



Synthesis, Characterization, X-Ray Diffraction Studies and Biological Properties of Ni(II) and Pd(II) Complexes of Tetradentate Schiff Bases

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Ni(II) and Pd(II) complexes of ONNO type tetradentate Schiff bases derived from 2:1 molar condensation of *o*-phenylenediamine and substituted salicylaldehydes have been synthesized and characterized by physico-chemical techniques such as elemental analysis, magnetic susceptibility measurements, conductivity measurements, electronic, IR, ¹H NMR spectral studies as well as X-ray diffraction studies. Analytical data suggest 1:1 (metal:ligand) stoichiometry of the metal complexes. The molar conductance data revealed the non-electrolytic behaviour of the complexes. Comparison of spectral data of Schiff bases and their metal complexes indicate that the Schiff bases act as dibasic tetradentate ligands and are coordinated to the metal ions *via* azomethine nitrogen and deprotonated phenolic oxygen atoms. Magnetic susceptibility and electronic spectral data confirm the diamagnetic nature and square planar geometry for the complexes. The powder X-ray diffraction data suggested monoclinic crystal system for these complexes. The ligands and their metal complexes have been screened for antimicrobial activities.

Keywords: Metal(II) complexes, Schiff bases, *o*-Phenylenediamine, Substituted salicylaldehyde, X-Ray diffraction studies.

INTRODUCTION

Schiff bases have an important position in the development of coordination chemistry due to their synthetic accessibility and physico-chemical properties. Transition metal complexes of azomethines have photochemical, catalytic, medicinal and electrochemical applications [1-3]. Tetradentate ONNO type Schiff bases have been reported for designing macrocyclic biomolecules that help in understanding biological processes [4,5]. Palladium(II) complexes have been investigated for its catalytic activity [6], photoluminescence properties as well as antitumor, anti-HIV and antimicrobial activities [7].

The reactions of tetradentate Schiff bases acquired from salicylaldehyde and diamines are a subject of interest of many authors [8,9] due to the ease of preparation and variable geometries. In the present paper, an attempt has been made to synthesize Ni(II) and Pd(II) complexes of tetradentate Schiff bases and further investigate the structure these complexes by spectral characterization and powder X-ray diffraction studies.

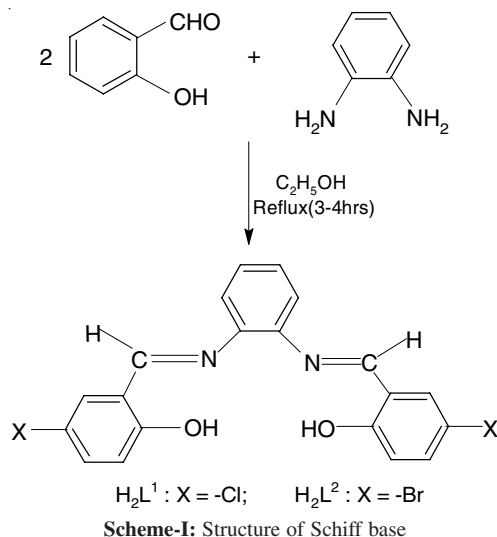
EXPERIMENTAL

All the chemicals used were of analytical reagent grade purchased from SDFCL Mumbai, India and used as such without further purification.

Elemental analyses were carried out in the micro-analytical laboratory, IIT Mumbai, India. Metal content was determined by gravimetric techniques in the laboratory [10]. The magnetic susceptibility measurements of the complexes were made on Guoy balance using Hg[Co(SCN)₄] as the standard. Molar conductivity of ligands and metal complexes were recorded using 1 × 10⁻³ M solution of DMSO on Equiptronics Conductivity meter EQ 660A. IR spectra were recorded using KBr pellets in the 4000-400 cm⁻¹ region on FTIR-Spectrum One FT-IR spectrometer supplied by Perkin-Elmer. The electronic absorption spectra of ligands and complexes were recorded in the UV-visible region using DMSO as solvent on UV-2401PC UV-Vis spectrophotometer supplied by Shimadzu. The ¹H NMR measurements were performed on a Bruker Advance 300 MHz spectrometer. The X-ray data was obtained from TIFR, Mumbai, India.

Synthesis of Schiff bases: The two Schiff bases H₂L¹ and H₂L² were synthesized by condensing 0.01 mol of *o*-phenylenediamine with 0.02 mol of 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde, respectively. The amine and aldehyde were refluxed in ethanolic medium for 3-4 h. The precipitate formed was cooled and filtered. The crude Schiff bases were then recrystallized with absolute ethanol (**Scheme-I**).

Synthesis of Ni(II) and Pd(II) complexes: The solution of metal chlorides (0.001 mol) in hot ethanol was added to ligand



solution (0.001 mol). The solution was refluxed with continuous stirring for about 4-5 h at 60 °C. The precipitated complexes were cooled and filtered, washed with cold methanol and dried in vacuum.

Biological studies: The *in vitro* growth inhibition assay of the compounds were tested for their antimicrobial activity against the bacterial species *Staphylococcus aureus*, *Escherichia coli* and fungi *Aspergillus niger* and *Candida albicans* by the agar well diffusion method [11].

RESULTS AND DISCUSSION

The crystalline solid complexes of Ni(II) and Pd(II) are bright in colour, stable in air and decompose at higher temperature (> 300 °C). The complexes are insoluble in water and other common organic solvents but soluble in DMF and DMSO. The elemental analysis data confirmed 1:1 (metal:ligand) stoichiometry for all the complexes (Table-1). The low values of molar conductance in DMSO (10^{-3} M) solution at room temperature indicate that these complexes are non-electrolytic in nature [12].

IR spectra: The preliminary identification regarding the formation of schiff bases and their complexes were obtained from IR spectral data (Table-2). The IR spectra of free ligands showed characteristic broad band of medium intensity in the region 3677-3468 cm^{-1} assigned to intramolecular hydrogen bonded $\nu(\text{O-H})$ stretching vibration [13]. The disappearance of this band in the corresponding metal complexes indicates involvement of phenolic oxygen in coordination to the metal after deprotonation. This is further confirmed by the shift in the position of $\nu(\text{C-O})$ band to lower wave numbers by 20-30

cm^{-1} [14]. The participation of azomethine nitrogen is proved by the shift of strong and sharp bands at 1613 and 1602 cm^{-1} for H_2L^1 and H_2L^2 , respectively to a lower frequencies after complexation [15]. All the complexes showed an additional non-ligand bands in the regions 550-510 and 466-409 cm^{-1} assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretching vibrations, respectively.

^1H NMR spectra: ^1H NMR spectra of Schiff base ligands and their metal complexes were recorded in DMSO solvent. The ^1H NMR spectra of the parent ligands H_2L^1 and H_2L^2 exhibited singlet signals at 12.89 and 12.94 ppm, respectively which was attributed to phenolic -OH proton [16]. These OH signals disappeared when ^1H NMR spectra were performed in presence of D_2O . Also, the two ligands H_2L^1 and H_2L^2 showed singlets at 8.93 and 8.89 ppm, respectively, corresponding to -CH=N moiety. On complexation the proton signals of azomethine carbon appeared to be deshielded as they were shifted downfield compared to the respective ligands indicating coordination through azomethine nitrogen atom [17]. The multiplets in the region 6.65-7.90 ppm were assigned to aromatic ring protons (Table-2).

Electronic absorption spectra and magnetic susceptibility: The electronic spectrum of Schiff base ligands and their metal complexes were explored in DMSO solution (1×10^{-5} M). The absorption spectra of the Schiff base ligands exhibited two high intensity bands at around 270 and 330 nm (Table- 2) which is attributed to benzene $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition of non-bonding electrons present on azomethine nitrogen in the Schiff bases, respectively. These two transitions were shifted in the spectra of all the complexes with appropriate shifts. The appearance of band around 480 nm in Ni(II) complexes is due to $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ transition favouring a square planar geometry [18]. The Pd(II) complexes display bands in the regions of 255-259, 353-378 and 455-477 nm. The broad bands in the region 455-477 nm were considered due to $d-d$ transition ($^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$) of square planar configuration [19]. Magnetic susceptibility measurements supported the diamagnetic behaviour of all the complexes.

Powder X-ray diffraction analysis: To understand the crystal structure, X-ray diffractogram of complexes were obtained in the range 5° to 70° (2 θ) value and an independent indexing for the X-ray powder diffraction data was done. The inter-planar spacing (d_{hkl}) were calculated by using Braggs equation for the major reflexes. The preliminary data in the form of $1/d^2$ were fed to the computer and all the differences were calculated as required for Hess and Lipson's method. The reflexes were indexed and refined for obtaining the Miller indices h, k, l using Back-cal program by computational method. The precise lattice parameters and deviations were then obtained by using program X-ray and program error matrix, respectively. There-

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE LIGANDS AND THEIR METAL COMPLEXES

Compound	m.w. (Colour)	m.p. (°C)	Microanalysis (%): Found (Calculated)				Λ_M (S $\text{cm}^2 \text{mol}^{-1}$)
			C	H	N	M	
H_2L^1 [$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2$]	385.00 (Bright orange)	220	62.71 (62.32)	3.11 (3.64)	7.36 (7.27)	—	—
NiL^1 [$\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2\text{Ni}$]	441.71 (Brownish red)	> 300	54.28 (54.33)	2.70 (2.77)	6.14 (6.33)	13.00 (13.29)	15.5
PdL^1 [$\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2\text{Pd}$]	489.42 (Yellow)	> 300	49.52 (49.04)	2.05 (2.45)	5.33 (5.72)	21.63 (21.74)	12.3
H_2L^2 [$\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2\text{Br}_2$]	473.80 (Yellow)	199	50.51 (50.65)	2.86 (3.98)	5.86 (5.91)	—	—
NiL^2 [$\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2\text{Br}_2\text{Ni}$]	530.51 (Brick red)	> 300	45.05 (45.23)	2.17 (2.26)	5.50 (5.28)	11.50 (11.07)	5.81
PdL^2 [$\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2\text{Br}_2\text{Pd}$]	578.22 (Ochre yellow)	> 300	41.58 (41.50)	2.12 (2.07)	4.78 (2.84)	18.88 (18.40)	9.22

TABLE-2
 SPECTRAL DATA OF THE LIGAND AND THEIR METAL COMPLEXES

Ligand/ complexes	IR (cm ⁻¹)					¹ H NMR (δ ppm)			λ _{max} (nm)		
	ν(O-H)	ν(C=N)	ν(C-O)	ν(M-O)	ν(M-N)	OH	CH=N	Aromatic	π→π*	n→π*	d-d transition
H ₂ L ¹	3468	1613	1271	—	—	12.89	8.93	6.90-7.78	271	334	—
NiL ¹	—	1603	1253	510	409	—	8.82	6.70-7.58	264	379	480
PdL ¹	—	1598	1250	536	467	—	8.85	6.76-7.69	255	353	455
H ₂ L ²	3677	1602	1373	—	—	12.94	8.89	6.97-7.68	269	324	—
NiL ²	—	1593	1352	517	430	—	8.75	6.65-7.90	259	373	479
PdL ²	—	1590	1350	550	466	—	8.77	6.79-7.84	259	378	477

 TABLE-3
 CELL DATA AND CRYSTAL LATTICE PARAMETERS FOR THE COMPLEXES

Complex	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Vol (Å) ³	D _{obs}	D _{cal}
NiL ¹	18.698 ± 0.063	18.445 ± 0.016	14.658 ± 0.053	90	122.27	90	2797.29	1.112	1.077
PdL ¹	20.113 ± 0.035	14.257 ± 0.064	15.467 ± 0.046	90	96.81	90	3875.77	1.183	1.246
NiL ²	18.160 ± 0.035	11.687 ± 0.046	15.425 ± 0.082	90	104.07	90	3839.14	1.182	1.073
PdL ²	18.618 ± 0.065	12.987 ± 0.021	16.015 ± 0.027	90	94.19	90	3340.93	1.272	1.223

after the densities of all the indexed compounds were determined using a 5 cm³ specific gravity bottle and toluene as displacing liquid. After indexing, the space group is determined using systematic and critical evaluation of each reflex in the powder pattern [20]. All the complexes were successfully indexed to monoclinic system with Z = 4 and space group P_{2/m}. The lattice parameters are summarized in Table-3. The closeness in the value of observed density and calculated density suggest that each reflex of X-ray diffraction pattern is indexed with perfectness.

Antimicrobial activity: The ligands and their metal complexes were assayed *in vitro* for their ability to inhibit the growth of representative Gram positive (*Staphylococcus aureus*) and Gram negative (*Escherichia coli*) bacteria and the fungus *Candida albicans* and *Aspergillus niger*. The susceptibilities of certain strains of bacteria and fungus were evaluated by measuring the size of the bacteriostatic diameter. The results (Table-4) indicated that (a) Schiff bases are more active against the fungus than their complexes, (b) all the complexes showed higher activity against the bacteria, and (c) Pd(II) complexes showed higher antibacterial and antifungal activities in comparison with Ni(II) complexes.

tetradentate ligands and coordinated to the central metal ions *via* deprotonated phenolic oxygen and azomethine nitrogen atoms with 1:1 (metal:ligand) stoichiometry (Fig. 1). A square planar structure is proposed for all Ni(II) and Pd(II) complexes. The powder X-ray diffraction data suggested monoclinic crystal system for these complexes with space group P_{2/m}. The antimicrobial results indicated that all the complexes are biologically active, however, Pd(II) complexes showed higher antimicrobial activity compared to Ni(II) complexes.

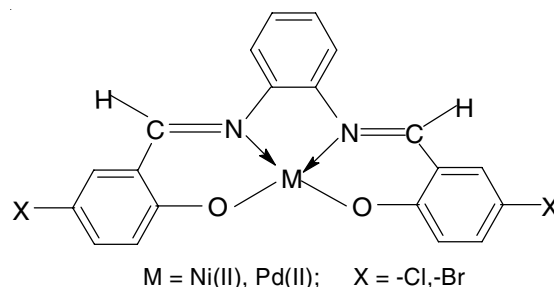


Fig. 1. Structure of the complexes

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Conclusion

On the basis of analytical and spectral studies, it is observed that the synthesized Schiff bases behave as dibasic, ONNO

TABLE-4 <i>in vitro</i> ANTIMICROBIAL ACTIVITIES OF LIGANDS AND THEIR COMPLEXES				
Compound	Diameter of inhibition zone (mm)			
	<i>C. albicans</i>	<i>A. niger</i>	<i>S. aureus</i>	<i>E. coli</i>
H ₂ L ¹	22	20	10	08
H ₂ L ²	20	18	12	06
NiL ¹	11	10	11	12
PdL ¹	16	14	14	15
NiL ²	10	12	13	11
PdL ²	15	16	16	14
Echinocandin	26	22	—	—
Gentamycin	—	—	25	22

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