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Research Article

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Biological Application of Schiff base Benzil Monohydrozone and its Metal complexes

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Abstract

Due to hydrazones anti-bacterial, anti-fungal, anti-cancer, anti-depression and anti-viral properties, hydrazone become active substance in pesticides discovery. Hydrazone used in stable complexes in coordination chemistry, and its metal complexes used in various formulations in pharmaceuticals. The metallic hydrazone compounds act as catalyst used in various organic complex reactions. Due to its numerous medicinal properties hydrazone become highlighted in last decades. The present review made attention towards the new drug delivery development process, it's aromaticity in organic chemistry, pharmaceutical formulations and molecular biology in relation to hydrazone and its metal complexes.

Keywords: Hydrazones, Coordination chemistry, Biological activity, Metal complexes, Schiff Base

Introduction

The title ligand (HMPPH) contains a reactive grouping O=C, -N-OH , which determines the characteristics reactions of isonitrosoketones[1]. Tautomericoxime 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.

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 AV300NMRSpectrometer' 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.

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%.

Synthesis of metal complexes: An ethanolic solution of title ligand (0.02mol) was mixed with aqueous solutionof 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.

Results 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), Pd(II), Zn(II), Cd(II) and Hg(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.

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 in general and isonitrosopropiophenone[6] in particular along with the spectra of thiosemicarbazide[6-9] 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 Cu, Pt ,Pd, Zn, Cd and Hg 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 1:-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 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)	----	----
Cu(MPPH)2	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)2	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)2	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
Zn(MPPH)2	Yellow	76.44	818.25	180	7.99 (8.12)	68.99 (69.10)	4.93 (4.98)	10.27 (10.34)	7.82 (7.88)	diamagnetic	0.8430
Cd(MPPH)2	Yellow	82.44	849.30	186	13.24 (13.28)	66.48 (66.50)	4.74 (4.76)	9.90 (9.94)	5.56 (5.60)	diamagnetic	0.7485
Hg(MPPH)2	Pale brown	74.88	953.45	176	21.75 (21.80)	59.96 (60.14)	3.98 (4.10)	9.12 (9.20)	5.40 (5.44)	diamagnetic	0.6645

Table 2:- Tentative assignments of Ligand

Tentative assignments	Ligand	Cu(II) complex	Pd(II)complex	Pt(II)complex	Zn(II) complex	Cd(II) complex	Hg(II) complex
νOH	3292	------	------	------	------	------	-----
νN=C	1638	1615	1610	1618	1612	1640	1610
νN=C (Oximino)	1540	1520	1530	1520	1530	1550	1528
νC=O	1620	1590	1590	1595	1580	1598	1580
νN-O	1023	1014	994	1006	1018	1000	1030
νN→O	---	1335,1536	1329,1541	1331,1540	1330,1530	1320,1538	1330,1540
νM-N	---	550	555	540	550	560	520
νM-O	---	---	---	---	---	---	---
νC=CAr.	3050	3054	3050	3055	3070	3060	3050

1HNMR 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 3:-PMR spectrum of HMPPH and its metal complexes in D_6DMSO

Compound	**Multiplicity**	**δppm**	**Assignment**
	Singlet 1H	11.80	Oximino>C=N–OH group
HMPPH	Singlet 3H	2.10	Methyl–CH_3
	Multiplet	7.10-8.10	Aromatic Protons
[Pd(MPPH)$_2$]	Singlet 3H	2.40	Methyl–CH_3
	Multiplet	7.20-7.80	Aromatic Protons
[Pt(MPPH)$_2$]	Singlet 3H	2.40	Methyl–CH_3
	Multiplet	7.20-7.80	Aromatic Protons

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[14,15].The observed diamagnetism, as shown by the room temperature magnetic moments of the Pd(II), Pt(II),Zn(II), Cd(II) and Hg(II) complexes shows that these complexes are diamagnetic in nature suggesting tetrahedral geometry.

Antimicrobial activity:

2-((2-(hydroxyimino)-1-phenylpropylidene) Hydrazono)-1, 2-diphenylethanone (HMPPH) and its metal complexes with Cu (II), Pd (II), Pt (II), Zn(II), Cd(II) and Hg(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 4 :- Antimicrobial activity

Compound	Test Microorganisms (zone of inhibition in mm)				
	E.coli	*S.aureus*	*Bacillus subtilis*	*V.cholarae*	*Yeast*
HMPPH	Nil	06	Nil	Nil	Nil
$Cu(MPPH)_2$	Nil	16	14	16	16
$Pd(MPPH)_2$	10	20	16	16	18
$Pt(MPPH)_2$	Nil	18	20	18	16
$Zn(MPPH)_2$	08	10	12	14	16
$Cd(MPPH)_2$	Nil	12	14	12	14
$Hg(MPPH)_2$	Nil	12	10	14	14

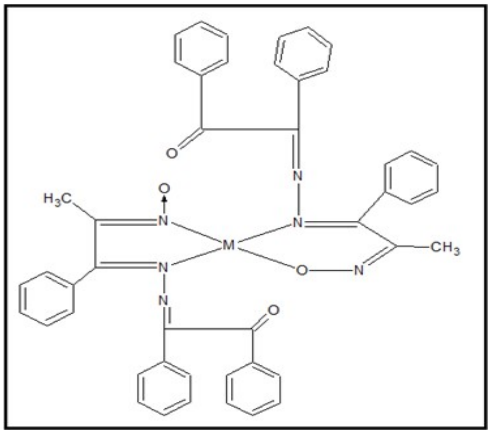
MIC data for Pd(MPPH)2 and Pt(MPPH)2 (in DMF)

Table 5 :- MIC data for Pd(MPPH)2 and Pt(MPPH)2 (in DMF)

Concentration in ppm	Zone of inhibition in mm			
	$Pd(MPPH)_2$		$Pt(MPPH)_2$	
	S.aureus	*Bacillus subtilis*	*S.aureus*	*Bacillus subtilis*
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	-	-	-	-

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, $Pd(MPPH)_2$ and $Pt(MPPH)_2$ 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 activitywas discernible. The MIC for $Pd(MPPH)_2$ was 80 ppm while it was 90 ppm for the Pt(MPPH)2. All complexes are non-electrolyte, high thermal stability and strong metal- ligand bond



Proposed structure of Cu(II), Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II) complexes of HMPPH

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