



SYNTHESIS AND SPECTROSCOPIC ANALYSES OF CO(II), NI(II), AND FE(II) COMPLEXES WITH SALICYLALDEHYDE DERIVATIVES OF BENZILMONOXIMEHYDRAZIDE

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ABSTRACT

New Co(II), Ni(II), and Fe(II) complexes with hydrazide Schiff bases have been synthesized. The complexes were characterized using elemental analyses, molar conductance, FT(IR), PMR, Electronic Absorption spectra as well as magnetic moment measurements. The low molar conductance values denote non-electrolytes. FT(IR) and PMR data reveal that ligand is coordinated to the metal ions by two bidentate centers via the nitrogen atom of the azomethine and oximino groups. The electronic absorption spectra as well as magnetic moment data reveal that formation of octahedral [ML₂] complexes.

Keywords: Co(II), Ni(II) and Fe(II) complexes, Hydrazine based ligands, Octahedral complexes.

1. INTRODUCTION

Schiff bases were the first effective chemotherapeutic agents employed systematically for the prevention and cure of bacterial infections in humans [1, 2]. The vast commercial success of these medicinal agents has made the chemistry of Schiff bases a major area of research and an important branch in pharmaceutical sciences [3]. Complex formation between metal ions and Schiff bases, combining antibacterial activity of Schiff bases and microbial activity of the metal ions, constitute an important field of research. Metal complexes of Schiff bases derived from hydrazides have gained considerable importance due to their pronounced fungicidal and antimicrobial activities [3-7]. Polynuclear metal ion complexes usually have peculiar spectroscopic and magnetic properties [8-11], besides wide applications in biological systems, catalysis, and material science [12-14]. In view of the bioinorganic and medicinal importance of Schiff base derived complexes, it was

thought worthwhile to synthesize and characterize some Co(II), Ni(II), and Fe(II) complexes with Schiff bases derived from condensation of salicylaldehyde and benzylmonoximehydrazide.

2. EXPERIMENTAL

All the chemicals used were of AR grade and used as supplied.

2.1. Synthesis of hydrazide Schiff bases

An ethanolic solution (20mL) of benzilmonoximehydrazide (10 mmol) was added to the solution (20 mL) of Salicylaldehyde (10 mmol) in ethanol, than few drops of concentrated hydrochloric acid were added to the reaction mixture, refluxed for 5 hours at 50-60°C, cooled and collected precipitated after filtration. After completion of reaction process, precipitate of ligand was formed as yellow solid and purity was checked by TLC [15].

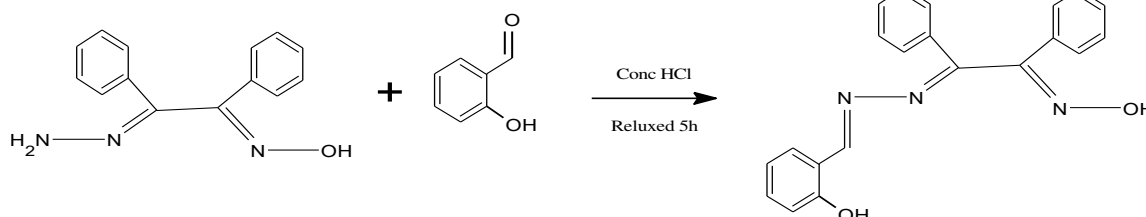


Fig. 1: Reaction scheme of preparation of ligand

2.2. Synthesis of the complexes

The following general procedure was used in the synthesis of all metal complexes. The metal chloride salts, (10mmol) were dissolved in water (20mL) and the solution was added to a warmed, stirred ethanolic solution (30 mL) of the ligand (20 mmol). The mixture was left under reflux with continuous stirring for 3 h and the solid complexes precipitated. The resulting solid was filtered off, washed several times with ethanol, and dried in vacuum over anhydrous calcium chloride.

2.3. Physical methods

The molar conductance of solid complexes in nitrobenzene was measured using a conductance bridge of the type 523 conductometer. Electronic spectra of all the synthesized compounds were recorded on JASCO V-650 spectrophotometer, using methanol as solvents. Perkin-Elmer spectrum 100 model was used for FT(IR) spectra in KBr discs. For PMR spectra of prepared compounds, Bruker AV300 NMR spectrometer was used. Magnetic measurements were performed by Gouy's method using magnetic susceptibility instrument (20 KG) at room temperature. Molar susceptibilities were corrected for diamagnetism of the component atoms applying Pascal's constants. Metal contents were determined complexometrically using standard ethylenediamine tetraacetic acid (EDTA) titration [16].

3. RESULTS AND DISCUSSION

The Schiff based ligand was prepared and purified by recrystallization several times from the appropriate

solvent until constant melting point. The purity of the ligand was confirmed by elemental and spectral analyses which gave a good agreement with the suggested molecular formula [17-21].

3.1. Elemental analysis and molar conductance data:

Elemental analyses (C, H, N, and metal content) of synthesized compounds are presented in table 1. The nitrobenzene solubility of the prepared complexes made determinations of the molar conductivity (Lm) of 10^{-3} mol solution at 25°C. The molar conductance of the synthesized complexes (table 1) is relatively low, indicating non-electrolytes in nature [22].

3.2. FT(IR) spectra and mode of bonding

Important FT(IR) spectral bands of the ligand and its complexes are shown in table 2. The ligand contains different coordination sites. The (C=N) of azomethine at 1615 cm^{-1} in the free ligand have higher shifts after complexation, indicating coordination of azomethine nitrogen [23-24]. Bands of the free ligand at 1571 cm^{-1} due to (C=NO) is shifted higher frequencies in spectra of metal complexes indicating participation of these groups in complex formation. The appearance of oximino (-OH) at 3272 cm^{-1} in the free ligand, is absent in its metal complexes, confirm coordinated ligand to metal ions via deprotonation of oximino group. So far FT(IR) spectra of all the complexes, non-ligand bands at $550\text{-}570$ and $490\text{-}495\text{ cm}^{-1}$ can be assigned to (M→N) and (M-N), respectively [25-27]. FT(IR) spectra reveal that the ligand coordinate to metal via azomethine and oximino nitrogen only.

Table 1: Analytical and Physical data of HBMHoHB ligand and its metal complexes

Compound	Color	% Yield	MP/ DP °C	Elemental Content Expected (Found)					Electrical Cond
				C	H	N	O	M	
HBMHoHB	Yellow	79.83	218	73.45 (73.11)	4.99 (4.90)	12.24 (12.11)	9.32 (9.30)	-	-
Co(BMH _o HB) ₂	Brown	76.82	253	67.77 (67.70)	4.30 (4.21)	11.30 (11.29)	8.61 (8.60)	7.93 (7.67)	5.18
Ni(BMH _o HB) ₂	Yellow	78.09	256	67.77 (67.71)	4.30 (4.29)	11.30 (11.22)	8.61 (8.58)	7.93 (7.90)	1.33
Fe(BMH _o HB) ₂	Ink Blue	79.99	254	68.11 (68.00)	4.32 (4.22)	11.35 (11.45)	8.65 (8.59)	7.55 (7.51)	1.99

Table 2: FT(IR) spectrum of HBMHSA ligand and its metal complexes

Compound	-OH (Oxo)	-OH (Phe)	Ar C-H	Ar C=C	>C=NN-	>C=NO-	Phe ring	M-N
HBMH _o HB	3272	3109	3078	2993	1615	1571	729	-
Co(BMH _o HB) ₂	-	3110	3079	2990	1635	1598	728	570, 495
Ni(BMH _o HB) ₂	-	3150	3079	2987	1633	1599	728	565, 490
Fe(BMH _o HB) ₂	-	3115	3076	2992	1640	1590	763	550, 495

3.3. Electronic and magnetic moment measurements:

The electronic absorption spectra of the metal complexes are studied as chloroform solution and compared with free ligand spectra (table 3). The shifts of the intra-ligand bands can be attributed to coordination to metal, while new bands (and change in color) of the complexes can be attributed to d-d transitions within the complexes. The electronic spectrum of the Co(II) complex displayed bands at 597nm ($\epsilon=300\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 488nm ($\epsilon=600\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$). These two bands are assignable $4A_{2g} \leftarrow 4T_{1g}(F)$ (ν_2) and $4T_{1g}(P) \leftarrow 4T_{1g}(F)$ (ν_3) transitions respectively [28-29]. The lowest band $4T_{2g} \leftarrow 4T_{1g}(F)$ (ν_1) could not be observed due to the limited range of the instrument used but could be calculated using the band fitting procedure $\nu_1 = \nu_2 - 10Dq$ suggested by Underhill and Billing [30] and is 1242nm. The value of $\nu_2/\nu_1 = 2.09$ close to in the range 2.1-2.2, reported for most of the

octahedral Co(II) compounds [31]. The spectral parameters for [Co(BMHoHB)] are $Dq = 870\text{cm}^{-1}$, $B' = 890\text{cm}^{-1}$, $B'/B = \beta = 0.90$ and $\beta\% = 9\%$. Reduction of Racah parameter from 971cm^{-1} (free ion value) to 886cm^{-1} and the $\beta\%$ value 9% indicate the covalent nature of the compound.

Ni(BMHoHB)₂ shows three bands at 1040nm ($\epsilon=5\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$), 583nm ($\epsilon=988\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) and 511nm ($\epsilon=3989\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) due to $3T_{2g} \leftarrow 3A_{2g}$ (ν_1), $3T_{1g} \leftarrow 3A_{2g}$ (ν_2) and $3T_{1g}(P) \leftarrow 3A_{2g}$ (ν_3) transitions, respectively, in an octahedral symmetry [32]. The value of ν_2/ν_1 is 1.78 which lies in the usual range (1.60-1.82), reported for the majority of octahedral Ni(II) compounds [30, 32]. The spectral parameters for [Ni(BMHoHB)₂] are $Dq = 950\text{cm}^{-1}$, $\beta' = 840\text{cm}^{-1}$, $B'/\beta = \beta = 0.80$ and $\beta\% = 19\%$. Reduction of Racah parameter from 1030cm^{-1} (free ion value) to 842cm^{-1} and the $\beta\%$ value 19% indicate the covalent nature of the compound.

Table 3: Electronic Absorption spectra of HBMHoHB ligand and its metal complexes

Compound	Solvent	λ_{nm}	ϵ	Transition
HBMHoHB	Methanol	339	13166	Oximino $\pi \rightarrow \pi^*$
		297	20899	Azomethine $\pi \rightarrow \pi^*$
Co(BMHoHB) ₂	Chloroform	597	300	$4T_{2g}(F) \rightarrow 4A_{2g}$
		488	600	$4T_{1g}(F) \rightarrow 4T_{1g}(P)$
Ni(BMHoHB) ₂	Chloroform	1040	5	$3A_{2g} \rightarrow 3T_{2g}$
		583	988	$3A_{2g} \rightarrow 3T_{1g}$
		511	3989	d-d transition
Fe(BMHoHB) ₂	Chloroform	598	233	$5T_{2g} \rightarrow 5E_g$
		483	2256	$5E_g \rightarrow 5B_{1g}$

The electron absorption spectra of [Fe(BMHoHB)₂] shows a symmetrical broad band around 598nm ($\epsilon = 233\text{dm}^3/\text{mol}/\text{cm}$), along with a small band at around 483nm ($\epsilon = 2256\text{dm}^3/\text{mol}/\text{cm}$). For Fe(II) high spin case, the ground state (5D) is supported to split into 5E_g and $^5T_{2g}$ states, as such are d-d transition corresponding to $^5T_{2g} \rightarrow ^5E_g$ may be expected. However, the 5E_g state is expected to further split into $^5B_{1g}$ and $^5A_{1g}$ owing perhaps, to Jahn-Teller distortion. As such Fe(II) high spin octahedral complexes could show two, fairly closely spectral bands. The bands observed at 598nm and 483nm are therefore assignable to d-d transitions.

Magnetic moment values of Ni(II) complexes (table 3) fall within the 3.00-3.30 range normally observed for octahedral Ni(II) complexes [27, 32].

3.4. PMR spectra

PMR spectra of HBMHoHB ligand was recorded in d₆ DMSO solution and TMS used as internal standard. The ¹H NMR data and their assignment are illustrated in table 4. Two singlets observed at δ 12.25ppm and δ 12.00ppm in HBMHoHB ligand. The oximino group is expected to release the proton much more easily than the phenolic proton of the salicylaldehyde moiety of the ligand, since the deshielding effect is more on the proton of the oximino group than that on the phenolic group, therefore the singlet at δ 12.25ppm ascribed to oximino proton of the ligand. The singlet at δ 12.00ppm in the PMR spectrum of the ligand (table 4) assigned for phenolic-OH group remains unaltered in the PMR spectrum of complexes confirm the non-coordination of phenolic-OH.

Table 4: ¹H NMR spectrum of HBMHoHB ligand and its metal complexes

Compound	-OH (oximino)	-OH Phenolic	-CH=	Phenyl Rings
HBMHoHB	12.25	12.00	8.30	6.8-7.8

4. STRUCTURAL INTERPRETATION AND CONCLUSION

Although many articles have been published on metal ion complexes of Schiff bases derived from benzilmonoxime due to their biological activity and wide applications in pharmaceutical sciences, most dealt with mononuclear metal complexes [3-7]. We reported preparation and characterization of some hydrazide Schiff base derivatives and their binuclear complexes. So, in this article we extend our research on preparation and characterization of Co(II), Ni(II) and Fe(II) complexes with some salicylaldehyde derivatives of benzilmonoximehydrazide Schiff bases. The structures proposed are based on octahedral geometries and the ligand coordinate to the metal ions via azomethine and oximino group nitrogen atoms. Conductance data reveal that the complexes are non-electrolytes. According to the above data, the structure of the complexes is given in fig. 2.

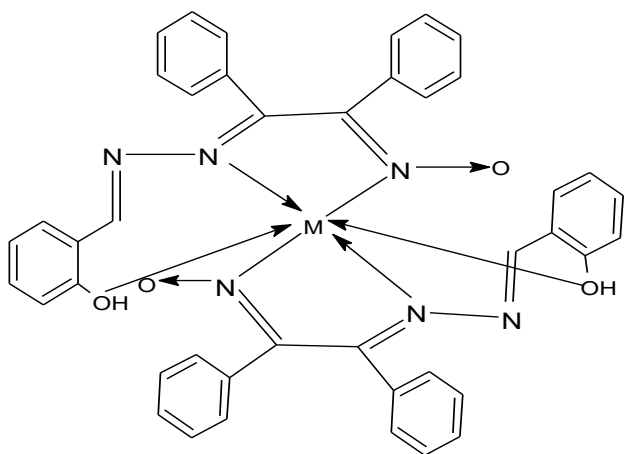


Fig. 2: Proposed structure of metal complexes of Ligand HBMHoHB [where M = Co(II), Ni(II) and Fe(II)]

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