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RESEARCH ARTICLE

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

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Abstract

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Reaction between hydrazine hydrate 80% aqueous solution and an alcoholic solution of α-benzilmonoxime yields α-benzilmonoximehydrazone (IUPAC Name: (1E, 2E) - 1, 2 - diphenylethane -1, 2 –diene hydrazine oxime).

The present work report the synthesis and characterization of α-benzilmonoximehydrazone along with its metal complexes with Fe(II) and Pd(II). The compounds synthesized have been characterized on the basis of various physico-chemical techniques. Electrical conductance studies on the metal complexes reveal their non-electrolytic nature. Spectral measurements and magnetic moment suggest an octahedral geometry for Fe(II) Complex, and square planar geometry for Pd(II) complex.

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Introduction:-

Ligands containing oxime also function as Schiff base containing an additional oximegroup are interesting as ligand both on account of the structural variation[1-5]of the metal complexes as well as wide range of application ranging from analytical to biological activities[1-5]**.** Oxime function is ambidentate i.e. nitrogen and oxygen with almost equal probability[6]. The second function due to the Schiff base moiety provides interesting complexation possibilities[7], it can coordinate with metal ion through nitrogen, in this view we wish to report Synthesis and Characterization of α-benzilmonoximehydrazone ligand and itsFe(II) and Pd(II) complexes. IUPAC name of the title ligand is (1E, 2E) - 1, 2 - diphenylethane -1, 2 –diene hydrazine 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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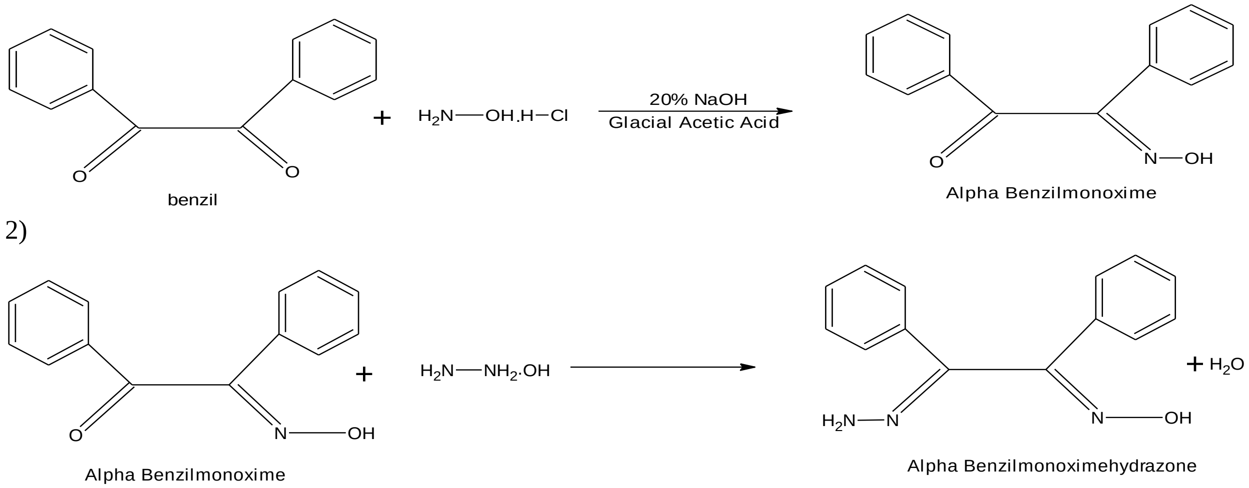
on Perkin - Elmer spectrum 100 model. PMR spectra were recorded on Brucker AV300 NMR spectrometer using TMS as internal standard.

Preparation of ligand:-

α-benzilmonoxime was prepared using benzil and hydroxyl amine hydrochloride[8]. 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.

1)



Two step preparation of α-Benzilmonoximehydrazone

Preparation of metal complexes:-

Ink blue Fe(BMOH)$_2$:-

A reaction between 1.0g (4mmol) of ligand in 25cm^3 of ethanol was added to an aqueous solution of (0.50g, 2mmol) FeSO$_4$, 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 25cm^3 of ethanol was added to a acidic solution of (0.50g, 2mmol) PdCl$_2$, 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	Elemental Analysis					Magnetic Moments (B.M.)	Electrical Conductance 10^{-3} M(in Nitrobenzene) mhos
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)		
HBMOH	Colorless	72.03	172	-	70.29 (70.27)	5.44 (5.32)	17.57 (17.58)	6.69 (6.75)	-	-
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 $FeSO_4$ gave $[Fe(BMOH)_2]$as ink blue, $PdCl_2$ gave $[Pd(BMOH)_2]$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 $[Fe(BMOH)_2]$, and $[Pd(BMOH)_2]$ complexes were 11.15, and 1.73 for 10^{-3} M respectively (**Table-1**), indicating that the complex to be non electrolyte[9].

^1H NMR Spectra:-

The pmr spectrum of HBMOH in (d_6) DMSO solvent (**Table-2**), reveals a broad singlet at 12.42δ, suggesting the highly acidic nature of this proton. Amultiplet 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 – NH_2 group in the ligand. The pmr spectra of Pd(II) complex shows a multiplate 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 12.45δin HBMOH is absent in its Pd(II) complex, suggesting the deprotonation of the hydroxyl group of the oxime in the ligand. The doublet peak '$–NH_2$' shows slightly changed region 7.8-7.9δ, suggests the amino group does not contribute to the coordination.

Table 2:- PMR spectral data of the HBMOH.

Compound	Signal	Assignment
HBMOH	δ 12.42 δ7.80 δ7.33-7.60	1H, O – H 2H, - NH_2 group 10H, Phenyl group
$Pd(BMOH)_2$	δ7.80 δ7.33-7.60	2H, - NH_2 group 10H, Phenyl group

IR spectra:-

A significant feature of the IR spectrum of α-benzilmonoximehydrazone is the absence of band between 1720-1680cm^{-1} due to the υC = O vibration reported[11] 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 '- NH_2' group present in the ligand. This band are 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 toN-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[11]. 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 $-NH_2$ group in bonding these complexes[12].The band at 1647cm^{-1} due to υ(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[14]. 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[15]. 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.The facts are further supported by the appearance of new bands in the regions 538 and 418, 511 and 503 in the Fe(II), Pd(II)complexes which were assigned to the N-M stretching vibration respectively[16].

Table 3:-FT(IR) spectral data for HBMOH and its metal complexes.

Compound	υ(O-H)	υ(N-H)	Ar. C-H	C=NO	C=NN	N - O	N-N	M-N
HBMOH	3287	3387	3058	1647	1493	926	1072	-
$Fe(BMOH)_2$	-	3400	3069	1658	1538	1000	1093	538, 418
$Pd(BMOH)_2$	-	3387	3025	1676	1550	1001	1099	582, 533

Magnetic moment:-

Ink blueFe(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[17]. However, the ^5T 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 contribution 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[17]. 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.Thespectral properties exhibited by the Pd(II) complex as well as the tendency of Pd(II) ion (d^8) 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[18]. 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[19]. This band is suffered as bathochromic shift compared to methanolic solution.

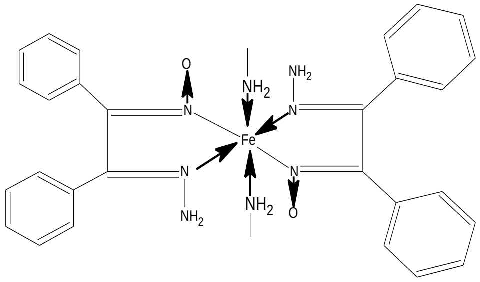
The electronic spectrum of the ink blueFe(II) complex in chloroform solution shows a symmetrical broad band around 15470cm^{-1}, along with a small band around 18000cm^{-1}(**Table-4**). The spectrum also shows a high intensity band at 26320cm^{-1}.The position of the last band along with the intensityshown, 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 ^5D is supported to split into ^5E_g and $^5T_{2g}$states. As such *d-d* transition corresponding to$^5T_{2g} \rightarrow {}^5E_g$may be expected. However, the ^5E_g state is expected to further split into $^5B_{1g}$ and $^5A_{1g}$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 at22780cm^{-1}and 28250cm^{-1}. The ligand field transitions are not clearly observed.

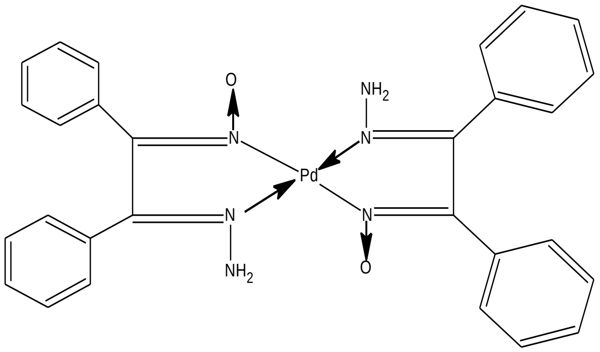
Table-4:- Electronic spectral data for HBMOH and its metal complexes.

No.	Compound	Solvent	Band position in cm^{-1}	Intensity ε	Assignment
1	HBMOH	Methanol	47620	12252	Oximino$\pi\rightarrow\pi^*$ transition
			42200	11181	Azomethine$\pi\rightarrow\pi^*$ transition
		0.1N NaOH	39520	12116	Oximino$\pi\rightarrow\pi^*$ transition
			32260	11288	Azomethine$\pi\rightarrow\pi^*$ transition
2	Fe(BMOH)$_2$	Chloroform	15470	271	$^5T_{2g} \rightarrow {}^5E_g$transition
			37170	5444	Charge transfer M$\rightarrow$Ltransition
3	Pd(BMOH)$_2$	Chloroform	22780	3958	Charge transfer M$\rightarrow$Ltransition
			28250	3465	Charge transfer M$\rightarrow$Ltransition
			33370	8633	Charge transfer M$\rightarrow$Ltransition

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 thatFe(II)complex ishigh spin octahedral and Pd(II) complex issquare 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;





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