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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND THERMAL STUDIES OF SOME TRANSITION METAL COMPLEXES OF NOVEL SCHIFF BASE LIGAND

R. K. PAWAR, M. A. SAKHARE and B. R. ARBAD*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University,
AURANGABAD – 431004 (M.S.) INDIA

ABSTRACT

The condensation of 4-chloro-2-amino phenol with 3-acetyl-6-methyl-(2H)pyran,2,4(3H)-dione (dehydroaetic acid (DHA) yielded 3-((E)-1-(5-chloro-2-hydroxyphenylimino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one. It's Pd(II) and Ir(III) complexes were synthesized by stoichiometric ratio of combination. The ligand and their metal complexes were further characterized by elemental analysis, ^{1}H NMR spectrum, mass analysis, conductivity measurement, UV/Visible and infrared spectroscopic studies. The ligand and it's metal complexes were screened *in vitro* for antibacterial activity against *Escherichia coli, salmonellatyphi* and *staphylococcus aureus* and for antifungal activity against *aspergillusflavus* and *candida albicans*.

Key words: 4-Chloro2-aminophenol, Schiff base ligand, Transition metal complexes, Antimicrobial activity.

INTRODUCTION

Novel Schiff base ligand with N_2O_2 donor atoms are well known to co-ordinate with various metal ions and have attracted a great deal of interest in recent years due to their rich co-ordination chemistry.[1] Schiff bases derived from dehydrocetic acid, diamines, amino phenols and amino alcohols are reported to have wide variety of applications including clinical[2],biological and analytical fields[3].

Many Schiff base ligands due to their great flexibility in structure have major contribution and their limited scope in earlier studies have enlarged to manifold[4]. Due to chelating nature of the azomethine nitrogen atom of Schiff bases, these are well recognized as antibacterial, antifungal, antitumor, antituberculosis, anticancer, DNA binding and cleavaging agents.[5] Because of excellent complexation ability with different metal ions

*Author for correspondence; E-mail: abr_chem@yahoo.co.in; Ph.: +91 0240 2403311;
Fax: +91 0240 2403335

Schiff base ligands have been employed intensively in analytical chemistry. Transition metals are most suitable candidates for the synthesis of cancer combating nonradioactive tools for chemotherapy and diagnosis. Co-ordination chemistry of transition metal complexes has become of increasing significance in the last few years due to their wide variety of applications in supramolecular photochemistry and in medicine.[6] One of the oxygen heterocyclic 3-acetyl-6-methyl-2H-pyran 2,4(3H)-dione (DHA) was reported to be an excellent chelating agent and it is also aversatile starting material for the synthesis of wide variety of heterocyclic ring systems[7]. In view of the above mentioned facts and our continued interest in the synthesis of novel Schiff bases based on DHA and their metal complexes, we report in this paper the synthesis and characterization of Pd(II)and Ir(III) complexes.

EXPERIMENTAL

Dehydroacetic acid purchased from sigma Aldrich was used as supplied. 4-chloro2-aminophenol of AR grade was used for the synthesis of ligand. AR grade metal chlorides were used for the complex preparation. The carbon, hydrogen and nitrogen contents were determined on perkin Elmer (2400) CHN analyzer. FTIR spectra were recorded on Jasco FTIR 4100 spectrometer using KBr pallets. ^{1}H NMR spectrum of ligand was measured in DMSO using TMS as internal standard. The TG/DTA were recorded on SDT Q600 V20.9 build 20. The UV-Visible spectra of complexes were recorded on JASCO UV-530 spectrometer. Magnetic susceptibility measurements of the metal complexes were determined on Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-3} m solution in DMF.

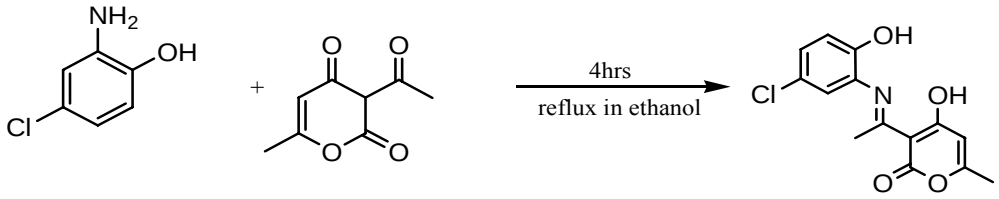
Synthesis of 3-(E)-1-(5-chloro-2-hydroxyphenylimino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one(LD)

The ligand was prepared by a reported method, a typical procedure for the synthesis of Schiff base is as follows. A 50 mL solution of 0.0029 mmol (0.5 g) of dehydroacetic acid, 0.0029 mmol (0.487 g) of 4-chloro 2-aminophenol in absolute ethanol were refluxed for about 4 h. The white precipitate thus formed was cooled to room temperature and collected by filtration, followed by recrystallization in ethanol[8-10] (yield 70 %) (**Scheme 1**).

Syntheses of Pd (II) and Ir(III) metal complexes of Ligand (LD)

To a hot methanolic solution (25 mL) ligand (0.0006 mol) of and methanolic solution (25 mL) of metal chloride (0.0003 mol) was added under constant stirring. The pH of reaction mixture was adjusted to (2-7) by adding 10% methanolic ammonia solution and refluxed for about 10-12 h. The precipited solid metal complex was filtered off in hot

condition and washed with hot methanol, petroleum ether and dried over calcium chloride in vacuum desiccator[8-10] (Yield 55%).



Scheme 1: Synthesis of ligand

Antimicrobial activity

The antimicrobial activity of ligand and metal complexes were tested in vitro against bacteria such as *staphylococcus aureus, Escherchia coli* and *salmonella typhi* by agar diffusion method[11-12]. Then compounds were tested at the concentrations at 250 ppm & 500 ppm in DMF and compared with known standaed viz. Gentamycin[13] (Table 1). For fungicidal activity compounds were screened *in vitro* against *aspergillusflavus* and *candida albicans* by agar diffusion method and compared with standard amphotericin B.

RESULTS AND DISCUSSION

Physical characterization, micro analytical, molar conductance data of ligand and metal complexes are given in Table 1. The analytical data of complexes reveals 1:2 molar ratio (metal : ligand). The magnetic susceptibilities of Pd(II) and Ir(III)complexes at room temperature are consistent with octahedral geometry for Ir(III) and square planner geometry for Pd(II) complexes. The metal chelate solutions in DMF show low conductance and these supports their non-electrolyte nature.[14-15.]

Table 1: Physical properties of ligand (LD) and it's Pd(II) and Ir(III) complexes

Compd.	Magnetic moment	Melting point (°C)	C	H	N	M	Mol. formula mol. wt	Conductance $Ohm^{-1} Lcm^{-2}$ mol
[LD]	-	222°C	56.68 (56.65)	3.85 (3.65)	9.02 (8.9)	-	$C_{14}H_{12}ClNO_4$ (293.4)	-
$[PdL_2]H_2O$	Diam.	>300°C	48.33 (48.14)	3.77 (3.36)	4.03 (4.02)	15.29 (15.41)	$C_{28}H_{26}Cl_2N_2O_8Pd$ (710.12)	17.9
$[IrL_2Cl]H_2O$	Diam.	>300°C	39.50 (41.85)	3.19 (3.31)	3.41 (3.90)	23.14 (24.69)	$C_{27}H_{26}Cl_3IrN_2O_9$ (869.12)	12.9

The elemental analysis of the ligand shows that the amount of carbon, hydrogen and nitrogen are close to the experimentally determined values.

Electronic spectra

The relevant electronic spectra of ligand and it's metal complexes are presented in Table 2. The bands around 299 nm and 281 nm assigned to π – π* and n→n* transitions, respectively.

Table 2: Electronic spectral data of ligand (LD) and it's Pd(II) and Ir(III) complexes

Compound	Bands (nm)	Bands (cm^{-1})	Assigned transitions
Ligand	299		π – π*
	381		n→n*
[Pd L_2] H_2O	372	18450	$^1A_{1g} \rightarrow {}^1B_{1g}$
	405	27750	$^1A_{1g} \rightarrow {}^1E_g$
[Ir L_2Cl] H_2O	382	27000	$^1A_{1g} \rightarrow {}^1T_2g$
	407	29100	$^1A_{1g} \rightarrow {}^1T_2g$
		32800	$^1A_{1g} \rightarrow {}^3T_1g$

The electronic transition of a Four coordinated Pd(II) complex have diamagnetic nature and the spectral bands at 18450 cm^{-1} and 27750 cm^{-1} assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow 1E_g$ transitions and band occurring 34546 cm^{-1} in UV region is ascribed to charge transfer transition. Hence, a square planer geometry may be assigned for Pd(II) complex[16]. The electronic transition of Six coordinated Ir(III) complex have three bands assignable to $^1A1g \rightarrow {}^1T2g$, $^1A1g \rightarrow {}^1T2g$, $^1Ag \rightarrow {}^3T1g$ are compatible with octahedral geometry.[17]

FT-Infrared spectra

FTIR spectral data is presented in Table 3. The FTIR spectrum of free ligand shows characteristic bands at 3060-3400, 1704, 1684, 1357 and 1319 cm^{-1} assignable to intermolecular hydrogen bonded ν (OH), lactone carbonyl ν(C=O), azomethine ν(C=N), aryl azomethine ν(C-N) and phenolic ν(C-O) stretching modes, respectively. The absence of weak broad band in the 3060-3300 cm^{-1} region, noted in the spectra of the metal complexes, indicates deprotonation of intermolecular hydrogen bonded OH group on complexation. This is further supported due to upward shift in phenolic ν(C-O) tothe extent of 20-30 cm^{-1} on complexation. The ν(C=N)[18], band is shifted to lower wavenumber with respect to free ligand, indicated that the nitrogen of the azomethine is co-ordinated to the metal ion. This is supported upward shift in ν(C-N) to the extent of 10-15 cm^{-1}. The FTIR spectra of metal

complexes showed new bands inthe range 524-550 cm^{-1} assigned to ν (M-N)[19] and also in the spectra of complexes there exist a weak band in the range 613-617 cm^{-1} assigned to ν(M-O)[20] modes. The infrared spectra of the complexes exhibited band in the range 545-568 cm^{-1}, assignable to τ(M-Cl)[21] streching vibration. The aromatic stretching frequency in free ligand shows band at 1500-1550 cm^{-1}, which is not so affected in complex and found at 1528 cm^{-1}. The presence of coordinated water in the complexes was revealed by the appearance of broad band in the region 3408-3482 cm^{-1}.[22]

Table 3: IR spectral data of the ligand (LD) and its Pd(II) and Ir(III) complexes

Compound	(OH)	(C=O)	(C=N)	(C-N)	(C-O)	(M-N)	(M-O)	(M-Cl)
Ligand	3139	1682	1654	1472	1375	-	-	-
$[PdL_2]\ H_2O$	2917	1548	1627	1483	1427	458	605	-
$[Ir\ L_2Cl]H_2O$	3103	1541	1617	1474	1281	413	673	515

^{1}H NMR spectral data of ligand (LD)

The ^{1}H NMR spectra of free ligand in DMSO at room temperature shows the following signals δ 2.1 (s, 3H-CH_3), 2.55 (s, 3H, N = C-CH_3), 10.37 (s, 1H, phenolic OH) 6.9 (s, 1H, ar-H), 7.0-7.9 (m, 2H, ar-H), 5.7 (1-H-(OH), 15.46 (s, 1H, enolic OH of DHA moiety).

Mass spectrum of the ligand (LD)

Mass spectral data confirmed the structure of the ligand (LD) as indicated by the peak corresponding to their molecular mass (Fig. 1).

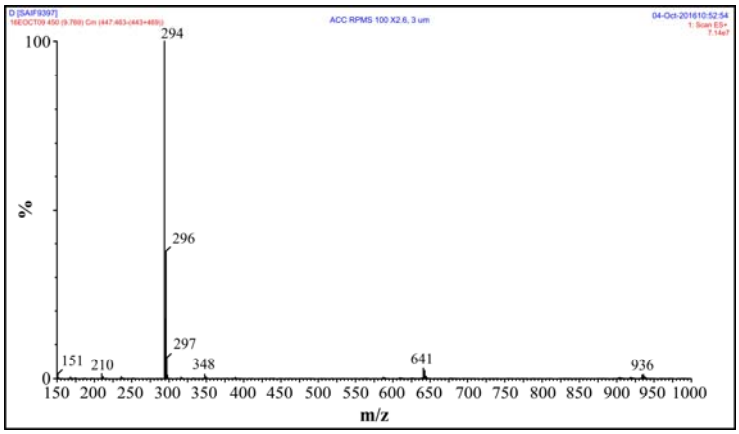


Fig. 1: Mass spectrum of Ligand (LD)

Thermal analysis

The simultaneous TG/DTA analysis of metal complexes was studied from ambient temperature to1000°c in nitrogen atmosphere using α-Al_2O_3 as reference. The Pd (II), Ir(III) complexes of ligand LD were chosen for thermal study. On the TG curve of Pd(II) the first step shows a steep slope between 50-100°C with mass loss of 2.396% (calcd. 2.5%) indicating the removal of one molecule of lattice water. An endothermic peak in the range 90-100°C (ΔT_{max} = 90°C) in the DSC curve corresponds to the ionic dehydration step. The second endothermic peak in the DSC curve observed in the range 400-470°C (ΔT_{max} = 100°C) corresponds to the decomposition of ligand. The mass of final residue corresponds to stable PdO44.78% (cal 42.19%)[23].

On TG curve of Ir(III) complex, the first step shows a mass loss 6.97 (cal. 6.40%) in the range 50°C-102.01°C indicating loss of two lattice water molecules and one ionic chloride. An endothermic peak in the region (ΔT_{max} = 100°C) in the DSC curve corresponds to the ionic dehydration and ionic dechlorination. Second endothermic peak observed in the range 400-450°C (ΔT_{max} = 497°C) in DTA may be attributed to the removal of non-coordinated part of ligand. The mass of final residue corresponds to stable Ir_2O_3 (cal. 3.23%)[24].

Table 4: The Kinetic data of ligand (LD) and it's Pd(II) and Ir(III) metal complex

Complex	Step	n	Method	E_a (kJ mol-1)	$A(s^{-1})$	$\Delta S^{\#}$ ($Jk^{-1}mol^{-1}$)	$\Delta G^{\#}$ ($KJ\ mol^{-1}$)	Correlation coefficient
Pd(II)	1	0.1	HM CR	29.61	1.07×10^5	117.6	39.77	0.997 0.995
				25.83		-85.2223	33.17	
Ir(III)	2	0.2	HM CR	30.86	5.30×10^3	-116.4	41.13	0.999 0.998
				28.36		-94.977	36.73	

Antimicrobial activity

The antibacterial activity of ligand and it's metal complexes were evaluated in vitro against bacteria such as gram +ve bacteria (*staphylococcus aureus*) and gram –ve bacteria (*Escherichia coli*) by agar diffusion method.[11-12]. Wells were made on petriplates containing solidified 20 mL Muller Hinton agar medium (250 ppm and 500 ppm) in DMF. These plates were inoculated for 20-24 hrs culture of bacterial strains. Different concentrations of the test samples were filled in the wells and incubated at 37°C for 24 hr. Control plates with Gentamycin and solvent were maintained. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the well. The results obtained were compared with known standard Gentamycin[13]. Three replicates were tested at the concentration 250 ppm and 500 ppm in DMF and compared with control. The culture of

fungi purified by single pore isolation technique. The wells were made on petriplates containing solidified 20 ml sabouroud dextrose agar medium. These plates were inoculated for36-40 hours. Control plates with amphotericin B and solvent were maintained. The antifungal activity was assayed by measuring the diameter of the inhibition zone formed around the well. Three replicates of each treatment were repeated in all experiments

The ligand and it's metal complexes does not exhibit any antifungal and antibacterial activity which may be due to low solubility of complexes.[25-30]

Table 5: Antibacterial activity of Ligand (LD) and its Pd (II) and Ir(III) metal complexes (Zone of inhibition in mm)

Compound	*Escherchia coli*	*Salmonella typhi*	*Staphylococcus aureus*
Ligand	00	00	00
$[PdL_2]\ H_2O$	00	00	00
$[Ir\ L_2Cl]\ H_2O$	00	00	00

Table 6: Antifungal activity of Ligand (LD) and its Pd (II) and Ir(III) metal complexes (Zone of inhibition in mm)

Compound	*Aspergillus flavus*	*Candida albicans*
Ligand	00	00
$[PdL_2]\ H_2O$	00	00
$[IrL_2Cl]\ H_2O$	00	00

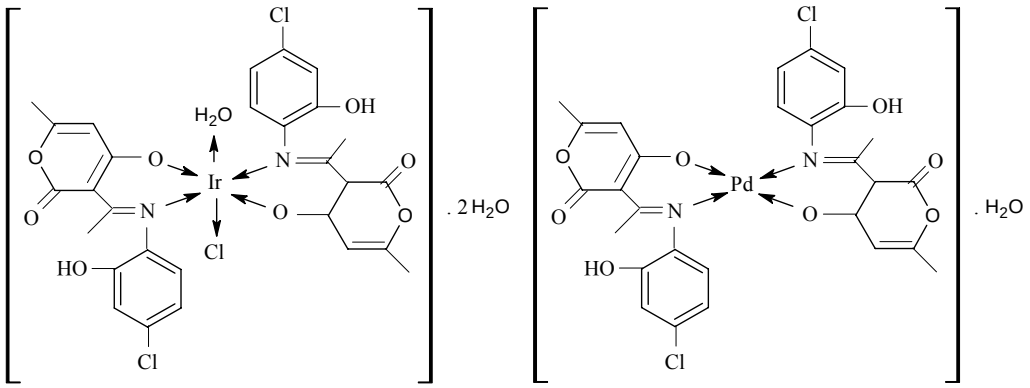


Fig. 2: Proposed structures of metal complexes

CONCLUSION

3-(E)-1-(5-chloro-2-hydroxyphenylimino)ethyl)-4-hydroxy-6-methyl-2H-pyran-2-one derived from 4-chloro-2-amino phenol and DHA. It's Pd(II) and Ir(III) complexes were synthesized and characterized using physicochemical and spectral data. On the basis of the physicochemical and spectral data discussed above, the ligand behaves as dibasic ON coordinating via enolic oxygen and imino nitrogen as illustrated in Fig. 2 and it's Pd(II) complex have square planar and Ir(III) complex have octahedral geometry. The ligand and it's metal complexes does not exhibit any antimicrobial activity.

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