

SYNTHESIS AND CHARACTERIZATION OF NEW  
PALLADIUM (II) AND PLATINUM(II) COMPLEXES  
CONTAINING 5-BUTYL-2,2'-BIPYRIDINE : XRAY CRYSTAL  
STRUCTURE OF BIS (3-METHYLPYRIDINE)-5- BUTYL-2,2'-  
BIPYRIDINE PALLADIUM (II) PERCHLORATE

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ABSTRACT

A series of new heteroleptic and homoleptic complexes of the type  $[M(5\text{-butbipy})Cl_2]$ ,  $[M(5\text{-butbipy})L_2]^{2+}$  and  $[M(5\text{-butbipy})_2]^{2+}$  ( $M = Pt(II)$  or  $Pd(II)$ , 5-butbipy = 5-butyl-2,2'-bipyridine.  $L =$  Pyridine or 3-methyl pyridine (3-picoline) were synthesized and characterized by  $^1H$ NMR and elemental analysis.

The crystal structure of bis(3-methyl pyridine)-5-butyl-2,2'-bipyridine palladium(II) perchlorate  $[Pd(5\text{-butbipy})(3\text{-pic})_2](ClO_4)_2$  was also determined by single crystal X-ray diffraction. The complex crystallized in the monoclinic crystal system and space group  $P2_1/c$  with  $a = 10.746(2)$ ,  $b = 17.569(6)$ ,  $c = 15.821(3)$  Å;  $\alpha = 90^\circ$ ,  $\beta = 97.38(2)^\circ$ ,  $\gamma = 90^\circ$  and  $z = 4$ .

The  $Pd(II)$  is in square planar environment and is coordinated by two *cis*-3-methyl pyridine ligands and a bidentate 5-butyl-2,2'-bipyridine ligand.

**Keywords:** 5-butyl-2,2'-bipyridine complexes, X-ray crystal structure.

1- INTRODUCTION

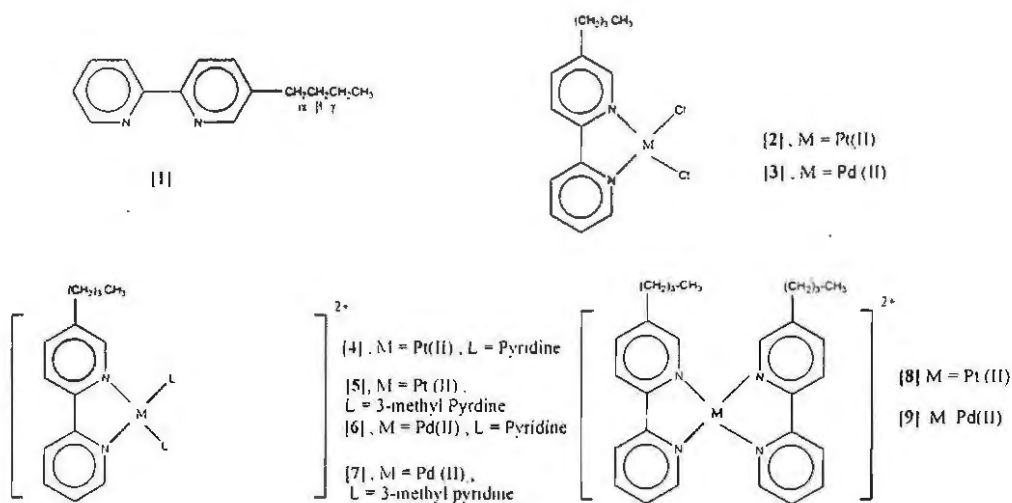
The growing number of studies on platinum(II) complexes is stimulated by their importance as antitumour chemotherapeutics, therefore since the discovery of the antitumour activity of *cis*-dichlorodiammineplatinum(II) [Rosenber et al., (1969)] efforts have

concentrated on the synthesis of new platinum (II) complexes, as well as those of palladium (II) which show antitumour activity [Hacker et al., (1984) and Nicolini et al., (1988)].

The coordination chemistry of platinum (II) and palladium (II) covers a huge field as shown by [Holloway & Melnik (2002, 2003, 2004 and 2005)] covering the crystallographic and structural data. However, the similarity of platinum (II) and palladium (II) is remarkable: for instance, they are both regarded as class b. or soft metals and this is reflected in their rich chemistry not only with soft bases such as sulfur and phosphorous but even with some hard ligands such as oxygen and nitrogen. The similarity extends even to sizes and bond lengths, thus the M-Cl bond in  $K_2[MCl_4]$  is  $2.318\text{\AA}$  for  $M = pd$  and  $2.316\text{\AA}$  for  $M = pt$  [Belluco (1973)].

The kinetic inertness of platinum (II) and palladium (II) complexes [Milink & Holloway (2006)] has allowed their extensive use in the characterization of geometrical isomerism and reaction mechanistic.

In view of the above, we have focused on the synthesis and characterization of a new series of Pt(II) and Pd(II) complexes with 5-butyl-2,2'-bipyridine[I] moiety along with the crystal structure analysis of  $[Pd(5\text{-butbipy})(3\text{-Pic})_2](ClO_4)_2$  [7]



## 2. EXPERIMENTAL

### 2.1: General

Proton nuclear magnetic resonance spectra were recorded on a Bruker WM 360(360MHZ) Pulsed Fourier transform spectrometer. Chemical shifts are quoted relative to tetramethylsilane ( $\delta$ ). Electronic spectra were recorded on a Kontron-Unikon 930 UV/vis Spectrophotometer provided with thermostated cell chambers whereas, the microanalytical data were collected with a perkin-Elmer 240C° elemental analyzer.

### 2.2: Syntheses

#### 2.2.1 5-Butyl-2,2'-bipyridine [1]

This compound [1] was prepared by dissolving the salt 1(2-acetylpyridine) pyridinium iodide [10] (8.0 g, 24.5 mmol) in methanol (50 ml) under nitrogen and treating it with a stoichiometric amount of 2-n-butylacrolein (2-methylenehexanal) (2.75 g, 24.5 mmol) and an excess (20 g, 260 mmol) of ammonium acetate. The solution was heated at 40-50° for 24 hours, after which the methanol was removed. The residue was dissolved in water (25 ml) and extracted with diethyl ether (4x10 ml) followed by hexane (4x10 ml).

The combined organic extracts were washed with water until the water layer was colourless. The organic layer was then dried over magnesium sulfate, filtered and evaporated under nitrogen. The product [1] was then purified on a basic alumina column (22x1.5 cm) eluting with hexane/acetone (1:1), and eventually isolated as a thick yellowish liquid (2.2 g, 43% yield).

$^1\text{HNMR}(\text{CDCl}_3)$  ( $\delta$ ppm) 8.46(1H,d,J=4.7Hz,H6'); 8.32(1H,s,H6); 8.24(1H,d,J=7.9Hz,H3'); 8.17(1H,d,J=8.1Hz,H3); 7.53(1H,dd,J=7.7,7.7Hz,H4'); 7.36(1H,d,8.1Hz,H4); 7.00(1H,dd,J=5.8,6.4Hz,H5'); 2.39(2H,t,J=7.6,7.7 Hz,  $\alpha$ -CH<sub>2</sub>); 1.38(2H, $\beta$ -CH<sub>2</sub>); 1.14(2H,m, $\gamma$ -CH<sub>2</sub>); 0.71(3H,t,J=7.3, 7.3 Hz,CH<sub>3</sub>).

#### 2.2.2 Dichloro-5-butyl-2,2'-bipyridineplatinum(II) [Pt(5-butbipy)Cl<sub>2</sub>][2]

A solution of 5-butyl-2,2'-bipyridine [1] (0.52 g, 2.4 mmol) in dilute hydrochloric acid (5ml, 1M) was added dropwise to a stirred

solution of potassium tetrachloroplatinate(II) (1.0 g, 2.4 mmol). This reaction mixture was heated ( $\approx 80\text{ C}^\circ$ ) for 20 minutes to give [Pt(5-butbipy)Cl<sub>2</sub>] [2] as an orange precipitate in 95% yield (1.1 g). The precipitate was recrystallized from acetone as a yellow solid.

<sup>1</sup>HNMR(DMSO-d<sub>6</sub>) ( $\delta_{ppm}$ ) 9.45(1H,d,J=5.8Hz,H 6'); 9.30(1H,s,H6);8.52 (1H,d,J=8.1 Hz,H 3'); 8.46(1H, d, J=8.4Hz,H<sub>3</sub>); 8.39(1H,dd,J=7.7, 7.9Hz, H 4');8.30(1H,d,8.3Hz,H4);7.81(1H,dd,J=6.0,6.1Hz,H<sub>2</sub>,H5')2.80(2H,t,J=7.7,7.6Hz, $\alpha$ -CH<sub>2</sub>);1.62(2H,m,J=7.5,7.0Hz,  $\beta$ -CH<sub>2</sub>);1.35 (2H,m,J=7.8, 7.4 H  $\gamma$ -CH<sub>2</sub>);0.93 (3H, t, J=7.2, 7.4Hz,CH<sub>3</sub>).

Calc. for C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> C <sub>12</sub> Pt	C=35.15	H=3.35	N=5.86
Found	C=35.0	H=3.4	N=6.0

### 2.2.3 Bis(pyridine)(5-butyl-2,2'- bipyridine) platinum (II) perchlorate [Pt(5-butbipy)(py)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> [4]

A solution of [Pt(5-butbipy)Cl<sub>2</sub>] [2] (0.10 g, 0.21 mmol) in water (10 ml) was set to reflux in the presence of pyridine (2 ml) for about 20 minutes. The resulting yellow solution was filtered and then treated with aqueous sodium perchlorate. The colourless precipitate which immediately formed was collected by filtration, washed with water, ethanol and dried in a vacuum to give [Pt(5-butbipy)(py)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> [4] in 41% yield (0.06 g)

<sup>1</sup>HNMR (DMSO-d<sub>6</sub>) ( $\delta_{ppm}$ ) 9.19 (4H,d, J=6.3Hz, Ho-py); 8.77, J = 9.1, 8.7Hz, H<sub>3</sub>, H<sub>3'</sub>); 8.55 (1H,ddd,J=5.4, 3.9, 4.5 Hz,H 4'); 8.47(1H,2H,dd, J=8.3Hz,H<sub>4</sub>); 8.25(2H,dd,J=8.6, 8.9Hz, H $\rho$ -py); 7.83 (4H,dd, J=6.8, 7.1Hz,H $m$ -py);7.75(2H,d,J=4.2,H 6', H5'); 7.47(1H,s,H6);2.67(2H,t,7.4, 7.6 Hz, $\alpha$ -CH<sub>2</sub>);1.48 (2H,m  $\beta$ -CH<sub>2</sub>);1.23 (2H, m,  $\gamma$ -CH<sub>2</sub>);0.85 (3H, t, J=7.2, 7.4Hz,CH<sub>3</sub>).

Calc. for C <sub>24</sub> H <sub>26</sub> N <sub>4</sub> Cl <sub>2</sub> O <sub>8</sub> Pt	C = 37.71	H = 3.34	N = 7.33
Found	C = 37.6	H = 3.4	N = 7.5%

### 2.2.4 Bis(5-butyl-2,2'- bipyridine) platinum(II) perchlorate [Pt(5-butbipy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> [8]

A solution of 5-butyl-2,2'-bipyridine [1] (0.20 g, 0.94 mmol) in ethanol (5 ml) was added dropwise to a stirred hot solution of [Pt(5-

butbipy)Cl<sub>2</sub>] [2] (0.20 g, 0.42 mmol) in water (100 ml). The mixture was set to reflux for three hours, until most of the complex [8] dissolved. The solution was allowed to cool then treated with a saturated solution of sodium perchlorate. The resulting yellow solution was filtered then evaporated ( $\approx 20$  ml). The precipitate was collected by filtration, washed with water, ethanol and acetone to give [Pt(5-butbity)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> [8] (0.22 g, 66% yield).

<sup>1</sup>HNMR (DMSO-d<sub>6</sub>) ( $\delta$ ppm) 9.09 (2H, dd, H6'(1), H6'(2)) 8.91, (2H, s, H6(1), H6(2)); 8.81 (2H, dd, J=8.0 Hz, H3'(1), H3'(2)); 8.76 (2H, d, J=8.3 Hz, H3(1), H3(2)); 8.63 [2H, dd, J, 7.8, 8.3, H4'(1), H4'(2)]; 8.54 [2H, d, J=8.3 Hz, H4(1), H4(2)]; 8.03 (2H, dd, J=5.3, 5.3 Hz, H5'(1), H5'(2)); 2.90 (4H, t, J=6.7, 7.5 Hz,  $\alpha$ -CH<sub>2</sub>); 1.72 (4H, d, 6.8 Hz,  $\beta$ -CH<sub>2</sub>); 1.41 (4H, dd, J=7.0, 6.8 Hz,  $\gamma$ -CH<sub>2</sub>); 0.95 (6H, t, J=7.2, 7.4 Hz, CH<sub>3</sub>).

Calc. for C <sub>28</sub> H <sub>32</sub> N <sub>4</sub> Cl <sub>2</sub> O <sub>8</sub> Pt	C = 41.08	H = 3.94	N = 6.83
Found.	C = 41.0	H = 4.2	N = 7.1%

### 2.2.5 Dichloro - 5 - butyl - 2,2' - bipyridine palladium (II) [Pd (5-butbipy) Cl<sub>2</sub>] [3]

A solution of 5-butyl-2,2'-bipyridine [1] (0.65 g, 3.1 mmol) in dilute hydrochloric acid (5 ml, 1M), was added dropwise to a stirred solution of potassium tetrachloropalladate (1.0 g, 3.1 mmol). The mixture was heated for about 20 minutes to give [Pd(5-butbipy) Cl<sub>2</sub>] [3] as a yellow precipitate in 79% yield (0.95 g).

Calc. for C <sub>14</sub> H <sub>16</sub> N <sub>2</sub> Cl <sub>2</sub> Pd	C = 43.11	H = 4.11	N = 7.18
Found	C = 43.4	H = 4.2	N = 7.3%

### 2.2.6 Bis(pyridine) (5-butyl-2,2'-bipyridine) palladium(II) perchlorate [Pd (5-butbipy) (py)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> [6]

A solution of [Pd(5-butbipy) Cl<sub>2</sub>] [3] (0.10 g, 0.26 mmol) in water (10 ml) was heated in the presence of pyridine (2 ml) for about 10 minutes. The resulting yellow solution was filtered, cooled and then treated with aqueous sodium perchlorate (0.1 g). The white precipitate which immediately formed was collected by filtration and recrystallized from hot water to give [Pd(5-butbipy) (py)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> [6] in 57% yield (0.10 g).

$^1\text{H}$ NMR (DMSO- $d_6$ ) ( $\delta$ ppm) 9.24(4H, d,  $J = 5.1, 4\text{Ho} - \text{py}$ ); 8.74 (2H, dd,  $J = 8.3, 8.5\text{Hz}$ , overlapped,  $H3'$  and  $H3$ ); 8.49(1H, dd,  $J = 7.8, 7.8\text{Hz}$ ,  $H4'$ ); 8.41 (1H, d,  $J = 8.3\text{Hz}$ ,  $H4$ ); 8.23(2H, dd, br. S,  $2\text{Hp} - \text{py}$ ); 7.84 (4H, dd,  $J = 6.1, 5.9\text{Hz}$ ,  $4\text{xHm} - \text{py}$ ); 7.70 (1H, dd,  $J = 6.1, 6.6\text{Hz}$ ,  $H5'$ ); 7.42(1H, d,  $J = 5.5\text{Hz}$ ,  $H6'$ ); 7.15 (1H, s,  $H6$ ); 2.63(2H, t,  $J = 7.4, 7.2\text{Hz}$ ,  $\alpha - \text{CH}_2$ ); 1.43[2H, m,  $J = 7.1, 7.3, 7.5\text{Hz}$ ,  $\beta - \text{CH}_2$ ]; 1.19 [2H, m,  $J = 7.5, 7.1, 7.2\text{Hz}$ ,  $\gamma - \text{CH}_2$ ]; 0.82[ 3H, t,  $J = 7.3, 7.1\text{Hz}$ ,  $\text{CH}_3$ ].

Calc. for $\text{C}_{24}\text{H}_{26}\text{N}_4\text{Cl}_2\text{O}_8\text{Pd}$	C = 42.65	H = 3.88	N = 8.29
Found	C = 42.4	H = 4.0	N = 8.5%

### 2.2.7 Bis(3-methylpyridine)(5-butyl-2,2'-bipyridine) palladium (II) Perchlorate [ $\text{Pd}(5\text{-butbipy})(3\text{-pic})_2(\text{ClO}_4)_2$ ] [7]

This compound [7] was prepared by a method similar to that used for [ $\text{Pd}(5\text{-butbipy})(\text{py})_2$ ] $^{2+}$  [6] except that 3-methylpyridine was used in place of pyridine. This product was recrystallized from a mixture of hot water (10 ml) and ethanol (5 ml), on standing for a few days at room temperature, the solution gave yellow crystals of [ $\text{Pd}(5\text{-butbipy})(3\text{-pic})_2$ ]( $\text{ClO}_4$ ) $_2$  [7] in 51% yield (0.09 g).

$^1\text{H}$ NMR (DMSO- $D_6$ ) ( $\delta$ ppm) 9.10(2H, s,  $\text{Ho}(1)3 - \text{pic}$ ); 9.04 (2H, d,  $J = 4.5, 2\text{Hz}$ ,  $\text{Ho}(2) - \text{pic}$ ); 8.68[2H, dd,  $J = 9.5, 9.1\text{Hz}$ , overlapped  $H3'$  and  $H3$ ]; 8.45(1H, dd,  $J = 7.8, 7.9\text{Hz}$ ,  $H4'$ ); 8.36 (1H, d,  $J = 8.3\text{Hz}$ ,  $H4$ ); 8.05(2H, dd,  $J = 6.7, 6.8\text{Hz}$ ,  $2\text{Hp}(3\text{-pic})$ ); 7.69 (3H, m, overlapping of  $\text{Hm}(3\text{-pic})$  and  $\text{H5}'(5\text{-butbipy})$ ); 7.36 (1H, d,  $J = 5.5\text{Hz}$ ,  $H6'$ ); 7.03(1H, d,  $H6$ ); 2.62 (2H, t,  $J = 7.2, 7.3\text{Hz}$ ,  $\alpha - \text{CH}_2$ ); 2.40[6H, s,  $2\text{xCH}_3 - 3\text{-pic}$ ]; 1.42[2H, m,  $J = 7.1, 7.4, 7.3\text{Hz}$ ,  $\beta - \text{CH}_2$ ]; 1.17 [2H, m,  $J = 7.3, 7.3, 7.2\text{Hz}$ ,  $\gamma - \text{CH}_2$ ]; 0.82[ 3H, t,  $J = 7.1, 7.3\text{Hz}$ ,  $\text{CH}_3 - 5\text{-butbipy}$ ].

Calc. for $\text{C}_{26}\text{H}_{30}\text{N}_4\text{Cl}_2\text{O}_8\text{Pd}$	C = 44.37	H = 4.30	N = 7.96
Found	C = 44.5	H = 4.5	N = 8.1%

### 2.2.8 Bis(5-butyl-2,2'-bipyridine)palladium(II) perchlorate [ $\text{Pd}(5\text{-butbipy})_2$ ]( $\text{ClO}_4$ ) $_2$ [9]

A solution of 5-butyl-2,2'-bipyridine [I] (0.28g, 1.32mmol) in ethanol (5ml) was added dropwise to a stirred solution of [ $\text{Pd}(5\text{-butbipy})\text{Cl}_2$ ] [3] (0.2g, 0.51mmol) in water (100ml). The mixture was set to reflux

until dissolution (1hour). The resulting yellow solution was filtered, cooled and then treated with aqueous solution of sodium perchlorate. The precipitate which immediately formed was collected by filtration, washed thoroughly with water and ethanol and then dried in vacuum. This was recrystallized twice from a mixture of warm water (10 ml) and ethanol (5 ml) and a few drops of dilute nitric acid. The mixture was left for a few days to give hair-like crystals of  $[\text{Pd}(5\text{-butbipy})_2](\text{ClO}_4)_2$  [9].

$^1\text{H}$ NMR (DMSO) - d6 ( $\delta$ ppm) 8.80 {2H,d,5.3Hz,H 6'(1),H 6'(1)}; 8.70 [2 H,d,J=7.7Hz, H 3'(1), H 3'(2)}; 8.66 [2H,d,J= 8.2Hz, H3(1), H3(2)]; 8.6 {2H.s.H6(1),H6(2)}; 8.53 [2H,dd,J=7.5,7.6Hz,H 4'(1),H 4'(2)}; 8.43 [2H. d. j=7.8Hz, 2H4(1), H4(2)]; 7.96 [2H,dd, J=6.2 . 6.3Hz, H 5'(1), H 5'(2)}; 2.87 [4H. t. J = 7.4, 7.7 Hz, 2x  $\alpha$ -CH<sub>2</sub>]; 1.68 [4H, m, J = 7.3, 7.5,7.3,7.9Hz,2x  $\beta$ -CH<sub>2</sub>]; 1.38 [4H,m,J=7.3,7.3,7.4Hz,2x  $\gamma$ -CH<sub>2</sub>]; 0.94 [6H. t. J= 7.3, 7.4, Hz, 2xCH<sub>3</sub>].

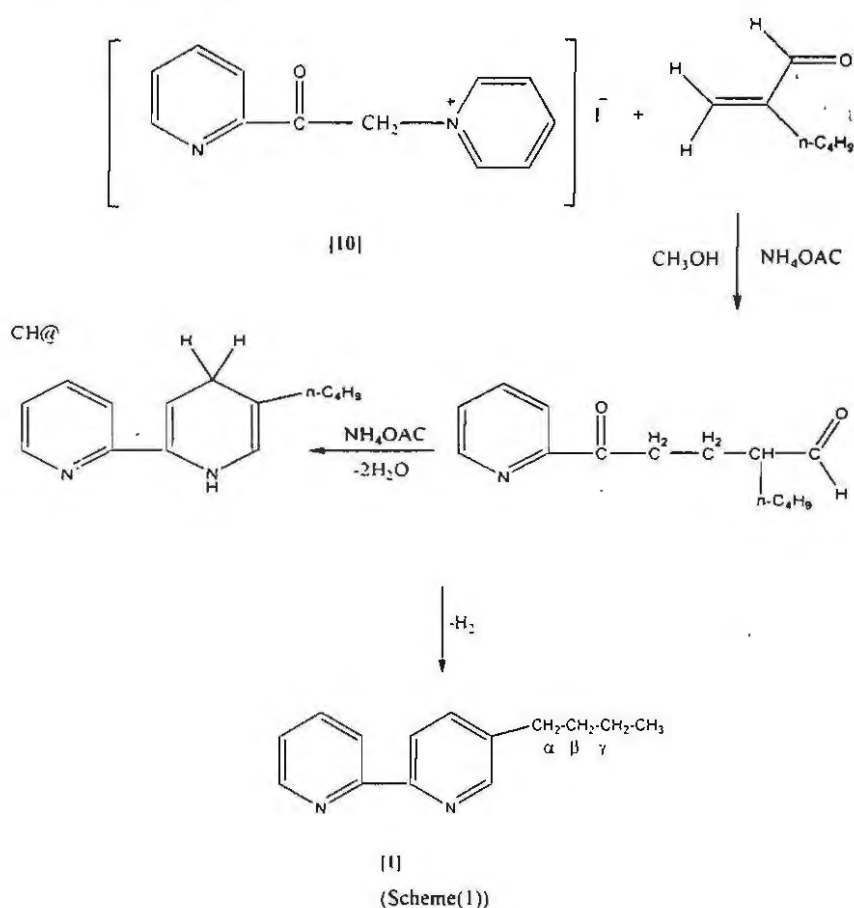
Calc. for C <sub>28</sub> H <sub>32</sub> N <sub>4</sub> Cl <sub>2</sub> O <sub>8</sub> Pd	C = 46.08	H = 4.38	N = 7.68
Found	C = 46.3	H = 4.4	N = 8.0%

### 3. RESULTS AND DISCUSSION

The ligand 5-butyl-2,2'-bipyridine[1] was deliberately designed and prepared in order to study the role played by the butyl group on the coordination geometry of both Pt(II) and Pd(II) complexes and also to investigate the possible existence of geometrical isomers (*cis* and *trans*) in case of bis (5-butbipy)<sub>2</sub>M<sup>2+</sup> (M=Pt(II) and Pd(II)).

Thus, the unsymmetrical ligand[1] was synthesized by cyclization technique. The synthesis was based on the following two steps. First, the formation of pyridinium salt [10], which was achieved according to the orteleva-king reaction [Krohnke (1963)], when one equivalent of 2-acetylpyridine reacts with a stoichiometric amount of iodine to give iodoacetylpyridine which then reacts with pyridine (also used as solvent) to give pyridinium salt [10] in reasonable yield(64%).

The 1-(2-acetylpyridinepyridinium iodide) salt [10] reacts with 2-n-butylacroleline (2-methylenehexanal) with excess of ammonium acetate in methanol as solvent [Weiss (1952) and Krohnke (1976)].



The reaction takes place rapidly under a nitrogen atmosphere to form, first the 1,5-diketone which then undergo ring closure in the presence of an excess of ammonium acetate to give the desired ligand 5-butyl-2,2'-bipyridine [1]

The complexes [Pt(5-butbipy)Cl<sub>2</sub>] [2] and [Pd(5-butbipy)Cl<sub>2</sub>] [3] were prepared when one equivalent of ligand[1] in dilute hydrochloric acid(1M) was heated with a stoichiometric amount of K<sub>2</sub>[PtCl<sub>4</sub>] and K<sub>2</sub>[PdCl<sub>4</sub>] respectively. However, the complexes [2] and [3] were obtained in a good yield and used as starting material for preparing the other complexes [4], [5], [6], [7], [8] and [9]. The perchlorate salt of



these complexes were recrystallized and isolated as shiny pale yellow crystals. These are described fully in the experimental section.

The  $^1\text{H}$ NMR spectrum (figure 1) of the complex  $[\text{Pt}(5\text{-butbipy})\text{Cl}_2]$  [2] showed clearly seven signals in the aromatic region due to resonance of unsymmetrical protons H6, H6', H3, H3'.....etc, and four signals in the aliphatic region due to resonance of butyl group .

The  $^1\text{H}$ NMR spectra of the complexes [4], [5], [6], and [7] in  $\text{DMSO-d}_6$  were assigned and the chemical shifts are summarized in table (1). Two sets of singles were observed for the inequivalent two halves of 2,2'-bipyridines due to the lack of symmetry : their H6, H6' protons are the most affected and shifted far towards H5, H5' compared with the dichloro - complexes and the free ligand . Their spectra showed also the split of unidentate ortho protons to two separate doublets of equal intensity.

This could be explained as one of the unidentate is trans to the substituted half of bidentate nitrogen and the other is trans to an unsubstituted half.

The bis complexes of 5-butyl-2,2'-bipyridine with platinum (II) [8] and palladium (II) [9] were prepared by refluxing the dichloro complexes [2] and [3] respectively in aqueous solutions with an excess of the ligand [1]. The complexes [8] and [9] were isolated from the solutions as hairy pale yellow crystals and then characterized by  $^1\text{H}$ NMR spectroscopy in order to investigate the possible existence of both geometrical isomers as a mixture . The low solubility of the above complexes (particularly as perchlorate salts) in  $\text{D}_2\text{O}$  and  $\text{CDCl}_3$  prevented measurement of  $^1\text{H}$ NMR spectra in these solvents. Therefore, these complexes [8] and [9] were measured in  $\text{DMSO-d}_6$  and clearly showed the same number of signals as their free ligand [1] but the chemical shifts of the complexes [8] and [9] appeared at lower field . This is presumably as a result of shielding of these protons by metal-nitrogen interaction (coordination effect).

The  $^1\text{H}$ NMR spectrum of the complex [9], (figure 2) showed no sign of the presence of both isomers as a mixture of *cis* and *trans*. However, as one isomer may have been isolated through crystallization, the second crop resulting from the filtrate of the first was also

characterized, and as a result showed no difference in chemical shifts from the original product.

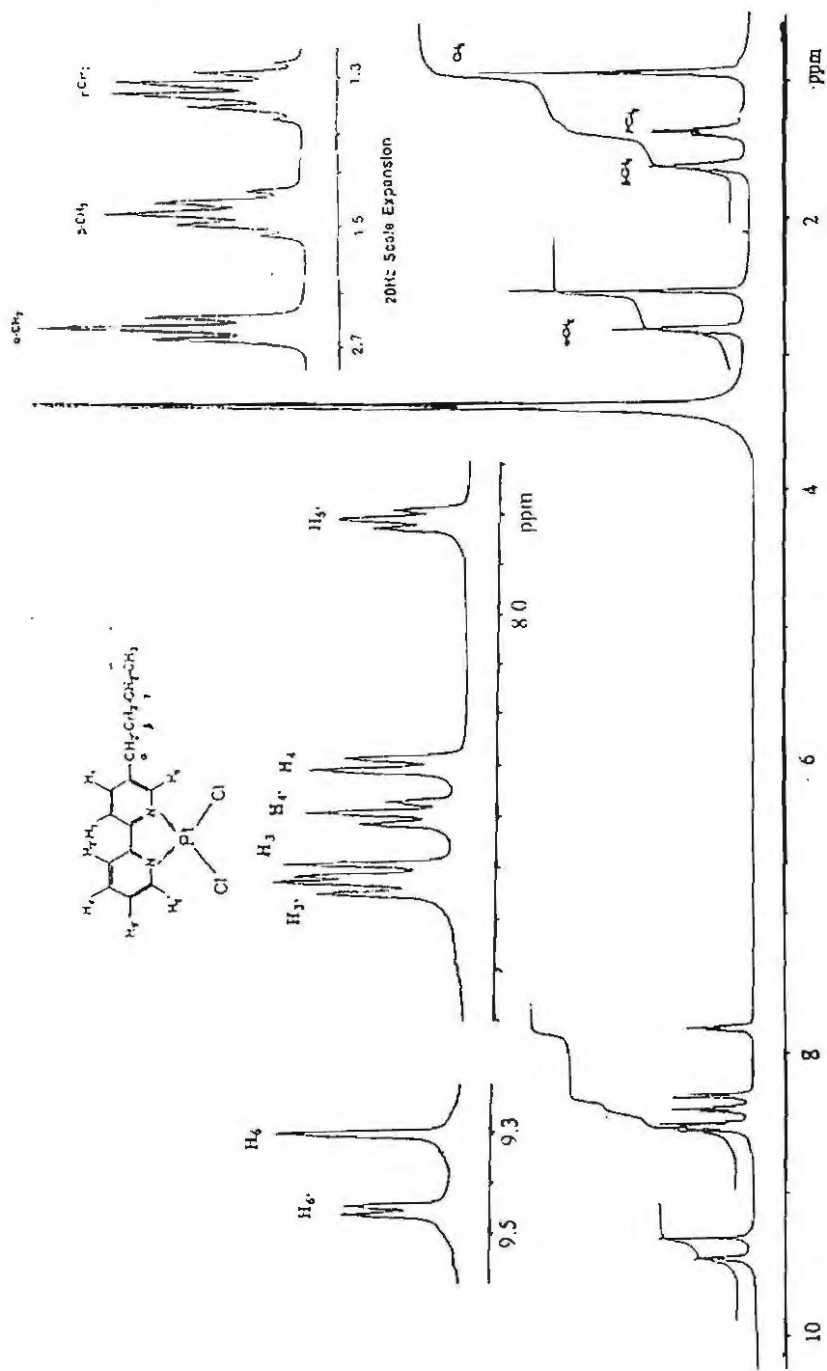
The electronic spectra of the complexes [8] and [9] were measured at different pH values (figure 3) and found to be strongly dependent on pH. The changes in wavelengths were relatively small, but internal transitions of the ligand showed changes in intensity from  $2.5 \times 10^4$  in neutral solutions to  $1.5 \times 10^4$  in alkaline solutions. The former extinction coefficients are of roughly the magnitude expected for a complex containing two substituted 5-butyl-2,2-bipyridine ligands per molecule, whereas the later value corresponds to one ligand per molecule. The observed spectral changes are analogous to those reported earlier for  $[\text{Pt}(\text{bipy})_2]^{2+}$  and  $[\text{Pt}(5,5\text{-dmbipy})_2]^{2+}$  [Gillard & Lyons (1973)] and [Gillard (1974)] interpreted the changes in the electronic spectra in terms of attack of the nucleophile adjacent to the nitrogen donor atom of the ligand.

In contrast, other workers [Nord (1975) and Wernberg (1986)] interpreted these changes in terms of a five or six coordinated intermediate.

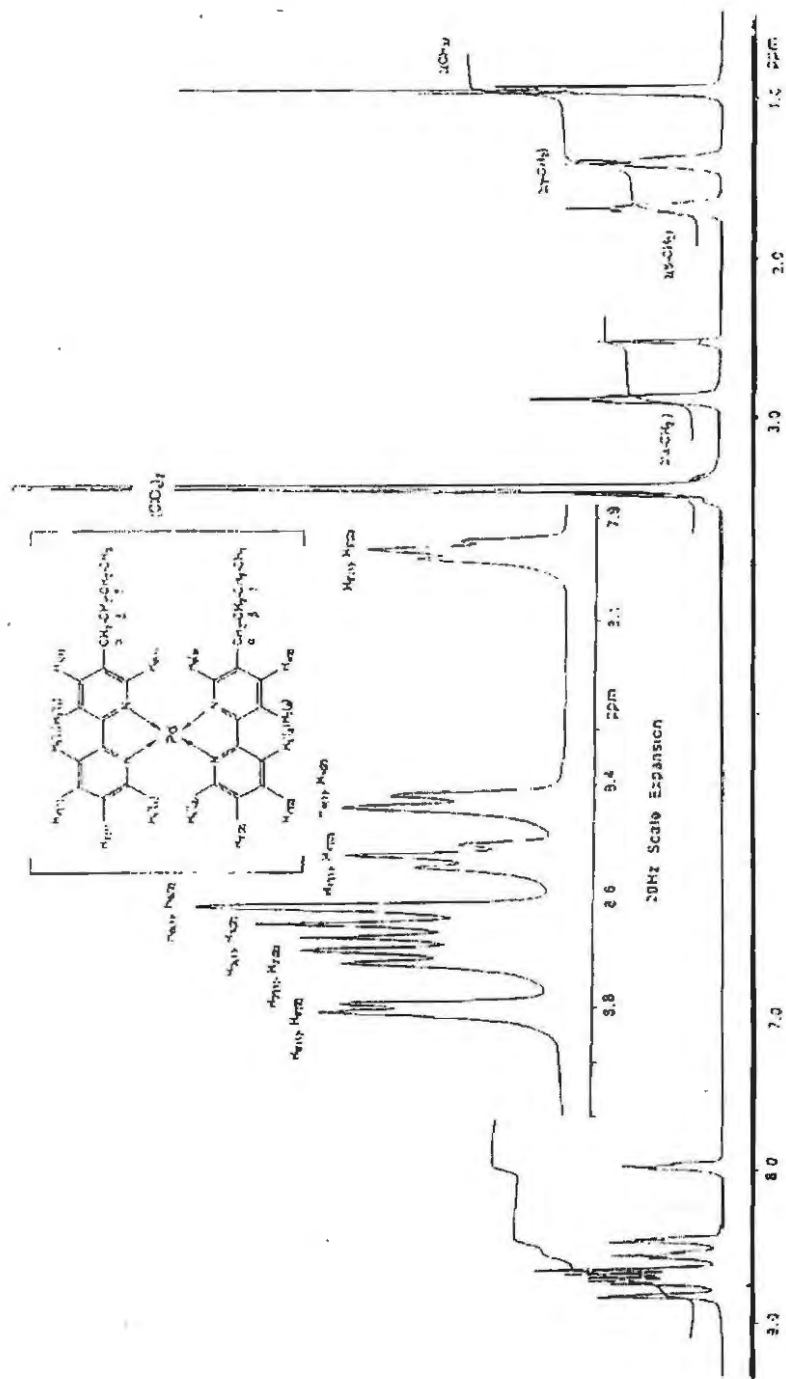
The single crystal X-ray structure determination of  $[\text{Pd}(5\text{-butbipy})(3\text{-pic})_2](\text{ClO}_4)_2$  [7] revealed that the palladium is coordinated to one unsymmetrical 5-butyl-2,2-bipyridine[1] and to two molecules of 3-methyl pyridine (3-Picoline) through their nitrogens roughly in a regular square planer geometry. A View of the complex [7] (figure 4) shows the disposition of the ligands and the chain of the n-butyl group attached to C(5). The average Pd-N distance is  $2.02 \text{ \AA}$ , and The planes of the two unidentate ligands lie perpendicular to the plane defined by the palladium and substituted bidentate.

One of the most interesting features of this structure is that one of the methyl groups in the unidentate ligands is above while the other is below the coordination plane (PdN4)

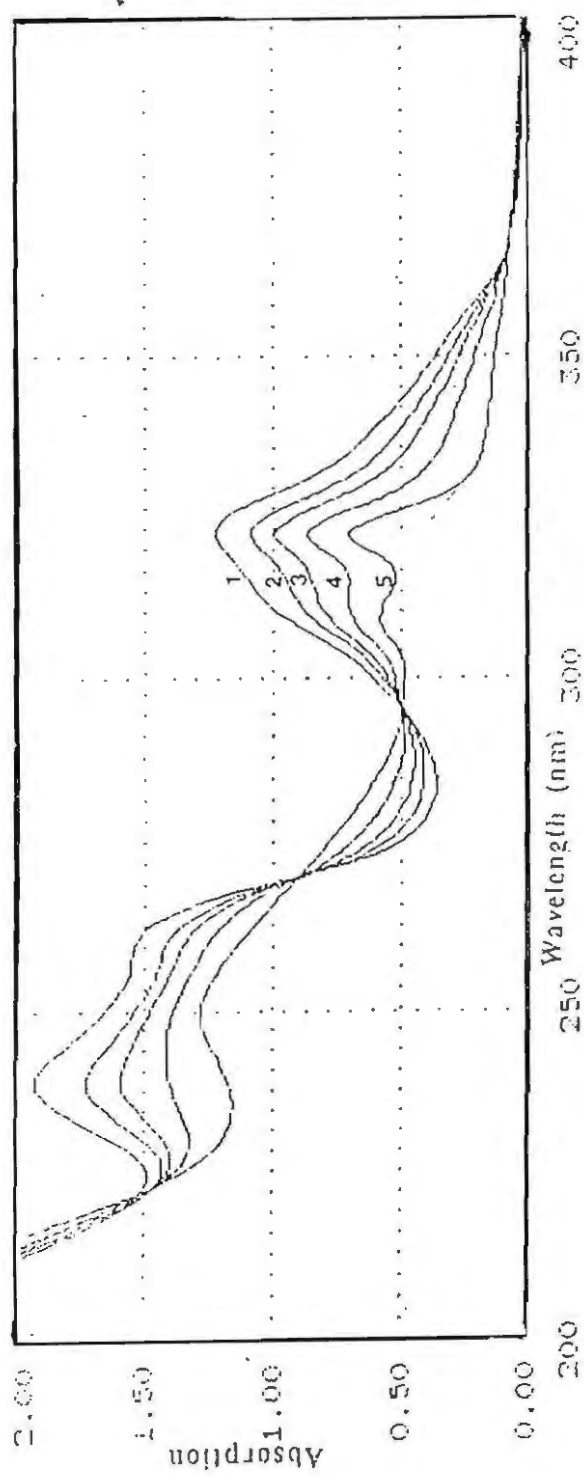
Crystal data, bond lengths, bond angles and the hydrogen coordinated ( $\times 10^4$ ) in addition to equivalent isotropic displacement parameters ( $\text{A}^\circ \times 10^3$ ) are given in tables 2, 3, 4, and 5 respectively.



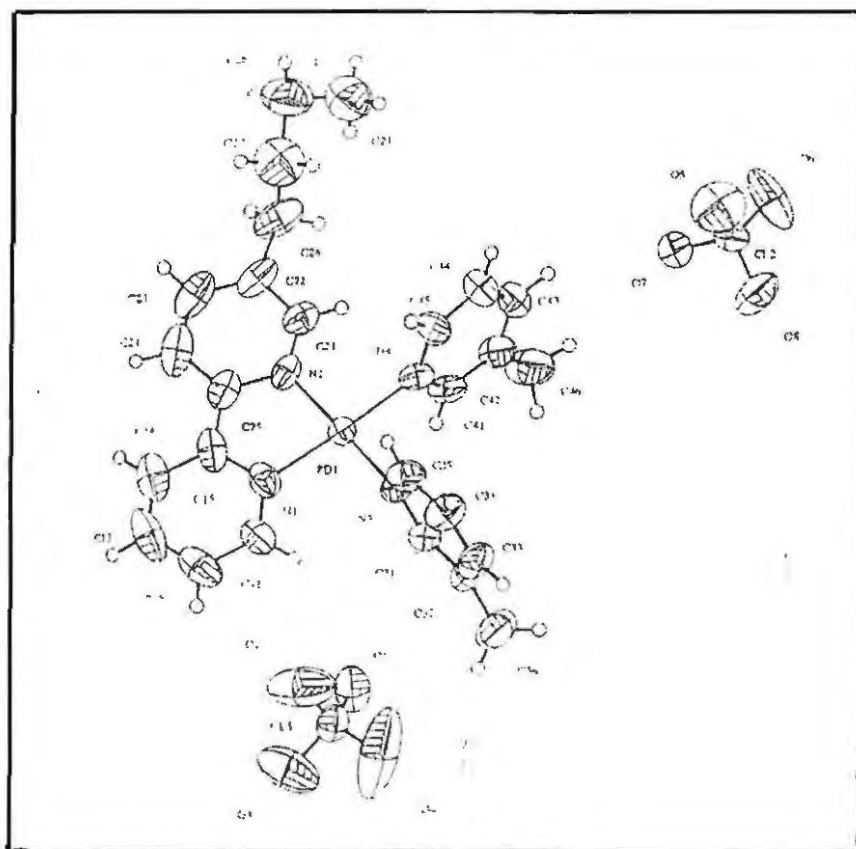
Fig(1) 360MHz  $^1\text{H}$  NMR spectrum of  $[\text{Pt}(\text{S-butbipy})\text{Cl}_2]$  [2] in  $\text{DMSO}-d_6$



Fig(2) 360MHz <sup>1</sup>H NMR spectrum of [Ru(5-butirpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> [9] in DMSO-d<sub>6</sub>.



Fig(3) UV spectra of  $[Pt(5\text{-butbipy})_2](ClO_4)_2$  [9] in water  $[4.45 \times 10^{-5}M]$  at pH (1) = 6.23, (2) = 9.85, (3) = 10.22, (4) = 10.68 and (5) = 11.58



Fig(4) The structure of  $[Pd(5\text{-butbipy})(3\text{-Pic})_2](ClO_4)_2[3]$

Table (1) Chemical shifts (ppm) of some 5-butyl-2,2' bipyridine compounds in DMSO-d<sub>6</sub>

Compound	H6'	H6	H3'	H3	H4'	H4	H5'	Ho	Hm	Hp	α-CH <sub>3</sub>	β-CH <sub>3</sub>	γ-CH <sub>3</sub>	CH <sub>3</sub>
5-butyl-2,2'-bipyridine [1] <sup>a</sup>	8.46	8.32	8.24	8.17	7.53	7.36	7.00	-	-	-	2.39	1.38	1.14	0.71
[Pt(5-butbipy)Cl <sub>2</sub> ] [2]	9.45	9.30	8.52	8.46	8.39	8.30	7.81	-	-	-	2.80	1.62	1.35	0.93
[Pt(5-butbipy) <sub>2</sub> ] <sup>2+</sup> [8]	9.09	8.91	8.81	8.76	8.63	8.54	8.03	-	-	-	2.90	1.72	1.41	0.95
[Pd(5-butbipy) <sub>2</sub> ] <sup>2+</sup> [9]	8.80	8.62	8.70	8.66	8.53	8.43	7.96	-	-	-	2.87	1.68	1.38	0.94
[Pt(5-butbipy)(Py) <sub>2</sub> ] <sup>2+</sup> [4]	7.75	7.47	8.77 <sup>b</sup>	8.77 <sup>b</sup>	8.55	8.47	7.75	9.19	7.83	8.25	2.67	1.48	1.23	0.85
[Pd(5-butbipy)(Py) <sub>2</sub> ] <sup>2+</sup> [6]	7.42	7.15	8.74 <sup>b</sup>	8.74 <sup>b</sup>	8.49	8.41	7.70	9.24	7.84	8.23	2.63	1.43	1.19	0.82
[Pd(5-butbipy)(3-Pic) <sub>2</sub> ] <sup>2+</sup> [7]	7.36	7.03	8.68 <sup>b</sup>	8.68 <sup>b</sup>	8.45	8.36	7.69	9.10 <sup>d</sup> 9.04 <sup>d</sup>	7.69	8.05	2.62	1.42	1.19	2.40 <sup>c</sup> 0.82

<sup>a</sup> in CDCl<sub>3</sub><sup>b</sup> Overlapped (H3, H3')<sup>c</sup> The methyl group of (3-Picoline)<sup>d</sup> Two pair of ortho protons (magnetically and environmentally different)

**Table (2):** Crystal data and structure refinement for  $C_{24}H_{16}N_6O_6Pd$ .

Empirical formula	$C_{24}H_{16}N_6O_6Pd$
Formula weight	590.85
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	P21/C
Unit cell dimensions	a = 7.046(2) Å alpha = 90 deg. b = 20.188(4) Å beta = 104.237(8) c = 14.977(2) Å gamma = 90deg
Volume	2064.8(8) Å <sup>3</sup>
Z	4
Density (calculated)	1.901 Mg/M <sup>3</sup>
Absorption coefficient	0.896 mm <sup>-1</sup>
F(000)	1184
Crystal size	0.15 x 0.08 x 0.04 mm
Theta range for data collection	2.46 to 25.08 deg
Index ranges	- 8 ≤ h ≤ 6, -22 ≤ k ≤ 23, -15 ≤ l ≤ 16
Reflections collected	8413
Independent reflections	3114 {R(int) = 0.0475}
Refinement method	Full-matrix Least-squares on F <sup>2</sup>
Data / restraints / parameters	3114/0/398
Goodness - of - fit - on F <sup>2</sup>	1.017
Final R indices [I>2sigma (I)]	R1=0.0349, WR2 = 0.0836
R indices (all data)	R1=0.0428, WR2 = 0.0853
Largest diff. Peak and hole	1.653 and -0.565 e. Å <sup>-3</sup>



Table (3): Bond lengths [ $\text{\AA}^\circ$ ].

Pd(1)-N(1)	2.011(5)
Pd(1)-N(4)	2.029(5)
Pd(1)-N(3)	2.029(5)
Pd(1)-N(2)	2.028(5)
N(1)-C(15)	1.344(9)
N(1)-C(15)	1.370(8)
N(2)-C(21)	1.305(8)
N(2)-C(25)	1.359(8)
N(3)-C(31)	1.321(8)
N(3)-C(35)	1.349(8)
N(4)-C(41)	1.323(8)
N(4)-C(45)	1.337(7)
C(11)-C(12)	1.386(9)
C(11)-H(11)	0.93
C(12)-C(13)	1.389(11)
C(12)-H(12)	0.93
C(13)-C(14)	1.379(11)
C(13)-H(13)	0.93
C(14)-C(15)	1.396(9)
C(14)-H(14)	0.93
C(15)-C(25)	1.441(10)
C(21)-C(22)	1.375(9)
C(21)-H(21)	0.93
C(22)-C(23)	1.381(10)
C(22)-C(26)	1.488(11)
C(23)-C(24)	1.357(11)
C(23)-H(23)	0.93
C(24)-C(25)	1.424(10)
C(24)-H(24)	0.93
C(26)-C(27)	1.525(11)
C(26)-H(26A)	0.97
C(26)-H(26B)	0.97
C(27)-C(28)	1.657(14)
C(27)-H(27A)	0.97
C(27)-H(27B)	0.97
C(28)-C(29)	1.51(2)
C(28)-H(28A)	0.97
C(28)-H(28B)	0.97
C(29)-H(29A)	0.96
C(29)-H(29B)	0.96

Cont. Table (3).

C(29)-H(29C)	0.96
C(31)-C(32)	1.393(8)
C(31)-H(31)	0.93
C(32)-C(33)	1.380(9)
C(32)-C(36)	1.517(10)
C(33)-C(34)	1.368(10)
C(33)-H(33)	0.93
C(34)-C(35)	1.379(9)
C(34)-H(34)	0.93
C(35)-H(35)	0.93
C(36)-H(36A)	0.96
C(36)-H(36B)	0.96
C(36)-H(36C)	0.96
C(41)-C(42)	1.390(9)
C(41)-H(41)	0.93
C(42)-C(43)	1.389(9)
C(42)-C(46)	1.474(10)
C(43)-C(44)	1.366(9)
C(43)-H(43)	0.93
C(44)-C(45)	1.364(9)
C(44)-H(44)	0.93
C(45)-H(45)	0.93
C(46)-H(46A)	0.96
C(46)-H(46B)	0.96
C(46)-H(46C)	0.96
Cl(1)-O(3')	1.28(2)
Cl(1)-O(2)	1.380(10)
Cl(1)-O(1)	1.422(5)
Cl(1)-O(4')	1.441(10)
Cl(1)-O(3)	1.481(7)
Cl(1)-O(2')	1.437(11)
Cl(1)-O(4)	1.418(9)
Cl(2)-O(6)	1.394(7)
Cl(2)-O(5)	1.405(4)
Cl(2)-O(8)	1.421(7)
Cl(2)-O(6')	1.40(2)
Cl(2)-O(8')	1.30(2)
Cl(2)-O(7)	1.463(7)
Cl(2)-O(7')	1.51(2)

Table (4): Bond angles (deg).

N(1)-Pd(1)-N(4)	175.0(2)
N(1)-Pd(1)-N(3)	96.3(2)
N(4)-Pd(1)-N(3)	88.6(2)
N(1)-Pd(1)-N(2)	82.0(2)
N(4)-Pd(1)-N(2)	93.2(2)
N(3)-Pd(1)-N(2)	176.7(2)
C(11)-N(1)-C(15)	120.3(6)
C(11)-N(1)-Pd(1)	126.8(4)
C(15)-N(1)-Pd(1)	112.9(4)
C(21)-N(2)-C(25)	120.0(6)
C(21)-N(2)-Pd(1)	127.7(4)
C(25)-N(2)-Pd(1)	112.0(4)
C(31)-N(3)-C(35)	119.9(5)
C(31)-N(3)-Pd(1)	121.6(4)
C(35)-N(3)-Pd(1)	118.4(4)
C(41)-N(4)-C(45)	120.0(6)
C(41)-N(4)-Pd(1)	118.2(4)
C(45)-N(4)-Pd(1)	121.7(4)
N(1)-C(11)-C(12)	122.5(7)
N(1)-C(11)-H(11)	118.7(4)
C(12)-C(11)-H(11)	118.8(5)
C(13)-C(12)-C(11)	117.0(7)
C(13)-C(12)-H(12)	1121.5(5)
C(11)-C(12)-H(12)	1121.5(5)
C(12)-C(13)-C(14)	121.6(7)
C(12)-C(13)-H(13)	119.2(5)
C(14)-C(13)-H(13)	119.2(4)
C(15)-C(14)-C(13)	118.9(7)
C(15)-C(14)-H(14)	120.6(5)
C(13)-C(14)-H(14)	120.6(4)
N(1)-C(15)-C(14)	119.7(7)
N(1)-C(15)-C(25)	115.7(5)
C(14)-C(15)-C(25)	124.6(7)
N(2)-C(21)-C(22)	125.9(7)
N(2)-C(21)-H(21)	117.0(4)
C(22)-C(21)-H(21)	117.0(4)
C(23)-C(22)-C(21)	114.1(7)
C(23)-C(22)-C(26)	122.6(7)
C(21)-C(22)-C(26)	123.3(7)
C(24)-C(23)-C(22)	123.3(7)
C(24)-C(23)-H(23)	118.3(4)
C(22)-C(23)-H(23)	118.4(4)
C(23)-C(24)-C(25)	118.3(6)
C(23)-C(24)-H(24)	120.9(4)

Cont. Table (4).

C(25)-C(24)-H(24)	120.8(4)
N(2)-C(25)-C(24)	118.4(6)
N(2)-C(25)-C(15)	116.8(6)
C(24)-C(25)-C(15)	124.8(6)
C(22)-C(26)-C(27)	111.0(7)
C(22)-C(26)-H(26A)	109.6(4)
C(27)-C(26)-H(26A)	109.5(5)
C(22)-C(26)-H(26B)	109.3(4)
C(27)-C(26)-H(26B)	109.4(5)
H(26A)-C(26)-H(26B)	108.0
C(26)-C(27)-C(28)	110.4(7)
C(26)-C(27)-H(27A)	109.6(5)
C(28)-C(27)-H(27A)	109.7(5)
C(26)-C(27)-H(27B)	109.5(5)
C(28)-C(27)-H(27B)	109.4(5)
H(27A)-C(27)-H(27B)	108.1
C(29)-C(28)-C(27)	107.1(9)
C(29)-C(28)-H(28A)	110.3(6)
C(27)-C(28)-H(28A)	110.4(5)
C(29)-C(28)-H(28B)	110.2(6)
C(27)-C(28)-H(28B)	110.3(5)
H(28A)-C(28)-H(28B)	108.5
C(28)-C(29)-H(29A)	109.5(6)
C(28)-C(29)-H(29B)	109.4(6)
H(29A)-C(29)-H(29B)	109.5
C(28)-C(29)-H(29C)	109.5(6)
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
N(3)-C(31)-C(32)	122.7(6)
N(3)-C(31)-H(31)	118.7(3)
C(32)-C(31)-H(31)	118.6(4)
C(33)-C(32)-C(31)	117.3(6)
C(33)-C(32)-C(36)	122.6(6)
C(31)-C(32)-C(36)	120.2(6)
C(34)-C(33)-C(32)	119.9(6)
C(34)-C(33)-H(33)	120.0(4)
C(32)-C(33)-H(33)	120.0(4)
C(33)-C(34)-C(35)	120.0(6)
C(33)-C(34)-H(34)	120.0(4)
C(35)-C(34)-H(34)	120.0(4)
N(3)-C(35)-C(34)	120.2(6)
N(3)-C(35)-H(35)	119.9(3)
C(34)-C(35)-H(35)	119.9(4)
C(32)-C(36)-H(36A)	109.4(4)

C(32)-C(36)-H(36B)	109.5(4)
H(36A)-C(36)-H(36B)	109.5
C(32)-C(36)-H(36C)	109.6(4)
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
N(4)-C(41)-C(42)	122.7(6)
N(4)-C(41)-H(41)	118.7(4)
C(42)-C(41)-H(41)	118.7(4)
C(43)-C(42)-C(41)	116.2(6)
C(43)-C(42)-C(46)	125.5(7)
C(41)-C(42)-C(46)	8.3(6)
C(44)-C(43)-C(42)	120.9(6)
C(44)-C(43)-H(43)	119.6(4)
C(42)-C(43)-H(43)	119.5(4)
C(43)-C(44)-C(45)	119.1(6)
C(43)-C(44)-H(44)	120.5(4)
C(45)-C(44)-H(44)	120.4(4)
N(4)-C(45)-C(44)	121.1(6)
N(4)-C(45)-H(45)	119.4(4)
C(44)-C(45)-H(45)	119.5(4)

Table (5): Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{C}_{24}\text{H}_{16}\text{N}_6\text{O}_6\text{Pd}$ .

	x	y	z	U(iso)
H(1)	2737(45)	763(16)	4285(22)	0(8)
H(2)	1791(55)	215(22)	2925(27)	27(12)
H(3)	280(50)	703(19)	1594(25)	15(10)
H(5)	-1122(46)	1761(17)	853(23)	5(9)
H(6)	-1782(50)	2863(17)	973(25)	2(9)
H(8)	-1602(47)	3910(18)	1962(24)	5(9)
H(9)	-848(54)	4334(21)	3427(25)	21(11)
H(10)	867(51)	3712(19)	4575(25)	13(10)
H(13)	1811(51)	755(18)	5502(24)	5(10)
H(14)	2551(56)	87(23)	6683(27)	32(12)
H(15)	4222(48)	564(18)	8067(24)	8(9)
H(17)	5538(51)	1579(19)	8933(26)	20(11)
H(18)	6295(53)	2720(17)	8858(26)	5(9)
H(20)	6432(56)	3756(20)	7979(27)	23(11)
H(21)	5617(59)	4263(22)	6554(28)	32(12)
H(22)	3932(60)	3692(22)	5294(28)	36(13)

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### REFERENCES

- Belluco U., *Organometallic and coordination Chemistry of platinum*, academic press, New York,(1973).
- Gillard R.D. and Lyons J.R., *J. Chem.Soc. Chem.commun.*, (1973)585.
- Gillard R.D., *inorg.Chim.Acta*.11(1974)L21
- Hacker M.P., Duple E.B. and Krakoff I.H., *Platinum coordination complexes in Cancer chemotherapy*, Martinus-Nijhoff, Boston(1984).
- Holloway C.E., Melnik M., *Rev.inorg. Chem.* 22(2002)163.
- Holloway C.E., Melnik M., *Rev. inorg. Chem.*23(2003)125.
- Holloway C.E., Melnik M., *Rev. inorg. Chem.*24(2004)301.
- Holloway C.E., Melnik M., *Rev. inorg. Chem.*25(2005)93.
- Krohnke F., *Angew chem.*, 75(1963)189.
- Krohnke F., *Synthesis*(1976)1
- Melnik M., Holloway C. E., *Coord. Chem. Rev.*, 250(2006)2261
- Nicolini M. *platinum and other metal coordination compounds in cancer chemotherapy*, Martinus-Nijhoff, Boston(1988).
- Nord G., *Acta Chem. Scand.A*,29(1975)270
- Rosenberg B., Van Camp L., Trosko J. F., Mansour V. H., *Nature* (London)222,285(1969).
- Weiss M., *J. Amer. Chem. Soc.*,74(1952)200
- Werberg O., *J. Chem .Soc .Dalton Trans.*,(1986) 725.

## المخلص العربي

تحضير وتشخيص معقدات جديدة للبلاتين الثنائي والبلاديوم الثنائي تحتوي على ٥- بيوتيل - ٢,٢ - ثنائي البيريدين : والتركيب البلوري باستخدام حيود الأشعة السينية للمعقد  $[pd(5-butbipy)(3-pic)_2] (ClO_4)_2$ .

تم في هذا البحث تحضير وتشخيص مجموعة من المعقدات الجديدة للبلاتين الثنائي والبلاديوم الثنائي مع ليكاند ثنائية السن غير مثنائية (Unsymmetrical) وهي ٥- بيوتيل - ٢,٢ - ثنائي البيريدين وقد تمت طريقة التشخيص باستخدام الرنين النووي المغناطيسي للبروتون والتحليل العنصري الدقيق.

كما تم تحديد التركيب البلوري للمعقد  $[pd(5-butbipy)(3-pic)_2] (ClO_4)_2$  باستخدام حيود الأشعة السينية واتضح أن أيون البلاديوم الثنائي يمتلك بنية المربع المستوى.