PREPARATION AND CHARACTERIZATION OF SOME MACROCYCLIC SCHIFF BASE DERIVED AND ITS PLATINUM COMPLEX

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Abstract - Macrocyclic ligand has been synthesized by reaction of 2-((6-((2-aminophenoxy) methyl) pyridin-2-yl)methoxy) benzealdehyde and 2-((6-((2-aminophenoxy) methyl) pyridin-2-yl) methoxy) benzenamine. Its complex Pt(II) has been synthesized by the reaction of ligand and $PtCl_2$.
Ligand and its metal complex have been characterized by Q-TOF MS, FTIR, ^{1}H NMR, ^{13}C NMR spectrums and elementel analysis. Complex of platinum (II) is diamagnetic and mononuclear.

Keywords - Macrocyclic Ligand, Platinum Complex, Schiff Base.

I. INTRODUCTION

Macrocyclic chemistry of metals is developing swiftly because of its importance of coordination chemistry [1]. The transition metal coordination chemistry of macrocyclic ligands has been developed extensively in recent years [2,3].
Schiff base metal complexes have played important role in the development of bioinorganic chemistry (4-6). These materials are the most widely used materials in the field of heterogeneous catalysis, molecular electronics and photographic chemistry (7) medical imaging [8], optical materials [9] and thin films (10,11).
There are numerous reports of antimicrobial activities of transition metal complexes containing O, N (12) and S, N (13) donor atoms. Palladium complexes are well known catalysts in bioinorganic chemistry. They play important roles in many catalytic industrial processes. In this papar, we report the preparation of a new type of macrocyclic ligand and its platinum (II) complex. This ligand has nitrogen and sulfur donor sites. The structures of synthesised ligand and their complex are explained by using data obtained from Q-TOF MS, IR, ^{1}H, ^{13}C spectrums and elementel analysis.

II. DETAILS EXPERIMENTAL

2.1 Materials and Instrumentation

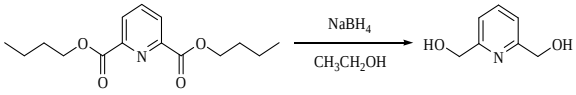
All chemicals and solvents were reagent grade and were used as purchased without further purification. FTIR spectra (KBr, 4000–400 cm^{-1}) were recorded using a Perkin Elmer BXII spectrophotometer. Routine ^{1}H (300 MHz) and ^{13}C (75 MHz) nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature in $DCCl_3$ and DMSO-d_6. Chemical shifts (d) are expressed in units of parts per million (ppm) relative to TMS. The analytical data and physical properties are summarized for each experiment. Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin-Elmer 2400 CHN elemental analyzer. Solid-state magnetic susceptibility data were collected on a powdered microcrystalline sample using a Sherwood Scientific Magnetic Susceptibility Balance at room temperature.

2.2. Synthesis

Pyridine-2,6-dicarboxylic acid dibutyl ester [I]

Thionyl chloride (88 mmol) was added dropwise to n-butanol (25 mL) with ice cooling under argon. A suspension of pyridine-2,6-dicarboxylic acid (44 mmol) in n-butanol (55 mL) was slowly added to it and the mixture was refluxed for 12 h under argon. The mixture was cooled and dropped into cold water (1000 mL). The solid was filtered, washed with water and dried in vacuo, obtained a white crystalline solid (79%) and Mp 62°C (14)
C15H21NO4 , 279.15; Found (calculated); C, 64.34 (64.50); H, 7.67 (7.58); N, 4.77 (5.01). FTIR(4000-450 cm^{-1}): 2965 cm^{-1} υ (C-H), 1720 cm^{-1} υ (C=O), 1242 cm^{-1} υ (C-O). ^{1}H NMR (300MHz, $CDCl_3$): δ 8.27 (d, *J* = 7.8 Hz, 2H), 8.03 – 7.97 (m, 1H), 4.43 (t, *J* = 6.8 Hz, 4H), 1.84 – 1.78 (m, 4H), 1.53 – 1.45 (m, 4H), 0.98 (d, *J* = 7.4 Hz, 6H) ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 164.92 (C), 148.89 (C), 138.38 (CH), 127.95 (CH), 66.34 (CH_2), 30.81 (CH_2), 19.43 (CH_2), 14.03 (CH_3) ppm

2,6-bis(hydroxymethyl)pyridine [II]



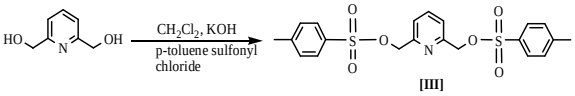
[II]

(I) (30 mmol) in ethanol (75 mL), $NaBH_4$ (145 mmol) in ethanol (45 mL) was added slowly for 2 h with ice cooling. The mixture was stirred at room temperature for 5h and then was relaxed further for 10h. After evaporation of the solvent, the residue was dissolved in 110 mL of water, adjusted to pH 4 with 2M HCl, and then adjusted to pH 9 with a saturated aqueous Na_2CO_3 solution. The solvent was evaporated and the dry residue was extracted with

CH_2Cl_2 (100 mL) by Soxhlet extraction for 96 h. Evaporation of the solvent produced a white solid (2.70 g, 65%) with Mp 112–114,8°C. (115–120,8°C) (15)

C7H9NO2 , 139.15; Found (calculated); C, 60.50 (60.42); H, 6.67 (6.52); N, 9.77 (10.07). FTIR(4000-450 cm^{-1}): 3350 cm^{-1} υ(O-H), 3094 cm^{-1} υ(C-H). ^1H NMR (300MHz, $CDCl_3$):δ 7.70 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 4.79 (s, 4H), 3.24 (s, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ161.51 (C), 137.72 (CH), 118.8 (CH), 64.83 (CH_2) ppm.

2,6-[(tosiloxy)methyl] pyridine [III]

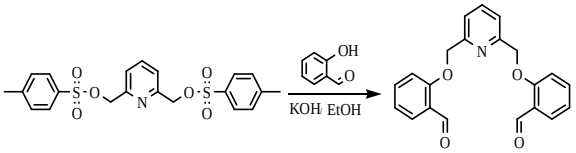


[III]

A solution of [II] (10 mmol) in 35 mL of CH_2Cl_2 was added to a 30% aqueous solution of KOH (45 mL). The reaction mixture was cooled at 0°C and stirred for 30 min, after which a solution of p-toluene sulfonyl chloride (20 mmol) was added in one portion. The reaction mixture was stirred for 1 h at 0 C and then at room temperature until complete conversion (TLC, 1/4 methanol/toluene). The reaction mixture was added to water (50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), the combined organic phase was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure to afford a white crystalline solid (70%) with Mp 119–122°C (121–122°C) (16).

C21H21NO6S2, 447.52; Found (calculated); C, 56.10 (56.36); H, 4.77 (4.73); N, 2.87 (3.13). FTIR (4000-450 cm^{-1}); 3076, 2936 cm^{-1} υ (C-H) 1586 cm^{-1} υ (C=C). ^1H NMR (300MHz, $CDCl_3$): δ 7.85 – 7.26 (m, 11H), 5.05 (s, 4H), 2.44 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 153.73 (C), 138.12 (C), 132.86 (CH), 130.15 (CH), 128.28 (CH), 121.61 (CH), 71.51 (CH_2), 21.90 (CH_3) ppm

2,6-bis(benzoxazol-20-ylthiomethyl)pyridine [IV]

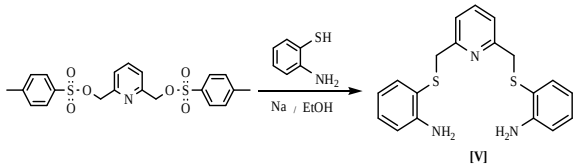


[IV]

A solution of [III] (2.23 mmol) in ethenol (5 mL) was added to ethanol (15 mL) solution of KOH (4.3 mmol). 2-hydroxybenzaldehyde (4mmol) was dropped in to the mixture in 1h. The mixture was stirred at room temperature for 2h and refluxed for 5h. After completion of the reaction (monitored by TLC Ethylacetate: Hexane (1:1)) the solid mass was filtered, washed with water. The product was recrystallized from EtOH, giving a white solid product. (64%, mp: 180-184 ˚C).

$C_{21}H_{17}NO_4$, 347.234; Found (calculated); C, 72.79 (72.61); H, 4.09 (4.93); N, 3.76 (4.03). FTIR (4000-400 cm^{-1}): 2862, 2758 cm^{-1} υ (C-N), 1680 cm^{-1} υ (C=O). ^1H NMR (300MHz, $CDCl_3$): δ10.63 (s, 2H), 7.92 – 7.02 (m, 11H), 5.34 (s, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ189.77 (CH), 160.70 (C), 156.27 (C), 138.35 (CH), 136.12 (CH), 129.40 (CH), 125.14(C), 121.50 (CH), 120.86 (CH), 113,14 (CH), 71.09 (CH_2) ppm.

2,6-bis(benzoxazol-20-ylthiomethyl)pyridine [IV]

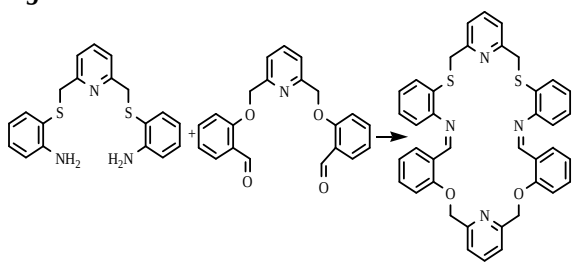


[V]

Na (4.3 mmol) was mixed together in 60 mL dry argon saturated ethanol and refluxed for 1 h in room temperature. A solution of [III] (2.23 mmol) in ethenol (5 mL) was added to mixture. 2-hydroxybenzaldehyde (4mmol) was dropped in to the mixture in 1h. The mixture was stirred at room temperature for 2h and refluxed for 5h. 2-aminobenzenethiol (4 mmol) was dropped in to the mixture in 1h. The mixture was refluxed for 6h. After completion of the reaction (monitored by TLC Ethylacetate: Hexane (1:1.5)) the solid mass was filtered, washed with water. The product was recrystallized, giving a white solid product. (Yield 78 %; mp. 79-82 °C).

$C_{19}H_{19}N_3S_2$, 353.356 (Yield % 78); Found (calculated); C, 63.1 (64.55); H, 5.1 (5.42); N, 11.76 (11.89). FTIR (4000-400 cm^{-1}): 3456, 3296 cm^{-1}υ (N-H), 3062, 2918 cm^{-1} υ (C-H), 1603 cm^{-1} δ (N-C). ^1H NMR (300MHz, $CDCl_3$): δ7.43 – 6.56 (m, 11H), 4.37 (s, 4H), 4.00 (s, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.99(C), 149.01 (C), 136.88 (CH), 136.76 (CH), 130.40 (CH), 121.70 (C), 118.41 (CH), 117.09 (CH), 115.12 (CH), 41.44 (CH_2) ppm

Ligand



10 mmol aldehyde and 10 mmol amine compound were mixed together in 60 mL dry argon saturated methanol and refluxed for 10 h. The solution was concentrated on a rotary evaporator and left for crystallization. A colored oily product was obtained. This oily product was loaded to alumina column for the purification. After purification colored (yellowlight brown) solids were obtained.

$C_{40}H_{32}N_4O_2S_2$ (Yield: 45%, 664.84) Found (calculated); C, 72.79 (72.26); H, 4.09 (4.85); N, 8.76 (8.43). FTIR (4000-450 cm^{-1}) 3040-2900 cm^{-1} υ(C-H)ar, 1616 cm^{-1} υ(CH=N), 1590-1580 cm^{-1} υ(C=C).

^{1}H NMR (300 MHz,) {14}: δ: 8.9 (s, 2H), 7.9 – 6.53 (m, 22H), 5.1 (s, 4H), 4.01 (s, 4H) ppm.

Metal complexes

The metal salt (10 mmol) was dissolved in 40 mL argon saturated ethanol and the solution was added to a stirred solution of azomethine (11 mmol) in 30 mL argon saturated ethanol solution at room temperature. On addition of metal to ligand solution immediate color change was observed according to the metal ions. Then the solution was warmed up to 50◦C and stirred for 10 h and then solution was concentrated on rotary evaporator. The solid substance dissolved in acetonitrile and loaded to a alumina column for the purification. The resulting precipitates were filtered by suction and then dried at vacuum oven at room temperature for 48 h.

[$PtLCl_2$] C40H32N4O2S2Cl2Pt (929.1) (Yield: 55 %). Found (calculated); C, 50.55 (51.61); H, 3.71 (3.47); N, 5.97 (6.02). FTIR (4000-450 cm^{-1}): 3030-2900 cm^{-1} υ(C-H)ar, 1593 cm^{-1} υ(CH=N), 1590 cm^{-1} υ(C=C). ^{1}H NMR (300 MHz) {19}: δ: 8.32 (s, 2H), 7.76 – 6.99 (m, 22H), 5.24 (s, 4H), 4.24 (s, 4H) ppm.

III. RESULTS AND DISCUSSION

FTIR spectra

The most relevant IR peaks of the ligand were compared and explained. The N–H stretching vibration is observed in the 3100–3250 cm^{-1}. The (C=N) band is observed at 1616 cm^{-1} in free ligand, and this band is shifted to 1593 cm^{-1} in the Pt(II) complex. The S–H stretching was observed in Ligand at 2546 cm^{-1}. The (C–O) bands are generally observed in the region of 1270–1330 cm-1 for free ligands and 1305–1330 cm^{-1} for complexes. Upon complexation, the frequencies of these modes are upshifted by 20 cm^{-1}(17).

Nuclear magnetic resonance

The ^{1}H spectra of the Ligand were carried out at room temperature in $CDCl_3$. Ligand show characteristic singlets at 8.90 ppm are observed for –CH N-, respectively. Aromatic protons appear in between 7.90 and 6.53 ppm. The (HC=N) is observed at 8.90 ppm in ligand, and this peak is shifted to 8.32 ppm in the Pt(II) complex. (18).

Molar conductance analyses

The measured molar conductivities of the Pt complex is 13.3 $\Omega^{-1}.cm^2.mol^{-1}$. The molar conductivity measurements show that complex is nonelectrolytes in DMSO. (1x 10^{-3} M) (19) and thus ensure the formation of the complex of [$Pt(L)Cl_2$] composition.

Magnetic Moments

The magnetic susceptibility of the solid-state complex under discussion was measured by the Gouy balance method. Magnetic moment of the Pt(II) complex was found to be diamagnetic. Pt(II) is suggested to possess a square-planar structure environment in the complex.

CONCLUSIONS

In this work, we presented platinum(II) complex of azomethine ligand. The metal center in complex is four coordinated with square planar Pt (II) complex is monometallic. The structures of the ligand and complex are well sustained by the spectral studies of ^{1}H NMR, ^{13}C NMR and FTIR, magnetic, and conductometric studies.

The measured molar conductivity of the complex indicate that the complexes have a [$Pt(L)Cl_2$] composition. The NMR spectra give additional features consistent with the formation of the complex in the [$Pt(L)Cl_2$] form. According to NMR spectra, coordination around the Zn and Pt ions occur through two nitrogen atoms and two Cl atoms. FTIR spectra of the complexes provides further evidence of the complexation.

Despite the crystalline nature of the product we could not succeed in obtaining single crystal suitable for X-ray structure determination. Proposed structures of the Pt (II) complex is shown in Fig1.

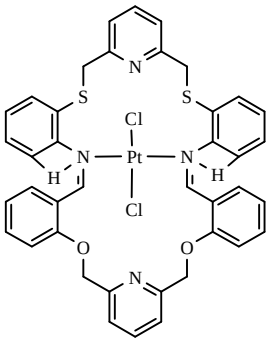


Fig. 1. The Structure of Pt(II) complex.

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