.5	108.3
C ₇	106.5	106.3	106.9
C ₈	102.3	102.3	102.1
C9	61.4	58.9	61.2
C ₁₀		32.08	28.7



Figure (13) : H^1 – NMR spectrum of the ligand (L^1)



Figure (14) H^1 – NMR spectrum of the ligand (L^2)



Figure (15) : H^1 – NMR spectrum of the ligand (L^3)



Figure (16) : C^{13} – NMR spectrum of the ligand (L^1)



Figure (17) : C^{13} – NMR spectrum of the ligand (L^2)



Figure (18) : C¹³ – NMR spectrum of the ligand (L³)

General properties of complexes

Atomic absorption data, molar conductivities, molecular weight and magnetic susceptibilities are listed in tables (9).

The reaction of the ligands L_1 , L_2 and L_3 with salt of Co(II) ion was 1:1 molar ratio for giving metal complexes as evidenced by atomic absorption measurements. Molar weight of the complexes (L¹Co), (L²Co) and (L³Co) was calculated by (Rast's Camphor Method) ⁽²⁹⁾ indicating that practical data were in good agreement with the suggested general formula of complexes. The molar conductivities of the complexes were measured by johns and brad ^(30,31) show methoat room temperature (1x10⁻³ M) in DMF. The molar conductance values of the complexes were high indicating that all the complexes behaved electrolytes presence of chorine ions outside the coordination sphere. This result was confirmed from the chemical analysis, where chloride ions give precipitate by addition of AgNO₃ solution⁽³²⁾ magnetic moment µeff of the ligand complexes was measured by Faraday method ⁽³³⁾ at room temperature. The µeff values for the complexes (CoL¹), (CoL²) and (CoL³) were 1.654 B.M, 1.721 BM and 2.468 B.M respectively indicating that complexes (L¹Co), (L²Co) are square planar geometry⁽³⁴⁾ while (L³Co) is tetrahedral⁽³⁵⁾.

 $Table \ (9): \underline{molecular} \ weight \ , \ molar \ conductivity \ , \ magnetic \ measurements \ and \ atomic \ absorption \ data \ of \ the \ complex$

		M.w	t	Moler	Metal %			Atomia magnetia	
Symbl.	Formula	Cam Met	phor hod	conductivity	found	Calcul	M:L ratio	susceptiblity	µeff (B.M.)
		found	Calcul	Onni .cm /moi				AA.10	
L ¹ Co	$[Co(L^1)(H_2O)_2] Cl_2$	488.25	489.97	269.72	12.02	11.9	1:1	1146.74	1.654
L ² Co	$[Co (L^2)(H_2O)_2] Cl_2$	504.1	503.99	119.35	11.69	11.57	1:1	1240.12	1.721
L ³ Co	$[Co (L^3)(H_2O)_2] Cl_2$	518.02	517.94	164.78	11.37	11.3	1:1	2553.49	2.468

Antibacterial activity of the ligands and complexes

Antibacterial activity of Schiff base ligands and their complexes was evaluated against gram positive and gram negative bacteria as shown in table (10). The data were indicated that all ligand showed high activity compared to the complexes due to the chalation hold the azomethine groups in complexes by coordination bonds with metal ion leading low inhibition in biological activity. The order of antimicrobial activity in the Schiff base ligands and complexes were $(L^1 > L^2 > L^3)$ ($L^3Co > L^2Co > L^1Co$). these data may be attribute to the biological activity increase with increasing molecular weight and distance between azomethine groups.

Table (10) : biological activity data of the ligand and complex

Compound	Gram positive bacteria	Gram negative bacteria
DMCO	-	-
L^1	++++	++++
L^2	+++	+++
L^3	+++	++
L ¹ Co	+++	+++
L ² Co	++	+++
L ³ Co	++	++

Inhibition zone diametr in mm (-) 0 , (+)7-10 , (++)10-15 (+++) 15-19 , (++++) 19-20

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