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Synthesis, Characterization and Antibacterial Studies of p-Dimethylaminobenzaldehyde Derivative of α-Benzilmonoximehydrazone ligand and its Zn(II), Cd(II) and Hg(II) Metal Complexes

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Abstract: *It is difficult to imagine life without biological metal complexes. Human being can't ignore the role of coordination compounds in the various physiological processes taking place inside our body. Hence coordination compounds synthesized compounds can compete with the vital biological reactions taking place in the body. Therefore, the metal complexes can inhibit the life cycle of various microbes and find their application in the medicine world. Here, we report the synthesis of divalent metal ions of Zn, Cd and Hg complexes with derivatives of Benzilmonoximehydrazone as ligand. Synthesized complexes were characterized by using traditional instrumental data and attempt to figure out the geometry of the complexes based on spectroscopic data. Antimicrobial studies were performed to assess the biological properties against the both the gram positive and negative* bacteria using streptomycin as a standard. The results obtained were encouraging.

Keywords: Coordination chemistry, Zinc, Cadmium, Mercury and Antibacterial Activity.

I. INTRODUCTION

Schiff bases and its derivatives are well known for its biological properties. Ligands with oxime functionality also considered as Schiff bases and they are equivalent in structural and application view point[1-5].

Oximes are ambidentate and it attempts to coordinate with its nitrogen and oxygen atoms with almost equal probability. In this view we wish to report synthesis, characterization and antibacterial studies of p-Dimethylaminobenzaldehyde derivative of α-Benzilmonoximehydrazone ligand and its Zn(II), Cd(II) and Hg(II) metal complexes. IUPAC name of the title ligand is 4-[-2-(hydroxyimino)-1,2-diphenylethylidene]hydrazinylidene}methyl]-*N*,*N*-dimethylaniline, for sake of convenience, it is abbreviated HBOHPDB. 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.

II. EXPERIMENTAL SECTION

All chemical used were of analytical reagent grade. Conductivity measurements were measured 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 where methanol/ 0.1N NaOH was used as a solvent for ligand, and Chloroform was 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 Brucker AV300 NMR spectrometer using TMS as internal standard.

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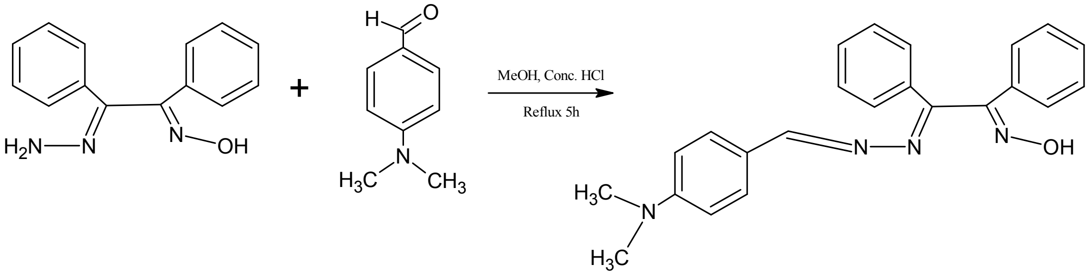
2.1 Preparation of ligand

α-Benzilmonoximehydrazone was prepared reported method[7].



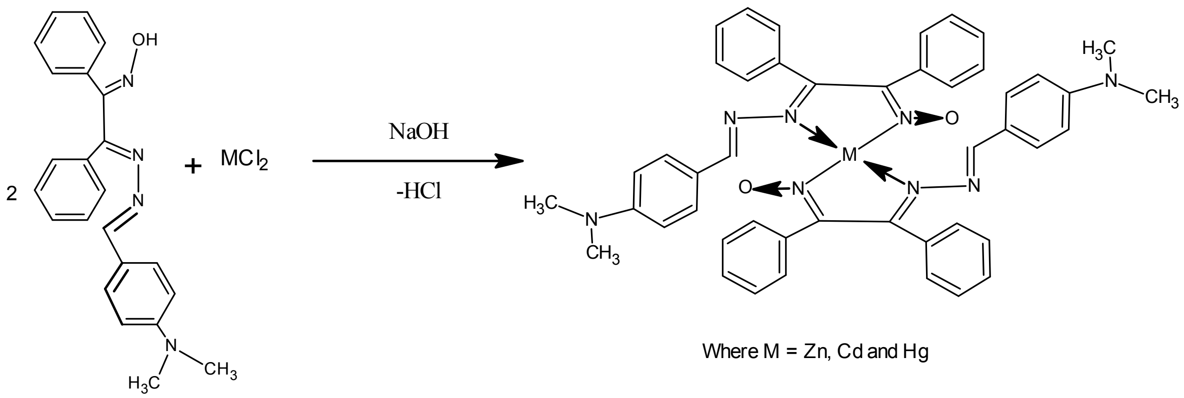
α-Benzilmonoximehydrazone
239gm

N,N-Dimethylaminobenzaldehyde
149g

α-Benzilmonoximehydazide-N,N-Dimethylaminobenzaldehyde
370g

2.2 Preparation of Metal Complexes

The metal complexes reported herein, were prepared by the reaction between an ethonolic solution of ligand and an aqueous solution of the corresponding metal chloride in 2:1 molar ratio. 0.5N NaOH was used as necessary to obtain the respective complexes.



Where M = Zn, Cd and Hg

2.2.1 Preparation of bis(benzilmonoxinehydrazone-p-dimethylaminobenzaldehyde)zinc (II)

A reaction between 1.48g (4mmol) of ligand in 25cm^3 of ethanol was added to a solution of (0.50g, 2 mmol) $ZnCl_2.6H_2O$, 0.5N NaOH was added to obtain a yellow precipitate which was digested in a waterbath for about 20-25 minutes and then filtered through Buchner funnel. The precipitate was washed with hot water and recrystallized from methanol, dried at 110^{o}C and analyzed for Zn(II) content. M.P.: 199^{o}C, UV-vis(Chloroform) λ_{max}: 328, 253nm; ^{1}H NMR (d_6 DMSO 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 $C_{46}H_{42}N_8O_2Zn$ (%) 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.

2.2.2 Preparation of bis(benzilmonoxinehydrazone-p-dimethylaminobenzaldehyde) cadmium(II)

A reaction between 1.48g (4mmol) of ligand in 25cm^3 of ethanol was added to a solution of (0.367g, 2mmol) $CdCl_2$, 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^{o}C and analyzed for Cd(II) content.m.p. 203^{o}C, UV-vis(Chloroform) λmax: 248nm; ^{1}H NMR (d_6DMSO 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 $C_{46}H_{42}N_8O_2Cd$ (%) 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.

2.2.3 Preparation of bis(benzilmonoxinehydrazone-p-dimethylaminobenzaldehyde) mercury(II)

A reaction between 1.48g (4 mmol) of ligand in 25cm^3 of ethanol was added to a solution of (0.543g, 2 mmol) $HgCl_2$, 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) λmax: 252nm; ^{1}H NMR (d_6DMSO 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 $C_{46}H_{42}N_8O_2Hg$ (%) 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.

2.3 Study of Antimicrobial Screening

The filter paper disc method was applied[8]. The test bacteria were seeded in tubes with nutrient broth (NB), the seeded NB (1mL) was homogenized at 45^{0}C in the tubes with 9mL of melted nutrient agar (NA) and the homogeneous suspensions were poured into petri-dishes. The discs of the filter paper (diameter 4mm) were ranged on the cooled medium. After cooling the formed solid medium of the investigated compounds were applied using a micropipette. After incubation for 24h in the thermostat at 25-27^{0}C, the inhibition (sterile) zone diameters of the discs were measured and expressed in mm. An inhibition zone of diameter over 7mm indicates that the tested compounds are active against the bacteria under investigation. The antibacterial activities of the investigated compounds were tested against three gram positive bacteria *(B. subilis, S. aureus, S. typhi) and* three gram negative bacteria *(E. coli, K. pneumoniae, P. aeruginosa)*. The concentration of 1000 ppm of each solution was prepared. Commercial DMF was employed to dissolve the test samples. Streptomycin was deployed as standard drug for comparison of findings with the values of prepared compounds.

2.4 Results and Discussion

The reaction of HBOHPDB (1) with $ZnCl_2.7H_2O$, $CdCl_2$, $HgCl_2$ gave [Zn(BOHPDB)$_2$] (2) as colorless, [Cd(BOHPDB)$_2$] (3) as colorless, [Hg(BOHPDB)$_2$] (4) as yellow complexes respectively. The ligand HBOHPDB were characterized on the basis of elemental analysis, FT(IR), ^{1}H NMR, electronic spectral data. The molar conductance of Zn(II), Cd(II), Hg(II) complexes were 3.32, 1.87, 2.65 for 10^{-3} M respectively, indicating that the complex to be non-electrolyte[7].

Table 1: Physical and analytical data of ligand (HBMHDAB) and its metal complexes

Compound (Colour)	M.W.	M.P. / D.T.	Yield(%)	Λ_m Scm^{2}mol^{-1}	Elemental analysis in % found (calculated)					μ_{eff} (B.M.)
					C	H	N	O	Metal	
HBMHDAB (Yellow)	370	191	79.63	---	74.59 (73.88)	5.97 (5.98)	14.14 (15.00)	4.32 (4.39)	---	---
[Zn(BMHDAB)$_2$] (Yellow)	804.29	211	90.59	3.32	68.63 (68.02)	5.22 (5.32)	13.93 (13.72)	3.98 (3.90)	8.13 (8.11)	Diamagnetic
[Cd(BMHDAB)$_2$] (Yellow)	851.29	235	81.12	1.87	64.84 (64.21)	4.93 (4.83)	13.96 (14.01)	3.76 (3.63)	13.20 (12.72)	Diamagnetic
[Hg(BMHDAB)$_2$] (Yellow)	939.47	280	84.72	2.65	58.76 (58.81)	4.47 (3.83)	11.92 (12.15)	3.41 (3.38)	21.35 (20.84)	Diamagnetic

2.4.1 Electronic Absorption Spectra

The electronic spectrum of HBOHPDB in methanol for the UV region reveals two high intensity bands at 230nm and 249nm respectively. These may be due to $\pi \rightarrow \pi^*$ transitions possible from the azomethine and oximino environments in the molecules. The UV spectrum of HBOHPDB in dilute alkali (0.1N NaOH) solution shows that, the band at 230nm in methanolic solution spectrum has suffered along with a bathochromic shift to 266nm. It means that this band could have its origin in the oximino linkage in the molecules as such; the band at 249nm 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 425 - 518nm 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.

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

Compound	λ_{nm}	*Assignments*
HBOHPDB (methanol)	230 and 249	$\pi \rightarrow \pi *$
(0.1N NaOH)	266 and 317	$\pi \rightarrow \pi *$
$Zn(BOHPDB)_2$	425	Metal to Ligand Charge Transfer
$Cd(BOHPDB)_2$	438	Metal to Ligand Charge Transfer
$Hg(BOHPDB)_2$	518	Metal to Ligand Charge Transfer

2.4.2 FTIR Spectra

Absence of any band between 3300-3400cm^{-1} in present ligand, in α-benzilmonoximehydrazone reported[19] at 3287cm^{-1} for $–NH_2$ group indicating successfully replacement of amino group during condensation. In order to study the binding modes of Schiff base to metal in the complexes, IR spectrum of the free ligand was compared with the spectra of the metal complexes. A strong and broad band is observed at 3267cm^{-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 was supported by insolubility in dilute alkali solution. The band at 1587cm^{-1} due to υ(C=NO) of the oximino group in ligand was shifted to higher frequencies at in the region 1597-1603cm^{-1} in its complexes suggests that the coordination of oximino group with the metal ion[11]. Also the band at 1549cm^{-1} which was assigned to the azomethine (C=NN) group of ligand was shifted to lower energy at in the region 1537-1540cm^{-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. The facts are further supported by the appearance of new bands in the regions 504-528cm^{-1} in the Zn(II), Cd(II), Hg(II) complexes which were assigned to the Zn-N, N→Zn, Cd-N, N→Cd, Hg-N, N→Hg, stretching vibrations respectively[12].

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

Tentative assignments	Ligand	Zn(II) complex	Cd(II) complex	Hg(II) complex
Hydrogen bonded νOH group	3267	-	-	-
νC=NOH	1587	1598	1597	1603
νC=NN	1549	1540	1537	1540
νN-O	1008	1009	1009	1007
νN→O	---	1287, 1540	1288, 1506	1289, 1488
νM-N	---	528	525	526
νM→N	---	508	504	505
νC=C Ar.	3053	3055	3056	3056

2.4.3 PMR Spectra

The ^1H NMR spectrum of the ligand and its complexes are done in d_6 DMSO solvent. The ^1H NMR spectrum of the prepared ligand exhibits a multiplet signal at 6.7-8.50δ (m, 14H) suggests that the aromatic groups present in ligand. This band is unshifted in complexes, indicate non-involvement of aromatic group in the coordination and also two methane group observed in the region 1.2- 1.6δ are unshifted in complex, suggests they are not involve in coordination. A sharp and singlet band observed at 10.20δ (s, 1H) in title ligand is absent in the prepared complex, confirm that the oximino group is deprotonated during complex formation. Other bands are unchanged in complex, suggests non-involvement of these group in coordination.

Table 4: PMR spectrum of HBMHDAB and its metal complexes in D_6 DMSO

Compound	multiplicity	δ ppm	assignment
HBMHDAB	Singlet 1H	11.80	Oximino>C=N–OH group
	Singlet 1H	0.30	Methane –CH= group
	Singlet 3H	2.50-2.90	Methyl $–CH_3$

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	Multiplet	6.80- 8.40	Aromatic Protons
[Zn(BMHDAB)$_2$]	Singlet 1H	0.30	Methane –CH= group
	Singlet 3H	2.50-2.90	Methyl –CH$_3$
	Multiplet	6.70- 8.50	Aromatic Protons
[Cd(BMHDAB)$_2$]	Singlet 6H	2.50-2.90	Methyl –CH$_3$
	Multiplet	6.80- 8.50	Aromatic Protons
	Singlet 1H	0.30	Methane –CH= group
[Hg(BMHDAB)$_2$]	Multiplet	6.80- 8.50	Aromatic Protons
	Singlet 1H	0.30	Methane –CH= group
	Singlet 3H	2.50-2.90	Methyl –CH$_3$

III. MICROBIOLOGICAL INVESTIGATION

The antibacterial activity of ligand and its Zn(II), Cd(II) and Hg(II) metal complexes were tested against bacteria, we used more than one test organism to increase the chance of detecting antibiotics principles in tested materials. The organism used in the present investigation included three gram positive bacteria *(B. subilis, S. aureus, S. typhi) and* three gram negative bacteria *(E. coli, K. pneumoniae, P. aeruginosa*) bacteria. The results of the bactericidal screening of the synthesized compounds are recorded in **Table-5**. An influence of the central ion of the complexes in the antibacterial activity against the tested gram positive and gram negative organism show that the complexes have an enhanced activity compared to the streptomycin standard.

Table 5: Antibacterial activity data of ligand and its complexes inhibition (in mm)

Compounds	*B. subilis*	*S. aureus*	*S. typhi*	*E. coli*	*K. pneumoniae*	*P. aeruginosa*
Ligand	18	17	17	10	16	11
Zn(II)	28	24	19	11	19	13
Cd(II)	23	21	18	13	17	12
Hg(II)	28	19	22	15	24	10
Streptomycin	30	28	28	25	31	24

IV. 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 and they are Zn(II), Cd(II) and Hg(II) metal complexes are non electrolytic nature. Spectral measurements data suggest that all metal ions are bonded with HBOHPDB ligand through nitrogen atom for M-N$_4$ composition and geometries for metal complexes are of tetrahedral shape. Zn(II), Cd(II) and Hg(II) metal complexes are screened for their biological activities against bacteria species. All synthesized compounds found to be better antibacterial species.

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