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Synthesis and Physico-Chemical Studies of Pd(II) Complexes Derived From Heterocyclic Schiff Bases

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Heterocyclic Schiff base ligands were prepared by condensing pyrrole 2-carboxaldehyde and pyridine-2-carboxaldehyde with *o*-toluidine, *p*-toluidine and aniline. The ligands were used to prepare Pd(II) complexes. Their structural features were studied on the basis of elemental analysis, diffused reflectance studies, magnetic susceptibility measurements, UV/visible and infrared absorption spectral data.

INTRODUCTION

The survey of literature reveals voluminous documentation of Schiff bases derived from substituted aldehydes and amines. The chelating properties of Schiff bases derived from *o*-hydroxyaldehyde and ketones display manifold applications in medicine, industry and agriculture[1]. The complexing behaviour of Schiff bases[2] and their biological activities[3] have been reported. But no attempts have been made to study the chelating behaviour of the Schiff bases derived from the condensation of substituted heterocyclic aldehyde and substituted anilines. The present paper reports the ligational behaviour of heterocyclic Schiff base containing N atom as a donor site with palladium(II).

EXPERIMENTAL

Pyrrole-2-carboxaldehyde, pyridine-2-carboxaldehyde, *o*-toluidine, *p*-toluidine and aniline of AR grade were used to prepare Schiff base ligands. 1 mg/ml $PdCl_2$ solution was used to synthesize Pd(II) complexes.

An ethanolic solution containing equimolar quantities of aldehyde and amine was refluxed for 3–4 h on a hot water bath. The reaction mixture was then poured on ice whereby solid Schiff base separated out. The Schiff base thus obtained was filtered, washed and dried at room temperature.

Pd(II) complexes were prepared by refluxing aldehyde, amine and metal salt solution in 2:2:1 molar ratio with ethanol at 100°C for 4–5 h. The pH of the resultant reaction mixture was gradually increased by addition of dilute NaOH up to 7.5 whereby the solid complexes separate out. The complexes were filtered, washed and dried at 80°C. The complexes were recrystallised from their solution in DMSO.

The elemental analysis was carried out by a well established method[4] and the metal content in the complex was found gravimetrically[5] using dimethyl glyoxime. The molar conductance was measured on Toshniwal instrument type CLO1.OTA using nitrobenzene as a solvent while the uv and visible spectra were rercorded on UV-2100, UV-Visible Spectrophotometer, manufactured by Shimadzu Corporation, Japan. The diffused reflectance spectra were obtained by Carl Zeiss VSU2P Spectrophotometer with reflectance attachments. The IR spectra of the compounds were recorded on FTIR-4100 manufactured by Shimadzu Corporation, Japan by KBr pellet method.

RESULTS AND DISCUSSION

The elemental and metal analysis values suggest a 1 : 2(M : L) stoichiometry for complexes with a general fomula $Pd(Ln)_2$ where n = 1, 2, ... , 6

L_1 = Schiff base of pyrrole 2-carboxaldehyde and *o*-toluidine
L_2 = Schiff base of pyrrole-2-carboxaldehyde and *p*-toluidine
L_3 = Schiff base of pyrrole 2-carboxaldehyde and aniline
L_4 = Schiff base of pyridine 2-carboxaldehyde and *o*-toluidine
L_5 = Schiff base of pyridine 2-carboxaldehyde and *o*-toluidine
L_6 = Schiff base of pyridine 2-carboxaldehyde and aniline

The various analytical data of the complexes are summarised in Table-1. The Schiff bases were brown in colour and were freely soluble in ehtanol. The palladium complexes were found to be insoluble in most of the common organic solvents. However, $Pd(L_4)_2$, $Pd(L_5)_2$ and $Pd(L_6)_2$ were found to be soluble only in DMSO and nitrobenzene.

The low molar conductances of the complexes suggest their nonelectrolytic nature.

TABLE-1
ANALYTICAL DATA OF COMPLEXES

Complexes	Color	Mol Weight	Thermal Stability (°C)	Molar conductance s cm^2 mole^{-1}	Elemental Analysis % [Exp (calcd)]			
					C	H	N	Pd
$Pd(L_1)_2$	dark brown	474.4	280	—	58.34 (60.71)	4.27 (5.09)	10.91 (11.80)	22.13 (22.41)
$Pd(L_2)_2$	dark brown	474.4	300	—	58.67 (60.71)	4.59 (5.09)	10.79 (11.80)	20.55 (22.41)
$Pd(L_3)_2$	dark brown	446.4	300	—	58.09 (59.14)	4.11 (4.51)	11.32 (12.54)	25.27 (23.81)
$Pd(L_4)_2$	ochre yellow	498.4	260	1.65	59.95 (62.59)	4.42 (4.85)	11.15 (11.23)	18.96 (21.33)
$Pd(L_5)_2$	ochre yellow	498.4	260	3.45	59.97 (62.59)	4.45 (4.85)	11.20 (11.23)	18.96 (21.33)
$Pd(L_6)_2$	brown	470.4	280	28.05	59.16 (61.22)	4.01 (4.28)	11.54 (11.90)	18.96 (22.60)

The salient features of the IR spectra of the ligands and complexes are summarised in Table-2. The spectra of all the ligands show a broad band of medium intensity in the range 1608–1587 cm^{-1} which can be assigned to ν(C=N). The lowering of this absorption band in complex spectra by 10–40 cm^{-1} from their respective positions in the ligand spectra suggests the co-ordination between palladium and the azomethine nitrogen.[6, 7]

The bands appearing due to ring stretching vibrations of 2-substituted pyrrole and pyridine rings in the ligand spectrum shift towards lower wave-numbers in the corresponding complex spectrum indicating the involvement of heterocyclic 'N' atom in the formation of complex.

In case of ligands L_1, L_2, L_3, a band appearing in the range 3200–2953 cm^{-1} is assigned to ν(N—H) which shifts from their original value, in the corresponding spectrum of Pd(II) complex. This gives an additional evidence of the involvement of N—H goup of pyrrole ring in the complexation.

The appearance of a new band in the range 594–562 cm^{-1} in the spectrum of Pd complex is assigned to ν(Pd—N). Similar type of assignment has also been reported by other researchers[8, 9].

TABLE-2
SALIENT FEATURES OF IR SPECTRA (cm^{-1}) OF LIGANDS AND COMPLEXES

Ligands Complexes	ν(N—H)	ν(C=N)	ν(Pd—N)
L_1	3196	1624	—
$Pd(L_1)_2$	2957	1603	594
L_2	3127	1618	—
$Pd(L_2)_2$	3200	1608	582
L_3	3221	1624	—
$Pd(L_3)_2$	2953	1610	584
L_4	—	1633	—
$Pd(L_4)_2$	—	1600	598
L_5	—	1626	—
$Pd(L_5)_2$	—	1599	574
L_6	—	1628	—
$Pd(L_6)_2$	—	1587	562

All the palladium complexes are yellow to brown in colour. Jain *et al.*[10] have reported that yellow-coloured Pd(II) complexes crystallize with square-planar geometry.

The electronic absorption and diffused reflectane spectra of complexes show three strong absorption bands in the range 18kK–22kK, 24kK–26kK and 30kK–35kK. These bands are assinged to the following d–d transitions respectively:

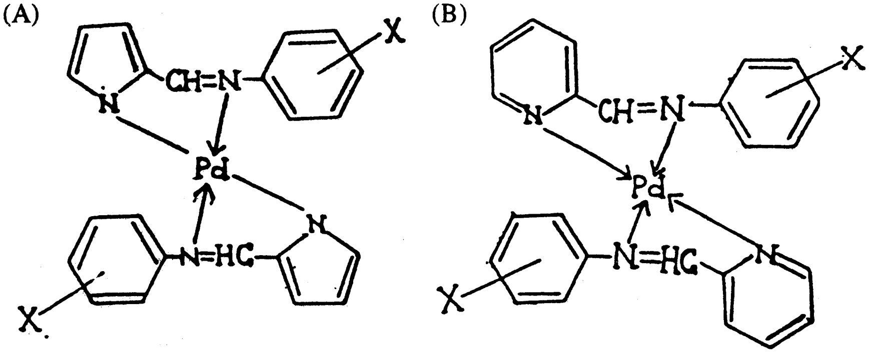
$$^1A_{1g} \rightarrow {}^1B_{1g}$$

$$^1A_{1g} \rightarrow {}^1E_{1g}$$

$$^{1}A_{1g} \rightarrow {}^{1}A_{2u}$$

Mehta and Mehta[11] have also reported these d–d transitions in the same range. The magnetic susceptibility measurements at room temperature for these complexes indicate diamagnetic nature and absence of any lone pair of electrons. Hence Pd(II) complexes can be assigned square-planar geometry. However, the appearance of d–d transitions at little higher values indicate distortion in the perfect square-planar geometry. Conclusively the Pd(II) complexes under present investigation may be assigned square-planar geometry as figured in structures A and B.

Pd(L_2)



L = L_1, L_2, L_3; X = *o*-Me, *p*-Me, H respectively

L = L_4, L_5, L_6; X = *o*-Me, *p*-Me, H respectively

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