SYNTHESIS AND CHARACTERIZATION OF (1E, 2E) - 1, 2 - DIPHENYLETHANE -1, 2 – DIENEHYDRAZONE OXIME LIGAND AND ITS Fe(II) AND Pd(II) METAL COMPLEXES.

Raj R. Badekar1*, R. S. Lokhande1, S. W. Kulkarni2 and R. M. Patil3.
1. School of Basic Sciences, Jaipur National University, Jaipur-302017, India.
2. Department of Chemistry, K.M. Agrawal College, Kalyan-421301, India.
3. Department of Chemistry, Institute of Science 15, Madam Cama Road, Mumbai- 400032, India.

Introduction:
Ligands containing oxime also function as Schiff base containing an additional oxime group are interesting as ligand both on account of the structural variation of the metal complexes as well as wide range of application ranging from analytical to biological activities. Oxime function is ambidentate i.e. nitrogen and oxygen with almost equal probability. The second function due to the Schiff base moiety provides interesting complexation possibilities, it can coordinate with metal ion through nitrogen, in this view we wish to report Synthesis and Characterization of α-benzilmonoximehydrazone ligand and its Fe(II) and Pd(II) complexes. IUPAC name of the title ligand is (1E, 2E) - 1, 2 - diphenylethane -1, 2 – diene hydrazone oxime, for sake of convenience able as HBMOH is likely to yield metal complexes with a variety of metal ions. Bonding in these complexes is also likely to show interesting features. The characterization of the ligand and its metal complexes were investigated by elemental analysis, physico-chemical methods, FT(IR) spectra, pmr, electronic spectra etc.

Experimental section:
All chemical used were of analytical reagent grade. Distilled water obtained from a glass distillation unit. Conductivity measurements were made on EQ - 660 laboratory conductivity meter using nitrobenzene as solvent. UV-visible spectra of the ligand and its metal complexes were recorded on JASCO V - 650 spectrophotometer, methanol/ 0.1N NaOH was used as a solvents to record UV spectrum of the ligand, while chloroform were used as solvent to record the spectra of the complexes in the UV-visible region. FT(IR) spectra in KBr discs were recorded.

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on Perkin - Elmer spectrum 100 model. PMR spectra were recorded on Brucker AV300 NMR spectrometer using TMS as internal standard.

**Preparation of ligand:**
α-benzilmonoxime was prepared using benzil and hydroxyl amine hydrochloride. The ligand was prepared by the reaction between 10g (4.4mmol) of α-benzilmonoxime and 2.25g (4.5mmol) of hydrazine hydrate (80% aqueous) was drop wise added with stirring. The reaction mixture was allowed to stand at room temperature overnight. The white crystals obtained in presence of ice cold water were filtered through a Buchner funnel, washed thoroughly with cold water, and recrystallized from 60% ethanol to yield ~ 77% (8.13g) of the ligand. m.p. 172 °C.

![Chemical structure of α-benzilmonoxime](image)

2)

![Chemical structure of α-benzilmonoximehydrazone](image)

**Preparation of metal complexes:**

**Ink blue Fe(BMOH)₂:**
A reaction between 1.0g (4mmol) of ligand in 25cm³ of ethanol was added to an aqueous solution of (0.50g, 2mmol) FeSO₄. 0.5N NaOH was added to obtain an ink blue precipitate which was digested in a water bath for 20-25 minutes and then filtered through Buchner funnel. The precipitate was washed with hot water and recrystallized from methanol, dried at 110°C and analyzed for Fe(II) content. m.p. 208°C

**Green Pd(BMOH)₂:**
A reaction between 1.0g (4mmol) of ligand in 25cm³ of ethanol was added to an acidic solution of (0.50g, 2mmol) PdCl₂, 0.5N NaOH was added to obtain a green precipitate which was digested in a water bath for 20-25 minutes and then filtered through Buchner funnel. The precipitate was washed with hot water and recrystallized from methanol, dried at 110°C and analyzed for Pd(II) content. m.p. 203°C.

**Result and Discussion:**

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

| Compound       | Color         | Yield % | M.P. / Dec. point° C | % M Found (Calcd) | % C Found (Calcd) | % H Found (Calcd) | % N Found (Calcd) | % O Found (Calcd) | Magnetic Moments (B.M.) | Electrical Conductance 10⁻³ M (in Nitrobenzene) mhos |
|----------------|---------------|---------|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|------------------------|-----------------------------------------------|
| HBMOH         | Colorless     | 72.03   | 172                  | -                 | 70.29             | 5.44              | 17.57             | 6.69              | -                      | -                              |
| Fe(BMOH)₂     | Ink Blue      | 75.06   | 208                  | 9.89 (10.50)      | 62.55 (63.18)     | 4.00 (4.15)       | 15.70 (15.79)     | 5.99 (6.02)       | 5.22                   | 11.15                          |
| Pd(BMOH)₂     | Green         | 7.29    | 2.03                 | 17.84 (18.29)     | 57.00 (57.73)     | 3.88 (4.12)       | 14.69 (14.43)     | 4.91 (5.50)       | -                      | 1.73                           |
The reaction of HBMOH with FeSO₄ gave [Fe(BMOH)] as ink blue, PdCl₂ gave [Pd(BMOH)] as green complex respectively. The ligand HBMOH were characterized on the basis of elemental analysis, FT(IR), ¹H NMR, electronic spectral data. The molar conductance of [Fe(BMOH)] and [Pd(BMOH)] complexes were 11.15, and 1.73 for 10⁻³ M respectively (Table-1), indicating that the complex to be non-electrolyte.

¹H NMR Spectra:-
The pmr spectrum of HBMOH in (d₈) DMSO solvent (Table-2), reveals a broad singlet at 12.42δ, suggesting the highly acidic nature of this proton. A multiplet observed around 7.33-7.60δ due to two phenyl rings in the ligand structure. The singlet observed at 7.8-7.9δ is suggested to be due to azomethine proton or –NH₂ group in the ligand. The pmr spectra of Pd(II) complex shows a multiplet in the aromatic region 7.33-7.67δ due to the phenyl ring, this is slightly unchangeable region, these described that the phenyl ring does not contribute the coordination in metal complexes. The singlet peak due to the N-OH proton at 12.45δ in HBMOH is absent in its Pd(II) complex, suggesting the deprotonation of the hydroxyl group of the oxime in the ligand. The doublet peak ‘―NH₂’ shows slightly changed region 7.8-7.9δ, suggests the amino group does not contribute to the coordination.

| Compound         | Signal       | Assignment     |
|------------------|--------------|----------------|
| HBMOH            | δ 12.42      | 1H, O – H      |
|                  | δ7.80        | 2H, - NH₂ group|
|                  | δ7.33-7.60   | 10H, Phenyl group|
| Pd(BMOH)₂       | δ7.80        | 2H, - NH₂ group|
|                  | δ7.33-7.60   | 10H, Phenyl group|

IR spectra:-
A significant feature of the IR spectrum of α-benzilmonoximehydrzone is the absence of band between 1720-1680cm⁻¹ due to the νC = O vibration reported at 1715cm⁻¹ in α-benzilmonoxime indicating a successful replacement of the carbonyl oxygen by the hydrazonyl group during Schiff base formation. The spectrum of HBMOH shows peak at 3390cm⁻¹, which are described to symmetrical vibration of the ‘―NH₂’ group present in the ligand. This band is absent of HBMO, indicating the replacement of carbonyl group to imine group. Rest of the bands observed in HBMOH is almost at the same frequencies in comparisons with bands of HBMO (Table-3).

A strong and broad band is observed at 3287cm⁻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. This observation is supported by insolubility in dilute alkali solution. All metal complexes of HBMOH exhibit medium intensity bands in the region 3387-3391cm⁻¹ that can be attributed at N-H vibrations. This suggests the non involvement of -NH₂ group in bonding these complexes. The band at 1647cm⁻¹ due to ν(C=NO) of the oximino group in ligand was shifted to higher frequencies at in the region 1675-1678 cm⁻¹ in its complexes suggests that the coordination of oximino group with the metal ion. Also the band at 1493cm⁻¹ which was assigned the azomethine (C=NN) group of ligand was shifted to higher energy at in the region 1538-1558cm⁻¹, in the metal complexes, indicating the participation of the azomethine group in the coordination. In the metal complexes with the ligand in which an oxime group coordination through its nitrogen atom, the formation of N → O linkages an essential feature.

Magnetic moment:-
Ink blue Fe(II) complex shows a room temperature magnetic moment of 5.22BM (Table-1), which is higher than the spin only magnetic moment of 4.89BM expected for the four unpaired electrons in high spin Ferrous complexes. However, the ⁷⁄₅ term for the high spin octahedral complexes of Fe(II) is expected to contribute significantly to the room temperature magnetic moment and the observed moment for most high spin complexes of Fe(II) is expected to be greater than the spin only moment and are often observed in the range between 5.1-5.7BM. Tetrahedral...
complexes of Fe(II) are expected to reveal moment in the range between 5.00-5.20BM. Where, the orbital
correlation to the observed moment is expected to be lower than for octahedral complexes. Further, for ligands
containing ‘N’ and ‘O donor atom, Fe(II) is known to coordinate to give octahedral complexes\(^1\). In HBMOH ‘N’ as
donor atom, therefore Fe(II) complex suggests a high spin octahedral geometry. The observation is amply supported
by the electronic absorption spectral data from the complex. The spectral properties exhibited by the Pd(II) complex
as well as the tendency of Pd(II) ion (\(d^9\)) to form square planar complexes suggests that the Pd(II) complex of
HBMOH to be diamagnetic.

Electronic Absorption Spectra:-
The electronic spectrum of HBMOH in methanol for the UV region reveals two high intensity bands at 42200cm\(^{-1}\)
and 47620cm\(^{-1}\) respectively (Table-4). These may be due to \(\pi \rightarrow \pi^*\) transitions possible from the azomethine
and oximino environments in the molecules\(^2\). The UV spectrum of HBMOH in dilute alkali (0.1N NaOH) solution
shows that the band at 42200cm\(^{-1}\) methanolic solution spectrum has suffered along with a bathochromic shift to
32250cm\(^{-1}\). It means that this band could have its origin in the oximino linkage in the molecules as such; the band at
39520cm\(^{-1}\) in the dilute alkali solution spectrum could be assigned to the azomethine linkage\(^3\). This band is suffered
as bathochromic shift compared to methanolic solution.
The electronic spectrum of the ink blue Fe(II) complex in chloroform solution shows a symmetrical broad band
around 15470cm\(^{-1}\), along with a small band around 18000cm\(^{-1}\) (Table-4). The spectrum also shows a high intensity
band at 26320cm\(^{-1}\). The position of the last band along with the intensity shown, suggests that it is originating from
charge transfer phenomenon. While, the earlier two bands could be said originate from the intra molecular transitions.
For high spin case, the ground state \(^5\)D is supported to split into \(^5\)E\(_g\) and \(^5\)T\(_2g\) states. As such \(d-d\) transition
corresponding to \(^5\)T\(_{2g}\)\(\rightarrow\)^5E\(_g\) may be expected. However, the \(^5\)E\(_g\) state is expected to further split into \(^5\)B\(_{1g}\) and
\(^5\)A\(_{1g}\) owing perhaps to Jahn-Teller distortion. As such Fe(II) high spin octahedral complexes could shows two fairly
closely bands. The bands observed at 15470cm\(^{-1}\) and 18000cm\(^{-1}\) are therefore assignable to \(d-d\) transitions. The green
colored Pd(II) in chloroform shows charge transfer bands at 22780cm\(^{-1}\) and 28250cm\(^{-1}\). The ligand field transitions
are not clearly observed.

Table-4: Electronic spectral data for HBMOH and its metal complexes.

| No. | Compound      | Solvent   | Band position in cm\(^{-1}\) | Intensity \(\varepsilon\) | Assignment                           |
|-----|---------------|-----------|-------------------------------|-------------------------|--------------------------------------|
| 1   | HBMOH         | Methanol  | 47620                         | 12252                   | Oximino \(\pi \rightarrow \pi^*\) transition |
|     |               | 0.1N NaOH | 42200                         | 11181                   | Azomethine \(\pi \rightarrow \pi^*\) transition |
|     |               |           | 39520                         | 12116                   | Oximino \(\pi \rightarrow \pi^*\) transition |
|     |               |           | 32260                         | 11288                   | Azomethine \(\pi \rightarrow \pi^*\) transition |
| 2   | Fe(BMOH)_2    | Chloroform| 15470                         | 271                     | \(T_{2g} \rightarrow E_g\) transition |
|     |               |           | 37170                         | 5444                    | Charge transfer M \(\rightarrow\) L transition |
| 3   | Pd(BMOH)_2    | Chloroform| 22780                         | 3958                    | Charge transfer M \(\rightarrow\) L transition |
|     |               |           | 28250                         | 3465                    | Charge transfer M \(\rightarrow\) L transition |
|     |               |           | 33370                         | 8633                    | Charge transfer M \(\rightarrow\) L transition |

Conclusion:
HBMOH ligand is insoluble in water but soluble in dilute alkali, common organic solvents. Its metal complexes are
insoluble in dilute alkali, indicates that deprotonation of oxime group during complex formation. These 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 Fe(II) complex is high spin octahedral and Pd(II)
complex is square planar geometry. FT(IR) spectral data suggests that complexes coordinate with metal ion through
nitrogen atom only. On the basis of magnetic and spectral data, structure of Fe(II) and Pd(II) tentatively assigned as;
References:
1. Srikanta A, Dixit NS and Patel CC; J. Inorg. Nucl. Chem., 42, 483 (1980).
2. Natrajan C and Hussain AM; Ind. J. Chem., 20A, 307 (1981).
3. Dhande PM and Halder BC.
   J. Ind. Chem. Soc., 55, 18 (1978).
   J. Ind. Chem. Soc., 56, 461 (1979).
4. Soleimani EJ; Chin. Chem. Soc., 60, 484 (2009).
5. Mohmound ASM and Naser MAS: Jorn. Chem. Soc. Pak., 18, 155-159 (1996).
6. Williams DR, Chem. Rev., 72, 203 (1972).
7. MacGarvey BR; J. Chem. Soc., 61, 1232 (1957).
8. Lever ABP; J. Chem. Educ., 45, 11, 711-712, (1968).
9. Kneubuhl; J. Chem. Phys. 33, 1074 (1960).
10. Low W; Paramagnetic Resonance in Solid P, 76, Acad Press, N.Y (1960).
11. Fujiwara S. et al; J. Chem. Soc. (Dalton), 600 (1979).
12. Badekar RR; M.Sc. Thesis, University of Mumbai (2012).
13. Badekar RR, Lokhande RS, Kulkarni SW and Patil RM; Inter. J. of Adv. Res. 4(7), 1093-1097 (2016).