

## КРАТКИЕ СООБЩЕНИЯ

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CHARACTERIZATION, LUMINESCENT PROPERTIES,  
AND CRYSTAL STRUCTURE DETERMINATION OF [Pt(Ph<sub>2</sub>bipy)Cl<sub>2</sub>]S. Shamaei<sup>1</sup>, A. Heidari<sup>2</sup>, V. Amani<sup>3</sup><sup>1</sup>Department of Chemistry, Faculty of Science, Khorramabad Branch, Islamic Azad University, Khorramabad, Iran  
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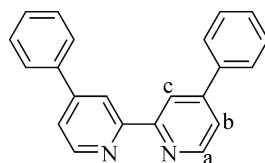
New complex [Pt(Ph<sub>2</sub>bipy)Cl<sub>2</sub>] (**1**) is obtained from the reaction of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O and 4,4'-diphenyl-2,2'-bipyridine (Ph<sub>2</sub>bipy) in a mixture of methanol, chloroform, and dimethyl sulfoxide. Suitable crystals of **1** for the diffraction experiment are obtained by slow evaporation of the resulted orange solution at room temperature. This complex is characterized by elemental analysis, IR, <sup>1</sup>H NMR, UV-Vis, and luminescence spectroscopy and its structure is studied by the single crystal X-ray diffraction method. X-ray structure determination shows that in the structure of this compound, the Pt(II) atom is four-coordinated in a distorted square-planar configuration by two nitrogen atoms from a bidentate 4,4'-diphenyl-2,2'-bipyridine ligand and two terminal chlorine atoms.

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**Keywords:** synthesis, crystal structure, platinum(II) complex, 4,4'-diphenyl-2,2'-bipyridine, luminescent properties.

Platinum complexes containing mono-, bi-, and tridentate N-donor ligands are important due to their application in electronics and optical devices, [1–3] bio-imaging materials [4, 5], medicine [6–8], and as catalysts [9, 10]. In particular, cisplatin *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] has been introduced in oncology for the treatment of diverse classes of cancer [6, 11, 12].

The synthesis and characterization of 4,4'-diphenyl-2,2'-bipyridine (Ph<sub>2</sub>bipy; Scheme 1) compound was reported by Case and Kasper in 1956 [13]. The Ph<sub>2</sub>bipy compound is a good bidentate ligand, and only a few complexes have been reported with this ligand, such as those of copper [14], tin [15], osmium [16], and ruthenium [17]. Also, three platinum(II) mixed-ligand complexes of [Pt(Ph<sub>2</sub>bipy)(3,5-Me<sub>2</sub>py)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> [18], [Pt(Ph<sub>2</sub>bipy)(C≡CPh)<sub>2</sub>] [19], and [Pt(Ph<sub>2</sub>bipy)(COMe)<sub>2</sub>] [20], including this ligand, have been reported. All of these complexes are fully characterized by spectroscopic methods and their structures are studied through single crystal X-ray diffraction. In continuation of these research works, herein, we report the synthesis, characterization and crystal structure of a new platinum(II) complex with chloride and 4,4'-diphenyl-2,2'-bipyridine.



Scheme 1. 4,4'-Diphenyl-2,2'-bipyridine

**Experimental. Materials and physical methods.** 4,4'-Diphenyl-2,2'-bipyridine was purchased from Aldrich and used as received. Other materials were purchased from Merck and used without further purification. Infrared spectra ( $4000\text{--}250\text{ cm}^{-1}$ ) of solid samples were taken as 1 % dispersion in CsI pellets using a Shimadzu-470 spectrometer. NMR was recorded on a Bruker AC-300 spectrometer for protons at 300.13 MHz in the DMSO- $d_6$  solvent. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. Melting point was obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus. UV-Vis spectra were recorded on a Shimadzu 2100 spectrometer using a 1 cm path length cell in DMSO at room temperature and luminescence spectra were recorded on a Perkin Elmer LS 45 using a 1 cm path length cell.

**Synthesis of [Pt(Ph<sub>2</sub>bipy)Cl<sub>2</sub>] (1).** A solution of 4,4'-diphenyl-2,2'-bipyridine (0.29 g, 0.90 mmol) in chloroform (10 ml) was added to a solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (0.38 g, 0.90 mmol) in methanol (10 ml) at room temperature and stirred for 5 min until a precipitate was formed. The precipitate started to disappear gradually when DMSO (10 ml) was added to the solution and the mixture was stirred at 50 °C for 1 h. The solution was filtered and allowed to crystallize at room temperature, whereupon orange prismatic crystals of **1** formed after two months (yield 0.37 g, 71.6 %, m.p. > 300 °C). IR (CsI, cm<sup>-1</sup>): 3081w, 3058w, 1619s, 1544m, 1473m, 1416m, 1359s, 1244w, 1085s, 990m, 852m, 764s, 687m, 634m, 536m, 408m, 316m, 281m, 255s. <sup>1</sup>H NMR (DMSO- $d_6$ , ppm): 7.62—7.82 (m, 5H), 8.17 (d, 1H), 9.05 (s, 1H) and 9.45 (d, 1H). UV-Vis:  $\lambda_{\text{max}}$  (DMSO, nm), 290, 340, 396. Elemental analysis: C<sub>22</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>Pt (%) (574.35); Anal. Calcd (%): C 46.00, H 2.79, N 4.88. Found: C 45.71, H 2.77, N 4.84.

**Single crystal X-ray diffraction analysis.** The X-ray diffraction measurements were made on a Bruker APEX II CCD area detector diffractometer at 298 K (MoK $\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073\text{ \AA}$ ). The structure of **1** was solved by SHELX-97 and absorption correction was applied using the SADABS programs [ 21 ]. Data collection, cell refinement, and data reduction were performed by APEX II, SAINT, SHELXTL, PLATON, and MERCURY [ 21—24 ]. Crystallographic and structure refinement data for **1**: C<sub>22</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>Pt, *M* 574.35, crystal system tetragonal, space group *P*4<sub>1</sub>2<sub>1</sub>2, *a* = 10.7807(11) Å, *b* = 10.7807(11) Å, *c* = 33.394(4) Å, *V* = 3881.1(8) Å<sup>3</sup>, *Z* = 8,  $\rho_{\text{calc}} = 1.966\text{ g/cm}^3$ ,  $\mu = 7.515\text{ mm}^{-1}$ , crystal size 0.35×0.32×0.31 mm,  $\theta_{\text{max}} = 26.98^\circ$  (completeness 99.9 %), number of measured reflections 24111, independent 4235 ( $R_{\text{int}} = 0.1601$ ),  $R_1 = 0.0497$ ,  $wR_2 = 0.0907$  over  $F^2 > 2\sigma(F^2)$ ,  $R_1 = 0.1039$ ,  $wR_2 = 0.1063$  over all, *S* = 1.118,  $\Delta\lambda_{\text{min/max}} = 1.933/ -0.681\text{ e/\AA}^3$ . Crystal chemical information on the structure investigated was deposited with the Cambridge Structural Database under number CCDC 1415869, from where it can be obtained free of charge on request at the following website: [www.ccdc.cam.ac.uk/products/csd/faqs](http://www.ccdc.cam.ac.uk/products/csd/faqs).

**Results and discussion. Synthesis of [Pt(Ph<sub>2</sub>bipy)Cl<sub>2</sub>] (1).** Complex **1** was obtained by the reaction of one equivalent of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O with one equivalent of 4,4'-diphenyl-2,2'-bipyridine in a mixture of methanol, chloroform, and dimethyl sulfoxide. Suitable crystals of **1** for X-ray diffraction studies were obtained by slow evaporation of the resulted orange solution at room temperature. It should be noted that in the presence of a mixture of these solvents and starting materials, auto-reduction of Pt(IV) to Pt(II) occurred in the title complex. Auto-reduction of Pt(IV) to Pt(II) in a methanol/water mixture, which was induced by UV irradiation, has been previously reported in the literature [ 25 ].

**Spectroscopic characterization of [Pt(Ph<sub>2</sub>bipy)Cl<sub>2</sub>] (1).** IR absorption of **1** is summarized in the EXPERIMENTAL section. The IR spectrum of this complex shows two weak bands at 3081 and 3058 cm<sup>-1</sup>, which are assigned to the C—H stretching vibrations of the phenyl and pyridine rings. The bands observed in the range 1619—1359 cm<sup>-1</sup> are assigned to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  vibrations. The medium to strong vibrations in the region 1085 to 536 cm<sup>-1</sup> are assigned to  $\delta(\text{C}=\text{C}=\text{N})$  and  $\delta(\text{C}=\text{C}=\text{C})$  bending vibrations in the phenyl and pyridine rings [ 26—30 ]. The far IR spectrum of complex **1** was recorded between 500 and 255 cm<sup>-1</sup>. The Pt—Cl stretching vibrations are seen at 408 and 316 cm<sup>-1</sup> and the Pt—N stretching vibrations are seen at 281 and 255 cm<sup>-1</sup> [ 31, 32 ].

According to the electronic absorption spectra of a DMSO solution of a free Ph<sub>2</sub>bipy ligand and complex **1**, the strong broad bands at around 265 nm for the free Ph<sub>2</sub>bipy ligand and 290 nm for **1** are

assigned to the intraligand  $\pi \rightarrow \pi^*$  transitions and the two weaker bands observed at around 340 and 396 nm for **1** are assigned to metal to ligand charge transfer (MLCT) [ 19, 33 ].

The  $^1\text{H}$  NMR spectrum of complex **1** was prepared in a DMSO- $d_6$  solution at room temperature and the results are listed in the EXPERIMENTAL section. The  $^1\text{H}$  NMR spectrum of **1** exhibited a multiple band at around 7.7 ppm for the phenyl groups, a doublet band at 8.17 ppm for Hb, a singlet band at 9.05 ppm for Hc, and a doublet band at 9.45 ppm for Ha (Scheme 1).

Luminescence emission spectra ( $\lambda_{\text{ex}} = 290$  nm) of the free Ph<sub>2</sub>bipy ligand and **1** were recorded in a DMSO solution at room temperature. The maximum emission of Ph<sub>2</sub>bipy at 360 nm is shifted to 368 nm in complex **1**, with a red-shift after the coordination to Pt(II) (8 nm red-shifted compared to the related emission band). Also, the luminescent emission of complex **1** is stronger than that of the free Ph<sub>2</sub>bipy ligand. The shapes of the luminescence emission spectra for the free Ph<sub>2</sub>bipy ligand and complex **1** are similar, therefore, the emission properties of this Pt(II) complex are assigned to either ligand-centred (LC,  $\pi^* \rightarrow \pi$  transitions) and MLCT states [ 34—37 ].

**Description of the molecular structure of [Pt(Ph<sub>2</sub>bipy)Cl<sub>2</sub>] (1).** The ORTEP view with the atom numbering scheme for this complex is shown in Fig. 1. As shown in this figure, each platinum(II) cation is four-coordinated in a distorted square-planar configuration by two nitrogen atoms from a bidentate 4,4'-diphenyl-2,2'-bipyridine ligand and two terminal chlorine atoms. The main contribution to the distortion of the square-planar configuration is made by a short bite angle of the coordinated Ph<sub>2</sub>bipy ligand (N1—Pt1—N2 = 79.1(4)°). Furthermore, the pyridine rings are slightly distorted from planarity. The mean planes of the rings *A* (N1/C1—C3/C10/C11), *B* (N2/C12—C14/C21/C22), and *C* (Pt1/N1/C11/C12/N2) make the following dihedral angles with each other: *A/B* = 3.28°, *A/C* = 3.41°, and *B/C* = 5.44°. Also, the phenyl rings *D* (C4—C9) and *E* (C15—C20) are oriented at a dihedral angle *D/E* = 5.17°. The Pt—N bond lengths are 1.998(9) and 2.007(8) Å and Pt—Cl bond lengths are 2.313(3) and 2.314(4) Å. The Pt—N and Pt—Cl bond lengths and angles are in good agreement with the corresponding values in [Pt(4,4'-dmbipy)Cl<sub>2</sub>], [Pt(5,5'-dmbipy)Cl<sub>2</sub>] [ 38 ], and [Pt(bipy)Cl<sub>2</sub>] [ 39, 40 ] (4,4'-dmbipy is 4,4'-dimethyl-2,2'-bipyridine, 5,5'-dmbipy is 5,5'-dimethyl-2,2'-bipyridine and bipy is 2,2'-bipyridine).

In the crystal structure of complex **1** (Fig. 2) intermolecular C—H...Cl hydrogen bonds (C9—H9...Cl1, H...A 2.72 Å, D...A 3.55(2) Å, D—H...A 150°; C16—H16...Cl1 2.72 Å, 3.599(17) Å, 158°) and the  $\pi$ — $\pi$  interactions between the phenyl and pyridyl rings, Cg2...Cg4<sup>i</sup>, Cg2...Cg5<sup>ii</sup>, Cg3...Cg4<sup>iii</sup> and Cg5...Cg5<sup>i</sup> [symmetry codes: (i)  $-1+y, 1+x, 2-z$ ; (ii)  $y, 1+x, 2-z$  and (iii)  $-1+y, x, 2-z$ , where Cg2, Cg3, Cg4 and Cg5 are the centroids of the rings *A* (N1/C1—C3/C10/C11), *B* (N2/C12—C14/C21/C22),

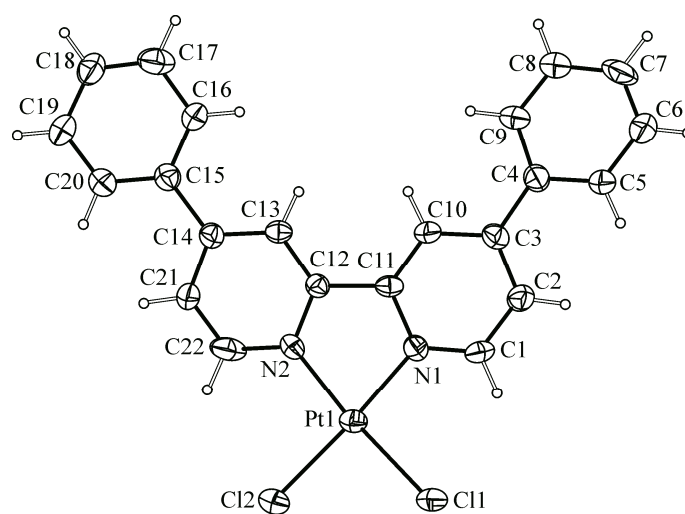


Fig. 1. The labeled diagram of **1**.  
Thermal ellipsoids are at 30 % probability level

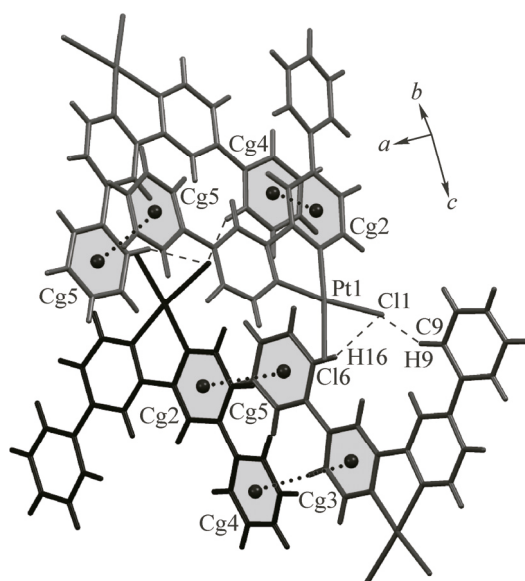


Fig. 2. Crystal packing diagram for **1**.

Intermolecular C—H...Cl hydrogen bonds and  $\pi$ — $\pi$  contacts are shown as dashed lines

*C* (C4—C9), and *D* (C15—C20), respectively] with centroid-centroid distances of 4.505(10), 3.636(9), 3.913(10), and 3.795(10) Å, respectively, are effective in the stabilization of the crystal structure and the formation of the 3D supramolecular complex.

In this work, a new complex [Pt(Ph<sub>2</sub>bipy)Cl<sub>2</sub>] (**1**) have 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(II) atom is four-coordinated in a distorted square-planar geometry. It is notable that in this compound, nonclassical C—H...Cl hydrogen bonds and  $\pi$ — $\pi$  interactions between the phenyl and pyridyl rings mostly stabilize the crystal lattice. Furthermore, luminescence studies show differences in the luminescence behaviour of complex **1** in comparison with the free Ph<sub>2</sub>bipy ligand. Luminescence emission of complex **1** was red shifted and is stronger than that of the free Ph<sub>2</sub>bipy ligand.

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#### REFERENCES

1. Cebrián C., Mauro M., Kourkoulos D., Mercandelli P., Hertel D., Meerholz K., Strassert C.A., Cola L.D. // *Adv. Mater.* – 2013. – **18**. – P. 437.
2. Ni J., Zhang L.Y., Wen H.M., Chen Z.N. // *Chem. Commun.* – 2009. – P. 3801.
3. Stengel I., Strassert C.A., Plummer E.A., Chien C.H., Cola L.D., Bäuerle P. // *Eur. J. Inorg. Chem.* – 2012. – P. 1795.
4. Mauro M., Aliprandi A., Septiadi D., Kehra N.S., Cola L.D. // *Chem. Soc. Rev.* – 2014. – **43**. – P. 4144.
5. Baggaley E., Botchway S.W., Haycock J.W., Morris H., Sazanovich I.V., Gareth Williams J.A., Weinstein J.A. // *Chem. Sci.* – 2014. – **5**. – P. 879.
6. Kelland L. // *Nat. Rev. Cancer.* – 2007. – **7**. – P. 573.
7. Wilson J.J., Lippard S.J. // *Chem. Rev.* – 2014. – **114**. – P. 4470.
8. Tabatabaei Rezaei S.J., Amani V., Nabil M.R., Safari N., Niknejad H. // *Polym. Chem.* – 2015. – **6**. – P. 2844.
9. Ogawa M., Ajayakumar G., Masaoka S., Kraatz H.B., Sakai K. // *Chem. Eur. J.* – 2011. – **17**. – P. 1148.
10. Du P., Schneider J., Li F., Zhao W., Patel U.I., Castellano F.N., Eisenberg R. // *J. Am. Chem. Soc.* – 2008. – **130**. – P. 5056.
11. Ting V.P., Schmidtman M., Wilson C.C., Weller M.T. // *Angew. Chem. Int. Ed.* – 2010. – **49**. – P. 9408.
12. Eljack N.D., Drucker H.Y.M.M.J., Shen C., Hambley T.W., New E.J., Friedrich T., Clarke R.J. // *Metallomics.* – 2014. – **6**. – P. 2126.

13. *Case F.H., Kasper T.J.* // J. Am. Chem. Soc. – 1956. – **78**. – P. 5842.
14. *Chesnut D.J., Kusnetzow A., Birge R., Zubieta J.* // J. Chem. Soc. Dalton Trans. – 2001. – P. 2581.
15. *Abram P.D., McKay D., Ellis D., Macgregor S.A., Rosair G.M., Welch A.J.* // Dalton Trans. – 2010. – **39**. – P. 2412.
16. *Lai S.W., Chan Q.K.-W., Zhu N., Che C.M.* // Inorg. Chem. – 2007. – **46**. – P. 11003.
17. *Yoshikawa N., Yamabe S., Kanehisa N., Kai Y., Takashima H., Tsukahara K.* // Inorg. Chim. Acta. – 2006. – **359**. – P. 4585.
18. *Cusumano M., Pietro M.L.D., Giannetto A., Nicoló F., Rotondo E.* // Inorg. Chem. – 1998. – **37**. – P. 563.
19. *Chan S.C., Chan M.C.W., Wang Y., Che C.M., Cheung K.K., Zhu N.* // Chem. Eur. J. – 2001. – **7**. – P. 4180.
20. *Werner M.L., Bruhn C., Steinborn D.* // J. Organomet. Chem. – 2008. – **693**. – P. 2369.
21. *Sheldrick G.M.* SADABS, Bruker AXS, Madison, WI, USA, 1998.
22. *Bruker SMART and SAINT.* – Bruker AXS Inc., Madison, WI, USA, 1998.
23. *Sheldrick G.M.* // Acta Crystallogr. – 2008. – **A64**. – P. 112.
24. *Mercury 141*, Copyright Cambridge Crystallographic Data Center, Cambridge, UK, 2001—2005.
25. *Gaballa A., Wagner C., Schmidt H., Steinborn D.* // Z. Anorg. Allg. Chem. – 2005. – **629**. – P. 703.
26. *Delbari A.S., Shahvelayati A.S., Jodaian V., Amani V.* // J. Iran. Chem. Soc. – 2015. – **12**. – P. 223.
27. *Abedi A., Amani V., Safari N.* // Main Group Chem. – 2012. – **11**. – P. 223.
28. *Alizadeh R., Amani V., Farshady A.A., Khavasi H.R.* // J. Coord. Chem. – 2010. – **63**. – P. 2122.
29. *Ghiasi Z., Amani V., Mirzaei P., Safari N., Abedi A.* // Aust. J. Chem. – 2013. – **66**. – P. 676.
30. *Amani V., Safari N., Khavasi H.R., Akkurt M.* // Polyhedron. – 2009. – **28**. – P. 3026.
31. *Pazderski L., Toušek J., Sitkowski J., Kozerski L., Szlyk E.* // Magn. Reson. Chem. – 2007. – **45**. – P. 1059.
32. *Falvello L.R., Garde R., Miqueleiz E.M., Tomás M., Urriolabeitia E.P.* // Inorg. Chim. Acta. – 1997. – **264**. – P. 297.
33. *Fielda J.S., Gertenbach J.A., Haines R.J., Munro O.Q., McMillin D.R.* // Z. Naturforsch. – 2007. – **62b**. – P. 447.
34. *Chen J.L., Tan X.Z., Chen X.X., Wang J.Y., Cao X.F., He L.H., Hua J.Y., Wen H.R.* // Inorg. Chem. Commun. – 2013. – **30**. – P. 120.
35. *Miskowski V.M., Houlding V.H., Che C.M., Wang Y.* // Inorg. Chem. – 1993. – **32**. – P. 2518.
36. *Abedi A., Saemian T., Amani V.* // J. Struct. Chem. – 2015. – **56**. – P. 1545.
37. *Allampally N.K., Daniliuc C.G., Strassert C.A., Cola L.D.* // Inorg. Chem. – 2015. – **54**. – P. 1588.
38. *Maheshwari V., Carlone M., Fronczek F.R., Marzilli L.G.* // Acta Crystallogr. – 2007. – **B63**. – P. 603.
39. *Canty A.J., Gardiner M.G., Jones R.C., Sharma M.* // Aust. J. Chem. – 2011. – **64**. – P. 1355.
40. *Connick W.B., Henling L.M., Marsh R.E., Gray H.B.* // Inorg. Chem. – 1996. – **35**. – P. 6261.