

Synthesis and characterization of dimeric palladium (II) complexes containing tetradentate N-donor ligands

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ABSTRACT

The N-donor tetradentate complexes of Pd(II) display considerable interesting properties. The N-donor tetradentate complexes of the type $[Pd_2LCl_4]$ {L=N1, N2-bis-(2-pyridinylmethylene)-1,4-diacetyldihydiimine(L1) and N1,N2-bis-(2-pyridinyl-methylene)-1,2-ethylenediimine(L2)} has been synthesized by refluxing a clear solution of $PdCl_2$ taken in acetonitrile with ligand L (L1 and L2). The synthesized complexes have been characterized by elemental analysis, molecular weight, magnetic susceptibility measurement, FT-IR, UV-Visible, ¹H NMR and conductivity measurements. The complexes have been conjecture to possess a tetra coordinate geometry around the Pd(II) centre where two Pd-atoms are in trans with respect to the C-C single bond.

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KEYWORDS

Tetradentate N-donor ligand;
Platinum (II);
Dinuclear;
IR;
¹H-NMR;
UV-Visible.

INTRODUCTION

The synthesis of coordination network with an organic helical molecule using N-donor ligands has been focused as divergent potential ligands to form double stranded dinuclear helicates^[1-6]. There is also considerable interest in the chemistry of complexes containing aromatic N₄ homotopic ligands. In the present paper we report synthesis of Pd(II) complexes with reported tetradentate ligand *viz* N1,N2-bis-(2-pyridinylmethylene)-1,4-diacetyldihydiimine(L1) and other Schiff base tetradentate ligand N1,N2-bis-(2-pyridinyl-methylene)-1,2-ethylenediimine(L2)^[7-11]. Both complexes have been characterized with various physico-chemical and spec-

troscopic techniques.

MATERIALS AND METHODS

All the chemicals used were of analytical grade. The Ligands L1 and L2 were prepared as by reported procedures^[7,8,12]. $K_2[PtCl_4]$, pyridine 2-carboxaldehyde, 2,4-butanedione and ethylenediamine were procured from Merck. All the solutions and reagents were freshly prepared before use. The FT-IR spectra were recorded on Perkin Elmer 983 spectrophotometer using KBr pellets. The ¹H-NMR and UV-Vis spectra recorded on Bruker-ACM 300 spectrometer and Systronics 106 spectrophotometer respectively at SAIF, NEHU Shillong. Room tem-

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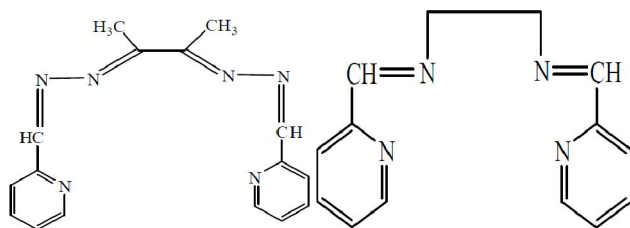
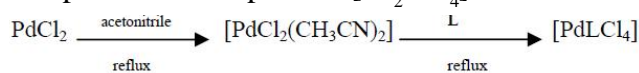


Figure 1 : (a) N1, N2-bis-(2-pyridinylmethylene)-1,4-diacetyldihydriimine(L1), (b)N1,N2-bis-(2-pyridinyl-methylene)-1,2-thylenediimine(L2)

perature magnetic susceptibilities of the complexes in powder form were measured on a Sherwood Scientific susceptibility balance. Micro-analyses were carried out at SAIF, NEHU, Shillong

Synthesis of the complex

PdCl_2 (0.18g, 1mmol) taken in acetonitrile (25 cm^3) was refluxed for 15 minutes. When a clear solution was obtained, ligand L (L1 and L2) (1mmol) was added to the solution and continued to reflux for another 4 hour. On standing at room temperature (25°C) a chocolate Brown coloured compound separated out which was isolated by centrifugation and washed with diethyl ether and dried *in vacuo*. The yield was recorded for both complexes (~75%). Reaction with L1 and L2 yielded complex of the composition $[\text{Pd}_2\text{LCl}_4]$



RESULT AND DISCUSSIONS

The tetradentate N_4 -donor ligands used for the preparation of Pd(II) complexes. Solution of a PdCl_2 in acetonitrile forms $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ ^[13] which on treatment with the ligands L ($\text{L} = \text{L1 and L2}$) result in the separation of dinuclear Pd(II) complexes with L ($\text{L} = \text{L1 and L2}$). The analytical results show that the complexes synthesized are having composition of general formula $[\text{Pd}_2\text{LCl}_4]$. The synthesized complex has been found stable in air at room temperature and insoluble in most

of the organic solvents but they are soluble in highly coordinating solvents like N, N'-dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The elemental analyses (TABLE 1) agree with the proposed formulation. Magnetic susceptibility measurements show that complexes are diamagnetic, thereby confirming low spin Pd(II), d^8 configuration. The complexes have molar conductance value in the region $0.5\text{-}3.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in DMSO solution at 10^{-3} M dilution. These values are consistent with the non-electrolytic nature of the complexes in this solvent^[15].

Infra-red spectral data

Infrared spectral data were supports the binding of tetradentate ligand to the metal centre. In the free ligand L1 and L2 showed a very strong absorption bands at 1589 cm^{-1} and 1658 cm^{-1} respectively, which is assigned to $\nu_{\text{C=N}}$ of the azomethine group. In complexes $[\text{Pd}_2\text{L1Cl}_4]$ and $[\text{Pd}_2\text{L2Cl}_4]$ this absorption has been shifted at 1606 cm^{-1} and 1600 cm^{-1} respectively indicating the coordination of the ligand with Pd(II) metal ion. For complex $[\text{Pd}_2\text{L1Cl}_4]$, $\nu_{\text{N-N}}$ stretching frequency showed a weak absorption bands at 1374 cm^{-1} compared to free ligand $\nu_{\text{N-N}}$ band observed at 1358 cm^{-1} . A medium intensity band for $[\text{Pd}_2\text{L2Cl}_4]$ at 1467 cm^{-1} compared to free ligand showed at 1480 cm^{-1} which is attributed to $-\text{CH}_2-$ bending mode of vibration. Besides these bands, all other characteristic vibrations are also observed in the complexes^[7,12,14].

UV-Visible Spectral data

Electronic absorption spectra of Pd (II) complexes in dimethylsulphoxide generally show one or two bands in the region 320-450nm with ϵ in the order of 10^3 . These bands may be assigned to the charge transfer type transition arising from the filled d-orbital of Pd (II) to the vacant π^* orbital of ligand. Further one band in the region 290-350nm with ϵ in the range $10^3\text{-}10^4$ are also observed. These bands may be assigned to the

TABLE 1 : Characteristic physical and analytical data [found(calculated)%] of the complex $[\text{Pd}_2\text{LCl}_4]$

Complex	Elemental analysis (% cal)					Molecular Weight
	Pd	C	H	N	Cl	
$[\text{Pd}_2\text{L1Cl}_4]$ (Chocolate Brown)	32.67 (32.79)	30.18 (29.61)	2.72 (2.79)	12.80 (12.95)	21.65 (21.85)	646±90
$[\text{Pd}_2\text{L2Cl}_4]$ (Brown)	37.56 (37.68)	29.27 (29.77)	2.55 (2.50)	4.33 (4.96)	24.99 (25.16)	

TABLE 2 : Structurally significant IR frequencies (cm⁻¹) of both complexes

Complex	IR cm ⁻¹	assignment
[Pd ₂ L1Cl ₄]	3098,3032	ν_{C-H}
	2853	ν_{C-H}
	1606	$\nu_{CH=N}$
	1474	ν_{C-CH}
	1361	ν_{C-CH}
[Pd ₂ L2Cl ₄]	3071,2925	ν_{C-H}
	1600	$\nu_{CH=N}$
	1467	ν_{C-CH}
	1374	ν_{C-CH}

intraligands transition of the type $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ [16]. The UV-Vis spectral data recorded in DMSO for both the complexes are given in TABLE 3

Molecular weight

The molecular weight data for the complexes (given in TABLE 1) have been determined in spectral grade DMSO by the freezing point depression method. The experimental values of the molecular weight for the two

TABLE 3 : The UV-Vis spectral data of synthesized complex

Complex	UV-Vis
[Pd ₂ L1Cl ₄] (Chocolate Brown)	432 (4.20x10 ³)
[Pd ₂ L2Cl ₄] (Brown)	320(2.51x10 ³), 288(3.13x10 ³),

complexes agree with their dimeric character. However, the experimental values of the molecular weights are slightly higher than those calculated based on the suggested dimeric compositions. Such higher of the molecular weights strongly suggest that the structure of the complexes is altered in the strongly coordinating solvent as compared to that in the solid state.

¹H NMR spectral data

¹H NMR spectra of Pd (II) complexes with ligands L1 and L2 viz. [Pd₂L1Cl₄] and [Pd₂L2Cl₄] in DMSO-d₆ showed multiplets in the region δ (7.35 – 9.70) ppm assigned to the aromatic protons of the pyridine ring present in the ligand. Signal due to azomethine protons (-CH=N) in [Pd₂L1Cl₄] observed as singlet at δ 8.45 ppm which shows down field shift by δ 0.25 ppm compared to the free ligand (δ 8.70ppm) and two methyl

TABLE 4 : Structurally significant ¹H NMR data (in δ ppm) of both complexes

Complex	¹ H NMR (ppm)
[Pd ₂ L1Cl ₄]	2.39 (s,-CH ₃), 2.48 (s,-CH ₃) 7.35-9.70 (m, aromatic), 8.45 (CH=N)
[Pd ₂ L2Cl ₄]	4.16 (s), 7.88 (d), 8.10(d), 8.30 (d), 8.68(s), 8.98 (d)

s= Singlet, d= Doublet, m= Multiple, ¹H-NMR were recorded in DMSO-d₆

protons showed a broad singlet at δ 2.39 and δ 2.48 ppm which is slightly up field in comparison to free ligand (δ 2.31 ppm)^[7,16]. ¹H- NMR spectrum of [Pd₂L2Cl₄] in DMSO-d₆ showed a sharp singlet at δ 4.16 ppm due to ethylene proton (-CH₂-CH₂-) which is slightly up field as compared to free ligand (δ 4.07). Signal due to azomethine protons (-CH=N) in [Pd₂L2Cl₄] observed as singlet at δ 8.68 ppm which is up field (δ 0.26 ppm) compared to the free ligand (δ 8.42 ppm).

Structural assessment

Complexes being insoluble in common organic solvent, no single crystal could be grown. A consistent effort to crystallize the complexes either from saturated solution or by diffusing into saturated solution in DMSO and DMF in a closed system led to the precipitation of amorphous products. Such behavior of the complexes with regard to their crystallization prevented their analyses by X-ray crystallography. Their solubility in solvent like dimethylsulphoxide has also restricted their physical studies. Complexes are diamagnetic confirming Pd(II), low spin complexes. From experimental data CHN, molecular weight & Pd analysis by Voldar's method confirm the presence of dinuclear complex. It can be concluded that the dinuclear complexes [Pd₂LCl₄], (L=L1 or L2), there are two possible structures: (i) in which the two Pd atoms are in *cis* with respect to the C—C single bond of diacetyldihydrazone or C—C single bond of ethylenediamine for L1 and L2 respectively Figure 2 (ii) where the two Pd atoms are in *trans* with respect to the C—C single bond of diacetyldihydrazone or C—C single bond of ethylenediamine for L1 and L2 respectively Figure 3. Here, we prefer the structures where two Pd atoms are in *trans* with respect to the C—C single bond, since a *cis* structure will lead to a steric hindrance around the two Pd atoms.

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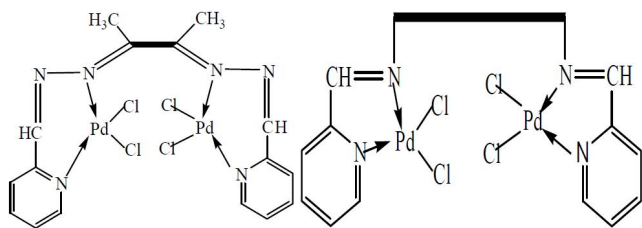


Figure 2 : Structure of $[Pd_2LCl_4]$, (L=L1 or L2), where two Pd (II) atoms are *cis* with respect to C—C bond

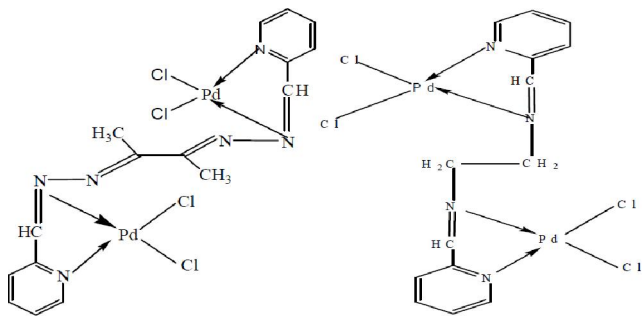


Figure 3 : Structure of $[Pd_2LCl_4]$, (L=L1 or L2), where two Pd (II) atoms are *trans* with respect to C—C bond

CONCLUSION

The complexes of Pd(II) with organic ligands enjoy global interest in scientific community due to their potential pharmacological activities. In this work, we have successfully synthesized the mixed chlorocomplex of Pd(II) using N-donor tetradentate ligands N1,N2-bis-(2-pyridinylmethylene)-1,4-diacetyldihydiimine(L1) and N1,N2-bis-(2-pyridinyl-methylene)-1,2-ethylenediimine(L2). Both the complexes have been characterized with various physico-chemical and spectroscopic techniques.

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