



SYNTHESIS, COMPLEXATION AND SPECTRAL STUDY OF NOVEL 2-BROMOBENZALDEHYDE DERIVED BENZILMONOXIMEHYDRAZONE

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ABSTRACT

In this newly approached method a novel series of Transition metal complexes were synthesized by the reaction of 2-bromobenzaldehyde react with benzilmonoximehydrazone in ethanolic solution at refluxed condition. Mononuclear complexes were synthesized by reaction with Cu(II), Ni(II) and Co(II) chloride salts. The ligand and its complexes were characterized by elemental analysis, UV, FTIR and PMR spectral studies.

Keywords: 2-Bromobenzaldehyde, metals, complexes, PMR, FTIR

1. INTRODUCTION

Schiff bases and their metal complexes are an extensively investigated area of chemistry. They are useful in the preparation of medicines, industrial catalysts, analytical reagents, agro chemicals and other industrial products. Schiff bases show high antiviral activity [1]. Several Schiff bases are found to possess anti-inflammatory, radical scavenging property, analgesic [2] and anti-oxidative action [3]. Schiff base derived Benzilmonoxime are known as chelating agents and frequently used in extractive and analytical chemistry. A number of benzilmonoxime have been reported show interesting stereochemistry. Benzilmonoxime are of special interest owing to their biological activities and semi-conducting properties [3]. In view of this and our continuing interest on the synthesized of α -Benzilmonoximehydrazone [4, 5] and its 2-bromobenzaldehyde derivative [6-9], we wish to report the synthesis, complexation and spectral study of novel 2-Bromobenzaldehydebenzilmoximehydrazone (HBMHOB). The properties of the synthesized ligand and its complexes were investigated by spectroscopic methods.

2. MATERIAL AND METHODS

All the chemicals used were of analytical grade and used as supplied by the manufactures. Conductivity measurements were carried out on Toshaniwal digital conductivity meter. The melting point of ligand and its metal complexes were determined by Electro thermal

melting point apparatus. FTIR spectra were recorded using (KBr pellets) $4000-400\text{ cm}^{-1}$ on FTIR tests Perkin-Elmer Infrared spectrophotometer. Uv-visible or electronic spectra were recorded on JASCO 650 spectrophotometer using methanol/0.1N NaOH solvents for ligands and methanol/ chloroform solvents for all metal complexes. Bohr magnetic properties recorded at The Institute of Science, Madam Kama road, Mumbai using Gouy electromagnetic balance at 4 amp and 6 amp at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ and $\text{Ni}(\text{en})_3\text{S}_2\text{O}_3$ as a calibrant. The diamagnetic corrections were made by Pascal's constant [10]. PMR spectra were recorded on Bruker AV300 NMR spectrometer using TMS an internal standard. The EPR spectra were recorded on a model 'E-112-ESR Spectrometer' using TCNE as standard at RT and LNT condition.

2.1. Preparation of ligand

2-Bromobenzaldehyde derivative benzilmoximehydrazone was prepared by reported method [11].

2.2. Preparation of metal complexes

Co(II), Ni(II) and Cu(II) complexes were prepared by mixing a hot ethanolic solution of ligand (2mol) and aqueous solution of metal chlorides (1mol). To the boiling solution of ligand (0.02 mol) in ethanol (50cm^3) was added metal chloride (0.01 mol) dissolved in a minimum quantity of water and adjusted the pH of the mixture to 7.5-8.0 with dilute NaOH solution. The complexes were recrystallized from methanol.

3. RESULTS AND DISCUSSION

The analytical data of the ligand and its metal complexes are shown in Table 1. The analytical data are consistent with proposed molecular formula. All the complexes are insoluble in water and varyingly soluble in common organic solvents like methanol, chloroform, benzene,

nitrobenzene etc. The soluble complexes have been found to be non electrolytes [12] in nitrobenzene. The ligand and its metal complexes were characterized on the basis of elemental analysis, FT(IR), magnetic susceptibility measurements, electronic spectra and EPR data.

Table 1: Analytical and physical data of the ligand and its metal complexes

Compound	Color	Yield %	M.P./Dec. point°C	Elemental Analysis					Magnetic Moments (B.M.)	Electrical Conductance 10^{-3} M(in DMF) mhos
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)		
HBMHOBB	Yellow	76.98	205	-	62.08 (61.92)	3.97 (3.88)	10.34 (10.02)	3.94 (3.85)	-	-
Co(BMHOBB) ₂	Brown	76.85	218	6.78 (6.64)	57.97 (57.88)	3.45 (3.40)	9.66 (9.59)	3.68 (3.63)	1.83	1.95
Ni(BMHOBB) ₂	Light Green	83.28	219	6.75 (6.34)	57.98 (57.83)	3.45 (3.45)	9.66 (9.68)	3.68 (3.88)	3.29	1.28
Cu(BMHOBB) ₂	Green	76.26	223	7.27 (6.78)	57.66 (57.29)	3.43 (3.41)	9.61 (9.58)	3.66 (3.56)	2.0	7.56

3.1. Magnetic moment

Brown color Co(II) complex shows a room temperature magnetic moment of 1.83 BM (Table 1), indicate the low spin octahedral Co(II) complex [13]. The light green colored Ni(II) complex shows room temperature magnetic moment of 3.29BM and observed magnetic moment expected for octahedral Ni(II) complexes. The green colored [Cu(BMHOBB)₂] shows a room temperature magnetic moment of 2.0 BM in solid state, suggests distorted octahedral geometry of this complex [13].

3.2. Electronic Absorption Spectra

The UV- spectra of the prepared compounds in the ultra-violet region show high intensity band at around 339nm ($\epsilon = 12723 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), 226nm ($\epsilon = 20905 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). These bands are due to the $\pi \rightarrow \pi^*$ (allowed) transitions of azomethine and oximino environment in the synthesized molecule. In many isonitrosoketones [16, 17], a band occurs at similar positions and intensity, reported as the ($\pi \rightarrow \pi^*$) transitions in the present compound.

The electronic spectrum of the orange color Co(II) complex, observed two bands at 895nm and 406nm respectively and assigned to ${}^2E_g \rightarrow {}^2T_{2g}(v_1)$ and ${}^2E_g \rightarrow {}^4A_{2g}(v_3)$ transitions respectively assuming low spin octahedral geometry around the metal ion. The transitions ν_1 and ν_3 yield fairly good values for 10Dq and B, therefore, using appropriate equations [14] and the values of 10Dq and B are found to be 798nm and 9860 cm^{-1} respectively. The values of β , covalency factor

can be obtained as 9860 cm^{-1} , taking the free ion B value for Co(II) as 9710 cm^{-1} . The percent character (B') can be calculated for the $B' = \frac{B-B'}{B} \times 100$ and is found to be 11.66%.

Table 2: Electronic spectral data for HBMHOBB and its metal complexes

Compound	λ_{nm}	ϵ ($\text{dm}^3/\text{mol}/\text{cm}$)	Transition
HBMHoBB	339	12723	$\pi \rightarrow \pi^*$
	249	20905	$\pi \rightarrow \pi^*$
[Co(BMHoBB) ₂]	895	~10	${}^2E_g \rightarrow {}^2T_{1g}$
	406	34482	${}^2E_g \rightarrow {}^2T_{2g}$
	298	36020	MLCT
[Ni(BMHoBB) ₂]	976	8	${}^3A_{2g} \rightarrow {}^3T_{1g}$
	619	62	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$
[Cu(BMHoBB) ₂]	435	14371	MLCT
	631	191	${}^2T_{2g} \rightarrow {}^2E_g$
	258	13530	MLCT

The bands observed at 976nm and 619nm in the Ni(II) complex electronic spectrum are assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_2)$ transitions respectively on the basis of idealized octahedral geometry [15]. The ratio ν_2/ν_1 is found to be 1.57, which falls in the range reported for the other octahedral complexes of Ni(II) supporting the assignment [16]. From the observed position of ν_1 and

ν_2 transitions, the frequency of the third transition ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) and B values has been calculated [17]. The third band ν_3 is expected to occur at 522nm. However, this band is not observed in the solution spectrum of the complex probably because, it is masked by the tail-end of the strong charge transfer band around 435nm. The value of the Racah interelectronic repulsion parameter B is 7420cm^{-1} , the covalency factor is found to be 8216cm^{-1} and is in close agreement octahedral Ni(II) complexes [18].

A band at 631nm is attributed to ${}^2E_g \rightarrow {}^2T_{2g}(D)$ transition suggesting a distorted octahedral geometry for Cu(II) complex.

3.3. IR spectra

The band at 3209cm^{-1} for the free ligand due to N-OH which is absent in metal complexes, suggests the deprotonation of the hydroxyl group of the oxime in the process of formation of the complexes. The observed bands at 1569cm^{-1} and 1625cm^{-1} due to the oximino $\nu(C=NO)$ and azomethine (C=NN) groups in ligand was shifted to higher frequencies in its complexes, indicating the participation of these groups in coordination [14]. This fact is further supported by the appearance of new bands in the regions $500\text{-}571\text{ cm}^{-1}$ in the complexes which were assigned to the $\nu(N-M)$ stretching vibration [16].

3.4. Proton Magnetic Resonance spectrum

The PMR spectrum of o-bromobenzaldehyde derived benzilmonoximehydrazide ligand in deuterated DMSO was recorded using tetramethylsilane as the internal standard. The PMR spectrum data of HBMHOBB is summarized in Table 4. The oximino proton appears as a singlet at 10.17ppm and all the 14 aromatic protons appears as a multiplet in the range 8.15-8.43ppm. In addition to this, there are aliphatic protons present as a bridge between azomethine ($>C=NN-$) groups. In NMR spectrum of HBMHOBB ligand, methine singlet proton observed at 8.70ppm.

3.5. EPR Spectra

The nature of the cEPR spectrum of Cu(II) complex suggest distorted octahedral structure as only two g values, which follow the trend $g_{\parallel} > g_{\perp} > 2.0023$, could be obtained [16]. Absence of any resolution at the g_{\perp} position may be implying that g_x and g_y are same or nearly same [17]. That g_{\perp} is not lower than 2.03 also indicate that the unpaired electron in the Cu(II) ion is in the $d_{x^2-y^2}$ orbital [18]. The $G \geq 4$, indicate absence of exchange coupling. The high G values found taken to imply negligible exchange interaction. The α^2 value is 0.702 for Cu(II) complex indicates appreciable covalent character for them.

Table 3: FT (IR) spectral data for HBMHOBB and its metal complexes

Compound	$\nu(O-H)$	Ar(C=C)	Ar. C-H	C=NN	C=NO	N - O	N-N	M-N
HBMHOBB	3209	3107	3082	1625	1569	1018	1095	-
Co(BMHOBB) ₂	-	3106	3073	1675	1586	1010	1093	515, 551
Ni(BMHOBB) ₂	-	3104	3069	1681	1589	1007	1109	505, 571
Cu(BMHOBB) ₂	-	3216	3082	1677	1571	1008	1099	505, 566

Table 4: PMR spectrum of o- -Bromobenzaldehyde derivative of α Benzilmonoximehydrazone ligands

Compound	-OH	-CH=	Phenyl Ring
HBMHoBB	10.17	8.70	8.15-8.43

Table 5: EPR spectral data for the metal complexes of HBMHOBB

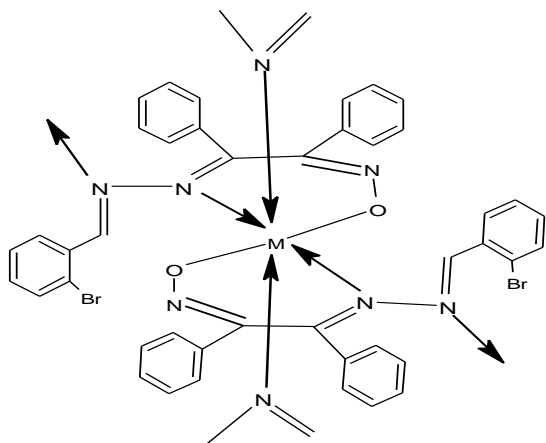
Compound	g_{\parallel}	g_{\perp}	g_{ave}	$A_{\parallel} (x 10^{-4}\text{cm})$	$A_{\perp} (x 10^{-4}\text{cm})$	$A_{ave}(x 10^{-4}\text{cm})$	α^2
Cu(HBMHOBB) ₂	2.192	2.041	2.091	20	08	12	0.7020

4. CONCLUSION

All complexes have high decomposition points which suggest high thermal stability for metal complexes and they are non-electrolytic in nature. The spectral and

magnetic data suggests that Co(II) complex is low spin octahedral, Ni(II) complex is high spin octahedral and Cu(II) complex is distorted octahedral environment. FT (IR) spectral data suggests that complexes coordinate

with metal ion through nitrogen atoms only. On the basis of magnetic and spectral data, structure of Co (II), Ni(II) and Cu(II) complexes tentatively assigned as;



Where: M = Co(II), Ni(II) and Cu(II)

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