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Synthesis and 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 Fe(II), Co(II) and Ni(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 [1]. Tautomeric oxime compounds are potentially ambient ligands capable of forming metal complexes with different types of structures/ bonding [2]. 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[3]. 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[4]. FT(IR) spectra were recorded in KBr medium on a 'Perkin- Elmer spectrum 100'. The pmr spectra recorded on a 'Brucker AV300 NMR Spectrometer' instrument in d6 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.

1) *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 100^0C in an oven and recrystallize from toluene. Completion of reaction was checked by using TLC. Melting point is 138^0C yield 86%.
2) *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 Fe(II), Co(II) and Ni(II) chlorides, yields complexes corresponding to the general formula ML2. 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[5]. High melting points of all metal complexes suggests strong metal-ligand bond.

Table (I): Analytical and physical data of the ligand and its metal complexes.

Compound	Color	Yield %	M.W	Melting point / Dec.point °C	Elemental Analysis					Magnetic Moments μ B.M.	Electrical Cond. 10^{-3} M(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)	----	----
Fe(MPPH)$_2$	Blue	80.23	792.60	194	7.05 (7.10)	69.70 (69.74)	4.58 (4.63)	10.60 (10.63)	8.07 (8.09)	5.32	0.4856
Co(MPPH)$_2$	Brown	88.25	795.74	176	7.41 (7.43)	69.43 (69.45)	4.56 (4.59)	10.56 (10.59)	8.04 (8.09)	4.93	0.0748
Ni(MPPH)$_2$	Red-Brown	96.22	795.50	180	7.39 (7.41)	69.45 (49.44)	4.56 (3.35)	10.56 (10.80)	8.05 (20.60)	3.14	0.01417

A. *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[6-8] in general and isonitrosopropiophenone[6-8] in particular along with the spectra of thiosemicarbazide[9] and related compounds. The spectrum shows a broad band at 3406cm^{-1} due the presence –OH groups (oximino) in the ligand. Assignment of this band was based on comparisons with other Isonitrosoketones and their hydrozonyl derivatives[6-9]. The band at 1670 cm^{-1} may be chiefly due to the perturbed >C=N- stretching vibrations of the azomethine (>C=N-N=) group in HMPPH and 1574 cm^{-1}is due to the aromatic >C=C< vibrations. The band observed at 979 cm^{-1} may be assigned to =N-N= stretching vibrations. The broad peak observed at 3292 cm^{-1} (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^{-1} and ~1540 cm^{-1} corresponds to presence of $N \rightarrow O$ group which indicate oximino group coordinate through nitrogen and not through oxygen[2]. Appearance of new band in the region 480-490 cm^{-1} in Fe, Co and Ni complexes corresponding to M-O bond. The coordination of oximino and azomethine nitrogen is confirmed by the disappearance of a band 1670 cm^{-1} (>C=NOH) and shifting of the band 1590 cm^{-1} (-C=N-) towards lower frequencies in all the complexes[10], which is assigned to azomethine nitrogen in the ligand.

Table (II): IR spectral bands of the ligand (HMPPH) and its metal complexes (cm^{-1}):

Tentative assignments	Ligand	Fe(II) complex	Co(II) complex	Ni(II) complex
νOH	3292	------	------	------
νN=C	1638	1620	1618	1615
νN=C (Oximino)	1540	1526	1520	1523
νC=O	1620	1588	1590	1580
νN-O	1023	1010	1014	1010
νN→O	---	1340,1535	1344,1539	1319,1530
νM-N	---	540	550	551
νM-O	---	480	489	490
νC=C Ar.	3050	3051	3057	3055

B. 1H NMR Spectra

The ^{1}Hnmr spectrum of HHBHPPO were recorded in deuteriated DMSO. Many isonitrosoketones[11,12] 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 thiocarbohydrazide of isonitrosopropiophenone[13] 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.

Table (III): PMR spectrum of HMPPH and its metal complexes in D_6 DMSO

Compound	multiplicity	δ ppm	Assignment
HMPPH	Singlet 1H	11.80	Oximino >C=N–OH group
	Singlet 3H	2.10	Methyl $–CH_3$
	Multiplet	7.10 - 8.10	Aromatic Protons

C. Magnetic Moment

The blue colored Fe(II) reveals magnetic moments at 5.32 B.M at room temperature possibly showing high spin octahedral geometry of this complex. The brown colored, $Co(MPPH)_2$, complex shows room temperature magnetic moments of 4.93B.M. Octahedral cobalt (II) complexes normally exhibit magnetic moments in the range of 4.7–5.2 B.M. The magnetic moment observed for $Ni(MPPH)_2$ complex lies in the range of 2.8–3.5B.M., showing room temperature magnetic moment of 3.14B.M. which is consistent with the octahedral geometry of the complex.

D. Electronic Absorption Spectra

The electronic absorption spectrum of the ink blue $Fe(MPPH)_2$ in chloroform solution shows a symmetrical broad band around 15.625kK (€=22777.82dm^3/mol/cm), along with a small band at around 19.2307kK (€=22275.78dm^3/mol/cm). The spectrum also shows a high intensity band at 23.3901kK (€=30370.37dm^3/mol/cm). The position of the last band along with the high intensity shown, suggests that it originating from a charge transfer phenomenon. While, the earlier two bands could be said to originate from the intra metal transitions.

For Fe(II) high spin case, the ground state (^{5}D) is supported to split into ^{5}Eg and $^5T_2$g states. As such are *d-d* transition corresponding to

$^5T_2$g $\longrightarrow$ ^{5}Eg may be expected. However, the ^{5}Eg state is expected to further split into $^5B_1$g and $^5A_1$g owing perhaps, to Jahn-Teller distortion. As such Fe (II) high spin octahedral complexes could show two, fairly closely spectral bands. The bands observed at 15.625kK and 19.2307kK are therefore assignable to *d-d* transitions.

The electronic spectrum of the Co(II) complex shows bands at 17.2413kK (Ɛ= 93.48093dm^{3}mol^{-1}cm^{-1}) and 20.8333kK(Ɛ= 512.315dm^{3}mol^{-1}cm^{-1}).These two bands are assignable to $4_{A_{2g}} \leftarrow 4_{T_{1g}}(F)$ (v_2) and $4_{T_{1g}}(P) \leftarrow 4_{T_{1g}}(F)$ (v_3) transitions respectively. The lowest band $4_{T_{2g}} \leftarrow 4_{T_{1g}}(F)$ (v_1) could not be observed due to the limited range of the instrument used but could be calculated using the band fitting procedure $v_1 = v_2 - 10Dq$ suggested by Underhill and Billing[12] and is 8.1010kK. The value of v_2/v_1 =2.1283 lies in the range 2.1–2.2, reported for most of the octahedral Co(II) compounds[13]. The spectral parameters for $[Co(MPPH)_2]$ are Dq = 0.919kK, B' = 0.9300kK, B′/B= β=0.9578 and β% = 5%. Reduction of Racah parameter from 0.971 kK (free ion value) to 0.9300kK and the β% value 5% indicate the covalent nature of the compound. $[Ni(MPPH)_2]$ shows three bands at 9.6153kK(Ɛ=56.29 dm^{3}mol^{-1}cm^{-1}), 15.625kK (Ɛ=77.7777dm^{3}mol^{-1}cm^{-1}) and 20.40kK(Ɛ=424.375dm^{3}mol^{-1}cm^{-1}) due to $3_{T_{2g}} \leftarrow 3_{A_{2g}}$ (v_1), $3_{T_{1g}} \leftarrow 3_{A_{2g}}$ (v_2) and $3_{T_{1g}}(P) \leftarrow 3_{A_{2g}}$ (v_3) transitions, respectively, in an octahedral symmetry. The value of v_2/v_1 is 1.62 which lies in the usual range (1.60–1.82), reported for the majority of octahedral Ni(II) compounds[14,15]. The spectral parameters for $[Ni(MPPH)_2]$ are 10Dq = 9.610kK, B' = 0.858kK, (B′/B)=β=0.83 and β% = 17% .Reduction of Racah parameter from 0.1030kK (free ion value) to 0.858kK and the β% value 17% indicate the covalent nature of the compound.

Table (IV): Electronic spectral data for HMPPH and its metal complexes

No.	Compound	Solvent	Band position in kk	Intensity ∈	Assignment
1	HMPPH	Methanol	2.7777	29733.33	π - π* transition
			3.5714	38978.79	π - π* transition
		0.1N NaOH	2.5600	25535.35	π - π* transition
			3.5087	29967.96	π - π* transition
2	Fe(MPPH)$_2$	Chloroform	15.625	22777.82	${}^5T_{2g} \longrightarrow {}^5Eg$
			27.02703	35274.88	Intra ligand transition
3	Co(MPPH)$_2$	Chloroform	17.2413	93.48093	$4_{A_{2g}} \leftarrow 4_{T_{1g}}(F)\ (v_2)$
			20.8333	512.315	$4_{T_{1g}}(P) \leftarrow 4_{T_{1g}}(F)\ (v_3)$
4	Ni(MPPH)$_2$.	Chloroform	9.6153	56.29	$3_{T_{2g}} \leftarrow 3_{A_{2g}}\ (v_1)$
			15.625	77.7777	$3_{T_{1g}} \leftarrow 3_{A_{2g}}\ (v_2)$
			20.40	424.3758	$3_{T_{1g}}(P) \leftarrow 3_{A_{2g}}\ (v_3)$

E. Antimicrobial Activity

2-((2-(hydroxyimino)-1-phenylpropylidene) Hydrazono)-1, 2-diphenylethanone (HMPPH) and its metal complexes with Fe (II), Co (II) and Ni (II) complexes with HMPPH were screened for their antibacterial activity in *vitro* using standard methods given by Sooner and Sykes[16].

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

Table E 1

Compound	Test Microorganisms (zone of inhibition in mm)				
	E.coli	S.aureus	Bacillus subtilis	V.cholarae	Yeast
HMPPH	Nil	06	Nil	Nil	Nil
Fe(MPPH)$_2$	12	14	10	14	12
Co(MPPH)$_2$	Nil	16	12	14	14
Ni(MPPH)$_2$	Nil	20	18	16	18

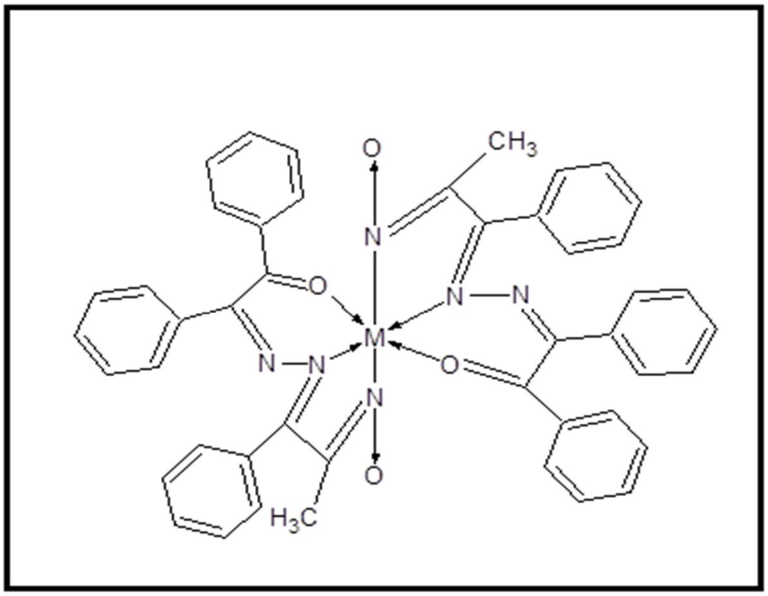
MIC data for Ni(MPPH)$_2$ (in DMF)

Table E 2

Concentration in ppm	Zone of inhibition in mm	
	Ni(MPPH)$_2$	
	S.aureus	Bacillus subtilis
300	12	10
250	12	9.0
200	10	7.0
150	8.0	6.5
100	7.0	5.5
90	6.5	5.0
80	6.0	5.0
70	5.0	-
60	-	-

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. The HMPPH complex, Ni(MPPH) showed maximum antimicrobial activity as is seen from Table E-2. Hence, that complex was further investigated to obtain the Minimum Inhibitory Concentration (MIC). The results show that the complex have measurable activity at about 300 ppm while below 70 ppm, no antimicrobial activity was discernible. The MIC for $Ni(MPPH)_2$ was 70 ppm. All complexes are non-electrolyte, high thermal stability and strong metal-ligand bond. On the basis of spectral and magnetic moment analysis, Fe(II) Co(II) and Ni(II) complexes are high spin octahedral geometry. The proposed structure of metal complexes of HMPPH fallows;



Proposed structure of Fe(II),Co(II) and Ni(II) complexes of HMPPH

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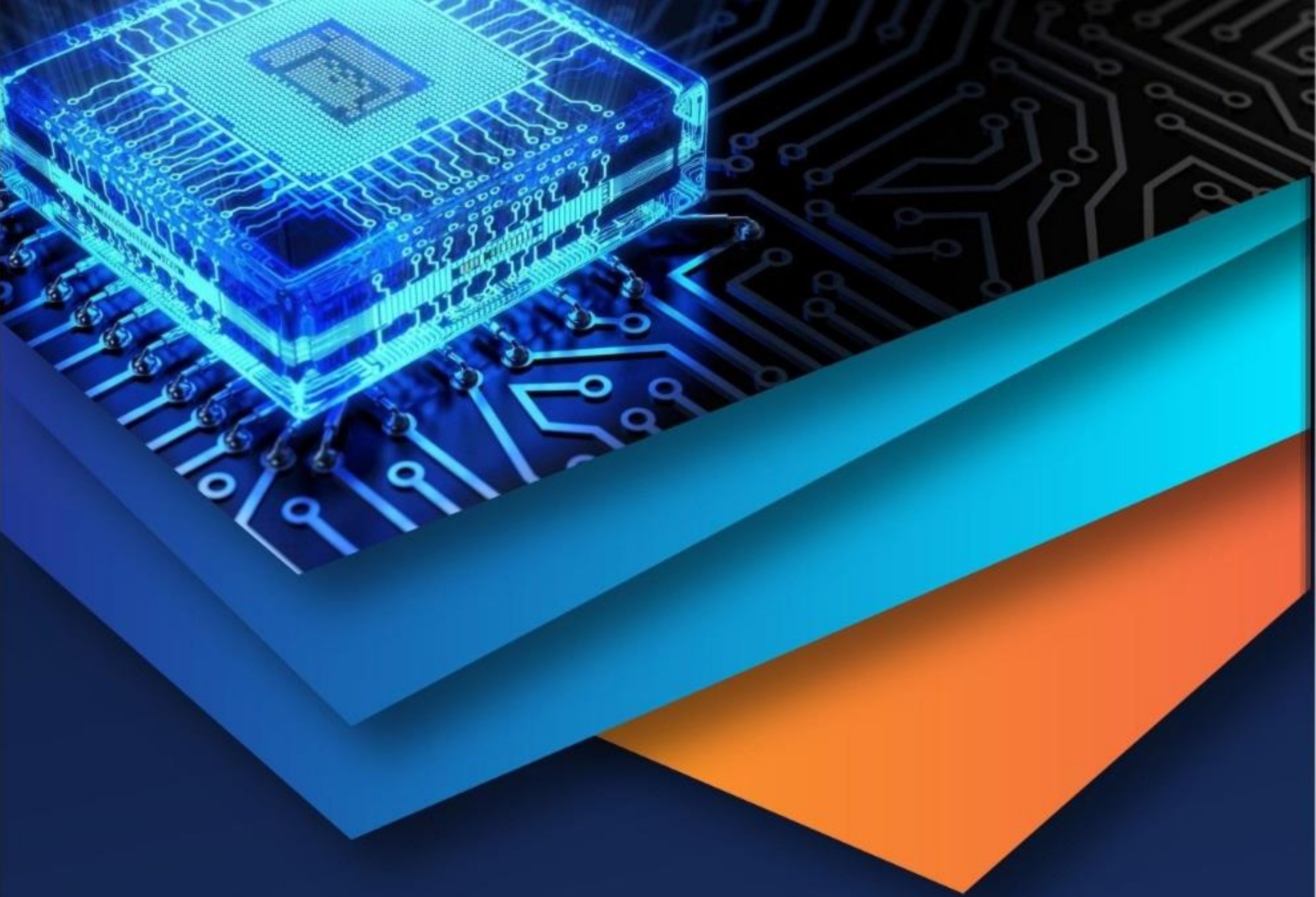

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