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RESEARCH ARTICLE

“Synthesis and Characterization of α - Benzilmonoximehydrazone ligand and its Zn(II), Cd(II) and Hg(II) metal complexes”.

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Manuscript Info Abstract

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Introduction:-

Ligands containing oxime also function as Schiff base containing an additional oxime group are interesting as ligand both on account of the structural variation¹⁻⁵ of the metal complexes as well as wide range of application ranging from analytical to biological activities¹⁻⁵. 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 Zn(II), Cd(II) and Hg(II) metal complexes. IUPAC name of the title ligand is (1E, 2E) - 1, 2 - Diphenylethane -1, 2 - Dione 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.

Result and discussion:-

Table:1:- Analytical and physical data for HBMOH and its Zn(II), Cd(II), Hg(II) metal complexes

Compound	Color (M.P. in °C)	% Yield	Percentage of					Conductance
			C	H	N	O	M	
HBMOH	Colorless (172)	72.03	70.29 (70.0)	5.44 (5.21)	17.57 (17.92)	6.69 (6.29)	-----	----
Zn(BMOH) ₂	Colorless (199)	83.12	63.83 (63.52)	4.45 (4.81)	15.68 (15.29)	5.88 (6.01)	10.98 (10.21)	1.90
Cd(BMOH) ₂	Colorless (203)	79.63	62.29 (62.82)	4.41 (4.00)	15.58 (15.03)	5.96 (5.28)	19.10 (18.62)	5.99
Hg(BMOH) ₂	Yellow (198)	79.99	49.66 (49.11)	3.54 (3.92)	12.41 (12.90)	4.72 (4.18)	29.65 (29.02)	1.78

The reaction of HBMOH (1) with $ZnCl_2 \cdot 7H_2O$, $CdCl_2$, $HgCl_2$ gave $[Zn(BMOH)_2]$ (2) as colorless, $[Cd(BMOH)_2]$ (3) as colorless, $[Hg(BMOH)_2]$ (4) as yellow complexes respectively. The ligand HBMOH were characterized on the basis of elemental analysis, FT(IR), 1H NMR, electronic spectral data. The molar conductance of Zn(II), Cd(II), Hg(II) complexes were 1.9, 5.99, 1.78 for 10^{-3} M respectively, indicating that the complex to be non-electrolyte [6].

Electronic Absorption Spectra:

Table – 2:- Electronic spectral data for HBMOH and its metal complexes in λ_{nm}

Transition type	Intra ligand charge transfer		Ligand to metal Charge transfer
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	
Compound			
HBMOH (1)	210	237	----
$Zn(BMOH)_2$ (2)	---	---	254, 328
$Cd(BMOH)_2$ (3)	---	---	248
$Hg(BMOH)_2$ (4)	---	---	256

The electronic spectrum of HBMOH in methanol for the UV region reveals two high intensity bands at 237nm and 210nm respectively. These may be due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition possible from the azomethine and oximino environments in the molecules. The UV spectrum of HBMOH in dilute alkali (0.1N NaOH) solution shows that, the band at 237nm in methanolic solution spectrum has suffered along with a bathochromic shift to 310nm. It means that this band could have its origin in the oximino linkage in the molecules as such; the band at 253nm in the dilute alkali solution spectrum could be assigned to the azomethine linkage. This band is suffered as bathochromic shift compared to methanolic solution. The electronic spectra of Zn(II), Cd(II) and Hg(II) complexes in exhibit absorption bands at 248 - 256nm and Zn(II) complex at 328nm with high molar extinction coefficient (**Table-2**). All metal complexes show only the charge transfer transitions, which can be assigned to charge transfer from the ligand to metal, no $d-d$ transition expected for d^{10} configuration and magnetic properties are diamagnetic. The electronic spectra and magnetic moments correlate with each other. It seems that all complexes are in tetrahedral geometry.

FTIR spectra:-

A significant feature of the FT(IR) spectrum of α -Benzilmonoximehydrazone is the absence of band between $1720 - 1680\text{cm}^{-1}$ due to the $\nu C = O$ vibration reported [8] at 1715cm^{-1} in HBMO indicating a successful replacement of the carbonyl oxygen by the hydrazone 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. Rests of the bands observed in HBMOH are 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 [9]. This observation is supported by insolubility in dilute alkali solution. All metal complexes of HBMOH exhibit medium intensity bands in the region $3057 - 3409\text{cm}^{-1}$ that can be attributed to N-H vibrations. This suggests the non-involvement of -NH₂ group in bonding these complexes. The band at 1647cm^{-1} due to $\nu(C=NO)$ of the oximino group in ligand was shifted to higher frequencies at in the region $1655 - 1678\text{cm}^{-1}$ in its complexes suggests that the coordination of oximino group with the metal ion [11]. Also the band at 1493cm^{-1} which was assigned to the azomethine (C=NN) group of ligand was shifted to higher energy at in the region $1550 - 1577\text{cm}^{-1}$, 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 \rightarrow O linkages an essential feature. The facts are further supported by the appearance of new bands in the regions 582, 533, 515, 490, 492, 458 cm^{-1} in the Zn(II), Cd(II), Hg(II) complexes which were assigned to the Zn-N, N \rightarrow Zn, Cd-N, N \rightarrow Cd, Hg-N, N \rightarrow Hg, stretching vibrations respectively [12].

Table-3:- Important IR bands(cm^{-1}) and their assignments for HBMOH and metal complexes

Vibration modes	$\nu(O-H)$	-NH ₂	C=N-O	C=N-N	N-O	M-N
HBMOH (1)	3287	3390	1647	1493	926	-----
$Zn(BMOH)_2$ (2)	---	---	3409	1677	1560	1009 582, 533
$Cd(BMOH)_2$ (3)	---	---	3361	1678	1551	1009 515, 490
$Hg(BMOH)_2$ (4)	---	---	3057	1676	1550	1000 492, 458

PMR Spectra:-**Table 4: PMR data of HBMOH**

<i>Compounds Phenyl ring -NH₂-OH</i>		
HBMOH(1) δ 7.33-7.60 (Broad, m)	δ 7.8-7.9(d)	δ 12.42(Broad, s, =NOH)
Zn(BMOH) ₂ (2) δ 7.37-7.63 (Broad, m)	δ 7.8-7.9(d)	-----
Cd(BMOH) ₂ (3) δ 7.35-7.67(Broad, m)	δ 7.8-7.9(d)-----	
Hg(BMOH) ₂ (4) δ 7.34-7.60 (Broad, m)	δ 7.7-7.8(d)	-----

The pmr spectrum of HBMOH in (d₆) DMSO solvent (Table 3), reveals a broad singlet at δ 12.42, suggesting the highly acidic nature of this proton. A multiplet observed around δ 7.33 to 7.60 due to two phenyl rings in the ligand structure. The singlet observed at δ 7.8-7.9 is suggested to be due to azomethine proton or -NH₂ group in the ligand. The ¹H NMR spectra of HBMOH complexes show a multiplet in the aromatic region δ 7.33 – 7.67 due to the phenyl ring, this is slightly changeable region, these described that the phenyl does not contribute the coordination in metal complexes. The singlet peak due to the N – OH proton at δ 12.42 in HBMOH is absent in its Zn(II), Cd(II) and Hg(II) complexes, suggesting the deprotonation of the hydroxyl group of the oxime in the ligand. The doublet peak ‘-NH₂’ shows slightly changed region δ 7.8 – 7.9, suggest the ‘-NH₂’ group does not contribute to the coordination,

Conclusion:-

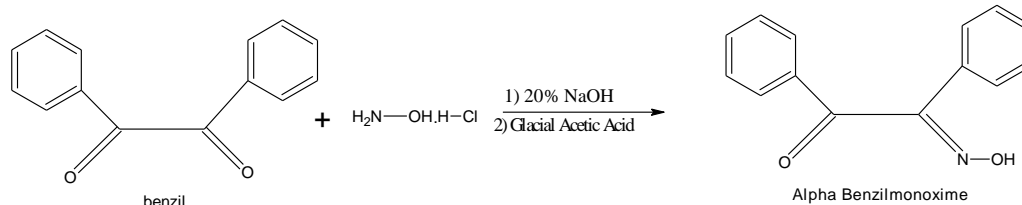
The title ligand is soluble in most of the organic solvents and dilute alkali, but its Zn(II), Cd(II) and Hg(II) metal complexes are insoluble in ethanol, dilute alkali and soluble in methanol, chloroform, DMF etc. Zn(II), Cd(II) and Hg(II) metal complexes are non electrolytic nature. Spectral measurements data suggest that all metal ions are bonded with HBMOH ligand through nitrogen atom for M – N₄ composition and geometries for metal complexes are of tetrahedral shape.

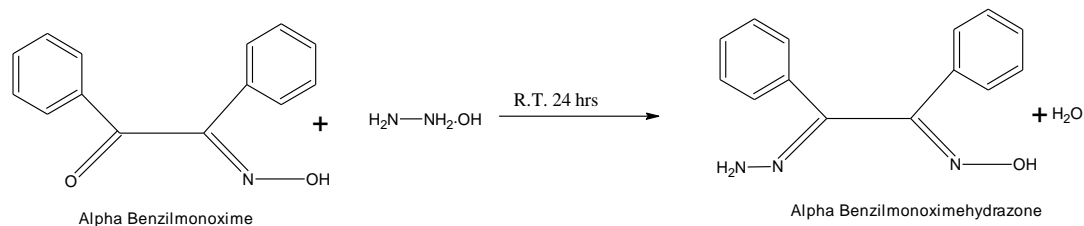
Experimental section:-

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

Preparation of ligand:-

α -Benzilmonoxime was prepared using benzil and hydroxyl amine hydrochloride [7]. The ligand was prepared by the reaction between 10g α -Benzilmonoxime and 2.25g of hydrazine hydrate (80% aqueous) 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, UV-vis(MeOH/0.1N NaOH) λ_{max} : 210, 237/ 253, 310nm; ¹H NMR (d₆ DMSO δ ppm) 7.8-7.9(m, 2H), 7.3-7.6(m, 10H), 12.4(s, 1H); IR (KBr Cm⁻¹) 3390, 3287, 1647, 1493, 1072, 926, 692. Anal. Calc. for C₁₄H₁₃N₃O (%) C 70.29, H 5.44, N 17.57, O 6.69; found C 70.00, H 5.21, N 17.92, O 6.29.





Scheme I:- Two step preparation of α -Benzilmonoximehydrazone

Preparation of metal complexes:-

The metal complexes reported herein, were prepared by the reaction between an ethanolic solution of ligand and an aqueous solution of the corresponding metal chloride, 0.5N NaOH was used as necessary to obtain the respective complexes.

Preparation of bis(benzilmonoximehydrazone)zinc(II):-

A reaction between 1.0g (4 mmol) of ligand in 25cm³ of ethanol was added to a solution of (0.50g, 2 mmol) ZnCl₂.6H₂O, 0.5N NaOH was added to obtain a colorless precipitate which was digested in a waterbath 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 Zn(II) content.m.p. 199 °C, UV-vis(Chloroform) λ_{max} : 328, 253nm; ¹H NMR (d₆DMSO δ ppm) 7.8-7.9(m, 2H), 7.3-7.6(m, 10H); IR (KBr cm⁻¹) 3409, 1677, 1560, 1098, 1009, 697, 582, 533. Anal. Calc. for C₂₈H₂₄N₆O₂Zn (%) C 63.83, H 4.45, N 15.68, O 5.88, Zn 10.98; found C 63.52, H 4.81, N 15.29, O 6.01, Zn 10.21.

Preparation of bis(benzilmonoximehydrazone)cadmium(II):-

A reaction between 1.0g (4 mmol) of ligand in 25cm³ of ethanol was added to a solution of (0.367g, 2 mmol) CdCl₂, 0.5N NaOH was added to obtain a colorless precipitate which was digested in a waterbath 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 Cd(II) content.m.p. 203°C, UV-vis(Chloroform) λ_{max} : 248nm; ¹H NMR (d₆DMSO δ ppm) 7.8-7.9(m, 2H), 7.3-7.6(m, 10H); IR (KBr cm⁻¹) 3361, 1678, 1551, 1083, 1009, 693, 515, 490. Anal. Calc. for C₂₈H₂₄N₆O₂Cd (%) C 62.29, H 4.41, N 15.58, O 5.96, Cd 19.10; found C 62.82, H 4.00, N 15.03, O 5.28, Cd 18.62.

Preparation of bis(benzilmonoximehydrazone)mercury(II):-

A reaction between 1.0g (4 mmol) of ligand in 25cm³ of ethanol was added to a solution of (0.543g, 2 mmol) HgCl₂, 0.5N NaOH was added to obtain a yellow precipitate which was digested in a waterbath 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 Hg(II) content.m.p. 198°C, UV-vis(Chloroform) λ_{max} : 252nm; ¹H NMR (d₆DMSO δ ppm) 7.7-7.8(m, 2H), 7.3-7.6(m, 10H); IR (KBr cm⁻¹) 3057, 1676, 1550, 1099, 1000, 695, 492, 458. Anal. Calcd for C₂₈H₂₄N₆O₂Hg (%) C 49.66, H 3.54, N 12.41, O 4.72, Hg 29.65; found C 49.11, H 3.92, N 12.92, O 4.18, Hg 29.02.

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