

# Antimicrobial Activity of 2-((2-(hydroxyimino)-1-phenylpropylidene) Hydrazono)-1, 2-diphenylethanone (HMPPH) and its Derivative

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**Abstract:-** A new series of Cu(II), Pt(II) and Pd(II) complexes were prepared with ligand 2-((2-(hydroxyimino)-1-phenylpropylidene) Hydrazono)-1, 2-diphenylethanone (HMPPH) corresponding to molecular formula ( $C_{23}H_{18}N_3O_2$ ) has been synthesized and reported for the first time. The Schiff base and its metal complexes were characterized on the basis of various spectroscopic investigation like IR, NMR, UV-VISIBLE spectroscopy, elemental analysis etc. While the geometry of the complexes was confirmed by electronic spectra, magnetic moment measurements. A preliminary screening of these compounds for biological activity against various microorganisms has indicated that they are microbial active against some microorganisms.

**Keywords:-** Schiff base, Antimicrobial activity, Metal complexes, Ligand.

## I. INTRODUCTION

The title ligand (HMPPH) contains a reactive grouping O=C, -N-OH, which determines the characteristics reactions of isonitrosoketones<sup>1</sup>. Tautomeric oxime compounds are potentially ambient ligands capable of forming metal complexes with different types of structures/ bonding<sup>2</sup>. These compounds find several applications as sensitive and selective reagents in the detection and determination of several metal ions. In addition, many of these compounds possess a wide spectrum of biological activity<sup>3</sup>. The present paper deals with the preparation and characterization of the title ligand, viz. 2-((2-(hydroxyimino)-1-phenylpropylidene) Hydrazono)-1, 2-diphenylethanone (HMPPH) corresponding to molecular formula ( $C_{23}H_{18}N_3O_2$ ). Various physicochemical techniques such as: element analysis, NMR and IR, have been employed to assign the structure of the ligand and its complexes. Their biological activity has been tested to find minimum inhibitory concentrations against various microorganisms.

## II. MATERIAL AND METHOD

All the chemicals used were of AR grade. The solvents were dried and distilled before use according to standard procedure<sup>4</sup>. FT(IR) spectra were recorded in KBr medium on a 'Perkin- Elmer spectrum 100'. The pmr spectra recorded on a 'Bruker AV300 NMR Spectrometer' instrument in  $d_6$  DMSO solvent using TMS as internal standard, The ultra-violet and visible spectra of the ligand and the metal complexes in solutions were taken on a Shimadzu UV-190 spectrophotometer, using quartz and glass cells of 1cm optical path. Methanol or Dimethylformamide (DMF) were used as solvent and blanks. The calibration of the spectrophotometer was checked with a 0.004% solution of potassium chromate in 0.05 M. Potassium hydroxide. The room temperature magnetic susceptibility of all the metal complexes reported in the present work were determined by the Gouy's method using  $Hg[Co(SCN)_4]$  as a calibrant.

**Synthesis of legand:** The synthesis of HMPPH was carried out by treating HINPP and benzilmonohydrazone in stoichiometric ratio in ethanol. The resulting solution was refluxed for 40 minutes the yellow colored solution formed was poured on ice cubes to get yellow puffy product was filtered through Buchner funnel, washed with distilled water, dried at 100°C in an oven and recrystallize from toluene. Completion of reaction was checked by using TLC. Melting point is 138°C yield 86%.

**Synthesis of metal complexes:** An ethanolic solution of title ligand (0.02mol) was mixed with aqueous solution of metals (0.01mol), pH was adjusted to 7.5-8.0 by using 0.1N NaOH, colored precipitated was separate out. Filtered and washed with hot distilled water and recrystallized from chloroform.

## III. RESULT AND DISCUSSION

The analytical data along with some physical properties of the ligand and its various metal complexes are summarized in Table 1. The ligand on interaction with Cu(II), Pt(II) and Pd(II) chlorides, yields complexes corresponding to the general formula  $ML_2$ . The analytical data show that the metal to ligand ratio is 1:2. They are insoluble in water, soluble in common organic solvents. The low molecular conductance value of the complexes reveals their non-electrolytic nature<sup>5</sup>. High melting points of all metal complexes suggests strong metal-ligand bond.

Compound	Color	Yield %	M.W	Melting point / Dec.point° C	Elemental Analysis					Magnetic Moments $\mu$ B.M.	Electrical Cond. $10^{-3} M(\text{in DMF})$ Mhos
					% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)		
HMPPH	Pale yellow	86.0	369.41	138	-----	74.78 (74.84)	5.18 (5.22)	11.37 (11.41)	8.66 (8.71)	----	----
Cu(MPPH) <sub>2</sub>	Brown	84.71	803.36	200	7.94 (7.96)	68.70 (68.74)	4.89 (4.92)	10.46 (10.49)	7.97 (8.01)	1.92	0.0804
Pd(MPPH) <sub>2</sub>	Red	83.67	846.23	178	12.58 (12.61)	65.29 (65.33)	4.65 (4.69)	9.93 (9.97)	7.59 (7.61)	diamagnetic	0.4603
Pt(MPPH) <sub>2</sub>	Brown	78.49	934.89	184	20.84 (20.87)	59.53 (59.57)	4.20 (4.23)	8.99 (9.02)	6.84 (6.87)	diamagnetic	0.7650

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

➤ *FT(IR) Spectra :*

An attempt has been made to assign some of the important bands on the basis of the reported infrared spectra of several Isonitrosoketones<sup>6-8</sup> in general and isonitrosopropiophenone<sup>6-8</sup> in particular along with the spectra of thiosemicarbazide<sup>9</sup> and related compounds. The spectrum shows a broad band at 3406cm<sup>-1</sup> due the presence -OH groups (oximino) in the ligand. Assignment of this band was based on comparisons with other Isonitrosoketones and their hydrozonyl derivatives<sup>6-9</sup>. The band at 1670 cm<sup>-1</sup> may be chiefly due to the perturbed >C=N- stretching vibrations of the azomethine (>C=N-N=) group in HMPPH and 1574 cm<sup>-1</sup> is due to the aromatic >C=C< vibrations. The band observed at 979 cm<sup>-1</sup> may be assigned to =N-N= stretching vibrations. The broad peak observed at 3292 cm<sup>-1</sup> (Table IV) in the IR spectrum of the ligand assigned to oximino (-OH), which is found to have disappeared in all the complexes. This reveals the involvement of oximino group in coordination. Appearance of two new bands in all complexes at ~1340 cm<sup>-1</sup> and ~1540 cm<sup>-1</sup> corresponds to presence of N → O group which indicate oximino group coordinate through nitrogen and not through oxygen<sup>2</sup>. Appearance of new band in the region 480-490 cm<sup>-1</sup> in Cu, Pt and Pd complexes corresponding to M-O bond. The coordination of oximino and azomethine nitrogen is confirmed by the disappearance of a band 1670 cm<sup>-1</sup> (>C=NOH) and shifting of the band 1590 cm<sup>-1</sup> (-C=N-) towards lower frequencies in all the complexes<sup>10</sup>, which is assigned to azomethine nitrogen in the ligand.

Tentative assignments	Ligand	Cu(II) complex	Pd(II) complex	Pt(II) complex
$\nu$ OH	3292	-----	-----	-----
$\nu$ N=C	1638	1615	1610	1618
$\nu$ N=C (Oximino)	1540	1520	1530	1520
$\nu$ C=O	1620	1590	1590	1595
$\nu$ N-O	1023	1014	994	1006
$\nu$ N→O	---	1335,1536	1329,1541	1331,1540
$\nu$ M-N	---	550	555	540
$\nu$ M-O	---	---	---	---
$\nu$ C=C Ar.	3050	3054	3050	3055

Table 2:- IR spectral bands of the ligand (HMPPH) and its metal complexes (cm<sup>-1</sup>)

➤ *<sup>1</sup>H NMR spectra:*

The <sup>1</sup>Hnmr spectrum of HHBHPPPO were recorded in deuteriated DMSO. Many isonitrosoketones<sup>11,12</sup> including isonitrosopropiophenone (HINPP) reveal the oximino proton (=N-OH) in the region 8δ to 12δ. In HMPPH the singlet at 11.8 δ may be assigned to oximino proton. The singlet at 2.3δ assigned to the methyl group in HMPPH. The pmr spectrum of the thiocarbohydraide of isonitrosopropiophenone<sup>13</sup> a broad singlet around δ12.4ppm is ascribed to the oximino proton. A multiplet in the range of 7.26 δ – 7.98 δ may be assigned to phenyl ring.

Compound	multiplicity	δ ppm	Assignment
	Singlet 1H	11.80	Oximino >C=N-OH group
HMPPH	Singlet 3H	2.10	Methyl -CH <sub>3</sub>
	Multiplet	7.10 - 8.10	Aromatic Protons
[Pd(MPPH) <sub>2</sub> ]	Singlet 3H	2.40	Methyl -CH <sub>3</sub>
	Multiplet	7.20 - 7.80	Aromatic Protons
[Pt(MPPH) <sub>2</sub> ]	Singlet 3H	2.40	Methyl -CH <sub>3</sub>
	Multiplet	7.20 - 7.80	Aromatic Protons

Table 3:- PMR spectrum of HMPPH and its metal complexes in D<sub>6</sub> DMSO

➤ *Magnetic Moment:*

Magnetic moments for Cu(II) complexes may occur due to antiferromagnetic coupling which may arise due to possible copper-copper interactions through oxo group. The observed diamagnetism, as shown by the room temperature magnetic moments of the Pd(II), Pt(II) complexes shows that these complexes are diamagnetic in nature suggesting tetrahedral geometry.

➤ *Electronic Absorption Spectra:*

For square planar Cu(II) complexes, the expected transitions are  $2_{A_{1g}} \leftarrow 2_{B_{1g}}$  and  $2_{E_g} \leftarrow 2_{B_{1g}}$  with the respective absorption bands<sup>13</sup>. In general, due to Jahn-Teller distortion, square planar Cu(II) complexes give a broad absorption band between 600 nm (16.666kK) and 700 nm (14.286kK). The electronic spectrum of [Cu(MPPH)<sub>2</sub>] (Figure X) exhibit a broad band centered at 660 nm

15.156kK,  $\epsilon=32.71\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$  indicating square planar geometry. A common feature of the electronic absorption spectrum in chloroform solution for palladium, and platinum complexes (Figures XI and XXII) is the absence of any appreciable absorption beyond 14.000kK. This is typical of square planar Pd(II) and Pt(II) complexes. Gray and Ballhausen<sup>15</sup> have reported an analysis of the electronic absorption pattern of square planar  $d^8$  complexes, such complexes are expected to show at least three closely spaced  $d-d$  transition weak bands. However, due to the proximity of this absorption to the high intensity charge transfer transitions, the former are masked. The high intensity transitions observed at 25.64kK ( $\epsilon=4125.413\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ), 31.25kK ( $\epsilon=16831.68\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ ) in Pd(MPPH)<sub>2</sub> are suggested to be charge transfer transitions

No.	Compound	Solvent	Band position in kk	Intensity $\epsilon$	Assignment
1	HMPPH	Methanol	2.7777	29733.33	$\pi - \pi^*$ transition
			3.5714	38978.79	$\pi - \pi^*$ transition
		0.1N NaOH	2.5600	25535.35	$\pi - \pi^*$ transition
			3.5087	29967.96	$\pi - \pi^*$ transition
2	Cu(MPPH) <sub>2</sub>	Chloroform	15.156	32.71	d-d transition
3	Pd(MPPH) <sub>2</sub>	Chloroform	25.64	4125.41	Charge transfer M→L transition
			31.25	16831.68	Charge transfer M→L transition
4	Pt(MPPH) <sub>2</sub>	Chloroform	26.31	4782.47	Charge transfer M→L transition
	32.25		18976.90	Charge transfer M→L transition	
	Cu(MPPH) <sub>2</sub>	Chloroform	15.156	32.71	d-d transition

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

➤ *Antimicrobial activity :*

2-((2-(hydroxyimino)-1-phenylpropylidene) Hydrazono)-1, 2-diphenylethanone (HMPPH) and its metal complexes with Cu (II), Pd (II) and Pt (II) complexes with HMPPH were screened for their antibacterial activity *in vitro* using standard methods given by Sooner and Sykes<sup>16</sup>.

Results of the agar ditch method for the antibacterial activity of HMPPH and its metal complexes (1000 ppm solution in DMF)

Compound	Test Microorganisms (zone of inhibition in mm)				
	<i>E.coli</i>	<i>S.aureus</i>	<i>Bacillus subtilis</i>	<i>V.cholarae</i>	<i>Yeast</i>
HMPPH	Nil	06	Nil	Nil	Nil
Cu(MPPH) <sub>2</sub>	Nil	16	14	16	16
Pd(MPPH) <sub>2</sub>	10	20	16	16	18
Pt(MPPH) <sub>2</sub>	Nil	18	20	18	16

Table 5

MIC data for Pd(MPPH)<sub>2</sub> and Pt(MPPH)<sub>2</sub> (in DMF)

Concentration in ppm	Zone of inhibition in mm			
	Pd(MPPH) <sub>2</sub>		Pt(MPPH) <sub>2</sub>	
	<i>S.aureus</i>	<i>Bacillus subtilis</i>	<i>S.aureus</i>	<i>Bacillus subtilis</i>
300	11	10	12	10
250	10	10	10	8.0
200	8.0	9.0	9.0	7.0
150	7.0	7.0	7.0	6.5
100	6.5	6.0	6.0	5.0
90	6.0	5.0	-	-
80	5.0	-	-	-
70	-	-	-	-
60	-	-	-	-

Table 6

#### IV. CONCLUSION

The appreciable antimicrobial activity shown by the metal complexes of HMPPH is significant in the absence of activity shown by the ligand, and holds forth a promise of fruitful further studies on these complexes. Amongst the HMPPH complexes, Pd(MPPH)<sub>2</sub> and Pt(MPPH)<sub>2</sub> showed maximum antimicrobial activity as is seen from Table E-II. Hence, these complexes were further investigated to obtain the Minimum Inhibitory Concentration (MIC). The results

show that the complexes have measurable activity at about 300 ppm while below 70 ppm, no antimicrobial activity was discernible. The MIC for Pd(MPPH)<sub>2</sub> was 80 ppm while it was 90 ppm for the Pt(MPPH)<sub>2</sub>. All complexes are non-electrolyte, high thermal stability and strong metal-ligand bond. On the basis of spectral and magnetic moment analysis, square planar geometry for Cu(II) Pd(II) and Pt(II). The proposed structure of metal complexes of HMPPH follows;

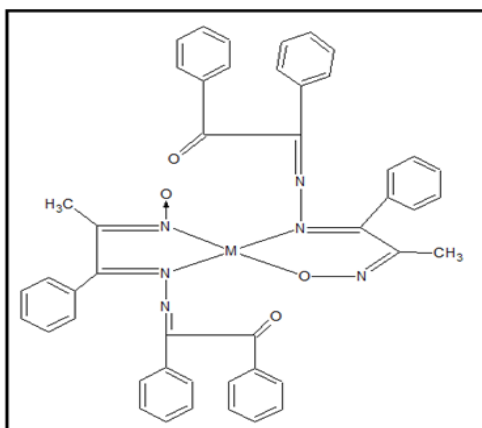


Fig 1:- Proposed structure of Cu(II),Pd(II) and Pt(II) complexes of HMPPH

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