

Synthesis, Characterization, Luminescent Properties, And Crystal Structure Determination Of a New Platinum(IV) Complex: *trans*-[Pt(4-mpy)₂Cl₄]

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Abstract

The new *trans*-[Pt(4-mpy)₂Cl₄] (**1**) complex (4-mpy is 4-methylpyridine) was prepared from the reaction of H₂PtCl₆.6H₂O with 4-methylpyridine in methanol. The synthesized complex was thoroughly characterized by elemental analysis, IR, ¹H-NMR, ¹³C{¹H}-NMR and ¹⁹⁵Pt-NMR spectroscopy. Elemental analysis data (C, H, N) support the general composition of the complex **1** and the structure has been established by single-crystal X-ray diffraction study. In this complex, the geometry platinum(IV) cation is octahedral, formed by two nitrogen atoms from two 4-mpy ligands and four chloride anions. Also, in this complex, the strong π...π interactions between the pyridine rings are effective on the stabilization of the crystal packing. Furthermore, the luminescence properties of the free 4-mpy ligand as well as the complex **1** were investigated in solution. Luminescence emission of complex **1** was red shifted compared to the free 4-mpy ligand in dimethyl sulfoxide solution

Keywords: crystal structure, platinum(IV) complex, 4-methylpyridine, luminescent properties.

1. Introduction

Platinum(IV) complexes containing pyridine ligands and chloride ions have been reported by for the first time by Hedin in 1886 and Jörgensen in 1900 [1, 2]. In this regard, there are several platinum(IV) complexes, with formula, [PtL₂Cl₄], such as *trans*-[Pt(pz)₂Cl₄] [3], *cis* and *trans*-[Pt(py)₂Cl₄] [4], *cis*-[Pt(py)₂Cl₄] [5], *cis* and *trans*-[Pt(pzH)₂Cl₄] [6], *trans*-[Pt(3phpy)₂Cl₄] [7] and *cis* and *trans*-[Pt(4-AcPy)₂Cl₄] [8, 9] (where pz is pyridine, pzH is

pyrazole, 3phpy is 3-phenylpyridine and 4-AcPy is 4-acetylpyridine) which have been synthesized and characterized by X-ray diffraction methods. The complexes of *trans*-[Pt(3phpy)₂Cl₄] and *cis* and *trans*-[Pt(4-AcPy)₂Cl₄] show anti-cancer properties [7-9]. In continuation of these research works, herein, we report the synthesis of a new platinum(IV) complex containing chloride and 4-methylpyridine ligands. The structure of this complex was studied by elemental analysis, X-ray crystallography as well as

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UV-Vis, IR and luminescence spectroscopic techniques.

2. Experimental procedure

2.1 Materials and method

The $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ salt, 4-methylpyridine ligand and all solvents were purchased from Merck Company and used as received without further purification. Infrared spectrum ($4000\text{--}250\text{ cm}^{-1}$) of solid sample was recorded on a Perkin Elmer Spectrum Rxi FT-IR spectrometer in CsI pellet. NMR spectra were recorded on a Bruker AC-300 for protons at 300.13 MHz and for $^{13}\text{C}\{^1\text{H}\}$ -NMR at 75.45 MHz in DMSO-d_6 solvent. ^{195}Pt -NMR spectrum was obtained in DMSO-d_6 solvent on a Bruker AC-500 spectrometer at 107.65 MHz and referred to a solution of Na_2PtCl_4 . Melting point was obtained on a Kofler Heizbank Rechart type 7841 melting point apparatus. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. UV-Vis spectra were recorded on a Perkin Elmer Precisely P-T-P1 Peltier System, using a 1 cm path length cell in DMSO at room temperature and luminescence spectra were recorded on a FP-6200 spectro fluorometer using a 1 cm path length cell in DMSO at room temperature.

2.2 Synthesis of *trans*-[Pt(4-mpy) $_2$ Cl $_4$] (1)

4-Methylpyridine ligand (0.08 g, 0.09 ml, 0.88 mmol) in 5 ml methanol was added gradually to a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ salt (0.23 g, 0.44 mmol) in methanol (10 ml) at room temperature and the resulting yellow suspension was stirred for 20 min. Yellow prismatic shape single crystals of complex **1** suitable for X-ray diffraction measurement were obtained by methanol diffusion into the yellow solution of **1** in dimethyl sulfoxide over five days (yield 0.25 g, 75.2%, m.p. 238 °C). Infrared frequencies (CsI, cm^{-1}) are reported in Table 1. ^1H -NMR (DMSO-d_6 , ppm): 2.41 (s, 3 H), 7.64 (d, $J = 5.4$, 1 H) and 8.72 (satellite, 1 H, $^4J_{\text{HPt}} = 26$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (DMSO-d_6 , ppm): 21.3, 125.4, 147.6 and 150.8. ^{195}Pt -NMR (DMSO-d_6 , ppm): 1712.5.

UV-Vis: λ_{max} (DMSO , nm), 299. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{Cl}_4\text{N}_2\text{Pt}$ (%): C, 27.55; H, 2.68; N, 5.35. Found: C, 27.26; H, 2.67; N, 5.30.

2.3 Crystal structure determination and refinement

The X-ray diffraction measurement was made on a Bruker SMART 1000 CCD area detector diffractometer at 298 K (Mo-K α radiation, graphite monochromator, $\lambda = 0.71073$ Å). The structure was solved by SHELX-97 and SHELXTL and absorption correction was done using the SADABS and APEX2 programs [10, 11]. Data collection, cell refinement and data reduction were done by APEX2, SAINT, SHELXTL and PLATON [10-14]. The molecular structure and crystal packing diagram for complex **1** were generated with the Mercury 2.4 program [15]. Crystallographic and structure refinement data for **1**: $\text{C}_{12}\text{H}_{14}\text{Cl}_4\text{N}_2\text{Pt}$, M 523.13, crystal system orthorhombic, space group *Pmna*, $a = 7.2658(9)$ Å, $b = 7.2658(9)$ Å, $c = 13.6808(14)$ Å, $V = 793.31(17)$ Å 3 , $Z = 2$, $\rho_{\text{calc}} = 2.190\text{ g/cm}^3$, $\mu = 9.504\text{ mm}^{-1}$, crystal size $0.40 \times 0.25 \times 0.39$ mm, $\theta_{\text{max}} = 26.11^\circ$ (completeness 99.9%), number of measured reflections 5674, independent 1143 ($R_{\text{int}} = 0.0424$), $R_1 = 0.0410$, $wR_2 = 0.1012$ over $F^2 > 2\sigma(F^2)$, $R_1 = 0.0610$, $wR_2 = 0.1121$ over all, $S = 1.004$, $\Delta\rho_{\text{min/max}} = 1.012\text{--}1.016\text{ e/Å}^3$. Complex **1** is deposited with CCDC number 1910994.

3. Results and discussion

3.1 Synthesis of *trans*-[Pt(4-mpy) $_2$ Cl $_4$] (1)

Compound *trans*-[Pt(4-mpy) $_2$ Cl $_4$] (**1**) was obtained from the reaction of one equivalent of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ with two equivalents of 4-methylpyridine in methanol at room temperature, in 75.2% yield. The suitable crystal of **1** for X-ray diffraction experiment was obtained by methanol diffusion into the yellow solution of complex **1** in dimethyl sulfoxide over five days.

3.2 Spectroscopic characterization of **1**

trans-[Pt(4-mpy) $_2$ Cl $_4$] (**1**) is stable in air and can be used directly for routine analyses. The infrared spectra for free 4-methylpyridine (4-mpy) ligand [16]

Table 1. Infrared frequencies of 4-mpyfree ligand and complex **1** (cm⁻¹).

Compound	$\nu(\text{C-H})_{\text{cycle}}$	$\nu(\text{C-H})_{\text{Me}}$	$\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N}), \nu(\text{C}-\text{C})$	$\delta(\text{C}=\text{C})$	$\delta(\text{C}=\text{N}), \delta(\text{C}-\text{C})$	$\nu(\text{Pt}-\text{Cl})$	$\nu(\text{Pt}-\text{N})$
4-mpy	3070m,	2992m	1606s, 1563m, 1611m, 1497m, 1445m,	1070w, 1042w, 995m, 981m,		-	-
	3029m		1415m, 1380w, 1224m, 1211w	972m, 802s, 726m, 516m, 486s			
1	3055m,	2984m	1620s, 1500w, 1445m, 1375w, 1284w,	1129w, 1064s, 1024m, 857w,		347s	266m
	3018m		1245w, 1210s	817s, 710w, 566m, 509m			

and complex **1** are presented in Table 1. The infrared spectra of 4-mpy free ligand and complex **1** show the weak and medium absorption bands in the range 3070-2984 cm⁻¹, which have been assigned to the C-H stretching vibrations of the pyridine ring and methyl group. In the infrared spectra of free ligand and complex **1**, the multiple absorption bands which appeared in the range 1620-1210 cm⁻¹ have been assigned to the C=C, C=N and C-C stretching vibrations. Also, the multiple weak to strong absorption bands which appeared in the range 1129–486 cm⁻¹ have been assigned to the C=C, C=N and C-C deformation vibrations in the pyridine ring [17-22]. In addition, the strong and medium absorption bands in the infrared spectrum of complex **1**, which appeared at 347 and 266 cm⁻¹ have been assigned to the Pt-Cl and Pt-N stretching vibrations, respectively [4, 23-26].

The NMR spectra for complex **1** was prepared in dimethyl sulfoxide-d₆ solution at room temperature, and the results are listed in the experimental section. The ¹H-NMR spectrum of title compound shows two signals at 7.64 and 8.72 ppm for two kinds of aromatic protons and a signal at 2.41 ppm for the methyl protons. The signal appeared at 8.72 ppm for one of the aromatic protons, which are close to the platinum center, is seen with satellites of the platinum nucleus. Other aromatic proton is split by this hydrogen atom as expected. The ¹³C{¹H}-NMR spectrum of title compound showed a signal at 21.3 ppm for the methyl groups and three signals between 125 and 151 ppm for the pyridine rings. The ¹⁹⁵Pt-NMR spectrum of title compound shows a signal at

1712.5 ppm, relative to the Na₂PtCl₄ reference to an external sample of Na₂PtCl₄ at -1642 ppm relative to H₂PtCl₆ at 0 ppm. Similar positions are reported for platinum(IV) bearing chloride and nitrogen ligands [23, 27].

The electronic absorption spectra of the dimethyl sulfoxide solution of complex **1** and free 4-mpy ligand are shown in Fig. S1. The UV-Vis spectra exhibited a broad strong absorption band at 278 and 299 nm, for free ligand and complex **1**, respectively. This absorption band was assigned to $\pi \rightarrow \pi^*$ that was red-shifted due to complexation [28-30].

The normalized luminescence emission spectra of free 4-mpy ligand and complex **1** were obtained in DMSO solution at room temperature and the results are displayed in Fig. 1. As it is clear from this figure, free 4-mpy ligand exhibits an emission broad band at 341 nm ($\lambda_{\text{ex}} = 299$ nm), which has been red shifted to 353 nm in complex **1**, and can be assigned to $\pi^* \rightarrow \pi$ transition. The shapes of the luminescence emission spectra for the free 4-mpy ligand and complex **1** are similar, therefore, the emission properties of this complex are assigned to either ligand-centred (LC, $\pi^* \rightarrow \pi$ transitions). The observed red-shift for complex **1** can be explained with a decrease of the energy gap between the ground and excited states in the 4-mpy ligand upon coordinated to Pt(IV) cation [30-36].

3.3 Description of the molecular structure of *trans*-[Pt(4-mpy)₂Cl₄] (**1**)

The yellow prismatic crystals of *trans*-[Pt(4-mpy)₂Cl₄] (**1**) were grown by methanol diffusion into the yellow solution of **1** in dimethyl sulfoxide over

five days. Selected bond lengths and bond angles are presented in Table 2. The asymmetric unit of this complex consists of one chloride ion, a half of 4-methylpyridine ligand and $\frac{1}{4}$ of Pt(IV) ion. ORTEP view with numbering scheme and packing diagram for this complex are shown in figures 2 and 3, respectively. This complex has octahedral geometry. In this complex, platinum has octahedral coordination with four chloride anions in equatorial position and two 4-methylpyridine ligands in axial position. In this complex, the Pt-N bond distance, 2.029(10)Å, is almost similar to that found in *trans*-[Pt(pz)₂Cl₄], 2.047(5)Å [3], *trans*-[Pt(py)₂Cl₄], 2.065(3)Å, [4], *trans*-[Pt(3phpy)₂Cl₄], 2.055(10)Å, [7] and *trans*-[Pt(4-Acpy)₂Cl₄], 2.053(3)Å, [8]. Also, the Pt-Cl bond distance, 2.316(2)Å, is almost similar to that found in *trans*-[Pt(pz)₂Cl₄], 2.3186(10)Å, [3], *trans*-[Pt(py)₂Cl₄], 2.327(2)Å, [4], *trans*-[Pt(3phpy)₂Cl₄], 2.314(5)Å, [7] and *trans*-[Pt(4-Acpy)₂Cl₄], 2.310(5)Å, [8] (where pz is pyrazine, py is pyridine, 3phpy is 3-phenylpyridine and 4-Acpy is 4-acetylpyridine). Furthermore, in this complex, the N1-Pt1-N1ⁱ and Cl1-Pt1-Cl1ⁱ (i is -x,-y,-z) bond angles are 180° and are similar to that found in *trans*-[Pt(pz)₂Cl₄], 180° [3]. In this complex, another Cl-Pt-Cl and N-Pt-Cl bond angles (Table 2) are in good agreement with the corresponding values of reported structures [3, 4, 7, 8].

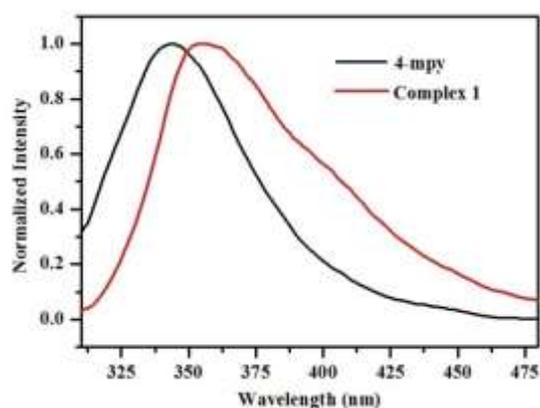


Fig. 1. The luminescence spectra of 3×10^{-4} M solution of 4-mpy ligand and complex **1** in DMSO at room temperature ($\lambda_{\text{exc}} = 299$ nm).

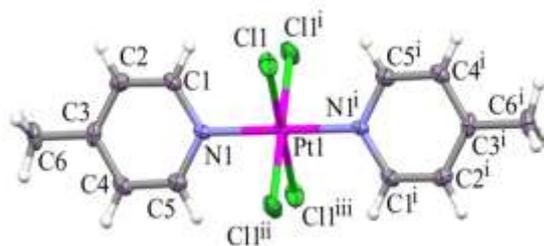


Fig. 2. The labeled diagram of *trans*-[Pt(4-mpy)₂Cl₄] (**1**). Thermal ellipsoids are at 30% probability level. Symmetry codes: (i) -x,-y,-z; (ii) -x,y,z and (iii) x,-y,-z.

Crystal packing diagram for this complex is shown in figure 3. As it is shown in this figure, there are no any hydrogen-bonding in the crystal packing. In the crystal packing of this complex, the coordinated 4-methylpyridine ligands form π bonding stacks in which each pyridine ligand lies between two pyridine ligands of adjacent platinum complexes. The centroid to centroid distance between adjacent aromatic rings is 3.830(2)Å. These several $\pi \dots \pi$ interactions causing on the stabilization of this complex in the crystal packing.

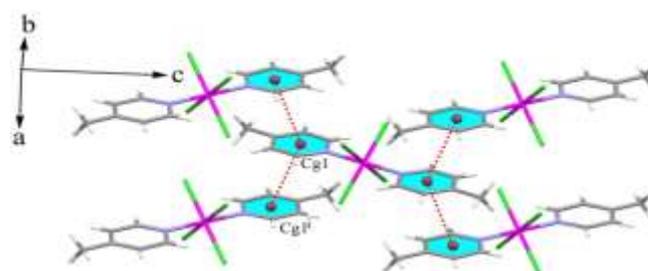


Fig.3. Crystal packing diagram of *trans*-[Pt(4-mpy)₂Cl₄] (**1**). The $\pi \dots \pi$ contacts are shown as dashed lines. Symmetry code: (i) -1/2-x,y,1/2-z.

Table 2. Selected bond distances (Å) and bond angles (°) for

Bond distances	
Pt1-N1	2.029(10)
Pt1-Cl1	2.316(2)
Bond angles	
N1-Pt1-N1 ⁱ	180
N1-Pt1-Cl1	90.0(2)
Cl1-Pt1-Cl1 ⁱ	180
Cl1-Pt1-Cl1 ⁱⁱ	90.80(15)
Cl1 ⁱ -Pt1-Cl1 ⁱⁱ	90.0(2)
Cl1 ⁱⁱ -Pt1-Cl1 ⁱ	89.20(15)
Cl1 ⁱⁱⁱ -Pt1-Cl1 ⁱ	90.80(15)
Symmetry codes: (i) -x,-y,-z; (ii) x,-y,-z; (iii) x,-y,-z.	

4. Conclusion

In this work, a new complex *trans*-[Pt(4-mpy)₂Cl₄] (**1**) has been synthesized. This complex was fully characterized by spectroscopic methods and its structure was determined by the single crystal diffraction analysis. In this complex, the Pt(IV) cation is six-coordinated in an octahedral geometry. It is notable that in this complex, the strong $\pi \dots \pi$ interactions between pyridine rings are effective on the stabilization of the crystal packing. Furthermore, the luminescence properties of the free 4-mpy ligand

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