



“Synthesis, Characterization and Physico-chemical Studies of Metal Complexes of Schiff Base derived from p-hydroxybenzaldehyde and benzilmonoximehydrazone”

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ABSTRACT

Tridentate Schiff base benzilmonoximehydrazone-p-hydroxybenzaldehyde (HL) derived from benzilmonoximehydrazone and p-hydroxybenzaldehyde and their Mn(II), Pd(II), Cd(II), Cu(II) and Zn(II) complexes have been prepared in 1:2 stoichiometric ratio and characterized on the basis of their solubility, metal analysis, FT(IR), electronic absorption spectra and magnetic measurements. The synthesized complexes have varying shades of color and decomposed at a temperature above 250°C. benzilmonoximehydrazone-p-hydroxybenzaldehyde acts a tridentate ligand coordinating to the metals through the azomethine nitrogen atom, the nitrogen atom of oximino. The electronic spectra are in consistent with the proposed octahedral geometry for Mn(II) and Cu(II) complexes around the metal ions. Successfully done by the biological activity studies on the representative.

Keywords: benzilmonoximehydrazone, p-hydroxybenzaldehyde, Schiff base.

1. INTRODUCTION:

Schiff bases derived hydrazide compound have been used as chelating ligands in the synthesis of diverse transition metal complexes^{1,2}. The Schiff bases derived from the reaction of aldehyde or ketone with amino acid are an excellence class of ligands which have a variety of applications including biological, clinical, industrial, analytical, as well as catalysis and organic synthesis³⁻⁵. hydrazide Schiff base complexes are an area of increasing attention, it has been reported that they possess anticarcinogenic, antimicrobial and antitumor activity⁶⁻⁸. Schiff bases containing benzilmonoximehydrazone and their metal complexes exhibit a variety of interesting properties⁹⁻¹⁰. From Literature antimicrobial activity against gram-positive and gram negative bacteria was reported for Schiff bases containing indole-3-carboxaldehyde and their transition metal (Cu, Ni, Co) complexes^{11,12}. A mononuclear copper(II) complex with a Schiff base derived from 5-bromohydrobenzaldehde and L-tyrosine mimics ascorbate oxidase activity¹³. Catalytic activity was reported for ruthenium(II) complexes with substituted o-hydroxysalicylaldehyde¹⁴. Here, we report a Schiff base formed from the reaction of benzilmonoximehydrazone and p-hydroxybenzaldehyde, their coordination complexes, and their spectral studies.

2. MATERIALS AND METHODS :

Materials and Reagents:

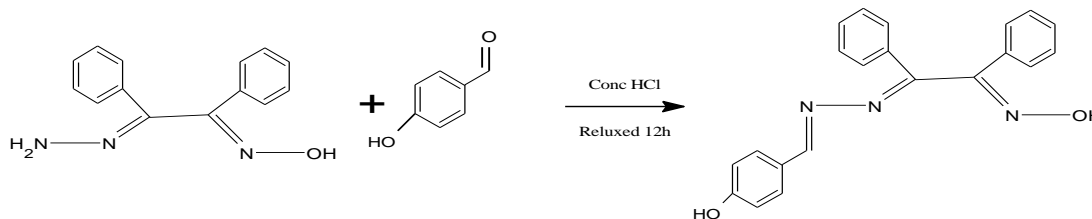
All reagents and solvents were of AR and used without further purification. P-hydroxybenzaldehyde, Copper (II) Chloride dihydrate, Manganese (II) Sulphate tetrahydrate, Palladium(II) chloride, Zinc (II) chloride and Cadmium (II) chloride were obtained from Loba chemie.

Physical measurements:

The electronic spectra of the complexes in chloroform were recorded on a JASCO V-650 Spectrophotometer and infrared spectra were recorded using KBr on a Perkin-Elmer Spectrum-100 spectrophotometer $4000-370\text{ cm}^{-1}$. The room temperature magnetic susceptibilities at 303K were measured on Gouys method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ and $[\text{Ni}(\text{en})_3\text{S}_2\text{O}_3]$ as calibrates and diamagnetic corrections were calculated using Pascal's constant, and melting points were determined with Stuart SMP30 Melting point apparatus. ^1H NMR spectra of ligand was recorded in DMSO-d₆ by using a Bruker AV300 NMR spectrometer using TMS as internal standard. Elemental analysis (C, H, N and O) were carried out with a Carlo Erba EA-1108 analyzer.

Preparation of HBMHpHB Ligand:

0.100M solution of α -benzilmonoximehydrazide (20ml ethanol) was added to 0.115M alcoholic solution of p-hydroxybenzaldehyde, than few drops of concentrated hydrochloric acid added to the reaction mixture, refluxed for 12 hours at 50-60°C, cool and collected precipitated after filtration, after complication reaction process precipitate of ligand is formed out yellow solid and purity checked by TLC.



Scheme-1: Preparation of ligand HBMHpHB

Synthesis of complexes $[ML_2]$, where M= Cu, Cd, Pd, Mn, Zn:

A mixture of the benzilmonoximehydrazone-p-hydroxybenzaldehyde (0.02mol) in 15 ml ethanol and the same amount of the same solvent of metal salt (0.01mol) (MX_2 , where M=Pd(II), Cd(II), Cu(II), Zn(II) and Mn(II) ; X=Cl/SO₄) were refluxed for five hours at 70-80°C on water bath . On cooling, colored solid product was collected by filtration and then washed several times with hot ethanol until the washing becomes colorless. The product was dried in air and stored in desiccators over anhydrous CaCl₂. All the metal complexes are colored and stable to air and moisture.

3. RESULTS AND DISCUSSION:

The condensation of benzilmonoximehydrazone and p-hydroxybenzaldehyde has yielded benzilmonoximehydrazone-p-hydroxybenzaldehyde Schiff base (HL). Complexes obtained from the reaction of benzilmonoximehydrazone-p-hydroxybenzaldehyde Schiff base with metal (II) salt of Mn, Cu, Cd, Pd and Zn are stable at room temperature exhibiting variety of colors with good yields as shown in **Table-1**. The complexes decompose on melting at temperature above 250°C, and are soluble mainly soluble in common organic solvents but insoluble in water. The analytical data are summarized in **Table-1**.

Table-1: Analytical and Physical data of HBMHpHB ligand and its metal complexes.

Compound	Color	% Yield	MP/DP °C	Elemental Content Expected (Found)					Electrical Cond
				C	H	N	O	M	
HBMHpHB	Yellow	76.98	205	73.45 (73.33)	4.99 (4.90)	12.24 (12.21)	9.32 (9.29)	-	-
Pd(BMHpHB) ₂	Green	76.48	266	63.72 (63.70)	4.05 (4.02)	10.62 (10.55)	8.09 (8.09)	13.40 (13.40)	2.98
Mn(BMHpHB) ₂	Brown	78.02	255	68.20 (68.09)	4.33 (4.29)	11.37 (11.31)	8.67 (8.62)	7.42 (7.39)	2.45
Cu(BMHpHB) ₂	Brown	71.44	270	67.38 (67.33)	4.28 (4.21)	11.23 (11.20)	8.56 (8.51)	8.50 (8.40)	1.52
Cd(BMHpHB) ₂	Yellow	79.68	272	61.28 (61.19)	4.02 (3.99)	10.55 (10.53)	8.04 (8.03)	14.06 (13.97)	5.87
Zn(BMHpHB) ₂	Yellow	76.74	262	62.25 (62.24)	4.53 (4.51)	11.20 (11.19)	8.54 (8.51)	8.73 (8.70)	2.69

3.1: FT(IR) Spectra:

FT(IR) spectra studies of synthesized compounds In order to clarify the mode of bonding and the effect of the metal ion on the ligand, the FT(IR) spectra of the benzilmonoximehydrazone-p-hydroxybenzaldehyde, and the metal complexes were studied and assigned based on careful comparison of their spectra. The FT(IR) data is presented in **Table-2**. All the complexes absent broad bands in the range of 3200–3300cm⁻¹, which is reported at 3295cm⁻¹, in the benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand, indicated oximino group deprotonated during coordination¹⁶. A sharp band at 1526cm⁻¹ in free the benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand (HL) is due to azomethine νC=NN- vibration. The shifting of this band to lower frequency (1500-1512cm⁻¹) in the metal complexes suggests the coordination of metal ion through nitrogen atom of azomethine group, as metal atom would reduce the electron density in the azomethine link and thus lower the HC=N absorption¹⁵. The involvement of another nitrogen atom of oximino group in bonding with metal ions was evident from the position as observed band at 1430cm⁻¹ in benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand (HL), but were shifted to lower frequency 1401-1409cm⁻¹ in the metal complexes^{15,17}. The ν(Ph-O) (Phenolic) stretching frequency observed at 3187cm⁻¹ in the ligand benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand (HL), was shifted to a lower frequency region in the Mn(II) and Cu(II) metal complexes in the range of 3135-3136cm⁻¹, this is indicative of bonding through phenolic oxygen¹⁸. In addition, the new bands at about 513-519cm⁻¹ and 489-494cm⁻¹ are assigned to M-N and M→O vibrations, respectively which support the involvement of N and O atoms in complexation with metal ions under investigation¹⁹.

Table-2: FT(IR) spectrum of HBMHpHB ligand and its metal complexes

Compound	-OH (Oxo)	-OH (Phe)	Ar C-H	Ar C=C	>C=NN-	>C=NO-	Phe ring	M-N
HBMHpHB	3295	3187	3070	2976	1526	1430	741	-
Mn(BMHpHB) ₂	-	3135	3070	2977	1505	1409	743	494, 515
Cu(BMHpHB) ₂	-	3136	3070	2978	1506	1407	742	493, 513
Pd(BMHpHB) ₂	-	3182	3072	2979	1512	1401	741	492, 515
Cd(BMHpHB) ₂	-	3178	3076	2980	1507	1409	743	489, 519
Zn(BMHpHB) ₂	-	3181	3073	2980	1500	1403	743	497, 517

Electronic spectra of synthesized compounds:

The electronic spectral absorptions of the ligand and complexes are presented in **Table-3**. The Intra ligand absorptions at 320, 235 and 220nm were assigned to $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectrum of the manganese(II) complex shows very weak absorptions in the visible region at 801, 758 and 608nm and these were assigned to ${}^6A_{1g}(F) \rightarrow {}^4E_g$; ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ which were spin forbidden transitions. The observed magnetic moment for Mn(II) complex was 5.75 B.M which is observed in the expected range (5.7-6.0 B.M) for a high spin Mn(II) complex. On this basis, the Mn(II) complex was suggested to be high spin octahedral geometry.

The electronic spectra of the Cu(II) complexes (**Table-3**) showed low energy bands at 580nm attributed to ${}^2E_g \rightarrow {}^2T_{2g}$ transition²⁴. The low-energy band in this position is expected for an octahedral configuration²⁵ and strong high energy band at 253nm assigned to $\pi \rightarrow \pi^*$ and metal to ligand charge transfer transitions. Also, the magnetic moment values 1.95 BM are indicative of antiferromagnetic spin-spin interaction through molecular association. Hence, the Cu(II) complexes appear to be in the octahedral geometry²⁶. The Pd(II) complex is diamagnetic, therefore the square planar arrangement of the HBMHpHB molecules around Pd(II) is assigned to this complex. The electronic spectrum of this complex shows absorption bands at 325 and 280nm due to the metal-ligand charge transfer transition. The Zn(II) and Cd(II) complexes show high energy band at the region 340-398nm and 265-299nm (**Table-3**) due to ligand to metal charge transfer transition.

Table-3: Electronic absorption spectra of HBMHpHB ligand and its metal complexes.

Compound	λ_{nm}	ϵ (dm ³ /mol/cm)	Assignments
HBMHpHB	320	11875	Phenolic $\pi \rightarrow \pi^*$
	235	8163	Azomethine $\pi \rightarrow \pi^*$
	220	8500	Oximino $\pi \rightarrow \pi^*$
Mn(BMHpHB) ₂	801	91	⁶ A _{1g} (F) \rightarrow ⁴ E _g
	758	514	⁶ A _{1g} \rightarrow ⁴ T _{1g}
	608	958	⁶ A _{1g} \rightarrow ⁴ T _{2g}
Cu(BMHpHB) ₂	580	1526	² E _g \rightarrow ² T _{2g}
	253	10546	$\pi \rightarrow \pi^*$
Pd(BMHpHB) ₂	325	4987	MLCT
	280	7563	MLCT
Cd(BMHpHB) ₂	340	3026	MLCT
	398	2489	MLCT
Zn(BMHpHB) ₂	398	4598	MLCT
	299	6647	MLCT

Study of a biological activity:

Six choice species of bacteria were used in this study *K. pneumonia*, *P. aeruginosa*, *E. coli* gram negative and *S. aureus*, *B. subtilis*, *S. typhi* as a gram positive bacteria²⁷, in nutrient agar medium against HL ligand and their Mn(II), Pd(II), Cu(II), Cd(II) and Zn(II) complexes. DMF used as a solvent and as a control were examined; the compound concentration in this DMF solvent was 25mg/1mL using this sensitivity test. This way of inhibition involves the exposure towards the microorganism's diffusion on agar plate²⁸. Incubated the plates at 37°C for 24h, after incubation recorded the average zone of inhibition. The obtained results are tabulated in **Table-6**.

The Cd(II), Mn(II) and Zn(II) complexes gave a similar zone of inhibition 5mm for all bacterial strains. The Pd(II) and Cu(II) complexes showed more activity against gram positive bacteria than gram negative bacteria.

Table-6: Antibacterial data as zone of inhibition for HBMHpHB ligand and its metal complexes

Compound	Gram (+) bacteria			Gram (+) bacteria		
	<i>S. aureus</i>	<i>B. subtilis</i>	<i>S. typhi</i>	<i>K. pneumonia</i> ,	<i>P. aeruginosa</i>	<i>E. coli</i>
HBMHpHB	5	5	5	5	5	5
Mn(BMHpHB) ₂	5	5	5	5	5	5
Cu(BMHpHB) ₂	4	4	4	3	3	2
Pd(BMHpHB) ₂	4	5	5	2	2	3
Cd(BMHpHB) ₂	5	5	5	5	5	5
Zn(BMHpHB) ₂	5	5	5	5	5	5

CONCLUSION:

The Schiff base benzilmonoximehydrazone-p-hydroxybenzaldehyde has been synthesized from the reaction benzilmonoximehydrazone and p-hydroxybenzaldehyde. The benzilmonoximehydrazone-p-hydroxybenzaldehyde metal(II) ions of Copper, Cadmium, Palladium, Zinc and manganese prepared have characterized by the spectroscopic methods. From the analytical and spectral data the benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand acts as a tridentate ligand and was found to coordinate to the metal ions through the azomethine and oximino nitrogen atom and phenolic oxygen to give an octahedral geometry. The HL ligand and its Mn(II), Pd(II), Cu(II), Cd(II) and Zn(II) complexes act as potent bacterial agents. Further work with analogs is needed.

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