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

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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-benzilmonoximehydrazone, 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 et al 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, et al 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, et al 2009; Chandra S and et al 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 et al 2001; Raman N, et al 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; Krishnankutty 2010). But literature reviews on benzilmonoximehyrazone condensation with bromobenzaldehyde derivative are not available. In view of this we wish to report condensation of bromobenzaldehyde derivatives with α-benzilmonoximehydrazine compounds and various transition metal complexes.

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)S_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 NMR Spectrometer’ 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):

![α-Benzilmonoximehydrazone + 3- bromobenzaldehyde](attachment:image)

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 aqous 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°C; yield - 81.12%.

The Synonyms of titled compound are:

N-[1(E),2E]-2-[(3-bromophenyl)methylidene]hydrazinylidene]-1,2-diphenylethyldienehydroxylamine; HBMHmBB;

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

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

1) Synthesis of Bis(α-Benzilmonoximehydrazone-m-bromobenzaldehyde)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) aqoues 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°C and recrystallized from methanol. The light green colored solid is having melting point 259°C with 77.28% yield.
2) Synthesis of Bis(α-Benzilmonoximehydrazone-m-bromo benzaldehyde) 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°C. It was filtered,
washed with hot water (25ml) and dried at 100°C. The product
obtained was recrystallized from methanol.

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

3) Synthesis of Bis(α-Benzilmonoximehydrazone-m-bromobenzaldehyde) 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)
aqueous NaOH solution, till a green color 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 and dried at 100°C. The product obtained was recrystallized from
methanol.

The Brown colored solid is having melting point 248° C with
77.56% yield
IV. RESULTS AND DISCUSSIONS

The ligand α-Benzilmonoximehydrazone-m-bromobenzaldehyde [HBMHmBB], IUPAC Name 2-[(3-bromobenzylidene)hydrazinylidene]-1,2-diphenylethanimine, chemical name- N-{(1E,2E)-2-[(2E)-[3-bromophenyl)methylidene]hydrazinylidene}-1,2-diphenylethlamidine 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 C₂₁H₁₆ON₃Br. The melting point of the ligand is 209°C. 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 dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and chloroform.

All newly synthesized metal complexes are in ML₂ 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 245-250°C. All these complexes are easily soluble in common organic solvents.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>% Yield</th>
<th>MP/DP in °C</th>
<th>% Element Content, Expected (Observed)</th>
<th>Magnetic Moment</th>
<th>Molar Cond.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>HBMHmBB</td>
<td>Yellow</td>
<td>81.12</td>
<td>209</td>
<td>62.08 (61.99)</td>
<td>3.97 (3.78)</td>
<td>10.94 (10.28)</td>
</tr>
<tr>
<td>[Co(BMHmBB)₂]</td>
<td>Brown</td>
<td>79.55</td>
<td>245</td>
<td>57.97 (57.56)</td>
<td>3.45 (3.31)</td>
<td>9.66 (9.54)</td>
</tr>
<tr>
<td>[Ni(BMHmBB)₂]</td>
<td>Green</td>
<td>80.99</td>
<td>248</td>
<td>57.98 (57.58)</td>
<td>3.45 (3.41)</td>
<td>9.66 (9.49)</td>
</tr>
<tr>
<td>[Cu(BMHmBB)₂]</td>
<td>Green</td>
<td>78.56</td>
<td>250</td>
<td>57.66 (57.51)</td>
<td>3.43 (3.35)</td>
<td>9.61 (9.42)</td>
</tr>
</tbody>
</table>

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 3110 cm⁻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 1605 cm\(^{-1}\) region in the individual FT(IR) spectrum which is representative of the azomethine group (Table-2). Another strong vibration band at 1545 cm\(^{-1}\) was observed which is assigned as oximino group of the Benzilmonoximehydrazone-m-bromobenzaldehyde. A medium band confirming to phenolic bromine was identified at 749 cm\(^{-1}\) of ligand Benzilmonoximehydrazone-m-bromobenzaldehyde. Another two bands observed at the 1067 and 1154 cm\(^{-1}\), which may be assigned as vN-O and vN-N bands respectively of the ligand Benzilmonoximehydrazone-m-bromobenzaldehyde.

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

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

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-diphenylethanamine in methanol, in the ultra-violet region reveals two high intensity bands at 392 nm (\(\varepsilon = 14385\) dm\(^3\)/mol/cm) and 243 nm (\(\varepsilon = 7867\) dm\(^3\)/mol/cm) respectively. These may be due to π→π* transitions possible from the azomethine and oximino environment in the molecule. The band observed at 392 nm in methanol spectrum of α-Benzilmonoximehydrazone-m-bromobenzaldehyde assigned oxime group and the band at 243 nm 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 analysed for its purity by Gas chromatography technique shows purity 99.31% (figure-2)

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 deuterated 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: H¹NMR 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 dm³/mol/cm), a hump at 599nm (ε = 1511dm³/mol/cm), and intense band observed at 506nm (ε = 6322 dm³/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 dm³/mol/cm). Another band is observed at 646nm (ε = 278 dm³/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 dm³/mol/cm).
Table-3: UV-Visible spectral data of HBMHmBB ligand and its metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>λnm</th>
<th>ε (dm³/mol/cm)</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBMHmBB</td>
<td>392</td>
<td>14385</td>
<td>π→π*</td>
</tr>
<tr>
<td></td>
<td>324</td>
<td>3845</td>
<td>π→π*</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>7867</td>
<td>π→π*</td>
</tr>
<tr>
<td>[Co(BHMmBB)₂]</td>
<td>900</td>
<td>~11</td>
<td>²E_g→²T₁g</td>
</tr>
<tr>
<td></td>
<td>599</td>
<td>4000</td>
<td>²E_g→²T₂g</td>
</tr>
<tr>
<td></td>
<td>506</td>
<td>8000</td>
<td>MLCT</td>
</tr>
<tr>
<td>[Ni(BHMmBB)₂]</td>
<td>970</td>
<td>~7</td>
<td>³A₂g→³T₁g</td>
</tr>
<tr>
<td></td>
<td>646</td>
<td>278</td>
<td>³A₂g→³T₁g(F)</td>
</tr>
<tr>
<td></td>
<td>576</td>
<td>1250</td>
<td>MLCT</td>
</tr>
<tr>
<td>[Cu(BHMmBB)₂]</td>
<td>637</td>
<td>350</td>
<td>²T₂g→²E_g</td>
</tr>
<tr>
<td></td>
<td>291</td>
<td>13541</td>
<td>MLCT</td>
</tr>
</tbody>
</table>

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 1605 cm⁻¹ and 1545 cm⁻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 1173-1178 cm⁻¹ and new absorption band vM-O/vM→N form at lower frequency 507-569 cm⁻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⊥ 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 gk > g⊥ > 2.0023, could be obtained. The A∥ and A⊥ 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-bromobenzaldehyde (ligand) is proposed. All transition metal complexes are stable up to 245-250°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 physicochemical 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)

REFERENCES

Chohan Z H, Munawar A, Supuran C T. Met based Drugs, 2001; 8:137-43
Dash D. C., Meher F. M., Monhanty P. C. and Nanda J. Indian J. Chem., 1987; 26(A); 698
Lee J D; Concise Inorganic Chemistry. 5th ed., 2007
Raman N, Joseph J, Senthil Kumara Velan A and Pothiraj C. Mycobiology, 2006; 34:214-218
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