

## **SYNTHESIS AND ANTIBACTERIAL ACTIVITIES OF SUGAR-CONTAINING PLATINUM ETHYNYL COMPLEXES**

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### **ABSTRACT**

New sugar-containing aryl ethynyl ligand [*N*-(4-trimethylsilylethynylphenyl)- $\beta$ -D-glucopyranosylamine] **2** has been prepared by the reaction of [*N*-(4-iodophenyl)- $\beta$ -D-glucopyranosylamine] **1** with trimethylsilylacetylene in the presence of Pd(OAc)<sub>2</sub>/CuI catalyst, in <sup>i</sup>Pr<sub>2</sub>NH and DMF solvent mixture. The trimethylsilyl group of compound **2** was deprotected using K<sub>2</sub>CO<sub>3</sub> in methanol to form terminal ethynylene ligand [*N*-( $\beta$ -D-glucopyranosyl)aniline-4-ethyne] **3**. Novel platinum mono-ethynyl complex *trans*-[(P(Bu)<sub>3</sub>)<sub>2</sub>PtCl(C $\equiv$ C-4-C<sub>6</sub>H<sub>4</sub>-NH-D-glucose)] **4** and bis-ethynyl complex *trans*-[(P(Bu)<sub>3</sub>)<sub>2</sub>PtCl(C $\equiv$ C-4-C<sub>6</sub>H<sub>4</sub>-NH-D-glucose)<sub>2</sub>] **5** were formed by the dehydrohalogenation reaction of *trans*-[Pt(P(Bu)<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] with terminal ethynyl ligand **3** in <sup>i</sup>Pr<sub>2</sub>NH/THF, in the presence of CuI, at 65°C. The complexes are hygroscopic in air, and are fairly soluble in methanol and CH<sub>2</sub>Cl<sub>2</sub>. The new compound **2** - **5** were characterized by FTIR and UV-Vis spectroscopy and elemental analysis. The compounds were tested for antibacterial activity using disk diffusion technique. The platinum complexes **4** and **5** displayed good resistivity against the following bacteria: *Escherichia coli*, *Proteus penneri*, *Klebsiella oxytoca* and *Pseudomonas aeruginosa*.

**Key words:** Sonogashira coupling, Dehydrohalogenation, Sugar-containing platinum acetylide, Antibacterial activity

### **INTRODUCTION**

Arylene ethynylene is an important building block for conjugated organic and organometallic complexes and polymers (Long *et al.* 2003, Bunz 2009). Conjugated organic polymers (poly (aryleneethynylene)s, PPEs) are semiconductors. These are stable and emissive, and for their fluorescent properties, they can be used as sensors to detect metals, proteins, bacteria and DNA (Bunz 2009, Disney *et al.* 2004). Introduction of metals (Pt, Pd, Fe, Ru, Os) into the arylene ethynylene may introduce redox, magnetic, optical, and electronic properties in the materials. As a consequence, these materials possess interesting properties such as optical nonlinearity, luminescence, liquid crystallinity (Long *et al.* 2003). Compared to the application of conjugated organic PPEs

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in biology (Kim *et al.* 2007, Yang *et al.* 2005, Dam *et al.* 2002, Phillips 2008, Babudri *et al.* 2003, Erdogan *et al.* 2002), little attention is given to their organometallic analogues (Wong *et al.* 2004, Ma *et al.* 2005). However, metal coordination complexes with tunable properties, such as radioactivity, cytotoxicity or photophysical features, would be good candidates for biomedical application, e.g. diagnostic tracers or therapeutic agents (Gottschaldt *et al.* 2009).

To design materials for biological applications, along with the designated properties such as fluorescence and photoactivity, it is necessary to improve the solubility and biocompatibility. One general principle used in nature is the attachment of biomolecules to active species to obtain binding domains, transport systems and enzyme activities. Monosaccharides are fundamental biomolecules, and they are the constitutional parts of complex lipids (glycolipids) and proteins (glycoproteins) and nucleic acid (Steinborn *et al.* 2000). The attachment of glycosidically bound carbohydrate moieties to metal ions may be a suitable option to create new materials with combined properties of both building blocks: carbohydrates and metal complexes (Wegner *et al.* 2001, Gottschaldt *et al.* 2009, Gottschaldt *et al.* 2004). Sugar fragments can be bound to metal centres either directly or through other atoms in the periphery. Introduction of sugar atom into the biological materials not only increases the solubility, but also influences their biocompatibility, primarily, acting as energy source and contributing to various recognition or specific transformation processes. Carbohydrate complexes of platinum group metals (Pd, Pt, Rh, Ir), where carbohydrate is directly bonded to metal atom, have been reported (Steinborn *et al.* 2000). In recent years, metal coordination complexes with sugar substituted chelating ligands were studied for the development of diagnostic tracers (Mindt *et al.* 2006, Ferreira *et al.* 2006), MRI contrast agents (Fulton *et al.* 2006, Duimstra *et al.* 2005) and therapeutic agents (Krishnamurthy *et al.* 2008, Ott *et al.* 2005, Ma *et al.* 2005). M-C  $\sigma$ -bonded and M-C  $\pi$ -bonded organometallic complexes with sugar moieties also demonstrated biosensing and medicinal activity (Monney *et al.* 2013). According to present knowledge, sugar-containing M-C  $\sigma$ -bonded ethynyl complexes are scarce (Ma *et al.* 2005).

The authors report herein, the first example of sugar-containing Pt-C  $\sigma$ -bonded ethynyl complexes with tri-*n*-butylphosphine as auxiliary ligand. The antibacterial activities of the new sugar-containing acetylene ligand and its Pt- ethynyl complexes are evaluated.

## MATERIALS AND METHODS

All solvents: dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), diisopropylamine (<sup>i</sup>Pr<sub>2</sub>NH), tetrahydrofuran (THF), dimethylformamide (DMF), ethanol (C<sub>2</sub>H<sub>5</sub>OH), methanol (CH<sub>3</sub>OH), ethyl acetate (EtOAc), n-hexane (C<sub>6</sub>H<sub>14</sub>), diethylether (Et<sub>2</sub>O), acetone (CH<sub>3</sub>COCH<sub>3</sub>); and reagents: D-

glucose, 4-iodoaniline, glacial acetic acid, trimethylsilyl acetylene, palladium acetate ( $\text{Pd}(\text{OAc})_2$ ), copper (I) iodide, triphenylphosphine ( $\text{PPh}_3$ ), palladium(II)chloride, diethyl sulphide ( $\text{Et}_2\text{S}$ ) *trans*- $[\text{Pt}(\text{P}(\text{Bu})_3)_2\text{Cl}_2]$ , nutrient agar, beef extract, peptone, NaCl, and standard antibiotic were purchased from Aldrich, Germany, and were used without further purification. Alumina (Aluminium oxide 90 active, neutral, 70-230 mesh ASTM) and silica gel (60G) for column chromatography were purchased from Merck, Germany.

Most of the reactions were performed under an inert atmosphere of nitrogen using standard techniques. Solvents were dried, distilled and degassed by nitrogen gas using standard procedure. Infrared spectra of all the compounds were recorded in FTIR spectrometer (Shimadzu: Prestige-21) using KBr (for solid) or dry  $\text{CH}_2\text{Cl}_2$  (for liquid) as background and UV-Vis spectra were recorded in UV-Vis spectrophotometer (Shimadzu: UV-1800). Melting points of the products were determined on a melting point apparatus (Stuart SMP-10). Elemental analysis of sample was carried out at BCSIR laboratories, Dhaka, Bangladesh.

*Synthesis of N-(4-iodophenyl)- $\beta$ -D-glucopyranosylamine 1:* 1 - 2 drops of glacial AcOH were added to a solution of D-glucose (2 g, 0.010 mol) and 4-iodoaniline (2.21 g, 0.010 mol) in ethanol (15 ml). The resulting solution was stirred at  $60^\circ\text{C}$  for 6 hrs and concentrated to one third of its volume. The pale brown crystalline precipitate that was formed upon cooling was filtered off using sintered crucible, washed with cold isopropyl alcohol and water, and the crude product was purified by recrystallization from ethanol and  $\text{H}_2\text{O}$  (3 : 1) mixture. Pure pale brown solid was obtained in 85% yield (m.p.  $113.8$ - $114.1^\circ\text{C}$ ). The product was highly soluble in acetone, ethanol, methanol,  $\text{PrNH}$  and DMF, but insoluble in  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$  and n-hexane. IR ( $\text{v}/\text{cm}^{-1}$ ):  $\nu$  (OH and N-H), 3600-3077;  $\nu$  (aromatic C-H), 3014.74;  $\nu$  (C-H stretching of  $\text{CH}_2$  group), 2953.02, 2916.37, 2885.51 and 2850.79;  $\nu$  (aromatic C = C), 1593.20, 1516.06 and 1485.19;  $\nu$  (pyranose form of glycoside of the residue), 1020;  $\nu$  ( $\beta$  configuration of the anomeric carbon), 881. Anal. Calc. for  $\text{C}_{12}\text{H}_{16}\text{INO}_5 \cdot \text{H}_2\text{O}$ : C, 36.11; H, 4.55, N, 3.51%. Found: C, 36.1; H, 4.53; N, 3.38%.

*Synthesis of N-(4-trimethylsilylethynylphenyl)- $\beta$ -D-glucopyranosylamine 2:* To a freshly dried and degassed mixture of diisopropylamine (20 ml) and dimethyl formamide (14 ml) were added **1** (500 mg, 1.32 mmol), trimethylsilylactylene (312.97  $\mu\text{l}$ , 2.23 mmol) and catalyst  $\text{Pd}(\text{OAc})_2$  (5.92 mg, 0.026 mmol, 2 mol %),  $\text{PPh}_3$  (13 mg, 0.052 mmol, 2 mol %), and CuI (5.027 mg, 2 mol %) with a positive flow of nitrogen, and the solution was stirred under inert atmosphere at  $0^\circ\text{C}$ . After 2 hrs, the reaction mixture was heated at  $70^\circ\text{C}$  temperature for 18 hrs. Then the reaction mixture was extracted by ethyl acetate and washed with saturated aqueous  $\text{NaHCO}_3$ , brine and dilute HCl solution, then dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure by a

rotatory evaporator. The crude product was purified by silica column chromatography using  $\text{CH}_2\text{Cl}_2$  and methanol as eluent. After removal of solvents under reduced pressure, the product was isolated as brick red paste in 68% yield. The product was highly soluble in acetone, ethanol, methanol,  $i\text{-PrNH}$  and DMF, but insoluble in  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$  and n-hexane. IR ( $\nu/\text{cm}^{-1}$ ):  $\nu(\text{OH})$  and  $\nu(\text{NH})$ , 3673-3090;  $\nu$  (aromatic C-H), 3032.10, 2958.80;  $\nu$  (alkyl group C-H), 2926.01;  $\nu$  ( $\text{C} \equiv \text{C}$ ), 2152.56;  $\nu$  (aromatic  $\text{C} = \text{C}$ ), 1654.92, 1610.56 and 1517.98;  $\nu$  (pyranose form of glycoside of the residue), 1012;  $\nu$  ( $\beta$  configuration of the anomeric carbon), 869. Anal. Calc. for  $\text{C}_{17}\text{H}_{25}\text{NO}_5\text{Si} \cdot 3.5\text{H}_2\text{O}$ : C, 49.26; H, 7.78, N, 3.38%. Found: C, 49.2; H, 7.79; N, 3.96%.

*Synthesis of N-( $\beta$ -D-glucopyranosyl) aniline-4-ethyne 3:* To a solution of compound **2** (109 mg, 0.3090 mmol) in methanol (6 ml),  $\text{K}_2\text{CO}_3$  (85.41 mg, 0.4635 mmol) was added. The reaction mixture was kept at room temperature for 18 hrs. After completion of the reaction, the crude product was obtained after removal of solvent in a rotatory evaporator. It was dissolved in ethyl acetate, washed with brine water and dried over  $\text{MgSO}_4$ . The crude product was purified by silica column chromatography using  $\text{CH}_2\text{Cl}_2$  and methanol as eluent. The pure product was obtained as a brick red paste in 68% yield. The product was highly soluble in acetone, ethanol, methanol, acetonitrile and THF, but insoluble in  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and n-hexane. IR ( $\nu/\text{cm}^{-1}$ ):  $\nu(\text{NH})$ ,  $\nu(\text{OH})$  and  $\nu(\equiv \text{C}-\text{H})$ , 3690-3077; 3283.63;  $\nu$  (aromatic C-H), 3039.81;  $\nu$  ( $\text{CH}_2$  group), 2924.09 and 2889.37;  $\nu$  ( $\text{C} \equiv \text{C}$ ), 2100.48;  $\nu$  (aromatic  $\text{C} = \text{C}$ ), 1610.56, 1519.91 and 1417.68;  $\nu$  (pyranose form of glycoside), 1012;  $\nu$  ( $\beta$  configuration of the anomeric carbon), 900.

*Synthesis of di[N-( $\beta$ -D-glucopyranosyl) aniline-4 ethynylene]bis (tributylphosphine) platinum(II) 4 and 5:* To a freshly dried and degassed mixture of diisopropylamine (6 ml) and THF (12 ml), were added *trans*-dichlorobis (tributylphosphine) platinum (II) (50 mg, 0.088 mmol), ligand **3** (73 mg, 0.264 mmol) and catalytic amount of copper (I) iodide (0.0046 mmol, 0.92 mg, 5 mol %) with a positive flow of nitrogen. The reaction mixture was allowed to stir under reflux at  $65^\circ\text{C}$  for 18 h under nitrogen atmosphere. During this period, the color of reaction mixture turned into yellow which was initially reddish in color. The formation of product was confirmed by taking IR spectroscopy. After completion of the reaction the solvent was removed under a reduced pressure. Product was purified by silica column chromatography. The first band, obtained by dichloromethane as eluant, was identified as *mono*-acetylide **4**. The second fraction, obtained from the column using 4/1 dichloromethane/methanol, was identified as *bis*-acetylide **5**. After recrystallization from hexane, *mono*-acetylide **4** was isolated in 58% yield which was solid at  $0^\circ\text{C}$  and pale yellow oil at room temperature. Complex **5** was isolated as reddish yellow oil in 24% yield.

IR ( $\nu/\text{cm}^{-1}$ ) of **4**:  $\nu(\text{NH})$  and  $\nu(\text{OH})$  3600-3176.76;  $\nu$  (aromatic C-H), 3091.89;  $\nu$  (C-H stretching of aliphatic group), 2958.80-2858.51;  $\nu$  ( $\text{C} \equiv \text{C}$  str. of mono Pt-acetylide),

2117.84;  $\nu$  (aromatic C = C), 1606.70, 1579.70 and 1400.32;  $\nu$  (pyranose form of glycoside), 1062;  $\nu$  ( $\beta$ -D configuration of the anomeric carbon), 910;  $\nu$  (Pt-C), 501.49. Anal. Calc. for  $C_{38}H_{70}ClNO_5P_2Pt \cdot 1/2$  Hexane: C 51.48, H 8.11, N 1.46%. Found: C, 51.2; H, 8.22; N, 2.37%.

IR ( $\nu/cm^{-1}$ ) of **5**:  $\nu$  (OH), 3690-3100;  $\nu$  (aromatic C-H), 3091.89;  $\nu$  (C-H stretching of aliphatic group), 2964.59, 2927.94 and 2835.36;  $\nu$  (C  $\equiv$  C), 2083.12;  $\nu$  (C = C str. of aromatic ring), 1608.63, 1579.70 and 1400.32;  $\nu$  (pyranose form of glycoside of the residue), 1016;  $\nu$  ( $\beta$ -D configuration of the anomeric carbon), 904;  $\nu$  (Pt-C) 501.49. Anal. Calc. for  $C_{52}H_{86}N_2O_{10}P_2Pt \cdot 2H_2O$ : C, 52.38; H, 7.61, N, 2.35 %. Found: C, 52.2; H, 7.88; N, 2.04%.

*Preparation of the culture media (bacteria solution):* Bacterium was grown in nutrient broth which was prepared by mixing 0.15 g beef extract, 0.25 g peptone and 0.25g NaCl in 50 ml of distilled water. The broth was heated for 15 minutes for complete dissolution, and was autoclaved for 15 minutes. Then single colony of *Escherichia coli*, *Proteus penneri*, *Klebsiella oxytoca* and *Pseudomonas aeruginosa* bacteria was added in 20 ml broth separately and incubated at 37°C for 24 hrs.

*Preparation of sample disk:* A stock solution of 3 mg-ml<sup>-1</sup> was made by dissolving the compound in distilled water. Paper discs of Whatman filter paper (0.45 micro pore) of uniform diameter (5 mm) and thickness (1 mm) were sterilized. 10 micro liters of stock solution (30  $\mu$ g sample) were soaked in each disk.

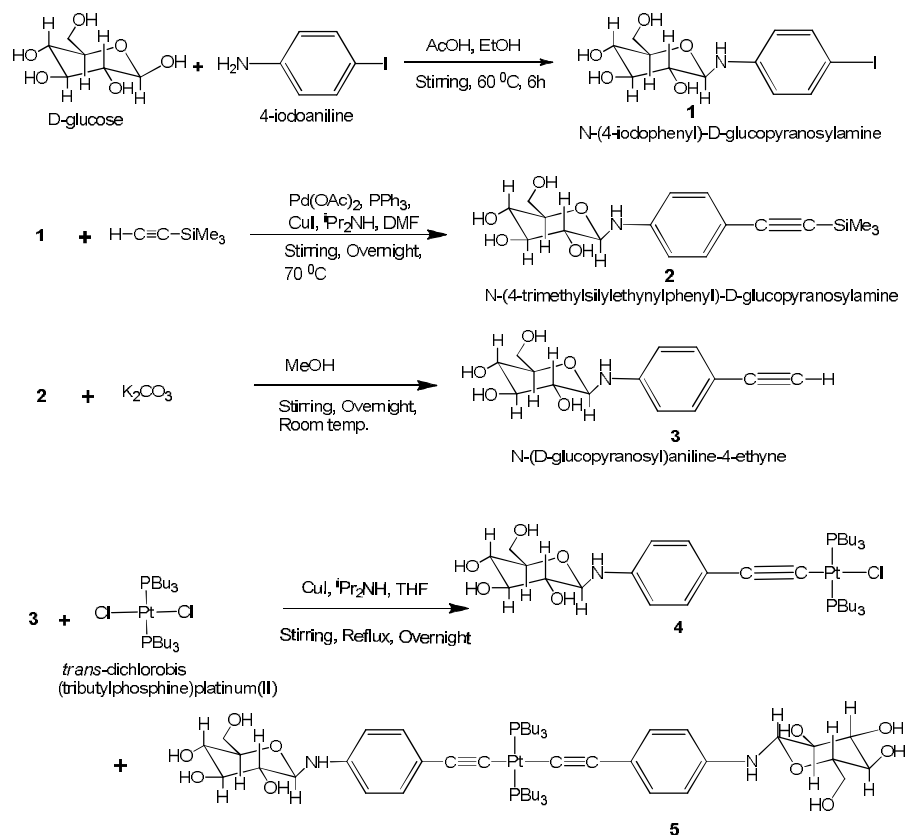
*Preparation of agar plates:* The medium was made up by dissolving bacteriological nutrient agar (3.2 g) in 100 ml distilled water. The mixture was autoclaved for 15 min at 120°C, dispensed onto a sterilized Petri dish, allowed to solidify, and then used for inoculation.

*Procedure of inoculation:* Inoculation was done with the help of micropipette with sterilized tips; 25  $\mu$ l of activated strain was placed onto the surface of an agar plate, and spread evenly over the surface by means of a sterilized bent glass rod (Bell *et al.* 2009).

*Application of disks:* Sample disks and antibiotic disks were applied in of the each earlier inoculated agar plates and incubated at 37°C for 24 hrs. The zone of inhibition (diameter) was then measured (in mm) around the sample and standard antibiotic disk. Antibiotic imipenem (IPM) was used against *Escherichia coli*, *Proteus penneri* and *Klebsiella oxytoca* bacteria and ciprofloxacin (CIP) was used against *Pseudomonas aeruginosa* bacteria as standard antibiotic disk. The antibacterial results of the compound were compared with the standard antibiotic disc.

## RESULTS AND DISCUSSION

*Synthesis and characterization:* The synthesis of D-glucose containing platinum-carbon  $\sigma$ -bonded ethynyl complexes **4** and **5** and their ethynyl precursor **3** is illustrated in scheme 1. Initially, hexose sugar-containing iodoaniline **1** was synthesized by glycosylation reaction of D-glucose with 4-iodoaniline, in the presence of 1-2 drops of glacial acetic acid catalyst, in ethanol, at 60°C, for 5-6 hrs (Wiebe *et al.* 2011). The pure pale brown product was isolated in 73% yield after recrystallization from ethanol and water. The trimethylsilyl protected ethynyl functional group was introduced into compound **1**, using Pd/Cu catalyzed cross-coupling reaction. Thus, the reaction between **1** and trimethylsilylacetylene, utilizing Sonagashira coupling route, gave compound **2** as viscous brick red oil in 68% yield. The removal of the silyl group by  $K_2CO_3$  provided expected sugar-containing terminal acetylene **3** in 65% yield. Air and light sensitive terminal ethynyl compound **3** was a hard solid under vacuum, but becomes redish yellow paste when exposed to air.

Scheme 1. Synthesis of compounds **1**, **2**, **3**, **4** and **5**.

Dehydrohalogenation is an established route for the synthesis of M-C  $\sigma$ -bonded platinum ethynyl complexes (Long *et al.* 2003). Utilizing this route, using one equivalent of *trans*-dichlorobis(tributylphosphine)platinum(II) and 2.5 equivalent of ethynyl ligand **3**, in the presence of CuI catalyst, gave mono-ethynyl complex **4** as major product (58 % isolated yield). Though the *bis*-complex **5** was also formed, its isolated yield is only 20 %. Dehydrogenation reaction always gives platinum *bis*-acetylide when ethynyl ligand is used in excess (Saha *et al.* 2005). Mono-acetylides of platinum is only obtained when platinum chloride precursor is used in excess under mild reaction condition (Zhou *et al.* 2009), sometimes even without catalyst (Amato *et al.* 2001). But when sugar substituted acetylene was used in this reaction, mono-substituted ethynyl complex was obtained as major product though the 2.5 equivalents ligand was used under elevated temperature. Both *mono*- and *bis*-ethynyl complex **4** and **5** were insoluble in water, but highly soluble in acetone, ethanol, methanol and dichloromethane.

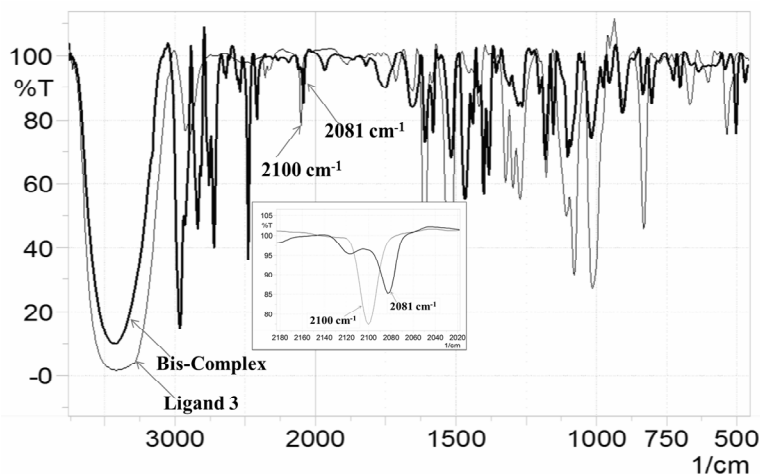


Fig. 1. IR (KBr) spectra of ligand **3** and *bis*-complex **5**.

The composition and structures of compounds **2-5** were confirmed by elemental analysis (Table 1) and IR and UV-Vis spectroscopy (Figs 1, 2). The selected IR spectral data of all compounds are presented in Table 1. The compound **1** showed peak at 881  $\text{cm}^{-1}$ , suggesting the  $\beta$ -configuration of the anomeric carbon. The three peaks observed at 1020  $\text{cm}^{-1}$ , 1053  $\text{cm}^{-1}$ , 1068  $\text{cm}^{-1}$  confirmed the pyranose form of the glycoside residue (Kulakov *et al.* 2008). In the IR spectrum of **2**, a shift of these two groups of peaks was observed when iodide of **1** was replaced by trimethylsilylacetylene group. A new strong peak at 2152  $\text{cm}^{-1}$  for the (C $\equiv$ C) group, and a broad peak at 3361 for the NH and OH groups were observed in the spectrum of **2**. A shift of the (C $\equiv$ C) stretching frequency from 2152  $\text{cm}^{-1}$  to 2100  $\text{cm}^{-1}$  was observed when the Me<sub>3</sub>Si group of the acetylene was

replaced by the H in terminal ethynyl compound **3**. The stretching frequency of (*sp* C-H) is generally observed at around 3300 cm<sup>-1</sup> for terminal acetylene which was obscured in the spectrum of **3** by the broad NH and OH band at 3200-3600 cm<sup>-1</sup>.

The IR spectrum of sugar substituted monoethynyl platinum complex **4** gave characteristic peaks at 2117 cm<sup>-1</sup> for the M-C  $\sigma$ -bonded (C $\equiv$ C) stretch and at 501 cm<sup>-1</sup> for the (M-C) stretch. The stretching frequency of (C $\equiv$ C) is shifted from 2117 to 2081 cm<sup>-1</sup> when the remaining chloride was replaced by the second acetylide group. The M-C and C $\equiv$ C stretching frequencies are used to determine the geometry of the square planar metal ethynyl complexes (Sonogashira *et al.* 1978, Long *et al.* 2002, Saha *et al.* 2005).

**Table 1. Selected IR and UV data and elemental analysis for compounds 1 - 5.**

Compound	Stretching frequency (v/cm <sup>-1</sup> )					Absorption band ( $\lambda_{\max}$ /nm)	Elemental analysis
	OH str. (broad peak) of glucose	Aromatic ring C-H str.	C $\equiv$ C str.	$\equiv$ C-H str.	Pt-C str.		
1	3600-3077	3014	×			252	Found C 36.1 H 4.5 N 3.38% Calculated for C <sub>12</sub> H <sub>16</sub> INO <sub>5</sub> •H <sub>2</sub> O (C 36.1 H 4.55 N 3.51%)
2	3673-3090	3032	2152			260	Found C 49.2 H 7.79 N 3.96% Calculated for C <sub>17</sub> H <sub>25</sub> NO <sub>5</sub> Si•3.5H <sub>2</sub> O (C 49.26 H 7.78 N 3.38 %)
3	3690-3077	3039	2100	3283		271	Not satisfactory, as the compound is air and light sensitive
4	3600-3176	3091	2117	×	542 and 501	275	Found C 51.2 H 8.22 N 2.37% Calculated for C <sub>38</sub> H <sub>70</sub> ClNO <sub>5</sub> P <sub>2</sub> Pt•½ hexane (C 51.48 H 8.11 N 1.46%)
5	3690-3100	3091	2081	×	542 and 501	278	Found C 52.2 H 7.88 N 2.04 % Calculated for C <sub>52</sub> H <sub>86</sub> N <sub>2</sub> O <sub>10</sub> P <sub>2</sub> Pt•2H <sub>2</sub> O (C 52.38 H 7.61 N 2.35 %)

For example, *cis*-[(PBu<sub>3</sub>)<sub>2</sub>Pt(C $\equiv$ C-C $\equiv$ CH)<sub>2</sub>] has a C<sub>2v</sub> symmetry and showed two absorption bands for each  $\nu$ (C $\equiv$ C) and  $\nu$ (M-C) (Sonogashira *et al.* 1978). In our case, only one absorption band for each of the  $\nu$ (C $\equiv$ C) and  $\nu$ (M-C) was observed, suggesting that compound **4** and **5** have *trans* geometry around the platinum metal centre.

UV-Vis spectroscopy is used to understand the  $\pi$ -interaction between the metal and ethynyl group in the metal ethynyl complexes (Saha *et al.* 2005, Younus *et al.* 1998, Fujikura *et al.* 1975). A broad band at 250-360 nm was observed in the spectrum of *mono*- and *bis*-ethynyl complex **4** and **5**. Compared to the ethynyl compound **3**, where



little hump was merely seen, the bands of **4** and **5** were clearly visible. These bands have been assigned to the  $\pi\text{-}\pi^*$  transition of the acetylenic fragment with LMCT character due to the mixing between  $\pi^*$  ( $\text{C}\equiv\text{C-R}$ ) and platinum  $(n + 1)p$  orbital. Similar spectroscopic features are reported in the related metal acetylide systems (Wong *et al.* 2004, Saha *et al.* 2005, Sina *et al.* 2015).

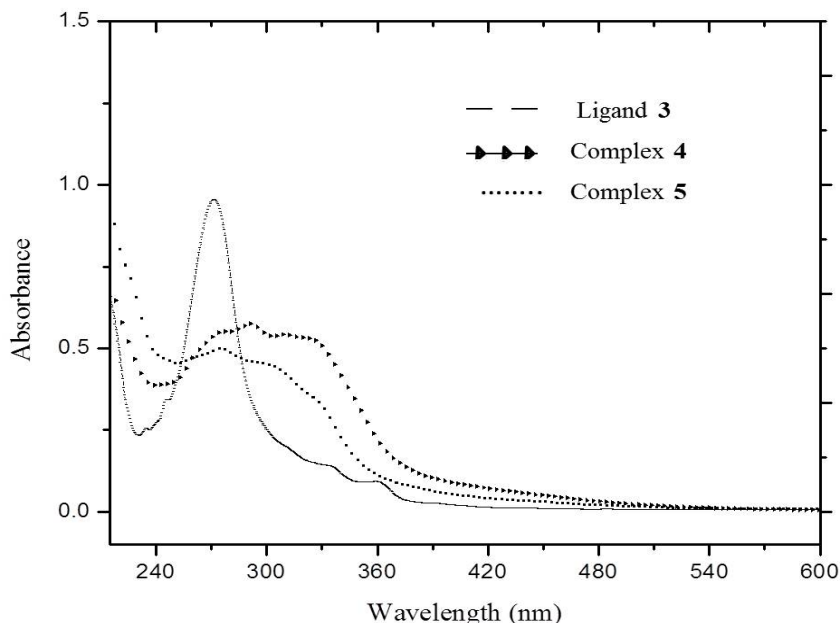


Fig. 2. UV-visible spectra of platinum complexes **4**, **5** and ligand **3**.

*Antibacterial activity:* The antibacterial activities of sugar-containing iodo compound **1**, ethynyl compounds **2** and **3**, and platinum complexes **4** and **5** were tested against bacteria *Escherichia coli*, *Proteus penneri*, *Klebsiella oxytoca* and *Pseudomonas aeruginosa*. The results are presented in Table 2. Platinum ethynyl complexes **4** and **5** were resistant to all four bacteria, whereas its ethynyl ligand **3** was only resistant to *Pseudomonas aeruginosa* bacteria (Table 2, Fig. 3). The activity of **4** and **5** can be explained by the increase in lipophilic character due to the ligand attached to the platinum centre. The complex penetrates the lipid layer of the cell membrane, blocks the metal binding sites in the enzymes of microorganism. As a result, the metabolism in the cell is stopped, and microorganism dies (Dai *et al.* 2013). The anticancer and antibacterial activity of the gold ethynyl complexes were reported recently (Hikisz *et al.* 2015), and previous report (Ma *et al.* 2005) of the sugar-containing platinum ethynyl complexes demonstrated 100 times higher anticancer efficiency than *cis* platin.

**Table 2. Quantitative antibacterial assay results (inhibition zone as annular radii) of compounds 1-5 (agar nutrient, air, 35-37°C, 48 hrs).**

Compound name	<i>Escherichia coli</i>		<i>Proteus penneri</i>		<i>Klebsiella Oxytoca</i>		<i>Pseudomonas aeruginosa</i>	
	Disc potency (µg)	Annular radii after 48hrs (mm)	Disc potency (µg)	Annular radii after 48 hrs (mm)	Disc potency (µg)	Annular radii after 48hrs (mm)	Disc potency (µg)	Annular radii after 48hrs (mm)
Antibiotic	10 (IPM)	17	10 (IPM)	16	10 (IPM)	15	2.5 (CIP)	17
1	30	7	30	8	30	8	30	6
2	30	7	30	8	30	×	30	6
3	30	×	30	×	30	×	30	5
5	30	4	30	5	30	4	30	4
4	30	5	30	4	30	4	30	5

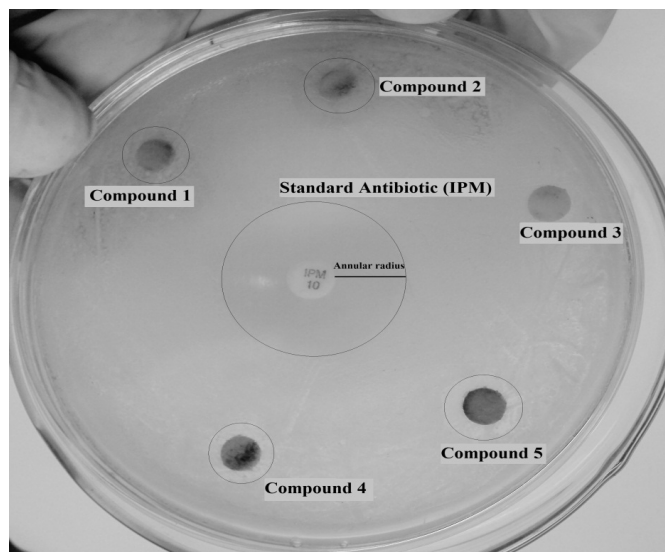


Fig. 3. Antibacterial activity of compounds **4**, **5** against *Escherichia coli* in the form of inhibition zone.

Hexose sugar-containing aryl ethynyl ligand **3** was formed by Sonogashira coupling reaction using N-(4-iodophenyl)- $\beta$ -D-glucopyranosylamine **1** and trimethylsilylacetylene, followed by the deprotection of trimethylsilyl group by  $K_2CO_3$ . Sugar-containing transition metals acetylide complexes **5** and **4** were synthesized by the dehydrohalogenation reaction between *trans*-[Pt(P(Bu) $_3$ ) $_2$ Cl $_2$ ] and ligand **3** in presence of CuI catalyst. The new products were fairly stable in air, and soluble in organic solvents. The compounds, **1** - **5** were characterized by IR, UV-Vis spectroscopy and elemental analysis. The antibacterial activities the compounds were studied by disc diffusion method.

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