

UV-Visible and IR Spectral Data of Pd(II) Complexes Derived from Bidentate Schiff Bases

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The present communication reports synthesis and characterisation of Pd(II) complexes of bidentate ligand prepared by condensation of 3-hydroxy benzaldehyde or 5-nitrosalicylaldehyde with primary amines. All the complexes were analysed and characterised with physico-chemical parameters. IR spectra suggest the co-ordination of ligand through nitrogen of azomethine group and phenolic oxygen. Magnetic properties and electron absorption spectra suggest square planar geometry for these complexes.

INTRODUCTION

In recent work¹ of Pd(II) complexes, the author has we have covered a brief survey about the importance of palladium complexes with various substituted Schiff bases. As a continuation of our comprehensive interest in characterising metal complexes with respect to the lattice parameters we have prepared Pd(II) complexes derived from Schiff bases. A wide range of spectral properties have been recently found in the literature which can be associated with some palladium complexes of some nitrogen containing ligands²⁻⁵. Structural configuration of Pd(II) complexes derived from various donor ligands will identify the potential ligands. A routine synthesis of these complexes and characterisation by physico-chemical properties are briefly covered in the present communication.

EXPERIMENTAL

All the chemicals used were chemically pure. The Schiff base ligands have been prepared by refluxing equimolar quantities of 3-hydroxybenzaldehyde and 5-nitrosalicylaldehyde with various primary amines in ethanolic solution on a water bath for 5 h. The precipitated Schiff base was filtered, washed and dried in oven at 60°C. The Schiff bases were recrystallised from their ethanolic solution. The pure crystals were characterised for their analytical parameters.

The Pd(II) complexes were synthesised by refluxing a mixture of aqueous solution of palladium chloride (0.01 M) and Schiff base (0.02 M) on a water bath for 6 h. The complexes were isolated by breaking the resulting solution over crushed ice. The product was filtered, washed and dried at 60°C in an oven. Each of these complexes was recrystallised from their ethanolic solution.

The recrystallised Pd(II) complexes were analysed for their constitutional elements to ascertain molecular formula to each one of them. The electronic absorption spectra of Pd(II) complexes were recorded using 0.001 M solution in DMSO. The IR spectra were recorded using KBr pellet technique. Room

temperature magnetic susceptibility was determined using Gouy's balance, whereas molar conductance was calculated using conductivity bridge supplied by M/s Toshniwal.

RESULTS AND DISCUSSION

The analytical data of Pd(II) complexes suggests that all the Pd(II) complexes were precipitated with 1 : 2 metal : ligand stoichiometry. All the complexes were crystalline, coloured, stable at room temperature and insoluble in common organic solvents. However, each one of them was easily soluble in DMF and DMSO. The molar conductance values of complexes in nitro-benzene are in the ranges corresponding to those of non-electrolytes in these solvents⁶ (Table-1). The conductance values suggest that the charge on metal ion is neutralised by the ligand; therefore the complex is neutral. The magnetic moment values of all the complexes suggest diamagnetic nature and hence it can be inferred that complexes possess square planar geometry.

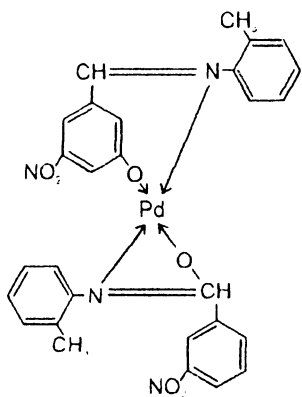
TABLE-1
PHYSICO-CHEMICAL PARAMETERS OF Pd(II) COMPLEXES
OF VARIOUS SCHIFF BASES

Complex	Molecular weight	Colour	Molar conductivity mhos cm ² mol ⁻¹	% Analysis, found (calcd.)				
				C	H	N	S	M
Pd(L ₁) ₂	498	Military green	1.31	61.32 (62.60)	3.87 (4.01)	5.61 (5.62)	—	21.05 (21.35)
Pd(L ₂) ₂	563	Dark yellow	0.59	54.42 (55.42)	3.43 (3.55)	4.47 (4.97)	11.10 (11.37)	18.74 (18.90)
Pd(L ₃) ₂	588	Light green	0.93	53.49 (53.02)	3.13 (3.09)	8.97 (9.52)	—	16.95 (18.08)
Pd(L ₄) ₂	616	Green	0.50	53.49 (54.51)	3.34 (3.57)	8.73 (9.09)	—	16.44 (17.26)
Pd(L ₅) ₂	616	Yellow green	1.82	53.91 (54.51)	3.07 (3.57)	8.98 (9.09)	—	16.80 (17.26)
Pd(L ₆) ₂	674	Dark green	1.90	49.62 (49.80)	2.66 (2.37)	7.97 (8.30)	—	14.36 (15.78)

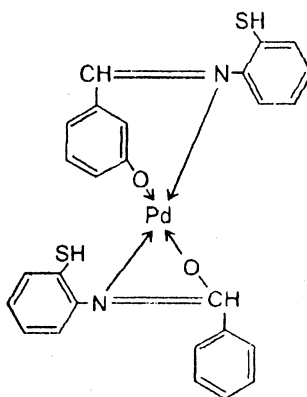
The bis-ligated complexes display absorption bands in the region 21740–18250 cm⁻¹ and 26320–22200 cm⁻¹ which may be assigned to the transition ¹A_{1g} → ¹B_{1g}(ν₁) and ¹A_{1g} → ¹E_{2g}(ν₂) respectively⁷.

The electronic absorption bands in the region 41670–33330 cm⁻¹ located in the solution spectra of palladium complexes is attributed to charge transfer transition. The electronic spectral data coupled with diamagnetic susceptibility of complexes favour square planar geometry for these complexes.

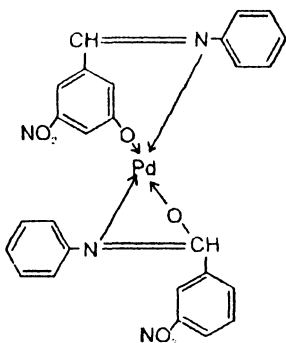
The IR spectra of ligands display IR bands near 3200 cm⁻¹ which are assignable to phenolic ν(OH) group. This band is absent in the corresponding spectra of Pd(II) complexes indicating involvement of phenolic oxygen in coordination of metal ion after deprotonation. The aldimino ν(C=N) of the Schiff bases was observed at

Structure of Newly Synthesised Pd(Ln)₂ Complexes

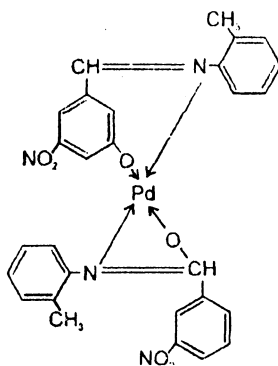
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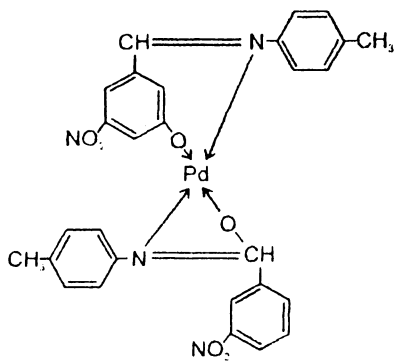
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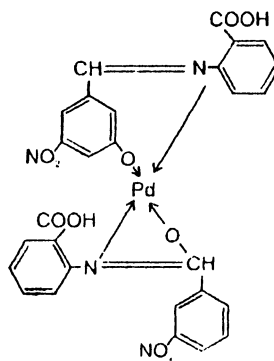
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6.

1650 cm^{-1} to 1594 cm^{-1} . The lowering of these stretching vibrations to the region (1623 cm^{-1} to 1568 cm^{-1}) in the Pd(II) complexes suggests involvement of aldimine nitrogen in the the co-ordination pattern⁸⁻¹⁰.

In far infra-red region prominent bands which are slightly different from the parent Schiff bases were observed in the spectra of Pd(II) complexes. It is very difficult to identify metal-ligand vibrations in the complexes. However, the bands observed in 589–480 cm^{-1} region are assignable to $\nu(\text{Pd}-\text{N})$ and $\nu(\text{Pd}-\text{O})$. Thus the infra-red spectral studies indicate that all the ligands are bonded as bidentate chelating molecules forming bond through phenolic oxygen and aldimino nitrogen atom. The important IR spectral bands of ligands and complexes are summarised in Table-2. The complexes can be assigned a structure as presented on page 399..

TABLE-2
IMPORTANT SPECTRAL DATA OF Pd(II) COMPLEXES

Complex	UV-visible spectral data (cm^{-1})			IR Spectral data (cm^{-1})		
	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}(\nu_2)$ cm^{-1}	${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_{2g}(\nu_2)$ cm^{-1}	Charge transfer transitions	$\nu(\text{C}=\text{N})$	$\nu(\text{Pd}-\text{N})$	$\nu(\text{Pd}-\text{O})$
Pd(L ₁) ₂	19230	22200	34480	1594 (1650)	589	557
Pd(L ₂) ₂	18250	26320	33330	1586 (1594)	576	457
Pd(L ₃) ₂	20830	26320	35710	1623 (1620)	569	—
Pd(L ₄) ₂	21280	24390	34480	1620 (1626)	557	519
Pd(L ₅) ₂	21740	26320	35710	1617 (1623)	589	546
Pd(L ₆) ₂	20410	—	41670	1600 (1636)	480	461

*Values in parentheses correspond to ligand.

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