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Research Article

SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE 3-[2-(HYDROPEROXYIMINO)-1,2-DIPHENYLETHYLIDENE]HYDRAZINYLIDENE} METHYL]PHENOL METAL (II) COMPLEXES

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ABSTRACT

A new series of Fe(II), Co(II) and Ni(II) complexes of the Schiff base ligand, 3-[2-(hydroperoxyimino)-1,2-diphenylethylidene]hydrazinylidene}methyl]phenol ($C_{21}H_{16}N_3O_2$), was synthesized in an ethanolic medium. The Schiff base was derived from the condensation reaction of 3-hydroxybenzaldehyde and benzilmonoximehydrazide at refluxed condition. Elemental analysis, FT(IR), Electronic absorption and PMR spectral data, molar conductance measurements and melting points were used to characterize the Schiff base and the metal complexes. From the physico-chemical analysis data, the prepared metal complexes formed had the general formulae [ML_2], where L = Schiff base ligand ($C_{21}H_{16}N_3O_2$) and M = Co, Ni and Fe. On the basis of FT(IR), electronic absorption spectra, and NMR data, "O" and "N" donor atoms of the Schiff base ligand participated in coordination with the metal (II) ions, and thus, a six coordinated octahedral geometry for all these complexes was proposed. Molar conductance studies on the complexes indicated they were non-electrolytic in nature.

Keywords: Benzilmonoximehydrazide, 3-hydroxybenzaldehyde, Octahedral, Electronic absorption spectra, Fe(II), Co(II) and Ni(II) complexes..

1. INTRODUCTION

The chemistry of transition metal complexes with Schiff base ligands containing oxygen and nitrogen as donor atoms has continued to attract the attention of researchers. These ligands are known to coordinate to metal atom in different ways under different reaction conditions. The ligands are derived from the condensation reaction of aldehydes and primary amines [1].

One of the major areas of research on the Schiff base metal complexes is their biological activity with the main aim being the discovery of safe and effective therapeutic agents for the treatment of bacterial infections and cancers. A number of Schiff base metal complexes have a diverse spectrum of biological and pharmaceutical activities. For instance, transition metal complexes of Schiff base ligands bearing "O" and "N" donor atoms are very important because of their biological properties such as antibacterial, anti-inflammatory [2], analgesic [3-4], antitubercular[5], antioxidant [6], antifungal, anticonvulsant [7], and anthelmintic [8]. The Schiff base transition metal complexes have also been used as biological models to understand the structure of bio-molecules and biological processes [9].

Ferrous, cobalt and nickel are life-essential metallic elements and exhibit greater biological activity when associated with certain metal protein complexes, participating in oxygen transport, electronic transfer reactions, or the storage of ions [10]. This has created enormous interest in the study of systems containing these metals [11, 12].

Fe(II), Co(II) and Ni(II) complexes of the Schiff base, 3-[2-(hydroperoxyimino)-1,2-diphenylethylidene] hydrazinylidene}methyl]phenol, which to the best of our knowledge has neither been synthesized nor reported and this was studied in our laboratories.

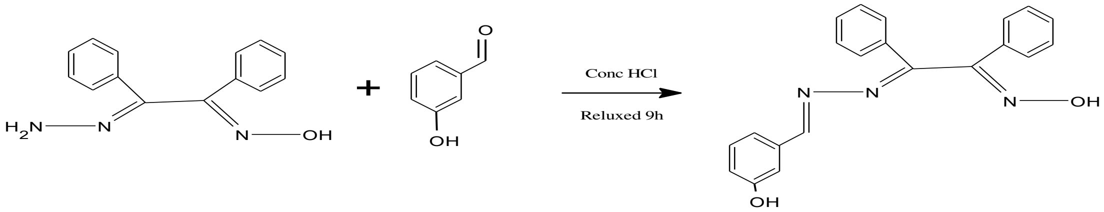
2. EXPERIMENTAL

2.1. Material and Methods

The chemicals and solvents used in this research work were of analytical grade sourced from Lob Chemie Company. Solvents and metal chlorides were purchased from Merck and used as received. An electronic spectrum of all the synthesized compounds was recorded on JASCO V - 650 spectrophotometer, using methanol as solvents. Perkin-Elmer spectrum 100 model was used for FT(IR) spectra in KBr discs. Brucker AV300 NMR spectrometer was used for PMR spectra of prepared compounds.

2.1.1. Preparation of HBMHmHB Ligand

A 0.100M solution of α-benzilmonoximehydrazide (20ml ethanol) was added to 0.125M alcoholic solution of m-hydroxybenzaldehyde, few drops of concentrated hydrochloric acid was then added to the reaction mixture, refluxed for 9 hours at 50-60°C, cooled and collected the precipitated after filtration. After completion of the reaction precipitate of ligand were formed as yellow solid and purity was checked by TLC.



Scheme 1: Preparation of ligand HBMHmHB

2.1.2. Synthesis of the α-benzilmonoxime-hydrazide-m-hydroxybenzaldehyde metal(II) Complexes

The metal complexes of α-benzilmonoximehydrazide-m-hydroxybenzaldehyde (HBMHmHB) ligand were prepared by mixing of 0.1M of HBMHmHB with 0.05M metal chlorides [Fe(II), Co(II) and Ni(II)] keeping ligand-metal ratio 2:1 in 25ml ethanol. The reaction mixture was refluxed for 5 hours on water bath (50-60°C). The reaction mixture was cooled and the pH was adjusted to 8, colored precipitated after filtration was collected.

3. RESULTS AND DISCUSSION

The Schiff base ligand α-benzilmonoximehydrazide-m-hydroxybenzaldehyde in this study was first synthesized by reflux method. The metal(II) complexes of the ligand are new and thus reported for the first time.

The Schiff base ligand is soluble in common organic solvents such as Choroform, ethanol, methanol, nitrobenzene, DMF and DMSO. The prepared ligand and its transition metal(II) complexes are colored solids which are stable in air [13]. The melting points of the complexes were higher than that of the Schiff base ligand indicating that the complexes are more stable than the ligand α-benzilmonoximehydrazide-m-hydroxybenzaldehyde [14].

3.1. Conductivity Measurements

The molar conductance values of the synthesized compounds in 10^{-3} M in nitrobenzene were measured at room temperature. The conductance values of the synthesized compounds were below 20 $Ohm^{-1}\cdot cm^{2}$ mol^{-1}, indicating their non-electrolytic nature [15-16]. This suggested that there were no anions present outside the coordination sphere of the complexes.

Table1: Analytical and Physical data of HBMHmHB ligand and its metal complexes

Compound	Color	% Yield	MP/DP °C	Elemental Content Expected (Found)					Electrical Cond
				C	H	N	O	M	
HBMHmHB	Yellow	74.82	209	73.45 (73.41)	4.99 (4.96)	12.24 (12.19)	9.32 (9.28)	-	-
$Co(BMHmHB)_2$	Brown	72.63	275	67.77 (67.66)	4. 30 (4.29)	11.30 (11.26)	8.61 (8.55)	7.93 (7.69)	5.09
$Ni(BMHmHB)_2$	Yellow	75.68	278	67.77 (67.68)	4. 30 (4.26)	11.30 (11.29)	8.61 (8.56)	7.93 (7.88)	2.66
$Fe(BMHmHB)_2$	Ink Blue	72.69	269	68.11 (68.08)	4.32 (4.26)	11.35 (11.29)	8.65 (8.61)	7.55 (7.54)	0.96

3.2. Electronic Spectral Analysis

The electronic spectral data of the Schiff base ligand α-benzilmonoximehydrazide-m-hydroxybenzaldehyde and its transition metal(II) complexes are given in the table 2. The ligand α-benzilmonoximehydrazide-m-hydroxybenzaldehyde showed three bands at 325 nm (ε=11875

dm^3/mol/cm), 230nm (8163 dm^3/mol /cm), and 215nm (8500dm^3/mol/cm). The band at 215nm (8500dm^3/mol/cm) is due to the π–transition in oximino group. The band appearing at 230nm (8163 dm^3/mol/cm) is assignable to *n*–transition of nonbonding electrons present on the nitrogen of the azomethine group (-HC=N). The band at 325 nm (ε=11875 dm^3/mol/cm) is due to *n*–transition of the phenolic group [17-18].

The electron absorption spectra of $[Fe(BMHmHB)_2]$ shows a symmetrical broad band around 591nm(ε = 249 dm^3/mol/cm), along with a small band at around 475nm (ε = 3096 dm^3/mol/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 591nm and 475nm are therefore assignable to *d-d* transitions.

In the Co(II) complex, two bands were observed at 278 nm (ε = 4869dm^3/mol/cm) and 397 nm (ε = 12396dm^3/mol/cm). This was a shift towards longer wavelength with respect to the spectrum of the Schiff base ligand. The band at 278nm was due to intra-ligand transition, and the band at 397 nm was as a result of *d-d* transition for $^3T_{1g}$ (F) ⟶ $^3T_{2g}$ which is within the range for octahedral configuration as reported in many other octahedral cobalt (II) complexes [19-21].

The electronic spectrum of Ni(II) complex showed three bands at 240nm (ε = 12396dm^3/mol/cm), 331 nm (ε = 9568 dm^3/mol/cm), and 436 nm (ε = 2061dm^3/mol/cm). The band at 240nm was probably due to intra-ligand transition, while the band at 331 nm was due to charge transfer. The observed band at 436 nm was as a result of *d-d* transition for $^3A_{2g}$ ⟶ $^3T_{2g}$ which favors an octahedral geometry for the Ni(II) complex [22].

Table 2: Electronic Absorption spectra of HBMHmHB ligand and its metal complexes

Compound	Solvent	λ_{nm}	ε	Transition
HBMHmHB	Methanol	325	11875	Phenolic $\pi\rightarrow\pi^*$
		230	8163	Azomethine $\pi\rightarrow\pi^*$
		215	8500	Oximino $\pi\rightarrow\pi^*$
$Co(BMHmHB)_2$	Chloroform	397	12396	$^3T_{1g}(F)\rightarrow{}^3T_{2g}$
		278	4869	MLCT
$Ni(BMHmHB)_2$	Chloroform	436	2061	$^3A_{2g}\rightarrow{}^3T_{2g}$
		331	9568	MLCT
		240	12396	MLCT
$Fe(BMHmHB)_2$	Chloroform	591	249	$^5T_{2g}\rightarrow{}^5E_g$
		475	3096	$^5E_g\rightarrow{}^5B_{1g}$

3.3. FT(IR) Spectral Analysis

The binding mode of the Schiff base ligand α-benzilmonoximehydrazide-m-hydroxybenzaldehyde to the metal ions in complexes was determined by comparing the FT(IR) spectrum of the free ligand with the spectra of the metal(II) complexes. The stretching frequency for the azomethine and C=N bond was observed at 1575 and 1460cm^{-1} respectively for the free ligand α-benzilmonoximehydrazide-m-hydroxybenzaldehyde [23-24]. The C=N stretching frequencies in the metal(II) complexes a shift to higher wave numbers [25-26]. This indicated coordination of α-benzilmonoxime-hydrazide-m-hydroxybenzaldehyde through the azomethine and oximino nitrogen [27]. Moreover, the appearance of additional weak bands in the region 490-570cm^{-1} attributed to υ(M-N) [28], further confirmed complexation [29]. This showed that the Schiff base ligand coordinated to the metal via "N" atoms.

In the free Schiff base ligand, the band at 3112 cm^{-1} due to υ(C-OH, phenolic) shifted to lower wave number by 40-60cm^{-1} in the complexes indicating the coordination of the phenolic oxygen atom to the metal ion [30]. Therefore, it can be concluded that coordination took place via phenolic oxygen and azomethine as well as oximino nitrogen of the Schiff base ligand molecule.

3.4. Elemental Analysis

The microanalysis data suggested that all the complexes were mononuclear where two moles of the ligand were coordinated to the central metal atom. The data, therefore, suggested that the metal to ligand ratio in the complex was 1:2 and the general formula for the complexes as [ML$_2$] (M = Co(II), Ni(II), Fe(II); L = α-benzilmonoximehydrazide-m-hydroxybenzaldehyde [31, 32]. The theoretical (calculated) values were found to be in good agreement with the experimental values (table 1).

3.5. NMR Spectral Analysis

The ^{1}H NMR spectra of the Schiff base was recorded in DMSO-d_6. PMR spectra of HBMHoHB ligand was recorded in d$_6$ DMSO solution and TMS used as internal standard. The ^{1}H NMR data and their assignment are illustrated in table 4. Two singlets observed at δ12.20ppm and δ11.70ppm in HBMHm HB ligand. The oximino group is expected to release the proton much more easily than the phenolic proton of the salicyaldehyde 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 δ12.20ppm ascribed to oximino proton of the ligand. The singlet at δ11.70ppm 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. The ^{1}H NMR spectrum of the α-benzilmonoximehydrazide-m-hydroxybenzaldehyde showed a singlet peak at 8.20 ppm corresponding to the azomethine proton (-N=CH-) [30, 31], an indication that the Schiff base was formed during the condensation reaction.

Table 3: FT(IR) spectrum of HBMHmHB ligand and its metal complexes

Compound	-OH (Oxo)	-OH (Phe)	Ar C-H	Ar C=C	>C=NN-	>C=NO-	Phe ring	M-N
HBMHmHB	3260	3112	3070	2960	1575	1460	729	-
Co(BMHmH)$_2$	-	3070	3079	2990	1611	1501	728	570, 494
Ni(BMHmHB$_2$	-	3098	3079	2987	1609	1525	728	575, 490
Fe(BMHmHB$_2$	-	3075	3076	2992	1608	1500	763	545, 499

Table 4: ^{1}H NMR spectrum of HBMHmHB ligand and its metal complexes

Compound	-OH (oximino)	-OH Phenolic	-CH=	Phenyl Rings
HBMHmHB	12.20	11.70	8.20	6.9-7.8

4. CONCLUSION

The Schiff base ligand α-benzilmonoximehydrazide-m-hydroxybenzaldehyde and its transition metal(II) complexes, [ML$_2$] (M = Co, Ni, and Fe), were successfully synthesized and characterized. The deprotonated tridentate Schiff base ligand α-benzilmonoxime-hydrazide-m-hydroxybenzaldehyde coordinated to the transition metal(II) ion via the azomethine and oximino nitrogen and phenolic oxygen resulting in the formation of a stable six-membered chelate ring. An octahedral geometry has been proposed for the metal(II) complexes based on the electronic spectra. The complexes formed are neutral with no free anions outside the coordination sphere. The metal (II) complexes exhibited better antibacterial properties than the parent Schiff base ligand under the same experimental conditions. It can also be deduced from this study that the antibacterial growth inhibition ability of the synthesized compounds increased with increasing concentration.

Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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