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## SYNTHESIS AND CHARACTERIZATION OF A SERIES OF COBALT (II) COMPLEXES WITH SALICYLALDEHYDE BASED UNSYMMETRICAL SCHIFF BASE LIGANDS

### PRIYANKA P.G. DEPT. OF CHEMISTRY L.S.COLLEGE.MUZAFFARPUR- 842001

### ABSTRACT

When 2- hydroxynaphthaldehyde, functionalized salicylaldehyde and ethan -1, 2- dihydrazide are refluxed together in equimolar proportion in ethanolic medium in presence of cobalt acetate, chelates of the type,  $[Co L^{1-4}]$  are formed. Characterization has been done on the basis of elemental analysis magnetic

are formed. Characterization has been done on the basis of elemental analysis, magnetic, conductivity and spectral studies suggesting structure of the complexes to be square planar.

### **KEYWORDS**

Co (II) complexes, unsymmetrical Schiff base ligand, spectral and magnetic studies.

### **1.0 INTRODUCTION**

A rejuvenated interest has been developed for Co (II) unsymmetrical Schiff base complexes in recent past<sup>1-23</sup> due to applications of Co (II) complexes in various fields such as catalysis, model system and pharmaceuticals.

In continuation of my earlier work<sup>24</sup> in the field, a series of square planar Co (II) complexes of the type [Co  $L^{1-4}$ ] is reported where L= unsymmetrical Schiff base formed by condensation of 2-hydroxynaphthaldehyde, substituted salicylaldehyde with ethane -1,2- dihydrazide.

### 2.0 EXPERIMENTAL

### 2.1 Unsymmetrical Schiff Bases:-

A series of new structural novel unsymmetrical Schiff base ligands were prepared by the condensation reaction in a 1:1:1 molar ratio of 2-hydroxy naphthaldehyde, ethane -1, 2- dihydrazide and substituted salicylaldehyde or salicylaldehyde and kept stirring at room temperature for four days with the help of a magnetic stirror.

All the ligands formed were orange yellow in color and melted at  $135 - 195^{\circ}$ c. They were also obtained in high yield and high purity (Table - I)

# Table – I Physical properties and analytical data for the Schiff bases and cobalt (II) complexes

		a				Microanalysis Found (Cal)			
Comp.	Empirical Formula	Formul Weight	Yield	Colo	M.P (°C)	%C	<mark>%</mark> H	%N	%M
$\mathrm{H_2L^1}$	C20H14N4O4	374	85	<mark>Orang</mark> e Yellow	194-195	64.17 (64.02)	3.73 (3.74)	14.90 (14.97)	
$H_2L^2$	C20H13N4O4Cl	410.5	72	Orange Yellow	134-135	58.18 (58.40)	3.15 (3.16)	13.61 (13.64)	
H <sub>2</sub> L <sup>3</sup>	C20H13N5O6	419	80	Orange Yellow	140-145	57.12 (57.27)	3.08 (3.10)	16.58 (16.70)	
$H_2L^4$	C22H18N4O5	418	78	Orange Yellow	185-186	62.98 (63.15)	4.28 (4.30)	13.26 (13.39)	
CoL <sup>1</sup>	[Co(C2OH12N4O4)]	431	92	Brown	>250	55.52 (55.68)	2.77 (2.78)	12.90 (12.99)	13.58 (13.69)
CoL <sup>2</sup>	Co[C20H11N4O4] Cl	465.5	89	Brown	>280	51.28 (51.34)	2.34 (2.35)	11.90 (11.98)	12.60 (12.62)
CoL <sup>3</sup>	[Co(C20H11N5O6)]	476	94	Brown	>250	50.02 (50.42)	2.30 (2.31)	14.68 (14.71)	12.36 (12.39)
CoL <sup>4</sup>	[Co(C <sub>22</sub> H <sub>16</sub> N <sub>4</sub> O <sub>5</sub> )]	475	90	Brown	>20	55.55 (55.57)	3.35 (3.37)	11.75 (11.79)	12.32 (12.42)

The following factors were found to affect the course of the synthesis:-

the sequence of addition of the reagents,

- ) temperature of the solution of the starting reagents (solution chilled to about  $4^{0}$ c)
- i) the nature of the dihydrazide used and
- *y*) the reaction time.

A change in reaction time from four days to just three hours or the use of warm solution of the starting reagents produced mixed products. From the above observation it seems that the condensation reactions occurred stepwise. The preparation of unsymmetrical Schiff base and their metal Co (II) complexes can be represented as follows.



Fig - 2.1 R=NO<sub>2</sub>(L<sup>1</sup>),Cl (L<sup>2</sup>), OC<sub>2</sub>H<sub>5</sub> (L<sup>3</sup>), H (L<sup>4</sup>)

### 2.2 Unsymmetrical Schiff base complexes of cobalt (II)

The cobalt (II) complexes were prepared by refluxing the relevant unsymmetrical Schiff bases with  $[Co (CH_3COO)_2.4H_2O \text{ in methanol.}]$  The resulting brown solids are stable in air.

### **3.0 RESULTS AND DISCUSSION**

### 3.1 <sup>1</sup>H NMR Spectra of the Schiff bases

The <sup>1</sup>H NMR spectral data of the free ligand were recorded in CDCl<sub>3</sub> against tetra methylislane as internal reference and are presented in table II.

The appearance of two different peaks for each of the azomethine protons and phenolic protons confirms the unsymmetrical nature of the Schiff in the series.

The higher of the two signals for both the azomethine and phenolic protons is assigned to the azomethine / phenolic proton attached to the napthaldehyde ring while the lower signal is assigned to the azomethine / phenolic protons attached to the Salicylaldehyde ring. Signals for the methane proton of the azomethine group were observed between 8.2 and 9.0ppm. The peak in the 6.8 to 8.1 ppm which appeared as a multiplet are assigned to chemical shifts for aromatic protons. The O-H protons of the phenolic group were observed as a singlet between 12.0 and 15.5ppm and were generally shifted downfield due to intermolecular hydrogen bonding. The signal due to the methyl protons on the ethoxy substituent in  $H_2L^3$  appeared as a triplet at 1.5ppm while the signal at 4.1ppm is assigned to the CH<sub>2</sub> protons.

For the unsymmetrical Schiff bases the observed difference in the signal of the phenolic proton is attributed to the greater electron withdrawing effect of the napthalaldehyde ring and hydrogen bonding between the phenolic protons and the azomethine nitrogen.

The deshielding effect of electron withdrawing groups and hydrogen bonding are responsible for the proton signal being moved further downfield. Similarly the same trend is observed for the azomethine proton of the unsymmetrical Schiff bases.

# Table – II<sup>1</sup>H NMR data for free ligands

Ligands	$\delta_{ m OH}$	$\delta_{ m Ar-H}$	δCH <sub>3</sub>	δCH <sub>2</sub>	δN=CH
$H_2L^1$	15.5(s,1H)	6.9,8.1(m,13H)			8.9(s,1H)
	10.2(s,1H)				9.0(s,1H)
$H_2L^2$	13.9(s,1H)	7.1,8.1(m,13H)			8.4(s,1H)
	15.2(s,1H)				8.8(s,1H)
$H_2L^3$	12.9(s,1H)	6.8,8.1(m,13H)	1.5	4.1	8.2(s,1H)
	15.0(s,1H)		(t,3H)	(q,2H)	8.7(s,1H)
$H_2L^4$	12.0(s,1H)	6.9,8 <mark>.0(m,14</mark> H)			8.6(s,1H)
	15.7(s,1H)				8.9(s,1H)

### **3.2 INFRARED SPECTRA**

The important infrared spectra bands of the metal complexes are presented in table III. A few representatives IR Spectra of cobalt (II) complexes have been shown in fig.

The tentative assignments of the observed band for the compounds were made by comparing the spectra with those reported in the literature on similar system<sup>1-7</sup>.

The absorption bands due to amino group disappeared in the IR Spectra of all the four ligands  $[H_2L^{1-4}]$  which showed that the amino group in the dihydrazide condensed with the aldehyde. The bands appearing at 1600-1640 cm<sup>-1</sup> due to azomethine group of the ligands is shifted to lower frequency at 1570- 1600 cm<sup>-1</sup> in the Co (II) complexes nitrogen in coordinating with the metal ion.

Similarly the V<sub>C-O</sub> band of the ligand which occurs at 1255-1330 cm<sup>-1</sup> is shifted to 1270 -1360 cm<sup>-1</sup> in the complexes indicating deprotonation and co – ordination of the phenolic oxygen to atom.

Thus it can be concluded that the Schiff bases acted as tetradentate ligands coordinating via the azomethine N and the phenolic O.

Further conclusive evidence of the co- ordination of the Schiff bases with the metal ions was shown by the appearance of new bands at 435-580 and 410-581cm<sup>-1</sup> assigned to the metal nitrogen (M-N) and metal oxygen (M-O) stretching vibrations respectively.

These bands were absent in the spectra of the uncomplexed Schiff bases thus confirming the participation of O and N atoms in the co-ordination. It has been established that the metal ligand vibrational mode are very sensitive to substituent effects.

The infrared spectra of both the ligands and complexes have no bands between 3100 and 4000 cm<sup>-1</sup> indicating the absence of uncoordinated N-H and uncoordinated –OH groups. Due to unsymmetrical nature of the ligands and the complexes two bands were observed for each of the following modes.  $v_{C=N}$ ,  $v_{C-O}$ ,  $v_{M-N}$  and  $v_{M-O}$ .

### 3.2.1 Unsymmetrical Schiff base complexes of cobalt (II)

The position of  $v_{C=N}$  bands of the ligands appeared at 1610-1620 cm<sup>-1</sup> and 1570-1580 cm<sup>-1</sup>. These are shifted to lower frequency at 1600-1610 cm<sup>-1</sup> respectively upon complexation indicating the involvement of the nitrogen atom of the azomethine group in co-ordination<sup>3</sup>.

On the other hand the (C-O) stretching frequencies which occur at 1313-1333 and 1276-1289 cm<sup>-1</sup> the ligands was moved to higher frequency by 15-30 cm<sup>-1</sup> for after complexation which indicates that the shifts are due to co-ordination of the phenolic oxygen of the ligands to the metal ion<sup>10</sup>. The new bands observed in the complexes in the region 453-580 and 508-554 cm<sup>-1</sup> were assigned to v (Co-N) while 463-575 are 423-428 cm<sup>-1</sup> and attributed to v (Co-O).

Complex	V C=N	<b>V</b> C-0	V M-N	V M-0
$H_2L^1$	1610,1580	1315,1275		10
$H_2L^2$	1620,1567	1335,1290		13-
$H_2L^3$	1610,1569	1315,1285	)	-
$H_2L^4$	1615,1568	1310,1285	-	-
CoL <sup>1</sup>	1604,1578	1325,1288	453,508	575,423
CoL <sup>2</sup>	1603,1574	1365,1310	454,539	568,428
CoL <sup>3</sup>	1606,1577	1340,1315	475,548	568,428
CoL <sup>4</sup>	1603,1571	1335,1315	580,554	463,428

	<b>Table III</b>		
<b>Infrared Sp</b>	ectral Data of Ligand <mark>s a</mark>	and Co (II) (	Complexes

### **3.2.2** Unsymmetrical Schiff base complexes of cobalt (II)

The electronic spectra of all the cobalt (II) complexes in CHCl<sub>3</sub> are very similar to each other and consist of three bands. One each at 18587-18939, 22272-22779 and 24876-25575cm<sup>-1</sup> region which clearly indicates the low spin square planer/distorted square planar geometry of the complexes . This is also corroborated by the observed effective magnetic moment of the complexes. The other intense bands between 28902 and 4149 cm<sup>-1</sup> are due to charge transfer transitions.

The electronic spectra of all the complexes in DMSO displayed a single d-d transition at 25063-25445 cm<sup>-1</sup> and a charger transfer transition at 29412-36101 cm<sup>-1</sup>.

The appearance of a single d-d transition in DMSO is attributed to the effect of the coordination of solvent which alters the stereochemistry to form low spin six co-ordinate distorted octahedral structure <sup>181</sup>. The slight differences in the peaks observed in the spectra of these complexes in both solvents are due to substituent effects of the different substituent on the Salicylaldehyde ring.

### 4.0 ELECTRONIC SPECTRA

### 4.1 Electronic spectra of the unsymmetrical cobalt (II) complexes Table IV

Electronic spectral bands of cobalt (11) complexes							
Comp	Solvent	d-d tr <mark>ansiti</mark> ons/cm <sup>-1</sup> (ε/cm <sup>-1</sup> mol <sup>-1</sup> )	C.T	Ligand#			
	CHCl <sub>3</sub>	18939(77),22523(205),24876(273)		31949(228)			
$CoL^1$				40323(606)			
	DMSO	25126(236)	29586(183)				
	CHCl <sub>3</sub>	18587(59),2272 (153),25575(227)		31447(202)			
CoL <sup>2</sup>				40816(364)			
	DMSO	25063(333)					
	Sec.		~~~	-			
	CHCl <sub>3</sub>	18868 (93),22523(233),24876(279)	28902(270)				
$CoL^3$			30675(274)				
	DMSO	25063(228)					
	CHCl <sub>3</sub>	18832(94),22779(250),25189(337)					
$CoL^4$							
	DMSO	25445(263)	29586(215)				

Electronic spectral bands of cobalt (II) complexes

The spectra were noisy in the UV and some of the band in the region could not be extracted.

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### **5.0 MAGNETIC MOMENT**

### **5.1** Unsymmetrical Schiff base complexes of Cobalt (II)

The observed values of magnetic moment for cobalt (II) complexes are generally diagnostic of the co-ordination geometry about the metal ion. The room temperature magnetic moments of low spin square planar cobalt (II) complexes are between 1.9 - 2.9 BM arising from one unpaired electron plus an apparently larger orbital contribution. Both tetrahedral and high spin octahedral cobalt (II) complexes possess three unpaired electron but may be distinguished by the magnitude of the deviation of effective magnetic moment from the spin only value. The octahedral and tetrahedral cobalt (II) complexes are reported to have magnetic moment between 4.9-5.2 and 4.2- 4.8 BM respectively. The effective magnetic moments of all the cobalt (II) complexes reported here lie in the range of 2.23- 2.61 BM corresponding to one unpaired electron for square planar stereo chemistry around d<sup>7</sup> cobalt (II) ion.

### **6.0 ELECTRO CHEMICAL STUDIES**

Extensive electrochemical studies on metal complexes with macrocyclic and unsymmetrical Schiff base ligands with and without  $\pi$  electron conjugation have been done and it has been established that system with extended double bond conjugation has higher stability<sup>25-26</sup>.

All the complexes of Co (II) under present study are found to undergo one step reduction reversibly or quasi – reversibly and the redox step is accompanied by one electron transfer. The thermodynamic parameter  $E_{1/2}$  for the complexes is found within the range -1.34 to -1.5V.  $E_{1/2}$  values change within a narrow range with changing substituent.

Thermodynamic consideration lead to believe that the electron transfer is accompanied by ligands anion radical formation.

 $[Co^{2+}(ligand)] + e \rightarrow [Co^{2+}(ligand)]$ 

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