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ChemTech

International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.2, No.1, pp 728-732, Jan-Mar 2010

Synthesis and structural studies of complexes of N-Salicylidine Amino acids (Glycine, L-Leucine with salicyldehyde) derived Schiff base with some bivalent transition metal ions

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Abstract : Co^{II}, Ni^{II} Cu^{II} and Zn^{II} complexes with Schiff bases viz. N-salicylidine amino acids ie. Sal. Glycine, Sal.L-Leucine have been synthesized and characterized with the help of micro analytical data, IR, NMR Spectroscopy, conductance and magnetic measurements. Ligand field parameters of some of the complexes have also been calculated.

Key words: - Schiff base, Bivalent metal complexes and Ligand field parameters.

Introduction

Studies of new types of Schiff bases and metal coordinated complexes are now attracting much attention. After suitable structural modifications, the derivatives of such compounds as such may be used as bio active materials as well as in industries. The aim of this study is to observe the impact of chelation on the organic compounds. Some Cu^{II}, Zn^{II}, Co^{II}, Ni^{II}, complexes have been synthesized involving the biopotent Ligand i.e. N-salicylidine Glycine (N-Sal. Gly) and N Salicylidine L-Leucine (N-Sal. L-Leu) and characterized.

Experimental

Chemicals and Reagents: All the used chemical and solvents were of A.R. grade. Elemental analysis, IR and NMR spectra were recorded at CDRI Lucknow. Melting point was determined on a Toshniwal CL-0301 apparatus. Molar conductance (10^{-3}M) was measured by Elico conductivity bridge at room temperature. Magnetic measurement was made by Gouy's method. Electronic spectra was recorded on Perkin-Elmer Lambda 2-B spectrophotometer Thermal decomposition of complexes have been noted on heating in muffle Furnace at above 150 and below. 600^{0}C in air.

Synthesis of Schiff Bases Ligands: The Schiff bases were synthesized by adding the ethanolic solution of salicyaldehyde with alkaline solution of amino acids. The mixture was again heated for 2-3 hours on a water bath at 50^{0}-60^{0}C when a clear yellow solution was obtained. The alkaline solution of Schiff bases are acidified by ice cold dil HCl at 5^{0}C and placed in ice bath for crystallization. The Schiff bases were dried in vacuum desicator over P_4O_{10} the purity of the synthesized compounds was monitored by TLC using silica gel (yield 55-65%).

I.R. absorption bands are observed at 3250-3100 cm^{-1} region which is on the lower wave number side as compared to the stretching frequencies of free-NH or OH group. This is due to presence of both types of hydrogen bonding, intermolecular O-H ….. O as well as intramolecular O-H …….. N in which phenolic hydrogen are hydrogenbonded either to the lonepair of azomethine nitrogen atom or to the oxygen atom of carboxylic group in the ligand[10]. Strong band at 1640 $^{cm-1}$ in Schiff base complexes due to azomethine group where as weak band at 1700-1725 $^{cm-1}$ is observed due to COOH carboxylic group in Schiff bases [11, 12].

NMR spectra of Schiff base with legand showed different peaks .

Sal- Glycine 4.78(2H, s, one of –COOH and other Phenolic –OH group), 7.05 -7.80(4H, m, Ar-H atoms), 8.50(1H, s, azomethine proton).

Sal.L-Leucine 4.65(2H s, one of –COOH and other Phenolic –OH group), 2.20 (3H, m, $-CH_3$ CH-CH2), 1.10(3H, d, $-CH_3$), 4.95(1H ,α , $-CH_3$), 6.80-7.70(4H, m, Ar-H), 8.20 (1H, m, Azomethine proton)

Prepration of complexes

(i) **Synthesis of Cu^{II} complexes:** Cold Aqueous solution of copper acetate us added to the Schiff base solution in equimolar ratio and the resulting solid product were washed with water, ether and dried in vacco over P_4O_{10} yield (55-67%)

(ii) **Synthesis of Zn^{II} complexes** – Cold Aqueous solution of zinc nitrate was added to Schiff base solution followed by 30% H_2O_2 and the mixture was cooled in ice and the resulting solid is washed with water, ether and then dried in vaccum over P_4O_{10} (Yield 55%-60%).

(iii) **Synthesis of Co^{II} complexes** – Aqueous ethanolic solution of cobalt acetate was added to hot ligand solution in 1:1 and 1:2 molar ratio the reactant were stirred for about 15 hour the resulting solid is washed with water-ethanol di ethyl ether and dried in vacco over P_4O_{10} (yield 80-90%).

(iv) **Syntheis of Ni^{II} complexes** – Aqueous ethanolic solution of Nickel Acetate was added in Schiff base solution. The reactant were stirred for about 15 hour. The resulting solid products were successively washed with water-ethanol diethyl ether and dried over P_4O_{10} (yield 75-85%).

The structure of metal complexes is proved by different analytical as well as spectral methods. Physical characterstics and elemental analysis of Cu^{II} Zn^{II}, Co^{II}, Ni^{II} complexes of some. Bifunctional Tridentate Schiff Bases are given in table I.

Result and discussion

(a) Complexes of Cu^{II}, Zn^{II}, Co^{II}, Ni^{II} with N-Salicylidine Glycine :-

The complexes show the metal to ligand stoichiometry in 1:1 for Cu^{II} and Zn^{II} and 1:2 for Co^{II} and Ni^{II} complexes. The conductivity values (in 10^{-3} M nitrobenzene) shows the non electrolytic behaviour of the complexes of Cu^{II}, Ni^{II}, Zn^{II} and Co^{II}. Electronic spectra of metal complexes were recorded in the range 200-1000nm in DMF(Table-2). The IR band of azomethine group in N-salicylidine Glycine ligand has shifted to lower side in the spectra of metal complexes due to co-ordination through azomethinenitrogen[1-3]. Other main characteristic bands of ligand remain almost unchanged in complexes Table -3.

NMR Spectra of Cu^{II} and Zn^{II} complexes were studied in $CDCL_3$ the δ values in ppm are given below.

Cu Sal. Glycine- 4.78 (2H,s, CH_2) 7.05-7.80 (4H, m Ar-H) 8.50 (1H, s, azomethine proton)

Zn (Sal Glycine), $3H_2O$ (5.05) (2H, s,CH_2) , 7.30-8.40 (6H, m, Ar-H) 9.50 (1H,s,azomethine proton)

(b) Complexes of Cu^{II}, Zn^{II}, Ni^{II}, Co^{II} with N-Salicylidine L-Leucine.

The Analytical data of the metal complexes indicates metal to ligand (Schiff base) stoichiometry for all the complexes is 1:1 for Cu^{II} Zn^{II} where as 1:2 for Ni^{II} and Co^{II} complexes. The molar conductance value (10^{-3} M in Nitro Benzene) suggests that the complexes show non electrolytic behaviour. Electronic spectra is also recorded in the range 200 - 1000 nm in DMF or in Nitro benzene. Absorption maxima and value of molar conductance and other values have been discussed in Table 1.

The IR absorption band due to azomethine group in N-Salicylidine L-leucine has shifted to lower side in complexes is due to co-ordination through azomethine Nitrogen A broad band around 3400 cm^{-1} and a sharp band 1390 cm^{-1} in the ligand spectrum can be assigned to phenolic OH stretching and phenolic -OH deformation [1-3] An intense band at 1320 cm^{-1} in the ligand due to the phenolic C-O, shifts higher in the complexes. Some IR frequencies in cm^{-1} of metal complexes with bifunctional tridentate Schiff bases are given in table 2.

NMR Spectra of Cu^{II} and Zn^{II} Complexes were studied in $CDCL_3$ The δ values (in ppm) are given in the following tables.

Cu (Sal-L-leuc.) 1.10 (3H, d, CH_3), 1.17 (3H, d, CH_3) 2.20 (3H, m, (CH_3)), 4.95 (1H, α , -CH), 6.80-7.70 (4H, m, Ar-H), 8.20 (1H, m, azomethine proton)

Zn (Sal-L-leuc.) 0.95 (3H, d, CH_3), 1.00 (3H, d, CH_3), 2.05 (3H, m, $(CH_3)_2$ CH CH_2), 4.85 (1H, m, α , -CH), 7.15-8.20 (6H, m, Ar-H), 9.3 (1H, s, azomethine proton)

NMR Spectra of Schiff bases are compared with the NMR spectra of complexes in D.M.S.O. the spectra of Schiff bases consists of a single azomethine proton resonance in addition of O-hydroxy proton and proton of –COOH group the –N =CH- Proton shows a singlet and the aromatic proton singlet occurs at the normal position.

Table 1: Physical characterstics and elemental analysis of Cu^{II} Zn^{II}, Co^{II}, Ni^{II} complexes of some. Bifunctional Tridentate Schiff Bases

Compd. No.	Emperical Formula	Molecular Weight	Colour	Elemental Analysis				Metal Ligand/ Ratio
				C%	H%	N%	M%	
L-1	N-Sal. Glycine $C_9H_7NO_3$							
01	Cu $(C_9H_7NO_3)$	240	Green	41.73	3.44	5.28	24.32	1:1
02	$Zn(C_9H_7NO_3)$ H_2o	296	White	36.40	4.35	4.70	22.04	1:1
03	$Ni(C_9H_7NO_3)_2$	412	Yellow	52.04	3.81	6.71	14.11	1:2
04	$Co(C_9H_7NO_3)_2$	414	Greenish	52.03	3.81	6.50	13.92	1:2
L-2	N-Sal-L-Leueine $(C_{13}H_{16}NO_3)$							
05	Cu $(C_{13}H_{16}NO_3)$	258	Yellow green	49.51	5.35	4.40	20.16	1:1
06	$Zn(C_{13}H_{16}NO_3)$ $3H_2o$	314	White	44.22	5.93	3.95	18.50	1:1
07	Ni $(C_{13}H_{16}NO_3)_2$	448	Yellow	59.20	6.05	5.30	11.13	1:2
08	Co $(C_{13}H_{16}NO_3)_2$	450	Greenish	59.18	6.03	5.28	11.14	1:2

Table-2 : Absorption maxima ,conductance and magnetic measurements of different Metal complexes

S.No.	Compound	Molar conductance In ohms^{-1} cm^2 mole^{-1} In Nitro Benzene	Magnetic Susceptibility		B.M. Value	λMax in nm.
			Specific Susceptibility χs x 10^{-6} C.G.S at 300K	Molar Susceptibility χm x 10^{-6} C.G.S at 300K		
	L-1					
1	Cu (Sal. Glycine)	4.2 x 10^{-1}	5.0	1513.85	1.89	250,405,500,540
2	Zn (Sal. Glycine) $3H_2O$	20	29.59	10420	5.02	238,270,306,425
3	Co (Sal. Glycine)$_2$	30	26.80	1040	4.95	238,272,305,350,690
4	Ni (Sal. Glycine)$_2$	35	10.65	3747	3.01	330,270,305,350,440
	L-2					
5	Cu (Sal-L-leucine)	5.0 x 10^{-1}	4.7	1585.17	1.93	255,410,505,550
6	Zn (Sal-L-leucine) $3H_2O$	27	27.39	10590	5.06	240,230,300,340,415
7	Co(Sal-L-leucine)$_2$	35	26.71	10010	4.92	240,278,310,350,700
8	Ni(Sal-L-leucine)$_2$	40	9.50	3672	2.98	338,272, 305,354,460

Table-3 : Some IR frequencies(in cm-1) of Cu^{II}, Zn^{II}, Co^{II}, Ni^{II} complexes-

S.No.	Compound	-OH Or -NH	C=N	Phenolic C-O-H	Carboxylic O- - C = O	M-N	M-O	Coordi-nated water molecule.
1	Cu (Sal. Glycine)	3465	1595	1300	1600	520	450	
2	Zn (Sal. Glycine) $3H_2O$	3550	1650	1290	1605	520	425	3150
3	Co $(Sal. Glycine)_2$	3500	1605	1290	1625	520	445	
4	Ni $(Sal. Glycine)_2$	3550	1605	1290	1650	522	445	
5	Cu (Sal-L-Leucine)	3500	1590	1320	1600	535	490	
6	Zn(Sal-L-Leucine) $3H_2O$	3550	1655	1295	1625	525	440	3200
7	Co $(Sal-L-Leucine)_2$	3515	1625	1295	1650	521	450	
8	Ni $(Sal-L-Leucine)_2$	3500	1635	1295	1655	525	440	

Electronic Spectra of Cu(II) and Zn(II) Complexes.

The electronic spectra of the Schiff bases in DMF showed two peaks in the near UV region (i.e. 310 and 395 nm) which arise from a change in the vibratrional energy in the hydrogen bonded structure as reported earlier[4,5]. The bathochromic shift of the bands may be due to metal ligand bonds. The low energy absorption band near 350nm was assigned to imine group. In copper complexes a high energy band around 500 & 550nm appeared.

Absorption spectra of Zn^{II} chelates in DMF show three different bands which are approximately at the same position in all complexes. These characterstic band correspond to the transitions

$^4T_1g(F) \longrightarrow {}^4T_2g(F)$,

$^4T_1g(F)\ ^4 \longrightarrow A_2g(F)$ and

$^4T_1g(F) \longrightarrow {}^4T_2g(F)$

Which support the Octahedral stereo chemistry of Zn^{II} complexes [6,7,8]

The absorption spectra of Co^{II} complexes in DMF show three different bands which are approximately at the same positions in all the complexes. These characteristic bands correspond to the transitions $^4T_1g(F) \longrightarrow {}^4T_2g(F)$, $^4T_1g(F) \longrightarrow {}^4A_2g(F)$ and $^4T_1g(F) \longrightarrow {}^4T_2g(F)$ which supports the octahedral geometry of Co^{II} complex [9].

The absorption spectra of Ni^{II} chelates correspond to the transitions $3A_2g\ (F) \longrightarrow {}^3A_1g$, $^3A_1g\ (F)$ and $^3A_2g \longrightarrow {}^3T_1g\ (P)$ this also shows the octahedral geometry of complexes

Thermogravimetric Analysis:

Pyrolytic curves of Cu^{II} complex show a stability upto 180^0C indicating that the complexes are highly stable due to dimeric structures. After 180^0C complex starts de composition till the formation of residue equivalent to CuO.

Zn^{II} complexes show a stability in T.G. curves upto 110^0-150^0C. Above these temperature the complexes start decomposition.

$Cu\ (Sal.Gly)_2 \xrightarrow{\sim 400^0C} CuO$

$Cu\ (Sal.\ L\text{-}\ Leucine)_2 \xrightarrow{\sim 450^0C} CuO$

$Zn\ (Sal.Gly.)3H_2O \xrightarrow{\sim 140^0C} Zn(Sal.Gly.) \xrightarrow{\sim 400^0C} ZnO$

$Zn(Sal.L\text{-}Leu).\ 3H2O \xrightarrow{\sim 150^0C} Zn(Sal.L\text{-}Leu) \xrightarrow{\sim 600^0C} ZnO$

The thermogravimetric analysis of Co^{II} and Ni^{II} complexes show a stability in T.G. curve at 550-600^{0}C above these temperatures the complexes start decomposition to their metal oxides which supports the molecular str. of complexes and the gravimetric evaluation of metals.

$$\mathrm{Co\ (Sal.Gly)_2} \xrightarrow{\sim 500^0\mathrm{C}} \mathrm{CoO}$$

$$\mathrm{Co\ (Sal.\ L\text{-}\ Leucine)_2} \xrightarrow{\sim 600^0\mathrm{C}} \mathrm{CoO}$$

$$\mathrm{Ni\ (Sal.Gly)_2} \xrightarrow{\sim 600^0\mathrm{C}} \mathrm{NiO}$$

$$\mathrm{Ni\ (Sal.Leucine)_2} \xrightarrow{\sim 600^0\mathrm{C}} \mathrm{NiO}$$

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