



SYNTHESIS AND CHARACTERIZATION OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH 2-[-(4-BROMOBENZYLIDENE)HYDRAZINYLIDENE]-1, 2-DIPHENYLETHANIMINE

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ABSTRACT

New Schiff base ligand 2-[-(4-bromobenzylidene) hydrazinylidene]-1,2-diphenylethanamine was synthesized via condensation of α -benzilmonoximehydrazone and 4-bromobenzaldehyde in ethanol. Complexes were obtained from 1:2 molar ratio reactions with metal ions and ligand, 2NA on reaction with $MCl_2 \cdot nH_2O$ salt yields complexes corresponding to the formulas $[M(L)_2]$, where $M = Co(II), Ni(II)$ and $Cu(II)$. The ¹H-NMR, FT-IR, electronic absorption spectra and elemental analysis were used for the characterization of the ligand. The geometry of complexes elucidated by FT-IR, electronic absorption spectra, conductance, and magnetic susceptibility measurements. All complexes are non-electrolytes in nitrobenzene solution. Octahedral geometries have been suggested for each of the complexes. The ligand is bidentate and leads to deprotonation coordination.

Keywords: α -benzilmonoximehydrazone, 4-bromobenzaldehyde, Diphenylethanamine, Octahedral geometries

1. INTRODUCTION

Schiff base is a class of organic compounds which are also known as azomethine, aniline or imines have attained significant position in the subject of coordination chemistry due to its various applications. It is utilized as a ligand in the formation of various transition metal complexes. The Schiff bases were acting excellent ligands [1] to form complexes with transitional metal ions due to its ability to donate proton/lone pair of electrons and having number of bonding sides [2]. This guides the different stereo-chemical structures and also provides the information related to the kinetic stability and thermodynamic stabilities of the complexes. However, mono-dented Schiff-base ligands were prepared and used for preparation of various types of metal ion complexes yet called as multi-denatad ligands, which are of great importance due to its chelating property. Hence extra stability of the metal ion complexes having interesting geometries was observed [4]. Compounds containing an azomethine group or imine are a class of important compounds in medicinal and pharmaceutical field [5]. The biological applications of these compounds have attracted remarkable attention. Some Schiff-bases exhibits antibiotic, antiviral and antitumor properties because of their specific

structure [6]. The wide use of antibiotics resulted in the serious medical problem of drugs resistance and public health concern.

The work presented in this paper concerns the Preparation and Characterization of Co(II), Ni(II) and Cu(II) complexes with novel Schiff base ligand derived from 2-[-(4-bromobenzylidene) hydrazinylidene]-1,2-diphenyle-thanimine in 1:2 (M:L) ratio.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals used were of reagent grade supplied by either S. D. fine chem and used as received.

2.2. Instrumentation

UV-Vis spectra were recorded on a JASCO 450 Spectrophotometer. FT (IR) spectra were taken on a Perkin-Elmer spectrum 100 Infrared spectrophotometer FT (IR) Spectrophotometer (4000 - 400) cm^{-1} with samples prepared as KBr discs. Molecular weight was determined by Rast Camphor method, confirming the monomeric nature of the compounds. Conductivities were measured for $10^{-3}M$ of complexes in nitrobenzene at 25°C using Toshaniwal digital conductivity meter. Bohr magnetic properties were 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. Nuclear magnetic resonance spectrum ^1H NMR for ligand was recorded in DMSO-d_6 using a Bruker 300 MHz instrument with a tetra methyl silane (TMS) as an internal standard. In addition melting points were obtained using (Stuart Melting Point Apparatus).

2.3. Preparation of ligand (HL)

The title ligand was prepared [7] by mixing of ethanolic solution of the α -Benzilmonoximehydrazone (0.100 mol) and p-bromobenzaldehyde (0.11mol) and adding 2ml of Hydrochloric acid. The resulting mixture was refluxed for 3h using water condenser. After complete reflux, the pH of solution was adjusted at 5 using 0.1N NaOH, cooled at room temperature, solid separated, dried at 110°C in oven.

2.4. Preparation of the divalent metal complexes of HBMHpBB ligand

2.4.1. Bis(α -Benzilmonoximehydrazone-p-bromobenzaldehyde) Co(II), $[\text{Co}(\text{BMMHpBB})_2]$

To a solution of 1.19g Copper chloride hexahydrate (5mmol) in 10cm^3 , water was added gradually with stirring a solution of 4.06g of HBMHpBB (10mmol) in 30cm^3 ethanol. The pH of the mixture raised slowly to 7.5 with dilute (0.10N) NaOH, when a green colored

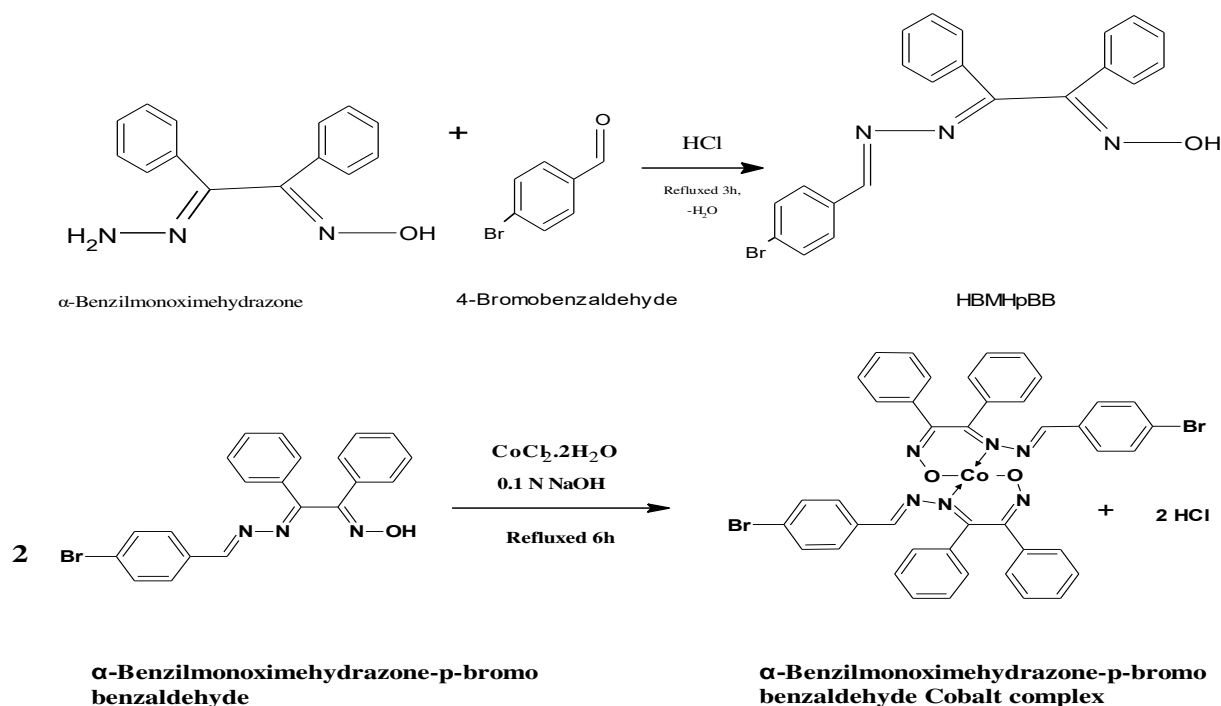
complex was separated, which was digested 30 min on waterbath and cooled, then filtered, washed with hot water (25cm^3) and dried at 100°C . It was recrystallized from methanol.

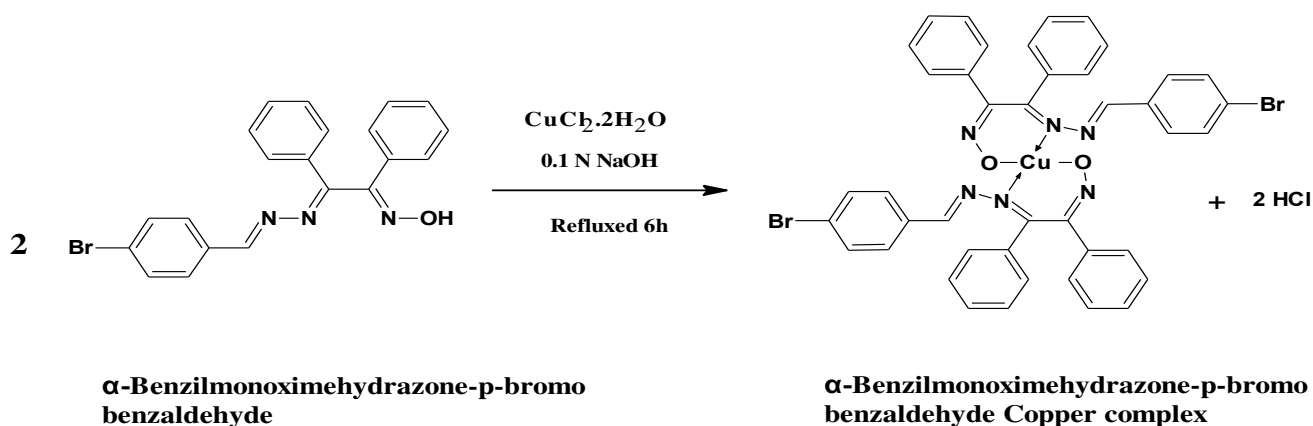
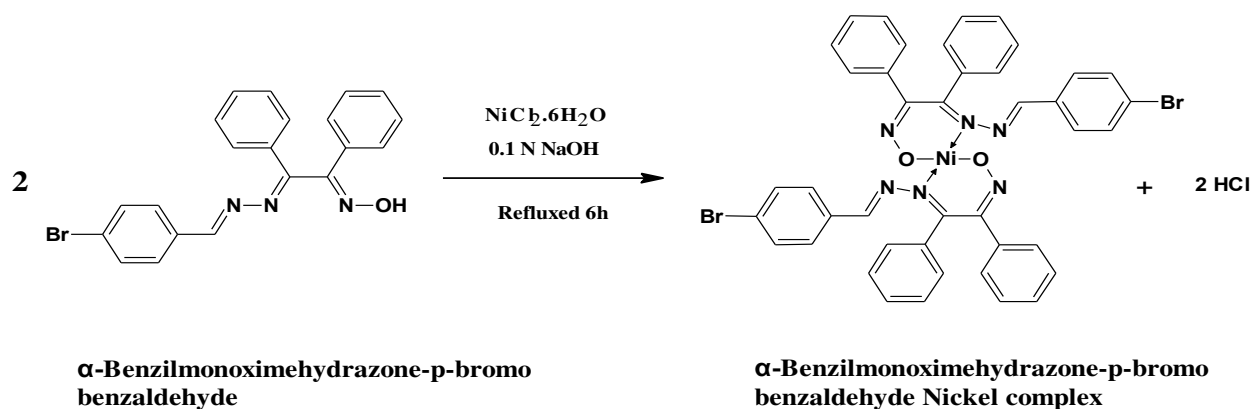
2.4.2. Bis(α -Benzilmonoximehydrazone-p-bromobenzaldehyde) Nickel(II), $[\text{Ni}(\text{BMMHpBB})_2]$

To a solution of 0.85g nickel sulfate heptahydrate (5mmol) in 10cm^3 , water was added gradually with stirring a solution of 4.06g (10mmol) of HBMHpBB in 35cm^3 ethanol. The pH of the mixture raised to 8.0 slowly with dilute (0.10N) NaOH, when a green colored complex separated, which was digested for 30 min on water bath and cooled, filtered, washed with hot water (25cm^3) and dried at 100°C . It was recrystallized from methanol.

2.4.3. Bis(α -Benzilmonoximehydrazone-p-bromobenzaldehyde) Copper(II), $[\text{Cu}(\text{BMMHpBB})_2]$

To a solution of 0.85g copper chloride dihydrate (5mmol) in 10cm^3 , water was added gradually with stirring to a solution of 4.06g (10mmol) of HBMHpBB in 30cm^3 ethanol. The pH of the mixture raised slowly to 8.0 with dilute (0.10N) NaOH, when a green colored complex separated, which was digested for 30 min on waterbath and cooled, filtered, washed with hot water (25cm^3) and dried at 100°C . It was recrystallized from methanol.





3. RESULTS AND DISCUSSION

Ligand (HL) and its transition metal complexes are soluble in (N,N-dimethylformamide (DMF), dimethylsulphoxide (DMSO), methanol (MeOH), ethanol (EtOH), acetone (C₃H₆O), 2-propanol (C₃H₈O) and are completely insoluble in water. From the physical and analytical data are presented in table 1. It was found that all the complexes were non-hygroscopic, stable at room temperature and appears as powders with high melting points [8]. Molar conductance values of the soluble complexes in DMSO show values (3.92-9.12 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) indicating that they are all non-electrolytic in nature [9].

3.1. FT-IR spectra

In order to study the binding mode of the Schiff base to the metal ion of the complexes [10], the IR spectrum of the free ligand was compared with the spectra of the complexes (table 2). The IR spectrum of the ligand shows band in the region 3239cm^{-1} , absence of this band in complexes indicates the deprotonation of hydrogen of oximino group [11]. The band observed at 1556cm^{-1} is characteristic of the oximino group in HBMTpBB ligand [12-13]. In the complexes, this band is shifted to higher

frequency *i.e.* $1571\text{-}1580\text{cm}^{-1}$, indicating the coordination of oximino nitrogen to the metal ions [14]. The ligand shows its characteristic azomethine ($-\text{C}=\text{NN}-$) band at 1614cm^{-1} , which are also shifted to higher frequencies in the spectra of the complexes in the range of $1644\text{-}1698\text{cm}^{-1}$. The spectra of chelate complexes showed new weak bands in the region $508\text{-}536\text{cm}^{-1}$, these bands were not present in the spectrum of ligand may be attributed to vibration $\nu(\text{M}\rightarrow\text{N})$ and $(\text{M}-\text{N})$ provide evidences concerning the bonding of oxygen and nitrogen the metal ions[15].

3.2. PMR Spectrum of α -Benzilmonoximehydrazone-p-bromobenzaldehyde ligand

The PMR spectra of the ligand α -Benzilmonoximehydrazone-p-bromobenzaldehyde is obtained in d_6 -DMSO, a singlet at $\delta = 10.20\text{ppm}$. Because oxime functional group is relatively expected to release the hydron with more ease, the hydron of an oxime group experiences more deshielding effect [16] and appears as a singlet at $\delta = 10.20\text{ppm}$. The ^1H NMR spectra of hydrazone derivative of isonitrosopro-piophenone (HPHOPD) exhibit oxime peak at $\delta = 8.10\text{ppm}$ [17] whereas in the nitrosalicylaldehyde derivative of

HPHOPD the hydron peak is reported at $\delta = 12.27$ ppm. This replacement of two hydrogens by the nitrosalicylaldehyde will make the oxime hydron easily releasable. With this view point it is suggested that the singlet at $\delta = 10.20$ ppm be possibly attributed to the oximino hydron, singlets observed [18] at $\delta = 9.10$ ppm

is ascribed for methyl hydrons, because of their similar electronic environment these are expected to resonate at same or nearly same δ values. The multiplet in the range of $\delta = 8.20-8.80$ ppm values may be attributed to the hydrogen atoms of aromatic ring [19].

Table 1: Physical and Analytical data of HBMHpBB ligand and its Complexes

Compound	Color	% Yield	MP/DP in °C	% Element Content, Expected (Observed)						Magnetic Moment	Molar Cond
				C	H	N	O	Br	M		
HBMHpBB	Yellow	72.68	207	62.08 (62.00)	3.97 (3.92)	10.94 (10.61)	3.94 (3.96)	19.67 (19.59)	-	-	-
[Co(BMHpBB) ₂]	Brown	77.56	248	57.97 (57.54)	3.45 (3.41)	9.66 (9.55)	3.68 (3.62)	18.93 (18.90)	6.78 (6.70)	4.80	3.92
[Ni(BMHpBB) ₂]	Light Green	77.28	259	57.98 (57.90)	3.45 (3.39)	9.66 (9.60)	3.68 (3.63)	18.93 (18.88)	6.75 (6.71)	3.10	4.58
[Cu(BMHpBB) ₂]	Green	75.66	262	57.66 (57.61)	3.43 (3.38)	9.61 (9.61)	3.66 (3.60)	18.29 (18.22)	7.27 (7.17)	2.03	9.12

Table 2: FT(IR) spectrum of HBMHpBB ligand and its Metal complexes

Compound	-OH	Ar C=C	Ar C-H	n(>C=NN-)	v(>C=NO-)	vN-O	vN-N	Ph-Br	M
HBMHpBB	3239	3100	3079	1614	1556	1010	1093	793	-
[Co(BMHpBB) ₂]	-	3095	3061	1662	1575	1008	1150	794	509, 536
[Ni(BMHpBB) ₂]	-	3102	3065	1698	1580	1009	1150	805	508, 536
[Cu(BMHpBB) ₂]	-	3110	3077	1644	1571	1003	1152	781	508, 530

3.3. Electronic Absorption Spectra

The electronic absorption spectral data of divalent metal coordination compounds were obtained in chloroform and is given in table 3.

The electronic spectrum of the Co(II) coordination compound shows bands at 610nm ($\epsilon = 21 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$) and 508 ($\epsilon = 472 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$). These two bands are assignable to ${}^4A_{2g} \leftarrow {}^4T_{1g}$ (ν_2) and ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}$ (ν_3) transitions respectively, the expected lowest energy band, i.e., ${}^4T_{2g} \leftarrow {}^4T_{1g}$ (ν_1) could not be seen in both the spectra, due to the limitations of instrument used to record the spectra, but could be calculated [20] and is about 1283nm. The value of $\nu_2/\nu_1 = 2.103$ falls in the range 2.1-2.2, and accounted often for the octahedral Co^{II} coordination complexes. The spectroscopic parameters for Co^{II} coordination compound of α -Benzilmonoximehydrazone-p-bromobenzaldehyde are $Dq = 891 \text{ cm}^{-1}$, $B' = 880 \text{ cm}^{-1}$, $B'/B = \beta = 0.91$ and $\beta\% = 10\%$. Depletion of Racah parameter from the so-called free-ion value of 971 cm^{-1} to 880 cm^{-1} indicates that the B in complex is only 91% of free-ion value [21]. Plausible ligand field transitions for octahedral Co(II) coordination compounds:

$${}^4T_{2g} \leftarrow {}^4T_{1g} \text{ -----}(\nu_1)$$

$${}^4A_{2g} \leftarrow {}^4T_{1g} \text{ -----}(\nu_2)$$

$${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g} \text{ -----}(\nu_3)$$

Calculation [22] of Dq:

$$\nu_2 = 610 \text{ nm}, \nu_3 = 510 \text{ cm}^{-1}$$

$$Dq = [(85 \nu_3^2 - 4(\nu_3 - 2\nu_2)^2) / 2 - 9(\nu_3 - 2\nu_2)] / 340$$

$$Dq = [(85 \times 198732 - 4(19873 - 2 \times 16700)^2) / 2 - 9(19873 - 2 \times 16700)] / 340$$

$$Dq = 302954.6 / 340$$

$$Dq = 891.0 \text{ cm}^{-1}$$

Calculation of B:

$$B = (\nu_3 - 2\nu_2 + 30 Dq) / 15$$

$$B = (19873 - 2 \times 16700 + 30 \times 891.0) / 15$$

$$B = 13203 / 15$$

$$B = 880.2 \approx 880$$

Calculating Nephelauxetic constant, β , and % free-ion value:

$$\text{Co(II) free-ion value, } B_0 = 971 \text{ and } B = 880$$

$$\beta = B/B_0$$

$$\beta = 880/971$$

$$\beta = 0.91$$

$$\% \text{ free-ion value for complex} = (B_{\text{cal}} \times 100) / B_{\text{free ion}}$$

% free-ion value for complex = $(880 \times 100)/971$

% free-ion value for complex = 90.62

So, the Racah parameter B in complex is only 91 % of free-ion value.

Calculation of ν_1 :

$$\nu_1 = 5Dq - 7.5 B + \frac{1}{2} (225 B^2 + 100Dq^2 + 180Dq B)^{1/2}$$

$$\nu_1 = 5 \times 891 - 7.5 \times 880 + \frac{1}{2} (225 \times 8802 + 100 \times 8912 + 180 \times 891 \times 880)^{1/2}$$

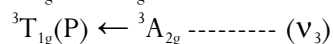
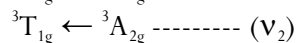
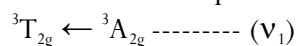
$$\nu_1 = 7789.32 \text{ cm}^{-1} \approx 7789 \text{ cm}^{-1}$$

The ultra-violet-visible absorption spectra of Ni^{II} coordination compound in chloroform solution reveals a peak at 951nm ($\epsilon = 8 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$) and 669nm ($\epsilon = 898 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$). The ³F ground state of the free divalent nickel ion for an octahedral symmetry of ligand fields, splits into ³A_{2g}, ³T_{2g}, and ³T_{1g}, whereas, the first excited state ³P of free ion remain unsplit and transforms into ³T_{2g}(P) in octahedral ligand field [23].

Table 3: UV-Visible spectral data of HBMHpBB ligand and its metal complexes

Compound	λ nm	ϵ (dm ³ /mol/cm)	Transition
HBMHpBB	391	10631	$\pi \rightarrow \pi^*$
	325	3998	$\pi \rightarrow \pi^*$
	244	5728	$\pi \rightarrow \pi^*$
[Co(BMHpBB) ₂]	610	21	${}^2E_g \rightarrow {}^2T_{1g}$
	508	472	${}^2E_g \rightarrow {}^2T_{2g}$
	408	7956	MLCT
[Ni(BMHpBB) ₂]	951	8	${}^3A_{2g} \rightarrow {}^3T_{1g}$
	669	898	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
	458	8952	MLCT
[Cu(BMHpBB) ₂]	549	110	${}^2T_{2g} \rightarrow {}^2E_g$
	291	13541	MLCT

Plausible ligand field transitions for octahedral Ni(II) coordination compounds.



The electronic spectra of the Ni(II) coordination compound in chloroform shows a peak at 951nm ($\epsilon = 8 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$, which can be ascribed to ${}^3T_{2g} \leftarrow {}^3A_{2g}$ (value may directly be taken as 10Dq for the Ni(II) octahedral complex, as ground state do not undergo second order interaction, so Dq is 951nm, another broad peak is seen at 508nm ($\epsilon = 898 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$, this is assignable to the ${}^3T_{1g} \leftarrow {}^3A_{2g}$. The ratio of ν_2/ν_1 is found to be 1.57, which falls in the range accounted for the other octahedral complexes of Ni(II) (1.50-1.82) supporting the assignment [24]. From the observed position of these two transitions viz., ν_1 and ν_2 , the value B, the frequency of the third, ligand-field transition, viz., ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$, and values is been calculated as follows [25].

Calculation of B

$$\nu_1 = 9510 \text{ cm}^{-1}, \nu_2 = 14928 \text{ cm}^{-1}, \text{ and } Dq = 951$$

$$B = [(\nu_2 - 2\nu_1)(\nu_2 - \nu_1)] / (15\nu_2 - 27\nu_1)$$

$$B = [(14928 - 2 \times 9510)(14928 - 9510)] / (15 \times 14928 - 27 \times 9510)$$

$$B = [-22170456] / (-32850)$$

$$B = 675$$

Calculation of ν_3

$$\nu_3 = 15Dq + 7.5B + \frac{1}{2}(225B^2 + 100Dq - 180Dq B)^{1/2}$$

$$\nu_3 = 15 \times 951 + 7.5 \times 755 + \frac{1}{2}(225 \times 7552 + 100 \times 9512 - 180 \times 951 \times 755)^{1/2}$$

$$\nu_3 = 19327.5 + \frac{1}{2}(-12935775)^{1/2}$$

$$\nu_3 = 19327.5 - \frac{1}{2}(-3596.634)$$

$$\nu_3 = 17529 \text{ cm}^{-1}$$

Calculating Nephelauxetic constant, β , and % free-ion value:

$$\text{Ni (II) free-ion value, } B_o = 1041, \text{ and } B = 675$$

$$\beta = B/B_o$$

$$\beta = 675/1041$$

$$\beta = 0.65$$

$$\% \text{ free-ion value for complex} = (B_{\text{cal}} \times 100) / B_{\text{free-ion}} \%$$

$$\text{free-ion value for complex} = (675 \times 100) / 1041$$

$$\% \text{ free-ion value for complex} = 64.8$$

the Racah parameter B in complex is only 65 % of free-ion value.

So, from the calculations, third band, ν_3 is expected to occur at 17529 cm^{-1} (570nm).

Spectra of Cu(II) coordination compound of α -Benzilmonoximehydrazone-p-bromobenzaldehyde, in principle, the d^9 case, with the free ion term 2D , of the Cu(II) ion in the so-called octahedral ligand field environment will split into lower 2E_g (t_{2g}^6, e_g^3) and the upper $^2T_{2g}$ (t_{2g}^5, e_g^4), yielding only one spin allowed transition ($^2T_{2g} \leftarrow ^2E_g$) in the visible region, however, because this six coordinated complex is non-linear and orbitally degenerate, it will be unstable in a regular octahedral environment, and will enjoy a static or dynamic Jahn-Teller distortions for stability reasons. Due to these thermodynamic distortions the 2E_g and $^2T_{2g}$ levels are further split into $^2B_{1g}$, $^1A_{1g}$, $^2B_{2g}$, and 2E_g electronic states, thus all together expected¹¹⁴ to give three bands, viz. $^2A_{1g} \leftarrow ^2B_{1g}$, $^2B_{2g} \leftarrow ^2B_{1g}$, $^2E_g \leftarrow ^2B_{1g}$. However, in many of the Cu(II) complexes the energy of the $^2A_{2g}$ state is fairly close to the 2E_g and $2B_{2g}$ resulting that all the three transitions cover under a broad envelope. Eventually, most Cu(II) six coordinated complexes gives only one broad absorption band, which may be attributed to so-called $^2T_{2g} \leftarrow ^2E_g$ transition. The

solution spectrum of α -Benzilmonoximehydrazone-p-bromobenzaldehyde complex in chloroform reveals an absorption peak at 549nm ($\epsilon = 110 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$) may be ascribed to $^2T_{2g} \leftarrow ^2E_g$ transition and is expected to show a distorted octahedral geometry.

3.4. Electron paramagnetic resonance (EPR) spectrum of Cu(II) complex

Electron Spin Resonance (ESR) also identified as Electron Paramagnetic Resonance (EPR) spectroscopy is the instrumental technique which involves microwave-induced resonance transitions between the magnetic energy levels of the electron, that possess a net spin moments. It can be used to investigate the paramagnetic species with one or many spin-free electrons, viz., free radicals, diradicals, metal coordination compounds with paramagnetic metal centers, defects in semiconductors, irradiation effects in solids, etc. ESR spectra of [Cu(BMHpBB)₂] is recorded at LNT in trichloromethane solution, on X-band at 9.1 GHz in the magnetic field of 0.3 T. Interpretation of the ESR spectra of the above said complex gives following values $g_{\perp} = 1.9812$, $g_{\parallel} = 1.8454$, $g_{\text{average}} = 1.9359$, $\mu_{\text{eff}} = 1.6765$.

Calculations of ESR parameters:

g_{\perp}	g_{\parallel}	g_{average}
$g_{\perp} = (g_{\text{std}} \times H_{\perp}) / H_{\text{std}}$	$g_{\parallel} = (g_{\text{std}} \times H_{\parallel}) / H_{\text{std}}$	$g_{\text{average}} = 1/3[2 \times g_{\perp} + g_{\parallel}]$
$g_{\perp} = (2.00277 \times 3210) / 3245$	$g_{\parallel} = (2.00277 \times 2990) / 3245$	$g_{\text{average}} = 1/3[2 \times 1.9821 + 1.8454]$
$g_{\perp} = 1.9812$	1.8454	$g_{\text{average}} = 1.9359$
μ_{eff}		Axial symmetry (G)
$\mu_{\text{eff}} = g_{\text{average}} [s(s+1)]^{1/2}$		$G = (g_{\parallel} - 2) / (g_{\perp} - 2)$
$\mu_{\text{eff}} = 1.9359 [1/2(1/2+1)]^{1/2}$		$G = (1.8454 - 2) / (1.9812 - 2)$
$\mu_{\text{eff}} = 1.6765$		$G = 8.2234$

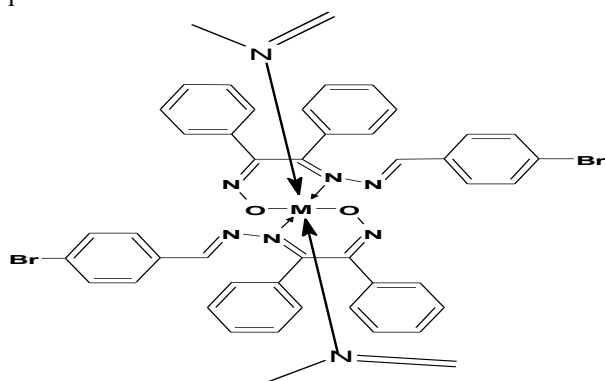
The electronic paramagnetic resonance (EPR) experiments on the Cu(II) complex of α -Benzilmonoximehydrazone-p-bromobenzaldehyde in polycrystalline form at liquid nitrogen temperature (LNT) on the X-band at 9.1 GHz under the magnetic field of 0.3 T, were attempted to obtain analytical information on the type of bonding in this complex. The room temperature spectrum of the [Cu(BMHpBB)₂] was poorly resolved with the LNT spectrum showing only slightly improved resolution. The low resolution of the spectrum is due to low crystallinity of the complex [26]. The nature of the EPR spectrum of this complex suggest distorted octahedral structure [27] as the two g values follows the trend $g_{\perp} > g_{\parallel}$ suggesting that the coordination com-

pound is tetragonally compressed [28] at ambient temperature. The g tensors were evaluated on the basis of Kneubuhl's analysis [29]. Hathaway et al have shown that a factor G which is $g_{\parallel} - 2 / g_{\perp} - 2$ can give important information on whether the observed g_{\parallel} and g_{\perp} values suggests the local Cu(II) environment. Their resonating was that since Kneubuhl's method ignores hyperfine coupling constants, the absolute g-values are possibly in error and further, that the components that affect the correlation between the g value of the local Cu(II) environment and the g values of the bulk true solid, may be measured with the interaction between the remote Cu(II) ions in a non dilute magnetic system. The authors also proposed that, if exchange coupling interaction is

larger than heat energy, imperfect spin-pairing may result. However, when the scene magnetic values that is higher than, the spin-only moments then, the coupling exchange interaction, whenever occurs, must have its energy lower than the heat energy. Then, such interactions influence the line shapes and do not reduce the magnetic moments below the spin-only values. When the exchange interactions takes up the value that is in between the equivalent ions crystallographically, than the sharp absorption lines appear and the obtained 'g' values gives the local 'g' values. If the interaction is among the non-equivalent crystallographically ion then it results in notable broadening of spectrum may occur and an isotropic spectrum would result. However, if the interaction is among the non-crystallographically equivalent ions then the observed g_{\perp} could be greater than the local g_{\perp} while the g_{\parallel} value could be similar than the local g_{\parallel} values. This would be reflected in the values of G being ≥ 4 . Therefore, values of $G >$ would per se indicate absence of exchange coupling. In the cupric complexes of α -Benzilmonoximehydrazone-p-bromobenzaldehyde then, the high G values found may be taken to imply negligible exchange interactions [30].

4. CONCLUSION

α -Benzilmonoximehydrazone-p-bromobenzaldehyde ligand abbreviated as HBMHpBB was prepared and reported first time.



Structure 1: Structures of metal complexes of α -benzilmonoximehydrazone-p-bromobenzaldehyde ligand (where; M = Co(II), Ni(II), Cu(II))

Physical data of the ligand compound to molecular formula $C_{21}H_{16}N_3OBr$ and correspond to the molecular mass of 406g/mol, which is determining molecular mass by Rast method. In the UV spectrum of ligand α -Benzilmonoximehydrazone-p-bromobenzaldehyde, oximino and azomethine $\pi \rightarrow \pi^*$ transitions are

observed at 325nm and 244nm. Proton magnetic resonance spectrum observed oximino proton at 10.20ppm methane (-CH=) group at 9.1ppm and aromatic group at 8.20-8.70ppm. On the basis of proton magnetic resonance spectral data, structure of the ligand may tentatively be assigned as given in structure 1.

Conflicts of interest

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

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