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Synthesis, Characterization and Spectral Studies of Hydrazide Schiff's Base with Metalions Such as Co (II), Ni (II) and Cu (II).

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ABSTRACT

A series of Cu(II), Ni(II) and Co(II), complexes have been synthesized from the schiff base ligands L₁ and L₂. The schiff base ligand L₁ N-(2-hydroxybenzylidene) (L) has been synthesized by the reaction between salicylaldehyde and benzoyl hydrazine, and the Schiff base ligand L₂ N,N'-Ethylene bis(salicylideneimine) has been synthesized by the reaction between salicylaldehyde and ethylene diamine. The nature of bonding and geometry of the transition metal complexes as well as schiff base ligand L₁ and ligand L₂ have been deduced from elemental analysis, FT-IR, UV-Vis, magnetic susceptibility, and molar conductance measurements. Cu(II), Ni(II) and Co(II) metal ions are forming 1:2 (M:L) complexes, Based on elemental, conductance and spectral studies, six-coordinated and four-coordination geometries was assigned for Cu(II), Ni(II) and Co(II) complexes. The complexes are 1:2 electrolytes in DMSO which is neutral in DMSO. The ligand L₁ acts as tridentate and coordinates through nitrogen atom of azomethine group, oxygen atom of carbonyl group Benzohydrazide and oxygen atom of hydrazoic group of benzoyl hydrazine and the L₂ acts as bidentate and coordinate through nitrogen atom of azomethine and oxygen atom of hydroxy group of salicylaldehyde.

Keywords: salicylaldehyde, benzoyl hydrazine, bi and Tri dentate Schiff base, Transition metal complexes,

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INTRODUCTION

Now a days the synthesis of azo compounds are very important, because widely used in the industry and caused a lot of harmful effective on the humans, there are different methos were used for removal of these organic materials such as adsorption process, photocatalytic degradation, etc [1-6]. But at the same time the synthesis steps consider a very important for getting a safety ways for preparation and lowest cost. The hydrazones have found wide applications in synthetic chemistry for preparation of compounds having diverse structures and for the applications in analytical chemistry for identification and isolation of carbonyl compounds and for detection of large number of metal cations the hydrazones and Schiff's bases (salcinaldehyde benzoyl hydrazone) were the subject of many interesting studies due to their important biological and technical applications Schiff's base ligands have been widely used for the preparation of transition metal complexes [8]. Particularly tridentate ONO/S, NNO/S functionalized ligands have recently attracted considerable interest but surprisingly NNO chelating ligands have to our knowledge been, little published[9]. Their metal complexes have found applications in various chemical processes like nonlinear optics, sensors, medicine etc [10]. Furthermore Hydrazones incorporating hetero cyclic moieties are well known for their metal binding ability and exhibit interesting co-coordinating behaviour with transition metal ions[11]. The in situ synthesis in the present of metal ions represents a prevalent means to obtain some interesting functional complexes[12]. In recent years the Hydrazones /Benzoylhydrazones have been drawing much attention from coordination chemists, because of the strong tendency of Benzoylhydrazones to chelate transition metals. In the context of the above mentioned applications we reported here the synthesis and spectroscopic studies on the complexes Salcinaldehyde benzoyl hydrazine [13]. Form stable complexes with most transition metal ions in the periodic table. The development of the field of bio inorganic chemistry has increased the interesting Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biological important species. The remarkable biological activity of acid hydrazides, a class of Schiff's base, their corresponding aroyl hydrazones, and the dependence of their mode of chelation with transition metal ions present in the living systems have been of significant interest. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications. Salcinaldehyde benzoylhydrazone is ONO tridentate donor[14]. The tautomerism of these ligands as well as the well known transition metal chelating properties allow various structural possibilities for the corresponding metal complexes. In addition, the versatile applications of Schiff base ligand complexes in the field of biological and industrial processes prompted us to synthesize the tridentate ONO Schiff base ligand complexes. As the part of our study of transition metal complexes with these legends, we have described the synthesis and spectroscopic properties for the Cu(II),Ni(II) and Co(II) metal complexes [15].

MATERIALS AND MEASUREMENTS

All chemical which are of analar grade are purchased from Aldrich, BDH, Merck and Sigma. All the solvents used Ethanol, methanol, The solvents were purified by distillation and double distilled water were used throughout the experiment. The infrared spectra of the ligand and their metal complexes were run as KBr discs in in range(4000-400)cm⁻¹ on a shimadzu 8400 FTIR spectrophotometer. Element analysis (C.H.N) were performed by using a Euro EA elemental analyzes. The magnetic susceptibility were measured on a MSB-Auto magnetic susceptibility Blance. Electrical conductivity measurements of the chelate complexes were recorded at room temperature in DMF (10-3M) using a 31 A digital conductivity meter. Electronic spectra in absolute ethanol (10-3M) solution were recorded by using shimadzu UV-vis. 1700 spectrophotometer 21-1885-0166..Experiments and preperation of soutions and washing all glass were using distilled water twice in doubly distilled water.

Synthesis of Benzohyrazide

A mixture of methyl benzoate and hydrazine hydrate (0.02 mol) was refluxed in ethanol (25 ml) for 4-6 hours. After the completion of reaction it was cooled and poured on to crushed ice; the solid thus obtained was filtered off, washed with water and recrystallized from ethanol) [16]. Results are shown in Fig. 1, m.p. - 112.50C, yield- 61%

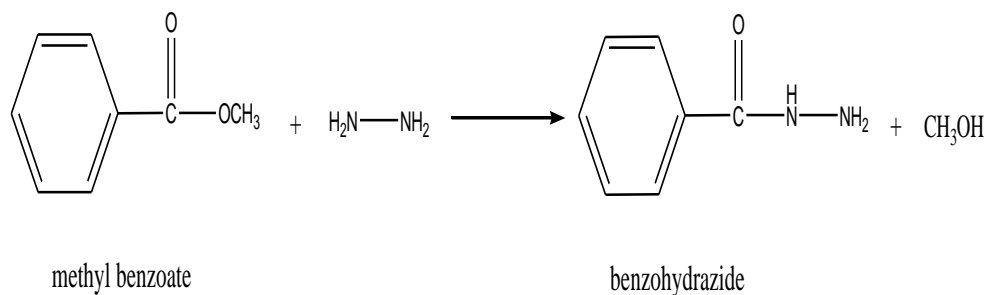


Figure 1: Synthesis of Benzohydrazide

Synthesis of N(2-hydroxybenzylidene)benzohydrazide

The ligand L_1 was synthesized by a solution of 2.61 mole of salicylaldehyde in 25 ml hot ethanol (95%) added to 2.91 mole of 2-hydroxybenzene (98%); the mixture solution was cooled after stirring for a few minutes. [16] The yellow precipitate formed was filter off, re-crystallized with ethanol and dried. Melting point is 168°C , results are shown in Fig. 2

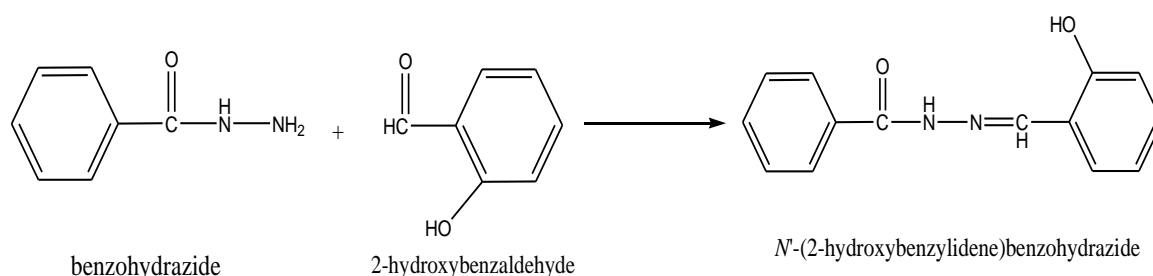


Figure 2: Synthesis of N(2-hydroxybenzylidene)benzohydrazide

Synthesis N,N'-Ethylene bis(salicylideneimine)

The ligand H_2L' was synthesized by a solution of 2.8 mmole of salicylaldehyde in 25 ml hot ethanol (95%) added to 1.4 mmole of ethylenediamine (98%); the mixture solution was cooled after stirring for a few minutes. The yellow precipitate formed was filter off, re-crystallized with ethanol and dried. [17] Melting point is 128°C . results are shown in Fig. 3

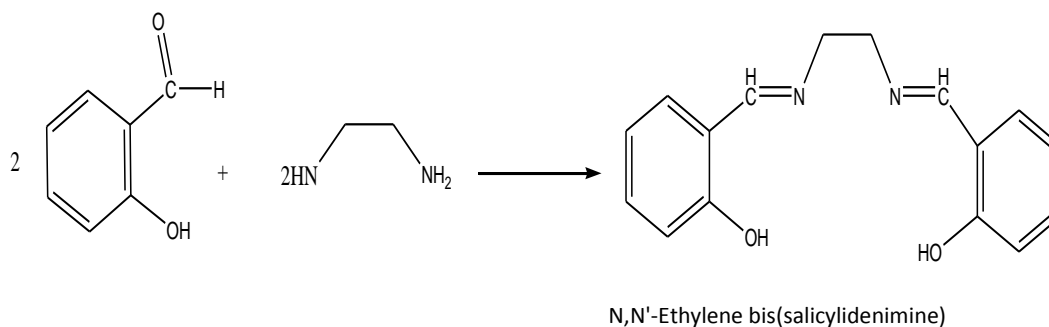


Figure 3: Synthesis N,N'-Ethylene bis(salicylideneimine)

Preparation Metal complexes:

EtOH solutions of the metal (II) acetates (0.01 mol dm^{-3}) and Schiff's base ligand L_1 (0.01 mol dm^{-3}) in 1:2 molar ratio under anhydrous conditions. were reacted in a beaker. The complexes precipitated immediately. The reaction mixture was heated to 60°C for 5-10 min. The precipitates were filtered off by

suction, washed several times with EtOH and dried in a desiccator over anhydrous CaCl_2 . [16], results are shown in Fig. 4

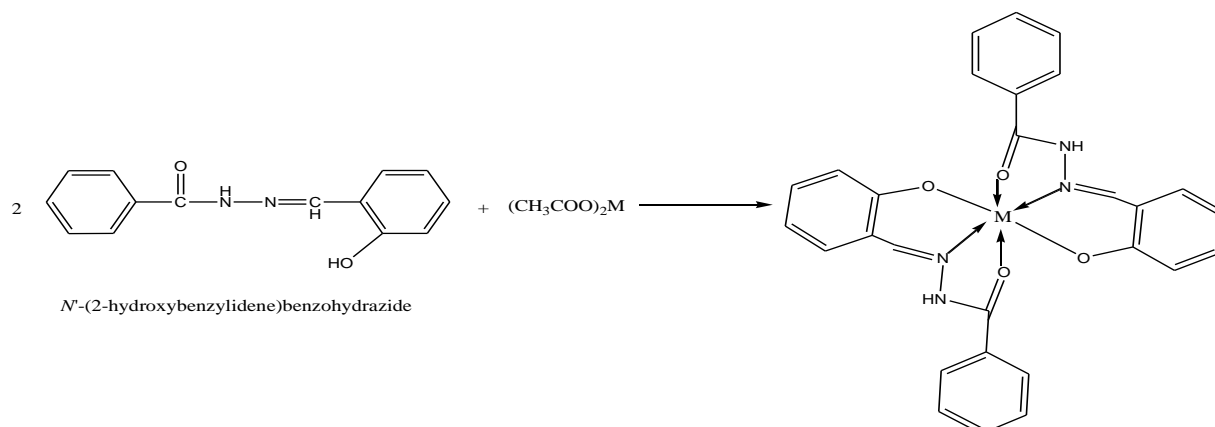


Figure 4: Preparation of N(2-hydroxybenzylidene) benzohydrazidemetal (II) ion M: Cu(II),Co(II),Ni(II)

Preparation Metal complexes:

EtOH solutions of the metal(II) acetates (0.01 mol dm^{-3}) and schiff base ligand L_2 (0.01 mol dm^{-3}) in 1:2 molar ratio under anhydrous conditions. were reacted in a beaker. The complexes precipitated immediately. The reaction mixture was heated to $60 \sim \text{C}$ for 5-10 min. The precipitates were filtered off by suction, washed several times with EtOH and dried in a desiccator over anhydrous CaCl_2 . [17], results are shown in Fig. 5

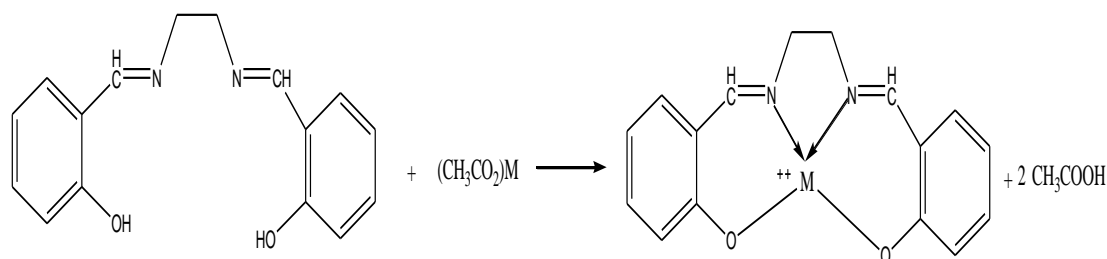
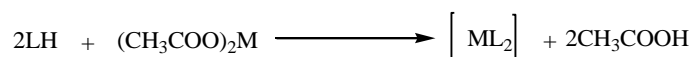


Figure 5: Preparation of metal complex: M: Cu(II),Co(II),Ni(II)

RESULTS AND DISCUSSION

It appears from the analytical data of the complexes (Table 1) that the ligands are doubly deprotonated and give 1:1 (M:L) complexes in EtOH medium, in contrast to similar monodeprotonated or neutral ligands in aprotic solvents t) or at low pH. The ligands are doubly deprotonated in solvents of high dielectric constants on heating) or at high pH. Since liberation of acetic acid in the reaction between the metal acetates and the ligands does not significantly affect the pH of the medium, the reaction may be written as. [18]



All the metal complexes are insoluble in common organic solvents such as ethanol, methanol, benzene, chloroform, acetone and ether, but are soluble in polar solvents such as DMF, DMSO and pyridine.

The low molar conductance values of $10^{-3} \text{ mol dm}^{-3}$ solutions of the complexes in DMF/DMSO at room temperature show that they are all non-electrolytes r 5). [19]

Electronic spectra: observed in several square planar complexes. In contrast to the normal range of μ_{eff} values (1.8-2.2BM) observed for copper(II) complexes, the slightly low values for [CuL] suggest dimeric or polymeric structures. The electronic spectra of the nickel(II) complexes suggest a square planar environment, which is supported by their diamagnetism. Similarly, the spectra of the cobalt(II) complexes suggest a square planar geometry. In contrast, the monodeprotonated and neutral ligands form 5- and 6-coordinated complexes, respectively, with copper(II) and nickel(II). [19]

Table 1: electronic spectral data and molar conductance values.

Complex	Colour	μ_{eff}	Λ_m	" \sim max
[CoL]	Reddish brown	2.1	32.8	1200, 445, 360 ${}^2B_{2g}, {}^2E_g, {}^2A_{1g}, CT$
[NiL]	Dark yellow	0.10	26.1	890, 540, 385 ${}^1A_{1g}, {}^1B_{1g}, {}^1B_{2g}$
[CuL]	Green	1.66	10.1	${}^2B_{1g}, {}^2A_{1g}, {}^2E_g$

Table 2: Important IR. spectral bands and assignments.

compound	$\nu(\text{NH})$	Amide $\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{N=C--O})$	$\nu(\text{C--O})$	$\nu(\text{N--N})$	$\nu(\text{M--O})$	$\nu(\text{M--N})$
LH2	3270s	1660s	1660	--	-	990s	-	-
[CoL]	--	-	1595m	1510s	1330w	1020s	440s	350w
[NiL]	--	-	1590s	1502s	1330w	1030s	400m	340w
[CuL]	---	-	1590s	1500s	1330w	1010w	450m	340w
H2La			1635s	----	1286	----	---	---
[CoLa]			1600	-----	1230	-----	534	534
[NiLa]			1626	-----	1290	-----	540	540
[CuL ^a]			1606	-----	1284	-----	478	478

IR Spectra

The IR. spectra of the free Schiff bases (Table 2) show strong $\nu(\text{NH})$ bands between 3270 and 3200 cm^{-1} . The bands at 1660, 1570 and 1300 cm^{-1} for LH₂ and at 1665, 1570 and 1330 cm^{-1} for L'H₂ may be assigned to amide suggesting that in the solid state the compounds exist primarily in the keto form. A strong band observed between 1630 and 1600 cm^{-1} may be assigned to $\nu(\text{C=N})$ of the azomethine. In the metal complexes, the absence of bands between 3400 and 3200 cm^{-1} ($\nu(\text{NH})$) and at 1660 cm^{-1} ($\nu(\text{C=O})$) and the appearance of a more intense band near 1600 cm^{-1} due to $\nu(\text{C=N})$ compared to the free Schiff base indicate that both CONH groups are enolized and deprotonated. $\nu(\text{C=N})$ bands of the ligands appear at a lower frequency (ca. 20 cm^{-1}) in the complexes. The appearance of $\nu(\text{N=C--O})$ at ca. 1500 cm^{-1} and $\nu(\text{C--O})$ at ca. 1330 cm^{-1} in the metal complexes also suggest bonding to metal through both deprotonated C--O groups. $\nu(\text{N--N})$ is observed at higher frequency (ca. 20 cm^{-1}) than the free Schiff bases, confirming coordination of the azomethine nitrogen to the metal. Unperturbed ring vibrations at 990, 650 and 400 cm^{-1} in the free Schiff bases and their complexes suggest non-involvement of the phenyl or pyridyl ring in bonding. Weak bands at 480-440 cm^{-1} and 360-340 cm^{-1} are tentatively assigned to $\nu(\text{M--O})$ and $\nu(\text{M--N})$.

The infra-red spectra data for ligand H2L^a and its complexes are given in Table 2. The table also includes infra-red data for the H2L' ligand and its complexes for the sake of comparison. The spectra in the region (3051 – 3059) cm^{-1} for both of the ligands, showed the presence of hydroxyl group - OH, which suggests existing of hydrogen bonding. Intra – hydrogen bonding is expected to occur in case of H2L as in case of H2L' due to the structural similarity of the two ligands. The relative small difference in absorbance between the two ligands can be explained in terms of more acidic hydrogen in case of H2L due to the withdrawal properties of the azo group attached.

The azo group is expected not to influence the coordination through structural factor as this group is quite far away from the coordination sites; formation of intra – hydrogen bonding in fact supports planar pattern of the ligand, inter – hydrogen bonding would also be formed in both ligands. The Phenolic - C – O spectra appeared at 1286 cm^{-1} and 1294 cm^{-1} for H2L, this reflects the higher acidity of OH group in H2L^a,

which in turn affects the strength of the C - O bond Values will be shifted towards lower frequency on coordination with metal ions, due to participation of oxygen in formation of the C - O - M bond. The band appear at 1635 cm^{-1} for H_2L^a ligands is assigned to the C=N stretching vibration again shifting occur on coordination as a result of Nitrogen engagement in this coordination the observed in the complexes in the region ($415 - 453$) cm^{-1} was attributed to ν (M - O), and the region ($534 - 535$) cm^{-1} was attributed to ν (M - N) this showed that the coordination occur through phenolic Oxygen, and imino nitrogen

CONCLUSION

In this paper we have reported the preparation of schiff base ligands derived from ligand L_1 N-(2-hydroxybenzylidene) (L) has been synthesized by the reaction between salicylaldehyde and benzoyl hydrazine The ligand L_1 and their complexes were characterized by spectral and analytical data. Based on these data on octahedral geometry has been assigned to Co(III),Ni(II)and Cu(II) complexes and the ligand L_2 N,N'-Ethylene bis(salicylideneimine)has been synthesized by the reaction between salicylaldehyde and ethylene diamine . The ligand L_2 and their complexes were characterized by spectral and analytical data. Based on these data on square planer geometry has been assigned to Co(III),Ni(II)and Cu(II) complexes. The schiff base ligand behaves a tridentate agent coordination through the position as nitrogen atom of azomethine group, oxygen atom of carbonyl group Benzohydrazide and oxygen atom of hydrazoic group of benzoyl hydrazine and the L_2 acts as bidentate and coordinate through nitrogen atom of azomethine and oxygen atom of hydroxy group of salicylaldehyde. All complexes not effect by air, light and a moisture suggesting high stability. The molar conductance measurements suggest the presence of chlorid ion inside the coordination sphere for Ni(II),Cu(II) and Co(III)-complex .

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