



## Crystal and Molecular Structure of Platinum(II) Complex with Bis(diphenylphosphino)methane

KARWAN OMER ALI<sup>1\*</sup>, HIKMAT ALI MOHAMMAD<sup>2</sup>,  
THOMAS GERBER<sup>3</sup> and ERIC HOSTEN<sup>4</sup>

<sup>1</sup>College of Science, University of Halabja, Halabja, Kurdistan Regional Government, Iraq.

<sup>2</sup>College of Education, Department of Chemistry, University of Salahaddin, Hewler, Kurdistan Regional Government, Iraq.

<sup>3,4</sup>Department of Chemistry, Nelson Mandela University, Port Elizabeth, South Africa.

\*Corresponding author E-mail: karwan.ali@uoh.edu.iq

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### ABSTRACT

Platinum(II) complex consisting of the tertiarydiphosphine (dppm) ligand had been prepared from PdCl<sub>2</sub> with one equiv of dppm ligand to form [PtC<sub>2</sub>(dppmCl)] complex where as dppmCl is bis(diphenylphosphino) chloromethane. Crystal was grown in dichloromethane by slow evaporation process and characterized by X-ray crystallography technic. The complex structure synthesized based upon the identification using X-ray Crystallography and FTIR was [PtC<sub>12</sub>(dppmCl)], the ligand dppm coordinated to the meta centre as bidentate chelating ligand and form square planar arrangement around Pt(II) metal centre. The bond distances of Pt-P1, Pt-P2, Pt- Cl1 and Pt-Cl<sub>2</sub> are 2.217 (2), 2.217 (2), 2.3661 (19) and 2.3661 Å<sup>o</sup> respectively. The characterized results of Pt(II) complex using X-ray analysis illustrated that [PtC<sub>12</sub>(dppmCl)] Complex form monoclinic crystal with unit cell dimensions of a = 16.2034(5), b = 7.8274(2), and c = 19.2496 (6) Å<sup>o</sup>, with β = 98.918 (1)<sup>o</sup>, Z=4, calculated density= 1.838 mg/m<sup>3</sup>, T= 200 k and space group C<sub>2</sub>/c.

**Keywords:** Bis(diphenylphosphino)methane (dppm), Bis(diphenylphosphino)chloromethane (dppmCl), Crystal structure, FT-IR spectroscopy, Pt(II) complex.

### INTRODUCTION

Phosphine ligands have been intensively used in coordination chemistry because of their electron releasing capacity<sup>1</sup>. The phosphine ligands can be organized based on the type of substituents bonded to the phosphorus atom<sup>2</sup>. Trivalent phosphorus compound are commonly

used as mono- and bi-dentate ligands in the organometallic and coordination compounds of the transition metals<sup>3</sup>. Bisphosphanes are class of bidentate ligand that contain two phosphine atoms joined by a bridge<sup>4</sup>. The bridge, for instance, could involve only one or more methylene bridge or a few phenyl rings with heteroatoms joined<sup>5</sup>. The structure of the methylene bridge and the substituents joined



to the phosphine atoms influence the chemical reactivity of the bisphosphanes ligand in coordination complexes by means of steric and electronic effects<sup>6,7</sup>. Phosphanes ligands usually attached to the metal center through the pair of valence electrons on the phosphorus<sup>8</sup>. The 'R' group substituents bound to the phosphorus can then influence the behavior of the phosphine as a ligand bound to a metal center<sup>9</sup>. Phosphine ligands are usually strong  $\sigma$ -donor ligands and only weak  $\pi$ -acceptors<sup>10</sup>. This impact can be expanded with electron-donating groups in the rest R, although electron with-drawing groups in 'R' favor the  $\pi$ -acceptor back bonding<sup>11</sup>. In the present work, the synthesized platinum complex has chlorine atom on the methylene group of dppm ligand that cause increase in the  $\pi$ -acceptor back bonding of dppm ligand and increase the stability of complex.

## EXPERIMENTAL

### Instrumentation and Materials

The FTIR spectra of complexes were recorded on a Shimadzu IRAffinity-1S FTIR Spectrophotometer in the range (4000-200  $\text{cm}^{-1}$ ) by using cesium iodide disc, and IR spectra of the compound were recorded on Shimadzu, FT-IR spectroscopy Mod IR Affinity-1CE spectrophotometer in the region (4000-400  $\text{cm}^{-1}$ ) by using potassium bromide disc. Melting point of the complex were recorded by Melting Point-MPD-100 Pixel Technology CO apparatus.

The compounds platinum dichloride and bis(diphenylphosphino)methane were commercially valid and be valid from Yacoo chem. China. All solvents used in this research were commercial products and were used without further purification.

### Synthesis of $[\text{PtCl}_2(\text{dppmCl})]$ complex

Bis(diphenylphosphino)methane (0.7687 g, 2mmol) was dissolved in (20  $\text{cm}^3$ ) dichloromethane and treated with a (20  $\text{cm}^3$ ) solution of platinum dichloride (0.5319 g, 3mmol) in a mixture of ethanol and concentrate hydrochloric acid in the same portion. The reaction mixture was stirred at 40°C for 3 h and allowed to evaporate slowly at 25°C. The yellow precipitate was formed. The yellow crystal was formed

by slow evaporation of a dichloromethane solution of the complex after one week, Yield: 1.300 g (87%), m. p.: (310°C). M.Wt: 650.378 g/mol.

## RESULTS AND DISCUSSION

X-ray data of  $[\text{Pt}(\text{k}^2\text{-dppmCl})\text{Cl}_2]$  complex were collected at 200 K in the Mo  $K\alpha$  radiation (0.71073 Å) on a Bruker Kappa Apex II diffractometer with graphite monochromated ( $\lambda = 0.71073$  Å). The program APEX-Trak was utilized to data accumulation and SAINT for cell refinement and data reduction<sup>12</sup>. The structure was carry out by straight manners applying SIR97<sup>13</sup> and refined by smallest-squares procedures utilizing SHELXL-97<sup>14</sup>. The needle yellow crystals were obtained by slow evaporation of dichloromethane solution of the complex at room temperature after seven days, these crystals were sent to X-ray analysis. Fig. 1 show the molecular geometry of the complex. The complex is composed of closely packed monoclinic molecule of  $[\text{Pt}(\text{k}^2\text{-dppmCl})\text{Cl}_2]$ . In the complex the Pt atom is surrounded to form square planer by two phosphorus atoms and two chlorine atoms. The bis(diphenylphosphino)methane contain two P as a donor atoms. The observed Pt-P1 and Pt-P2 length of 2.217(2) and 2.217(2) Å. The Pt-Cl1 and PtCl2 length of 2.3661(19) and 2.3661 Å respectively of  $[\text{Pt}(\text{k}^2\text{-dppmCl})\text{Cl}_2]$  metal complex<sup>15</sup>. A summary of crystal data, experimental details, and refinement outcomes is shown in Table 1.

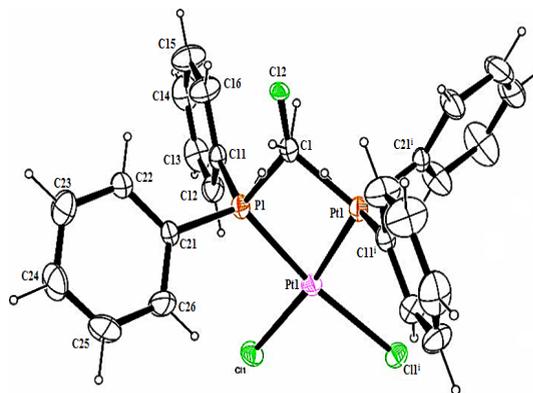


Fig. 1. Molecular structure of  $[\text{Pt}(\text{dppmCl})\text{Cl}_2]$  complex

### X-ray Crystal structure

Suitable crystals of the complex were produced by slow evaporation of a methylene chloride solution. A yellow crystal with approximate dimensions 0.04 x 0.20 x 0.21  $\text{mm}^3$  was formed and the crystal was sent to X-ray analysis. The molecular

structure is given in Fig. 1. Crystals of complex are monoclinic, space group C2/c with  $a = 16.2034(5)$ ,  $b = 7.8274(2)$ ,  $c = 19.2496(6)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 98.918(1)^\circ$ ,  $Z = 4$ . The R value is 0.03 (WR2=0.1178, S=1.30). The platinum center adopts a square planar geometry with Cl1-Pt1-P1 and Cl1-Pt1-P2 bonds angle of  $98.10(7)^\circ$  and  $98.10(7)^\circ$  respectively, the phosphine ligand is coordinated in bidentate fashion through two phosphorus atom, and the two chlorine atoms also coordinated to the metal center<sup>16,17,18</sup>. Table 2 gives the selected bond length and bond angles of metal complex.

### Infrared spectral

The IR spectra of the metal complex are in agreement with X-ray analysis data with respect to the condition of coordination. The infrared spectrum of bis(diphenylphosphino)methane ligand have bands at 3064, 2899, 1431 and  $511\text{ cm}^{-1}$  are attributed to the stretching vibration of aromatic  $\nu$  (C-H), aliphatic  $\nu$  (C-H),  $\nu$  (P-Ph) and aliphatic  $\nu$  (P-C) respectively<sup>19,20,21</sup>. The IR spectrum of complex also shows stretching vibrations assigned to the Pt-P bond at  $280\text{ cm}^{-1}$  and Pt-Cl bond at  $371\text{ cm}^{-1}$ <sup>22,23</sup>.

**Table 1: Crystallographic and structure refinement data for [Pt(dppmCl)Cl<sub>2</sub>] complex**

Compound	[Pt(dppmCl)Cl <sub>2</sub> ]
Empirical formula	C <sub>24.27</sub> H <sub>21.46</sub> Cl <sub>2</sub> P <sub>2</sub> Pt(Cl) <sub>0.725</sub> (H) <sub>0.54</sub>
Formula weight (g/mol)	667.43
R	0.03
Temperature (K)	200
Wave length (°Å),	0.71073, Monoclinic
Crystal system	
space group	C2/c
a(°Å)	16.2034(5)
b(°Å)	7.8274(2)
c(°Å)	19.2496(6)
$\alpha$ (°)	90
$\beta$ (°)	98.918(1)
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	2411.92(12)
Calculated density (mg/m <sup>3</sup> )	4, 1.838
Z	4
Crystal size	0.04 x 0.20 x 0.21 mm
Theta range for data collection	2.9,28.4 deg
Reflections collected/unique	16294,3007,[R(int)= 0.030]
Observed Data [I > 2.0 sigma(I)]	2930
R, wR2, S	R= 0.0478 wR2= 0.1178 S= 1.30
Min. and Max. Resd. Dens	[-1.71, 4.83] e/Ång <sup>3</sup>

**Table 2: Selected Bond length [Å] And Bond Angles [Degree] of [Pt(k2-dppmCl)Cl<sub>2</sub>] Complex**

Bond distance		Bond angle		Bond angle	
Pt1-Cl1	2.3661(19)	Cl1-Pt1-P2	98.10(7)	C14-C13-H13	120.00
Pt1-P2	2.217(2)	Cl1-Pt1-P1	98.10(7)	C13-C14-H14	119.00
Pt1-P1	2.217(2)	Cl1-Pt1-Cl1_a	90.02(6)	C15-C14-H14	119.00
Pt1-Cl1_a	2.3661(19)	Cl1-Pt1-P2_a	171.58(7)	C14-C15-H15	121.00
Pt1-P2_a	2.217(2)	Cl1_a-Pt1-P2	171.58(7)	C16-C15-H15	121.00
P1-C21	1.816(7)	C14-C15-C16	118.6(9)	P2-C11-C16	122.9(6)
P1-C1	1.85(3)	C11-C16-C15	121.1(9)	C12-C11-C16	119.7(7)
P1-C11	1.808(8)	P2-C21-C22	121.9(6)	P1-C11-C12	117.5(6)
P2-C11	1.808(8)	P2-C21-C26	117.9(6)	P1-C11-C16	122.9(6)
P2-C21	1.816(7)	P1-C21-C22	121.9(6)	P2-C11-C12	117.5(6)
C21-C26	1.362(12)	P2-Pt1-P2_a	73.87(8)	C11-C12-C13	119.2(8)
C21-C22	1.386(12)	Cl1_a-Pt1-P1	171.58(7)	C11-C16-H16	119.00
C22-C23	1.381(13)	Cl1_a-Pt1-P2_a	98.10(7)	C15-C16-H16	119.00
C23-C24	1.387(14)	C1-P1-C11	107.4(5)	C21-C22-H22	120.00
C24-C25	1.358(17)	C1-P1-C21	108.0(5)	C23-C22-H22	120.00
C25-C26	1.390(13)	P1-C21-C26	117.9(6)	C22-C23-H23	120.00
C12-H12	0.9500	C22-C21-C26	120.2(7)	C24-C23-H23	120.00
C13-H13	0.9500	C21-C22-C23	120.2(8)	C12-C13-C14	119.8(9)
C14-H14	0.9500	C22-C23-C24	119.6(9)	C13-C14-C15	121.7(9)
C15-H15	0.9500	C23-C24-C25	119.5(9)	C24-C25-H25	119.00
P2-H2	1.0000	Pt1-P1-C1	97.0(9)	C26-C25-H25	119.00
C11-C12	1.388(11)	Pt1-P1-C11	117.7(3)	C23-C24-H24	120.00
C11-C16	1.391(12)	Pt1-P1-C21	117.2(3)	C25-C24-H24	120.00
C12-C13	1.394(12)	C11-P1-C21	108.1(3)	C21-C26-H26	120.00
C13-C14	1.364(16)	C11-P2-C21	108.1(3)	C25-C26-H26	120.00
C14-C15	1.384(15)	C24-C25-C26	121.4(10)		
C15-C16	1.369(14)	C21-C26-C25	119.2(9)		
C16-H16	0.9500	C11-C12-H12	120.00		

**CONCLUSION**

In conclusion, new Pt(II) metal complex of tertiarydiphosphine (dppm) can be readily obtained by the reaction of 1,1-Bis(diphenylphosphino)methane with Pt(II) chloride as given in the Fig. 1. The central platinum atom is bonded by two chlorine and two phosphorus atoms of 1,1-Bis(diphenylphosphino) methane ligand, thus forming the  $[Pt(k^2\text{-dppmCl})Cl_2]$  square planar compound. The chlorine atom bonded to methylene group of dppm ligand that make the complex new.

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**Conflicts of Interest**

The authors declare no conflict of interest.

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