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Preparation and Characterization of Novel α-Benzilmonoximhydrazide *m*-Bromo benzaldehyde and its Metal Complexes with Cobalt, Nickel and Copper Chlorides

Yadav Premkumar[1], Nag Purnima[2], Badekar Raj[3] and Lokhande Rama[4]

[1]School of Basic Sciences, Jaipur National University, Jaipur, India; premkumaryadav@rediffmail.com
[2]School of Basic Sciences, Jaipur National University,Jaipur, India; purnima_nag007@yahoo.com
[3]Riva Industries, Ambernath MIDC, Dist-Thane, Maharashtra, India; badekarrr@gmail.com
[4]School of Basic Sciences, Jaipur National University, Jaipur, India; rama.lokhande@yahoo.com

Abstract: **A novel α- Benzilmonoximhydrazide m-Bromobenzaldehyde is synthesized by condensation of m-bromobenzaldehyde with α- Benzil monoxime hydrazone. Solid transition metal complexes were further prepared by reacting this ligand with corresponding metal chlorides. The newly prepared ligand and its metal complexes were characterized by several techniques including elemental analysis, molar conductance, magnetic measurements, electronic, IR and proton NMR spectroscopic studies. The Novel ligand and its colored metal complexes are having applications in Dyes and Pigment industry.**

Key words: α-benzilmonoximehydrazide, m-bromobenzaldehyde, Metal complexes, Spectral studies.

I. INTRODUCTION

Bidentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds (Raman N etal 2008). Schiff base metal complexes have played a major role in the development of bioinorganic chemistry because many of these complexes provide biological models in understanding the structure of bimolecular and biological processes (Abd El-Wahab,etal 2005; Makode J T 2009). Schiff base complexes derived from α-benzilmonoxime are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal ions. A large number of reports are available on the biochemistry and the microbial activities of transition metal complexes containing O and N donor atoms(Bagihalli G B, etal ,2009; Chandra S and etal 2005). In this paper, we report the preparation of a new type of bidentate ligand formed by the condensation of α-benzilmonoximehydrazone with m-bromobenzaldehyde and its transition metal complexes with Co(II), Ni(II) and Cu(II) metal ions which are having applications in Pigment and Dyes Industry due to their colored Crystal nature (Chohan Z H and etal 2001; Raman N, etal 2007; Ibotomba singh 2012). All newly synthesized compounds were characterized by various physico-chemicals as well as spectral studies.

II. LITERATURE SURVEY

Scanning of the literature reveals that the hydrazonyl derivative of α-Benzilmonoxime and its Fe(II), Co(II), Ni(II), Pd(II), Cu(II), Zn(II), Cd(II), Hg(II), Ti(III), Cr(III), Mn(III), Fe(III), Ru(III), Co(III), Ir(III), Ni(III), Cu(III), Au(III) complexes and pyridine adducts of Co(II), Ni(II) and Cu(II) ions along with their biological activities have been studied and reported (Loredana Dianu M, Kriza 2010; K Krishnankutty 2010). But literature reviews on benzilmonoximehrrazone condensation with bromobenzaldehyde derivative are not available. In view of this we wish to report condensation of bromobezaldehyde derivatives with α-benzilmonoximehydrazone compounds and various transition metal complexes.

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III. EXPERIMENTAL

A. Materials and methods:

The analytical Grade (AR) chemicals were used in all the experiments. The melting point of ligand and its metal complexes were determined by Electrothermal melting point apparatus. 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 $Hg[Co(SCN)_4]$ and $Ni(en)_3S_2O_3]$ as a calibrant. FT-IR spectra were recorded using KBR pellets in Mumbai University using Perkin - Elmer Infrared spectrophotometer. Conductivity measurements were carried out on Toshaniwal digital conductivity meter. UV-visible spectra were recorded on JASCO 450 spectrophotometer using methanol/0.1N NaOH solvents for ligands and methanol/ chloroform solvents for all metal complexes. The proton magnetic resonance spectra were recorded on 'Brucker AV300 NMRSpectrometer' using TMS as internal standard. The EPR spectra were recorded on a model 'E-112-ESR Spectrometer' using TCNE as standard at RT and LNT condition.

B. Preparation of α-Benzilmonoximehydrazide m-Bromobenzaldehyde (Ligand) :

The title ligand was prepared by mixing of methanolic solution of the α-Benzilmonoximehydrazone (0.100mol) and 3-bromobenzaldehyde (0.125mol) in 1ml of glacial acetic acid, The resulting mixture was refluxed for 7 hours. After complete reflux the pH of solution was adjusted to 5 using 0.1N aquoues NaOH solution, Reaction mass further cooled to room temperature, a yellow coloured solid was separated which was dried at 110°C in hot air oven.

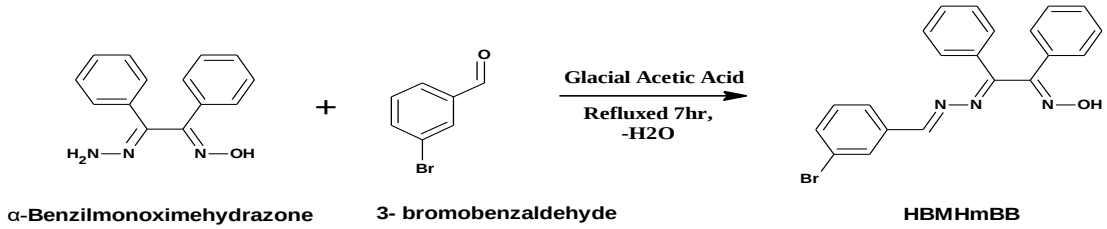
Melting point - 209^0 C; yield - 81.12%.

The Synonyms of titled compound are:

N-[(1*E*,2*E*)-2-{(2*E*)-[(3-bromophenyl)methylidene]hydrazinylidene}-1,2-diphenylethylidene]hydroxylamine;

HBMHmBB;

α-Benzilmonoximehydrazidem-Bromobenzaldehyde;2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine

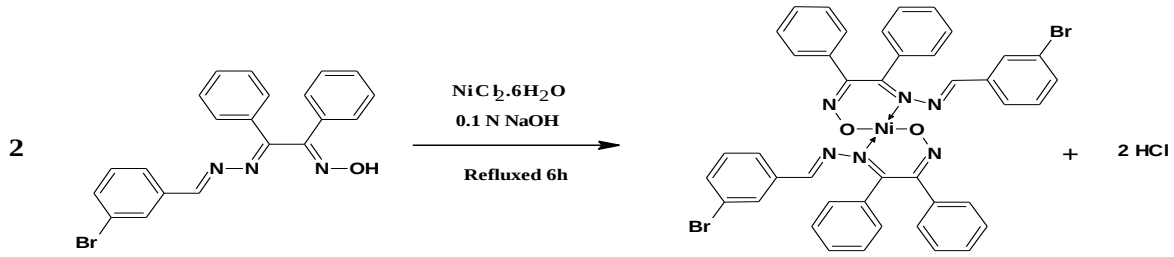


α-Benzilmonoximehydrazone 3- bromobenzaldehyde HBMHmBB

C. Preparation of Novel Transition metal complexes of α-Benzilmonoximehydrazide m-Bromobenzaldehyde:

1) Synthesis of Bis(α-Benzilmonoximehydrazone-m-bromobenzaldeyde)Nickel(II) complex, $[Ni(BMHmBB)_2]$:

To a solution of 0.85g nickel chloride hexahydrate (5mmol) in 10ml water, a solution of 4.06g (10mmol) of HBMHmBB in 35ml ethanol was added gradually with stirring. The reaction mass is heated and refluxed for 6hrs under stirring. The pH of the mixture was raised to 8.0 slowly with dilute (0.10N) aquoues NaOH solution, a green colored complex was separated, which was digested 30 min on water bath and cooled to 20-30°C. It was then filtered, washed with hot water (25ml) and dried at 100^0C and recrystallized from methanol. The light green colored solid is having melting point 259^0 C with 77.28% yield



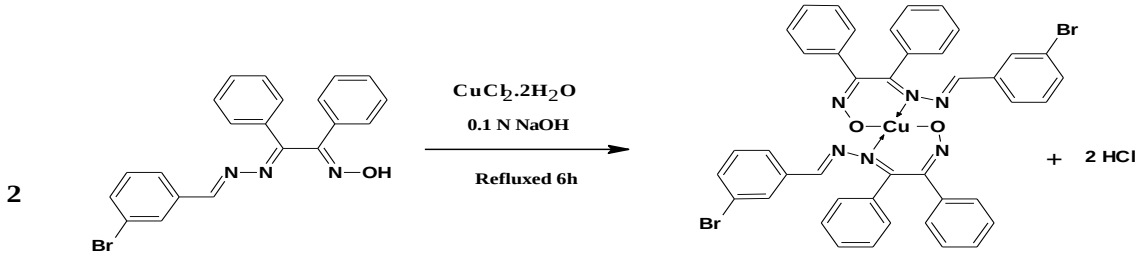
α-Benzilmonoximehydrazone-m-bromo benzaldehyde

α-Benzilmonoximehydrazone-m-bromo benzaldehyde Nickel complex

2) Synthesis of Bis(α Benzilmonoximehydrazone- m-bromobenzaldeyde) Copper(II) complex, [Cu(BMHmBB)$_2$]:

To a solution of 0.85g copper chloride dihydrate (5mmol) in 10ml water was added gradually with stirring to a solution of 4.06g (10mmol) of HBMHmBB in 30ml Ethanol. The reaction mass is heated and refluxed for 3hrs under stirring. The pH of the mixture was raised slowly to 8.0 with dilute (0.10N) NaOH, when an green colored complex separated, which was digested 30 min on water bath and cooled to 20-30^{0}C. It was filtered, washed with hot water (25ml) and dried at 100^{0}C. The product obtained was recrystallized from methanol.

The Green colored solid is having melting point 262^0 C with 75.66% yield



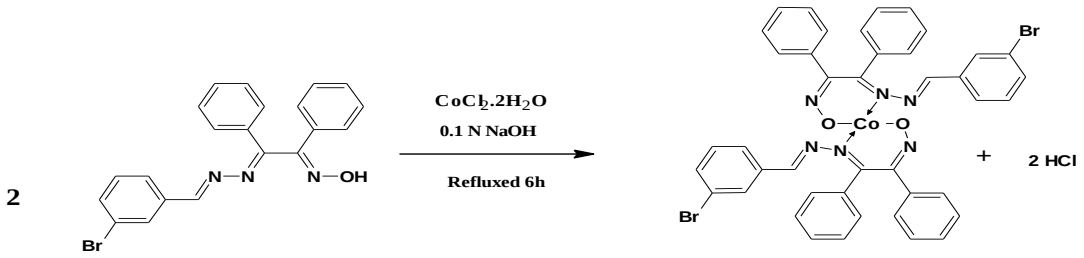
α-Benzilmonoximehydrazone-m-bromo benzaldehyde

α-Benzilmonoximehydrazone-m-bromo benzaldehyde Copper complex

3) Synthesis of Bis(α-Benzilmonoximehydrazone- m-bromobenzaldeyde) Cobalt (II) complex,
[Co(BMHmBB)$_2$]:

To a solution of 1.19g Cobalt chloride dihydrate (5mmol) in 10ml water, a solution of 4.06g of HBMHmBB (10mmol) in 30ml Ethanol was added gradually with stirring. The reaction mixture was heated and refluxed for 6hrs under stirring. The pH of the mixture was raised slowly to 7.5 with dilute(0.10N) aquoues NaOH solution, till a green color complex was separated, which was digested 30 min on water bath and cooled to 20-30^{0}C. It was then filtered, washed with hot water and dried at 100^{0}C. The product obtained was recrystallized from methanol.

The Brown colored solid is having melting point 248^0 C with 77.56% yield



α-Benzilmonoximehydrazone-m-bromo benzaldehyde

α-Benzilmonoximehydrazone-m-bromo benzaldehyde Cobalt complex

IV. RESULTS AND DISCUSIONS

The ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde [HBMHmBB], IUPAC Name 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine, chemical name- *N*-[(1*E*,2*E*)-2-{(2*E*)-[(3-bromophenyl)methylidene]hydrazinylidene}-1,2-diphenylethylidene] hydroxylamine is reported for the first time, where H signifies the presence of one replaceable proton. The Physical data of the ligand is given in the Table-1. The molecular weight of the ligand is determined by Rasts method and found to be 406g/mol, which was corresponds to the molecular formula $C_{21}H_{16}ON_3Br$. The melting point of the ligand is 209^0C. The purity of Ligand is 99.50% by Gas Chromatography technique. The newly prepared ligand is insoluble in water but soluble in dilute alkali solutions, which reveals the acidic nature of ligand. It is variably soluble in common organic solvents like methanol, ethanol, and dimethyl-formamide (DMF), dimethyl sulfoxide (DMSO) and chloroform.

All newly synthesized metal complexes are in ML_2 composition, (where M = transition metal ion and L = α-benzilmonoximehydrazone-o-bromobenzaldehyde ligand.). Elemental analysis data of metal complexes found nearby expected values, suggested metal complexes found to be 1:2 ratio.

All transition metal ion complexes of α-benzilmonoximehydrazone-m-bromobenzaldehyde ligand have high decomposition points and are thermally stable and shows strong metal-ligand bond. These complexes are having high decomposition points as shown in **Table-1,** with melting Range $245\text{-}250^0$C.All these complexes are easily soluble in common organic solvents.

Table-1: Physical and Analytical data of HBMHmBB ligand and its Complexes.

Compound	Color	% Yield	MP/DP in ^{o}C	% Element Content, Expected (Observed)						Magnetic Moment	Molar Cond.
				C	H	N	O	Br	M	-	-
HBMHmBB	Yellow	81.12	209	62.08 (61.99)	3.97 (3.78)	10.94 (10.28)	3.94 (3.85)	19.67 (19.66)	-	-	-
$[Co(BMHmBB)_2]$	Brown	79.55	245	57.97 (57.56)	3.45 (3.31)	9.66 (9.54)	3.68 (3.71)	18.93 (18.59)	6.78 (6.48)	3.12	3.92
$[Ni(BMHmBB)_2]$	Green	80.99	248	57.98 (57.58)	3.45 (3.41)	9.66 (9.49)	3.68 (3.53)	18.93 (18.75)	6.75 (6.54)	3.22	4.58
$[Cu(BMHmBB)_2]$	Green	78.56	250	57.66 (57.51)	3.43 (3.35)	9.61 (9.42)	3.66 (3.67)	18.29 (18.00)	7.27 (7.11)	1.87	9.12

A. FT(IR) spectrum studies of the α-Benzilmonoximehydrazone-m-bromo benzaldehyde (Ligand):

The significant FT(IR) stretching frequencies of the α-Benzilmonoximehydrazone-m-bromobenzaldehyde compound are represented in **Table-2.** The FT(IR) spectra of the ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde shows bands at 3229, 3154 and 3110cm^{-1} assignable to ν(-OH), Ar C=C and Ar C-H respectively. The free ligand α-

Benzilmonoximehydrazone-m-bromobenzaldehyde show very strong vibrational band at 1605cm^{-1} region in the individual FT(IR) spectrum which is representative of the azomethine group (**Table-2**). Another strong vibration band at 1545cm^{-1} was observed which is assigned as oximino group of the Benzilmonoximehydrazone-m-bromobenzaldehyde A medium band confirming to phenolic bromine was identified at 749cm^{-1} of ligand Benzilmonoximehydrazone-m-bromobenzaldehyde. Another two bands observed at the 1067 and 1154cm^{-1}, which may be assigned as νN-O and νN-N bands respectively of the ligand Benzilmonoximehydrazone-m-bromobenzaldehyde**.**

Table-2: FT-IR Spectrum of ligand Benzilmonoximehydrazone-m-bromobenzaldehyde and its metal complexes**.**

Compound	**-OH**	**Ar C=C**	**Ar C-H**	**ν(>C=NN-)**	**ν(>C=NO-)**	**νN-O**	**νN-N**	**Ph-Br**	**ν (M-O)/ ν (M→N)**
HBMHmBB	3229	3154	3110	1605	1545	1067	1154	749	-
[Co(BMHmBB)$_2$]	-	3147	3114	1658	1588	1015	1123	726	507, 556
[Ni(BMHmBB)$_2$]	-	3167	3159	1649	1587	1028	1179	724	514, 523
[Cu(BMHmBB)$_2$]	-	3184	3180	1644	1589	1024	1178	724	541, 569

B. The electronic spectral studies of the ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde (Figure-1):

The electronic absorption spectrum of 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine in methanol, in the ultra-violet region reveals two high intensity bands at 392nm (ε = 14385 dm^3 /mol/cm) and 243nm (ε = 7867 dm^3 /mol/cm) respectively. These may be due to $\pi \rightarrow \pi^*$ transitions possible from the azomethine and oximino environment in the molecule. The band observed at 392nm in methanol spectrum of α-Benzilmonoximehydrazone-m-bromobenzaldehyde assigned oxime group and the band at 243nm could be due azomethine group.

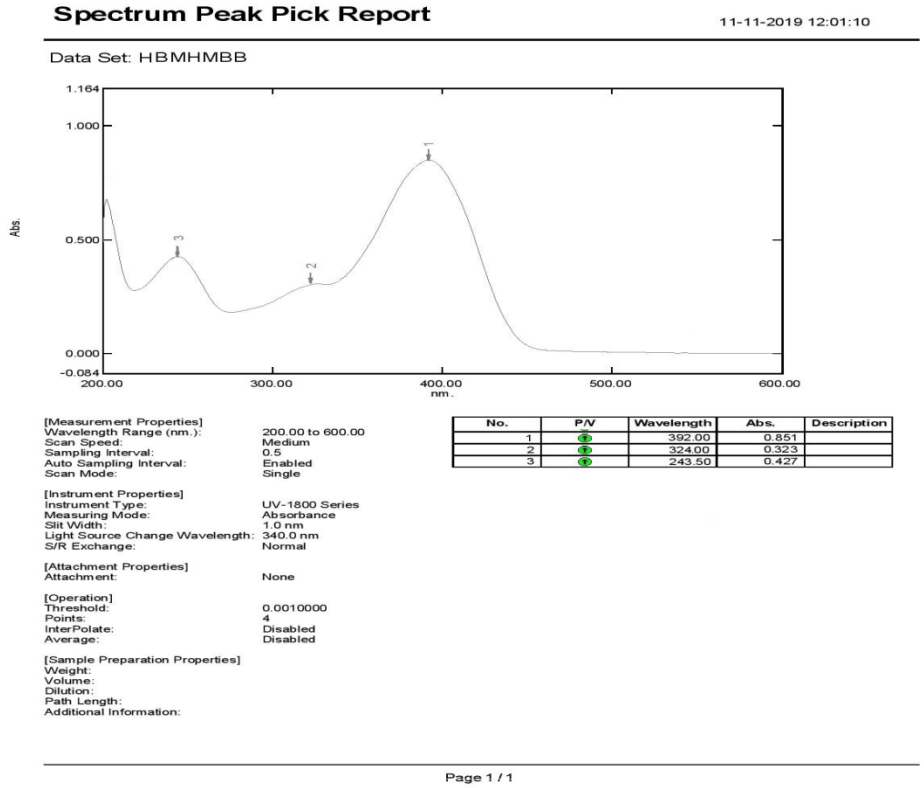
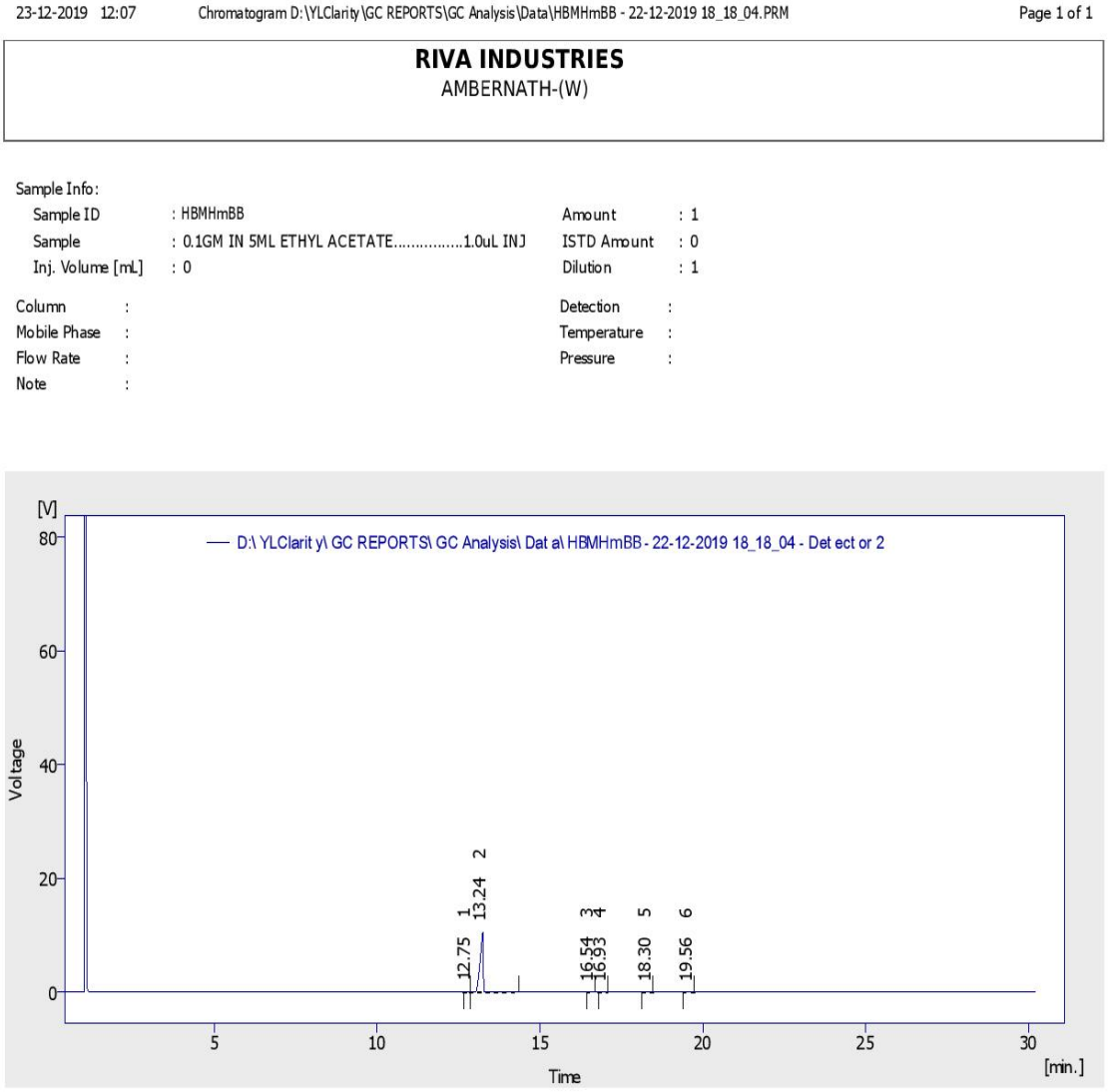


Figure-1: Electronic spectra of the ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde.

C. Gas chromatographic purity of Ligand:

The isolated α-Benzilmonoximehydrazone-m-bromobenzaldehyde [HBMHmBB] ligand is anlaysed for its purity by Gas chromatography technique shows purity-99.31% (figure-2)



Result Table (Uncal - D:\YLClarity\GC REPORTS\GC Analysis\Data\HBMHmBB - 22-12-2019 18_18_04 - *Detector 2)*

	Compound Name	Reten. Time [min]	Area [mV.s]	Height [mV]	Height [%]	Area [%]
1		12.753	213.188	49.921	0.472	0.30
2	HBMHmBB	13.243	70180.419	10512.492	99.317	99.50
3		16.537	26.044	4.444	0.042	0.04
4		16.933	71.105	12.725	0.120	0.10
5		18.297	19.991	2.516	0.024	0.03
6		19.563	23.931	2.645	0.025	0.03
		Total	70534.679	10584.742	100.000	100.00

Figure-2: GC spectrum of α-Benzilmonoximehydrazone-m-bromobenzaldehyde Ligand

D. The PMR spectra of ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde (Figure-3):

The PMR spectrum of α-Benzilmonoximehydrazone-m-bromobenzaldehyde ligand in deuturated DMSO was recorded using tetramethylsilane as the internal standard. The oximino proton appears as a singlet at δ10.50ppm and all the 14 aromatic protons appears as a multiplet in the range δ7.0 to δ7.7 ppm. In addition to this, aliphatic protons present as a bridge between azomethine (>C=NN-) groups appears at δ 8.5ppm.

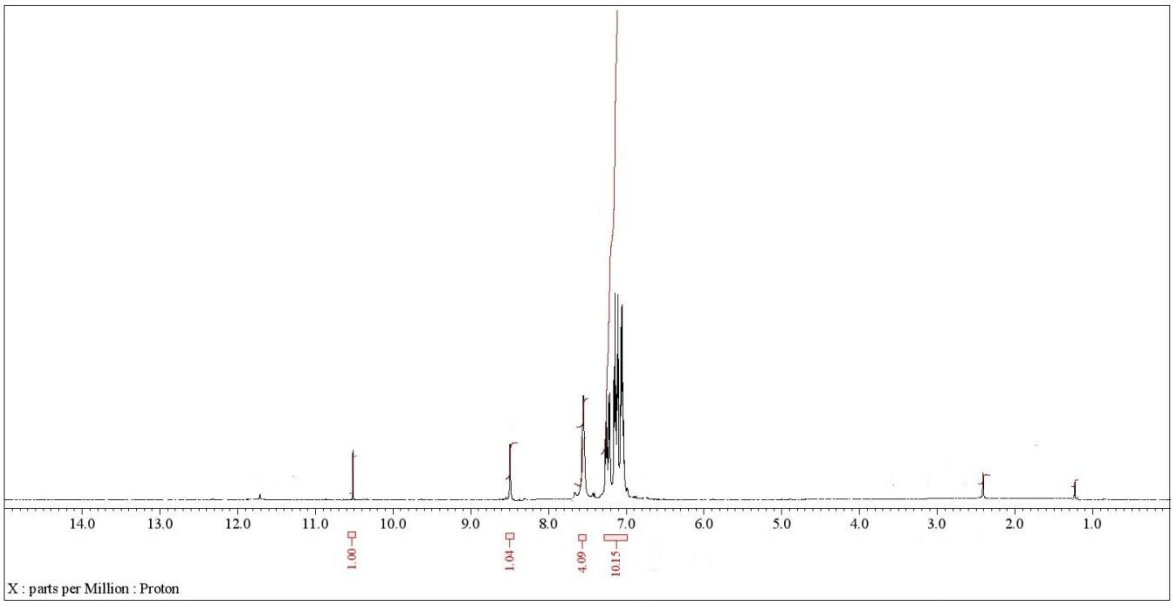


Figure-3: H^1NMR spectrum of α-Benzilmonoximehydrazone-m-bromobenzaldehyde [HBMHmBB],

E. Magnetic susceptibility Measurements of metal Complexes:

The Brown colored, $[Co(BHMmBB)_2]$ complex shows magnetic moment of 3.12 B.M. at room temperature, [Table 4.1] which is in the range expected for square Co(II) complexes. The green colored $[Ni(HBHmBB)_2]$ complex shows magnetic moment of 3.22 BM room temperature. High spin Ni(II) complexes expected to be paramagnetic properties due to the two unpaired electrons. The high spin Ni(II) octahedral complexes are expected to show magnetic moments in the range 3.0 to 3.3 BM. while slightly higher moments of 3.45- 4.0 BM. are expected for tetrahedral Ni(II) complexes. Green $[Cu(BHMmBB)_2]$ complex shows a room temperature magnetic moment of 1.87BM,

F. Electronic spectra of metal complexes:

The electronic spectra of α-Benzilmonoximehydrazone-m-bromobenzaldehyde and their metal complexes were recorded in chloroform and DMF solutions at room temperature. Electronic spectra data and their assignements of α-Benzilmonoximehydrazone-m-bromobenzaldehyde ligand and their transition metal ion complexes are given in **Table-3.**

The electronic absorption spectrum of the brown $[Co(BHMmBB)_2]$ complex exhibits weak intensity band at 900nm (ε = ~ 11 dm^3/mol/cm), a hump at 599nm (ε = 1511dm^3/mol/cm), and intense band observed at 506nm (ε = 6322 dm^3/mol/cm) these band assigned as charge transfer transition.

The Electronic spectrum of light green $[Ni(BHMmBB)_2]$ in chloroform solution reveals a peak at 970nm (ε = ~7 dm^3 /mol/cm). Another band is observed at 646nm (ε = 278 dm^3/mol/cm) which assigned to the *d-d* transition.

The green $[Cu(BHMmBB)_2]$ in DMF exhibits an intense well defined absorption band due to d-d transition is observed at 637nm (ε = 1250 dm^3/mol/cm).

Table-3: UV-Visible spectral data of HBMHmBB ligand and its metal complexes			
Compound	**λnm**	**ε (dm³/mol/cm)**	**Transition**
HBMHmBB	392	14385	$\pi \rightarrow \pi^*$
	324	3845	$\pi \rightarrow \pi^*$
	343	7867	$\pi \rightarrow \pi^*$
$[Co(BMHmBB)_2]$	900	~11	$^2E_g \rightarrow {}^2T_{1g}$
	599	4000	$^2E_g \rightarrow {}^2T_{2g}$
	506	8000	MLCT
$[Ni(BMHmBB)_2]$	970	~7	$^3A_{2g} \rightarrow {}^3T_{1g}$
	646	278	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
	576	1250	MLCT
$[Cu(BMHmBB)_2]$	637	350	$^2T_{2g} \rightarrow {}^2E_g$
	291	13541	MLCT

G. FT-IR Spectra of Metal Complexes:

The bonding between the ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde (HBHMmBB) and metal ion can be revealed by comparing the FT(IR) spectra of solid complexes with its ligand (**Table-2**).The IR spectra of the metal complexes of α-Benzilmonoximehydrazone-m-bromobenzaldehyde contain numerous bands of varying intensities. A common feature of the infrared spectra of all the metal complexes in KBr discs is the absence of any absorption bands attributable to the O-H vibration, due to oxime group in the spectrum of α-Benzilmonoximehydrazone-m-bromobenzaldehyde. This observation is also supported by the fact that all the complexes are insoluble in dilute alkali solutions indicating an absence of free oxime function in them. The two absorption bands observed in between 1605cm^{-1} and 1545cm^{-1}, these are tentatively proposed to be due to the azomethine and oximino C=N stretching vibration respectively. These two bands observed at around 1644-1658 and 1587-1589 cm^{-1} respectively in metal complexes of ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde, means shifted to higher frequencies. An oxime function is known to coordinate to the metal ion either through its nitrogen or oxygen atoms. In free ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde N-O band observed at 1018 cm^{-1}. During formation of the metal complexes such N-O band shifted to higher frequency as linkage N→O. In metal complexes, oxime group coordinated through oxygen atom to metal ion, such N→O band observed at in between 1173-1178cm^{-1} and new absorption band νM-O/νM→N form at lower frequency 507-569cm^{-1}.

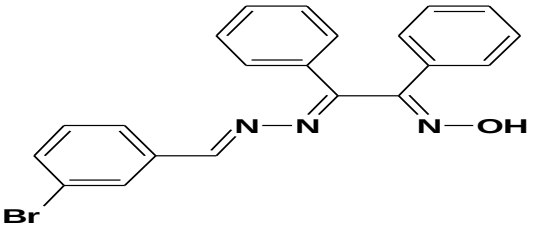
H. ESR Spectra of metal complex of HBMHmBB ligand:

Electron Spin Resonance is powerful tool to investigate the structure of complex in which transition metal ion is coordinated by several ligand. The ESR experiment on the Cu(II) complexes of α-Benzilmonoximehydrazone-m-bromobenzaldehyde at room temperature and liquid nitrogen temperature(LNT) in chloroform solution were attempted to obtain analytical information on the type of bonding in these complexes. The room temperature spectrum of the orange $[Cu(BHMmBB)_2]$, was poorly resolved. While at LNT, the ESR spectrum showing improved resolutions. The poor resolution of the spectrum could be due to low crystallinity of the complex. The green colored $[Cu(BHMmBB)_2]$, however, showed a four line hyperfine structure at the $g_{||}$ position in the spectrum at LNT. In either of the complexes, the $g_{\perp}$ line did not show any superhyperfine splitting due to nitrogen nucleus. This is suggestive of dissimilar field strength and probably also of the mixed Cu-N and Cu-O bonding as inferred from the infrared spectral studies on these complexes. The nature of the EPR spectra of these complexes suggests elongated tetragonal structure as only two g values, which follow the trend $g_k > g_{\perp} > 2.0023$, could be obtained. The $A_{||}$ and $A_{\perp}$ are well within the range for covalent cupric complexes.

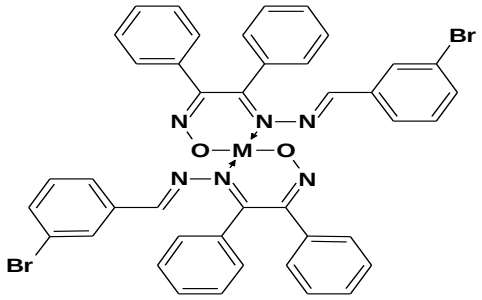
CONCLUSION

Based on various physicochemical results and spectral studies, the structure-I, for α-benzilmonoximehydrazone-*m*-bromobenzaldeyde (ligand) is proposed.

All transition metal complexes are stable up to 245-250^{0}C, indicating high thermal stability and strong metal-ligand bond. Ligand moiety is coordinated through oxygen and nitrogen atoms to the metal ions in all the complexes. On the basis of physiochemical data and spectral studies, Magnetic moment data and electronic spectral data, Structure II is proposed for metal complex.



Structure-I: α-Benzilmonoximehydrazone-m-bromobenzaldehyde



Structure II: α-Benzilmonoximehydrazone-m-bromobenzaldehyde metal complex (M= Ni,Cu,Co)

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