



X – RAY DIFFRACTION STUDIES OF Pd(II) COMPLEXES OF TETRADENTATE SCHIFF BASES

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Abstract:

Pd(II) Complexes with N_2O_2 tetradentate Schiff bases derived from o-phenylenediamine and various salicylaldehydes were synthesized and characterised by elemental analysis, magnetic susceptibility, molar conductivity as well as IR, 1H -NMR and electronic spectroscopy. Elemental analysis data proved 1 : 1 stoichiometry. The molar conductance data revealed the non electrolytic behaviour of the complexes. The analytical and spectral data confirm that the Schiff bases act as dibasic tetradentate ligands and coordinated to metal via the two azomethine nitrogens and the two phenolic oxygens. 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.

Keywords: Pd(II) complexes, Schiff bases, o-phenylenediamine, X- ray diffraction studies.

Introduction:

Coordination complexes with substituted salicylaldehydes have shown diverse structures and properties generating a variety of stereochemistries and wide range of bonding interactions [1,2]. These compounds can be used in photochemical, catalytic, medicinal and electrochemical applications [3-5]. Some of the complexes of tetradentate Schiff bases have received considerable attention because of their potential as catalysts for the insertion of oxygen into an organic substrate [6] and have shown to be useful models in understanding biological systems such as irregular binding of peptides [7]. These compounds play an important role in advancement of inorganic biochemistry as they may statistically mimic the spectroscopic or other physical properties of enzyme [8-9].

The synthesis and Characterisation of tetradentate Schiff base complexes derived from salicylaldehyde and diamines have been studied intensively by many authors [10,11]. However literature survey reveals that much less attention has been focused on their XRD studies hence it was thought worthwhile to carry out their crystallographic studies. In the present investigation three Pd(II) complexes have been synthesized, characterized and studied using powder X – ray diffractometer.

Materials and Methods

All chemicals used were of A. R. grade purchased from S. D. Fine chemicals (Mumbai) and used without further purification.

Synthesis of Schiff bases: The Schiff base was synthesized by condensing ethanolic solution of 0.01 mol of o-phenylenediamine with 0.02 mol of salicylaldehyde, 5-chlorosalicylaldehyde and 5-nitrosalicylaldehyde respectively and refluxed for

3-4 hours. The precipitate formed was cooled, collected by filtration washed with methanol and then recrystallized from ethanol. The purity of ligands was checked by thin layer chromatography and elemental analysis. The yield of the ligands was about 80-95%.

Synthesis of the Pd complexes: To the hot solution of 0.001 mol of ligand in chloroform, ethanolic solution of $PdCl_2$ (0.001 mol) was added. The reaction mixture was refluxed for about 4-5 hours at $50^\circ C$ with continuous stirring. The complexes which precipitated were filtered off, washed with cold methanol and recrystallized finally dried in vacuum over fused $CaCl_2$.

Experimental Analysis: Metal content was determined in the laboratory by the reported methods [12]. C, H and N analysis were performed at the IIT Mumbai. The infra-red spectra of the ligands and of their metal complexes were recorded in KBr pellets in the $4000-400\text{ cm}^{-1}$ region using a FTIR supplied by Perkin Elmer instrument. The electronic Spectra were recorded in DMSO solution using a UV-visible 2100 Spectrophotometer supplied by M/s Perkin Elmer lambda 25. The 1H NMR spectra were recorded in DMSO using a Bruker Advance 300 MHz spectrometer. The X-ray analysis was carried out at TIFR Mumbai.

Results and Discussion:

All the metal complexes are crystalline solids and decompose at high temperature. The complexes are insoluble in water, ethanol, methanol, chloroform, carbon tetrachloride etc. but soluble in DMF and DMSO. The analytical data along with some physical properties of the ligand and metal complexes are reported in Table 1. The molar conductivities of $1 \times 10^{-3}\text{ S}$

$\text{cm}^2 \text{mol}^{-1}$ solutions of the complexes in DMSO indicate their non-electrolytic nature [13].

IR Spectra: The IR spectra of the free ligands showed characteristic bands at around 3000 cm^{-1} assigned to intramolecular hydrogen bonded $\nu(\text{O-H})$ stretching vibration. The absence of this band in the metal complexes indicates deprotonation of OH proton due to its coordination to the metal. This is further supported by the shift in the stretching frequency of the $\nu(\text{C-O})$ to lower wave numbers by $20\text{-}30 \text{ cm}^{-1}$ from its position in the free ligands [14]. The coordination of azomethine nitrogen is confirmed by the presence of bands in the $1620\text{-}1610 \text{ cm}^{-1}$ region in the ligand which underwent a shift to a lower frequency after complexation [15]. All complexes show new bands in the $550\text{-}530 \text{ cm}^{-1}$ and $470\text{-}450 \text{ cm}^{-1}$ region assigned to $\nu(\text{Pd-O})$ and $\nu(\text{Pd-N})$ stretching vibrations respectively (Table 2).

^1H NMR Spectra: The ^1H NMR spectra of the ligands and Pd(II) complexes were recorded in DMSO solvent (Table 2). The proton signals of azomethine carbon appeared to be deshielded as they are shifted downfield compared to the respective ligands indicating coordination through azomethine nitrogen atom; also the OH signal of the free ligand ($\sim 13 \text{ ppm}$) is absent in the spectra of Pd complexes confirming the deprotonation and subsequent participation in complexation [16]. The multiplets in the region $6.09\text{-}8.65 \text{ ppm}$ were assigned to aromatic ring protons.

Electronic Absorption Spectra and Magnetic Susceptibility: The electronic spectrum of Pd(II) complex display bands in the region $19120\text{-}21598 \text{ cm}^{-1}$, $24923\text{-}26691 \text{ cm}^{-1}$ and $28700\text{-}30069 \text{ cm}^{-1}$ which may be assigned to $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$ transitions respectively. These transitions correspond to the

three d-d spin forbidden transitions from the lower lying d levels to the empty $\text{dx}^2\text{-y}^2$ orbitals, the ground state $^1\text{A}_{1g}$ and excited states corresponding to the transitions are $^1\text{A}_{2g}$, $^1\text{B}_{1g}$ and $^1\text{E}_{1g}$ in order of increasing energy. Hence, a square planar geometry may be assigned for Pd(II) complex [17]. This is further supported by diamagnetic behaviour of Pd(II) from the magnetic susceptibility measurements.

XRD Analysis: In X-ray diffractogram of the complexes, major reflexes were recorded in the range 5° to 60° 2θ value. The major reflexes were measured and corresponding d-values were obtained using Bragg's equation. The independent indexing of major reflexes was carried out using least square method. The miller indices h, k, l were calculated and refined by using Back – cal program on computer. The complexes were successfully indexed to monoclinic system with $Z = 4$ and space group $\text{P}_{2/m}$ for all the complexes [18, 19]. The lattice parameters are summarized in Table 3. The correctness of d-values was confirmed by comparing the observed density with that calculated from the X-ray diffractogram.

Conclusion:

The Schiff base and their Pd(II) complexes were characterized by elemental analysis, conductance measurements, IR, ^1H -NMR, uv-vis spectra and XRD studies. The results showed that these Schiff bases behave as tetradentate ligand coordinating through the deprotonated phenolic oxygens and azomethine nitrogens and exhibit square planar structure. The X-ray diffraction data was of great help in the determination of lattice parameters of crystal structures which form the basis of crystallographic studies providing valuable information leading to confirmation of geometrical structure.

Table 1. Analytical and Physical Data of the compounds

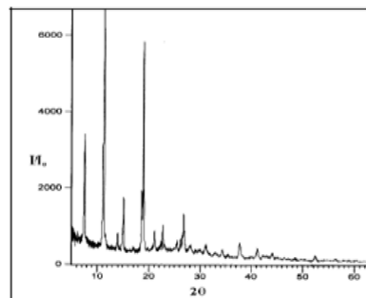
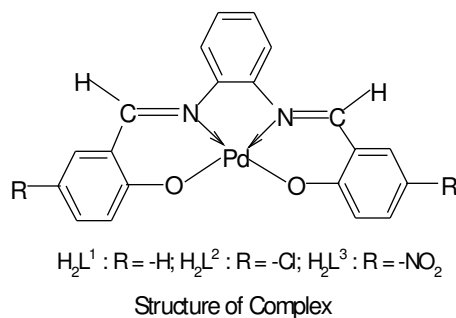
Compound	MolWt (Colour)	M.P ($^\circ\text{C}$)	Microanalysis % Calculated (Found)				χ_M ($\text{S cm}^2 \text{mol}^{-1}$)
			C	H	N	M	
H_2L^1 $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$	316.00 (mustard yellow)	183	75.94 (75.68)	5.06 (5.10)	8.86 (8.73)	--	--
PdL^1 $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2\text{Pd}$	420.42 (greenish yellow)	>250	57.08 (57.50)	3.33 (3.28)	6.66 (6.81)	25.31 (25.87)	8.5
H_2L^2 $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2$	385.00 (bright orange)	220	62.34 (62.71)	3.64 (3.11)	7.27 (7.36)	--	--
PdL^2 $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2\text{Pd}$	489.42 (yellow)	>250	49.04 (49.52)	2.45 (2.05)	5.72 (5.33)	21.74 (21.63)	12.3
H_2L^3 $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_6$	406.00 (orange)	>250	59.12 (58.79)	3.47 (3.49)	13.79 (13.55)	--	--
PdL^3 $\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_6\text{Pd}$	510.42 (brown)	>250	47.02 (47.37)	2.35 (2.18)	10.97 (10.63)	20.85 (20.17)	9.2

Table 2. IR Spectral data (cm⁻¹) and ¹H NMR spectra of Ligand and Complexes.

Ligand/ complexes	IR (cm ⁻¹)					¹ H NMR(δppm)		
	ν(O-H)	ν(C=N)	ν(C-O)	ν(Pd-O)	ν(Pd-N)	OH	CH=N	Aromatic
H ₂ L ¹	3054	1613	1361	---	---	12.95	8.57	6.92-7.70
PdL ¹	---	1602	1338	543	457	--	8.95	6.10-7.69
H ₂ L ²	3077	1611	1271	--	--	13.20	8.43	6.57-7.94
PdL ²	--	1598	1250	536	466	--	8.80	6.09-7.84
H ₂ L ³	3086	1619	1288	--	--	13.54	8.79	7.00-8.65
PdL ³	--	1605	1261	540	470	--	9.01	6.70-8.62

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}
PdL ¹	18.432 ±0.020	19.662 ±0.012	14.822 ±0.017	90	89.64	90	2604.31	1.852	1.745
PdL ²	20.113 ±0.035	14.257 ±0.064	15.467 ±0.046	90	96.81	90	3875.77	1.183	1.246
PdL ³	20.400 ±0.015	18.717 ±0.016	15.385 ±0.027	90	93.07	90	2732.09	1.502	1.563

X-ray spectrum of PdL²

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