

Synthesis and Characterization of Complexes of Pd(II) and Pt(II) with Steryl Derivatives of 2-Alkylbenzimidazole

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Dichloro and dithiocyanato complexes of Pd(II) and Pt(II) with steryl derivatives of 2-alkyl benzimidazole (L) of composition PdLX₂ (L = Bzmb1, Bzebl, Bzprbl and Bzpmbl X= Cl⁻ or NCS⁻) and PtL₂X₂ (X= Cl⁻ or SCN⁻ and L = Bzmb1, Bzebl, Bzprbl or Bzpmbl) where Bzmb1 = 1-(1*H*-benzimidazol-2-yl)methylbenzylidene, Bzebl = 1-(1*H*-benzimidazol-2-yl)ethylbenzylidene, Bzprbl = 1-(1*H*-benzimidazol-2-yl)propylbenzylidene, bzpmbl = 1-(1*H*-benzimidazol-2-yl)phenyl-1-methylbenzylidene have been synthesized and characterized by electrical conductance, UV and infrared spectral studies. The IR spectral studies of PdLCl₂ complexes showed shifting of steryl group $\nu(\text{CH}=\text{CH})$ vibrations to lower frequencies indicating involvement of HC=CH double bond to Pd(II). The UV and magnetic moment value of Pd(II) and Pt(II) complexes are consistent with square planar structure.

Keywords: Palladium(II), Platinum(II), Benzimidazolylsteryl complexes.

INTRODUCTION

Metal complexes based on flexible *bis*(imidazole) and *bis*(triazole) ligands containing different functional groups has been characterized crystallographically [1,2]. However, *bis*-(benzimidazole) ligands, a class of aromatic N-donor organic linkers, exhibited important physiological and pharmacological activity due to the presence of substitutions at the 1, 2 and 5 positions [3,4] and also some applications are found in the treatment of several diseases including epilepsy, diabetes and infertility [5,6]. The metal complexes of benzimidazole derivatives have been studied extensively [7-12]. From the literature survey, it is found that complexes of Pd(II) and Pt(II) with steryl derivatives of 2-alkylbenzimidazoles have little been studied [13]. The benzimidazole derivatives have immense medicinal utility [6] which aroused interest towards the studies of their metal complexes.

In present paper, we reported the synthesis and characterization of the complexes of Pd(II) and Pt(II) with four steryl derivatives of alkyl benzimidazoles namely 1-(1*H*-benzimidazol-2-yl)methylbenzylidene (Bzmb1), 1-(1*H*-benzimidazol-2-yl)ethylbenzylidene (Bzebl), 1-(1*H*-benzimidazol-2-yl)-1-phenylmethylbenzylidene (Bzpmbl) and 1-(1*H*-benzimidazol-2-yl)propylbenzylidene (Bzprbl) (Fig. 1). These ligands coordinated with Pd(II) and Pt(II) as potent nitrogen donor ligand. In some cases, it appears that steryl double bond (-C=CH) is also involved in bonding with Pd(II).

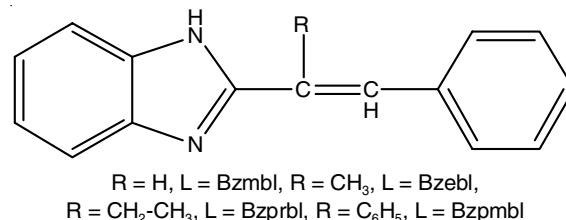


Fig. 1. Structure of steryl derivatives of alkyl benzimidazole ligand

EXPERIMENTAL

The stock solutions of PdCl₂ and PtCl₂ were prepared by dissolving 1 g of palladium(II) chloride in 10 mL hot water containing 1 mL (4 N) HCl. The clear solution was diluted with ethyl alcohol to 50 mL to get millimolar solution of PdCl₂. Platinum (II) chloride (1 g) was dissolved in 40 mL aqueous ethanol to get 1 mmol stock solution.

Synthesis of [PdLCl₂] (L = Bzmb1, Bzebl, Bzpmbl or Bzprbl): About 5 mmol of ethanolic solution of the corresponding ligand (10 mL) was taken in a round bottom flask and treated with 5 mmol of palladium(II) chloride solution and heated on a steam bath for 0.5 h and concentrated to half of its bulk when brownish yellow precipitate separated. The product was filtered, washed with cold ethanol and dried in a desiccator over CaCl₂.

Synthesis of [PdL(NCS)₂]: About 0.05 g of synthesized PdLCl₂ was suspended in 20 mL ethanol and treated with 0.1 g of potassium thiocyanate and refluxed on a steam bath for 1 h when orange yellow solution was formed. The solution was concentrated to 5 mL till orange yellow dithiocyanato complex separated. The product was filtered, washed with few drops of water to remove separated KCl and excess of KCNS. The residue was finally washed with aqueous ethanol and dried over CaCl₂.

Synthesis of PdL₂Cl₂ (L = Bzmb1, Bzebl and Bzprbl): About 10 mmol of ethanolic solution of the corresponding ligand was treated with 5 mmol solution of Pd (II) chloride and stirred for a few min when cream yellow product separated on concentration. The products were collected on a filter washed with cold aqueous ethanol and dried over CaCl₂ in a desiccator.

Synthesis of [PtL₂X₂] (X = Cl⁻ or SCN⁻ and L = Bzmb1, Bzebl, Bzprbl and Bzprbl): About 10 mmol of appropriate ligand was dissolved in 20 mL hot ethanol and treated with 5 mmol of platinum(II) chloride solution taken from stock solution. The mixed solution was refluxed on a steam bath in flask to get orange yellow solution. The resulting solution on concentration yielded cream yellow product. The product was filtered, washed with aqueous ethanol and dried in a desiccator over CaCl₂. The complex PtL₂(SCN)₂ were prepared by metathesis reaction with PtL₂Cl₂ and KCNS.

The electronic absorption spectra of complexes were determined in the range 200-650 nm and electronic absorption band positions of ligands and thier complexes are shown in Table-B. The I.R spectra of complexes were recorded as KBr disc in the range 4000-400 cm⁻¹ and the prominent IR bands of some complexes are given in Table-3.

RESULTS AND DISCUSSION

The analytical data of the synthesized complexes of Pd(II) and Pt(II) of substituted steryl benzimidazoles are given in Table-1.

The steryl derivatives of 2-alkylbenzimidazole (L) form bis-ligated complexes PdL₂Cl₂, PtL₂Cl₂ as well as PdL₂(SCN)₂ mono-ligated dichloro or dithiocyanato complexes of composition PdLCl₂ and PdL(SCN)₂, (L = Bzmb1, Bzebl, Bzprbl or Bzprbl). The complexes dissolved slightly in ethanol and

methanol but sparingly soluble in dimethyl formamide. The diluted and freshly prepared DMF solution of complexes show low electrical conductance value (8-15 ohm⁻¹ mol⁻¹ cm²) at 300-310 °C. The low electrical conductance value of complexes suggested coordinated nature of chloride or thiocyanate group in complexes [14]. As expected, the complexes PdLX₂ (X = Cl⁻ or SCN⁻), PtL₂X₂ (X = Cl⁻ or NCS⁻) and PdL₂Cl₂ are diamagnetic and complexes possess four coordinated square planar structure [15,16]. However, Pt(II) monoligated complexes PtLX₂ could not be isolated.

The electronic absorption spectra of complexes were recorded in ethanol in the range 200-650 nm and prominent band positions are shown in Table-2. In ultraviolet region these ligands show two bands near 212 and 268 nm for Bzmb1 and these are assigned as $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transition. These transitions are observed in other steryl derivatives between 205-214 nm and 265-272 nm. The $\pi \rightarrow \pi^*$ transition of ligand is shifted to lower wavenumber in complexes on complexation [17]. The complexes show strong absorption below 300-320 nm probably charge transfer transition [16,17]. Palladium(II) and platinum(II) have *nd*⁸ electronic system and in planar complexes with *dsp*² hybrid bonding which generates ¹A_{1g} as the ground state. The Pt(II) and Pd(II) complexes in planar field can show ¹A_{1g} $\rightarrow$ ¹B_{1g}, ¹A_{1g} $\rightarrow$ ¹A_{2g} transition in visible region and other transition will shift to ultraviolet region. The Pd(II) complexes show a medium band in the region 445-455 nm (Table-2) assigned as ¹A_{1g} $\rightarrow$ ¹A_{2g} transition in square planar field. Platinum (II) complexes show ligand field transition in ultraviolet region. The electronic absorption band near 285-290 nm for Pt(II) complexes is assigned to $\pi \rightarrow \pi^*$ transition. The complexes [Pt(Bzmb1)₂Cl₂] shows a medium band in visible at 415 nm and Pt(Bzebl)₂Cl₂ display a shoulder at 421 nm (Table-2) assigned as ¹A_{1g} $\rightarrow$ ¹A_{2g} transition in four coordinated square planar field [17].

The IR spectra of steryl derivatives and their Pd(II) and Pt(II) complexes showed a characteristic IR vibration of steryl bond (HC=CH) stretching vibrations in the range 1658-1624 cm⁻¹ in free ligands and their complexes PdLCl₂ and PtL₂Cl₂. The ligand [(1*H*-benzimidazol-2-yl)methylbenzylidene] shows benzimidazole ring NH stretch at 3197 cm⁻¹ and phenyl ring ν (C-H) and steryl group ν (C-H) between 3120-2973 cm⁻¹ and

TABLE-1
ANALYTICAL DATA OF Pd(II) AND Pt(II) COMPLEXES OF SUBSTITUTED STERYL BENZIMIDAZOLE

Complexes	Elemental analysis (%): Found (calcd.)					Ω^{-1} molar conductance
	M	N	C	H	Cl	
[Pd(Bzmb1)Cl ₂]	26.61 (26.80)	6.89 (7.04)	45.13 (45.29)	3.21 (3.02)	17.71 (17.87)	10
[Pd(Bzmb1)(NCS) ₂]	23.91 (24.05)	12.73 (12.66)	46.21 (46.11)	3.10 (2.71)	—	7
[Pd(Bzebl)Cl ₂]	25.71 (25.86)	6.51 (6.81)	46.51 (46.67)	3.45 (3.40)	17.31 (17.26)	8
[Pd(Bzebl)(NCS) ₂]	23.11 (23.31)	12.01 (12.27)	47.21 (47.33)	3.21 (3.07)	—	10
[Pd(Bzprbl)Cl ₂]	22.19 (22.45)	5.79 (5.91)	53.13 (53.23)	3.41 (3.38)	14.69 (14.98)	9
[Pd(Bzprbl)(NCS) ₂]	20.41 (20.52)	10.92 (10.80)	53.13 (53.24)	3.12 (3.09)	—	6
[Pd(Bzprbl)(NCS) ₂]	22.74 (22.62)	11.79 (11.90)	48.31 (48.47)	3.51 (3.40)	—	6
[Pd(Bzprbl)Cl ₂]	25.11 (25.01)	6.51 (6.58)	47.79 (47.95)	3.81 (3.76)	16.73 (16.69)	14
[Pt(Bzmb1) ₂ Cl ₂]	27.53 (27.62)	7.88 (7.93)	50.83 (50.99)	3.51 (3.40)	10.11 (10.06)	15
[Pt(Bzebl) ₂ Cl ₂]	26.41 (26.57)	7.49 (7.63)	52.37 (52.32)	3.92 (3.81)	9.78 (9.67)	12
[Pt(Bzprbl) ₂ Cl ₂]	22.81 (22.73)	16.59 (16.53)	58.63 (58.74)	3.89 (3.73)	8.11 (8.27)	11
[Pt(Bzprbl) ₂ Cl ₂]	25.41 (25.59)	7.46 (7.35)	53.31 (53.54)	4.10 (4.20)	9.41 (9.32)	12
[Pt(Bzmb1) ₂ (NCS) ₂]	25.83 (26.01)	11.01 (11.18)	50.91 (51.13)	3.31 (3.19)	—	13
[Pt(Bzebl) ₂ (NCS) ₂]	25.01 (25.08)	10.61 (10.78)	51.84 (52.37)	3.68 (3.59)	—	10

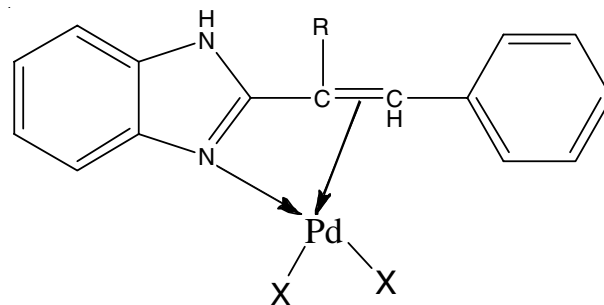
TABLE-2
ELECTRONIC ABSORPTION BAND POSITION OF
LIGAND AND SOME COMPLEXES (nm)

Compound	Electronic band position and assignment
BzmbI	212 ($\sigma \rightarrow \sigma^*$), 268 ($\pi \rightarrow \pi^*$)
Bzebl	214 ($\sigma \rightarrow \sigma^*$), 268 ($\pi \rightarrow \pi^*$)
Bzpmbl	205 ($\sigma \rightarrow \sigma^*$), 212 ($\sigma \rightarrow \pi^*$), 265 ($\pi \rightarrow \pi^*$)
BzprmbI	208 ($\sigma \rightarrow \pi^*$), 215 ($\sigma \rightarrow \pi^*$), 272 ($\pi \rightarrow \pi^*$)
Pd(BzmbI)Cl ₂	278 ($\pi \rightarrow \pi^*$), 450 ($A_{1g} \rightarrow A_{2g}$)
Pd(Bzebl)Cl ₂	240 ($\sigma \rightarrow \sigma^*$), 286 ($\pi \rightarrow \pi^*$), 440 ($A_{1g} \rightarrow A_{2g}$)
Pd(Bzpmbl)Cl ₂	225 ($\sigma \rightarrow \sigma^*$), 275 ($\pi \rightarrow \pi^*$), 455 ($A_{1g} \rightarrow A_{2g}$)
Pd(BzmbI)(NCS) ₂	215 ($\sigma \rightarrow \sigma^*$), 280 ($\pi \rightarrow \pi^*$), 445 ($A_{1g} \rightarrow A_{2g}$)
Pd(Bzebl)(NCS) ₂	216 ($\sigma \rightarrow \sigma^*$), 285 ($\pi \rightarrow \pi^*$), 450 ($A_{1g} \rightarrow A_{2g}$)
Pt(BzmbI) ₂ Cl ₂	290 ($\pi \rightarrow \pi^*$), 415 ($A_{1g} \rightarrow A_{2g}$)
Pt(Bzebl) ₂ Cl ₂	275 ($\pi \rightarrow \pi^*$), 420 ($A_{1g} \rightarrow A_{2g}$)
Pd(BzmbI) ₂ Cl ₂	272 ($\pi \rightarrow \pi^*$), 430 ($A_{1g} \rightarrow A_{2g}$)
Pd(Bzebl) ₂ Cl ₂	282 ($\pi \rightarrow \pi^*$), 435 ($A_{1g} \rightarrow A_{2g}$)

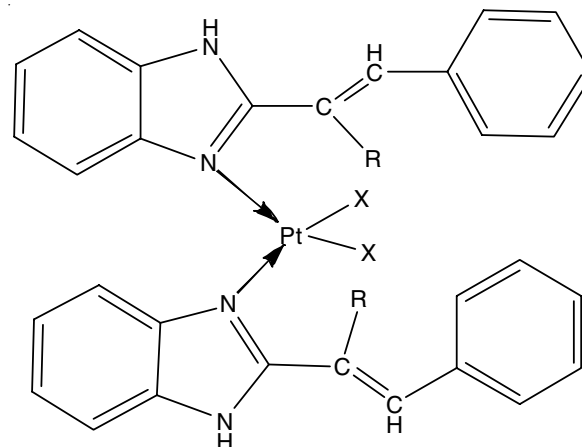
these vibrations are retained with slight change in band positions and intensity in complexes. The $\nu(C=C)$ stretching band was observed at 1642 cm^{-1} which is retained in Pt(II) complexes PtL_2Cl_2 but shifted to lower frequency by $20\text{--}30\text{ cm}^{-1}$ in $PdLCl_2$ suggesting involvement of $C=C$ double bond in coordinate bond formation. The $\nu(C=N)$ of benzimidazole ring was located at 1595 cm^{-1} is shifted by $15\text{--}10\text{ cm}^{-1}$ to lower frequency in complexes, supporting coordination of benzimidazole pyridine nitrogen in bond formation. The benzimidazole (NH) bending band is observed at 1520 cm^{-1} which is retained in almost all complexes indicating that it is not the bonding site of ligand in Pd(II) or Pt(II) complexes. The (CH) out of plane bending band of 2-steryl benzimidazole is located at 745 cm^{-1} as strong band in free ligand and in metal complexes [18]. The key IR bands of different steryl derivatives and their representative complexes are given in Table-3.

The IR spectrum of benzyldiene derivative of 2-ethylbenzimidazole (Bzebl) shows $\nu(NH)$ benzimidazole ring at 3215 cm^{-1} and (C-H) stretch of steryl group at 3135 cm^{-1} and these vibrations are retained in complexes. The $\nu(C=C)$ vibration of steryl group was located at 1652 cm^{-1} and $\nu(C=N)$ at 1605 cm^{-1} . The $\nu(C=C)$ and $\nu(C=N)$ of ligand shifted to lower frequency in $PdLCl_2$ indicating the coordination of both (C=C) π electrons and (C=N) nitrogen with palladium(II). The $\nu(C=N)$ of ligands are shifted to lower wave number in bisligated complexes PdL_2Cl_2 and PtL_2Cl_2 , but steryl ($-C=C$) stretch remains unaffected sugges-

ting monodentate bonding through (C=N) nitrogen of ligand [19]. The free ligand and its complexes show a number of IR bands in finger print region due to various mode of IR vibration of phenyl and benzimidazole ring. The thiocyanato complex $Pd(BzmbI)(SCN)_2$ shows a sharp and strong band at 2105 cm^{-1} due to $\nu(C=N)$ and a medium $\nu(C=S)$ vibration at 725 cm^{-1} indicating coordination of thiocyanate group through sulphur atom in dithiocyanato complexes [18]. Thus, from IR spectra, it is concluded that in $PdLCl_2$ type of complexes, steryl group double bond ($CH=CH-C_6H_5$) appears to be coordinated and the ligand is bidentate in which and second donor site is benzimidazole ring pyridine nitrogen. In case of PtL_2Cl_2 , the ligands are N donor mono-coordinated unidentate molecule. The probable structures of complexes are shown below:



Structure of $PdLX_2$ ($X = Cl^-$ or SCN^-) ($R = H, -CH_3, -CH_2-CH_3$ and C_6H_5)



Structure of PtL_2X_2 ($X = Cl^-$ or SCN^-) ($R = H, -CH_3, -CH_2-CH_3$ and C_6H_5)

TABLE-3
KEY IR BANDS (cm^{-1}) OF Pd(II) AND Pt(II) COMPLEXES OF SUBSTITUTED STERYL BENZIMIDAZOLE

Compound	$\nu(NH)$	$\nu(C-H)$	$\nu(C=C)$ steryl	$\nu(C=N)$	$\delta(N-H)$	Out-of-plane (C-H) phenyl	Ring deformation
BzmbI	3197	3120	1642	1595	1520	745	680, 540
Pd(BzmbI)Cl ₂	3220	3156	1626	1590	1520	742	670, 526
Pt(BzmbI) ₂ Cl ₂	3207	3150	1643	1590	1504	748	665, 527
Bzprbl	3312	3170	1658	1605	1512	738	692, 518
Pd(Bzprbl)Cl ₂	3300	3168	1630	1590	1508	738	691, 525
Pt(Bzprbl) ₂ Cl ₂	3290	3150	1655	1595	1507	742	685, 525
Bzpmbl	3245	3140	1655	1605	1498	748	668, 527
Pd(Bzpmbl)Cl ₂	3240	3130	1621	1592	1488	745	670, 527
Pt(Bzpmbl) ₂ Cl ₂	3247	3150	1653	1585	1490	742	670, 527
Bzebl	3272	3162	1662	1610	1507	738	675, 538
Pd(Bzebl)Cl ₂	3268	3152	1628	1590	1512	735	670, 530
Pt(Bzebl) ₂ Cl ₂	3270	3148	1665	1595	1510	740	672, 540

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