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ARTICLE

Synthesis and Structure of Trimethylplatinum(IV) Iodide Complex of 4′-(4-Methoxyphenyl)-2,2′:6′,2′′-terpyridine Ligand and its Halogen Bonding Property

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Abstract. The synthesis and structural characterization of a new trimethylplatinum(IV) iodide complex of 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine ligand L, {$PtMe_3IL$} (**1**) is reported. The X-ray crystal structure shows that the terpyridine ligand L binds the platinum(IV) metal center in bidentate fashion, which is well supported by the ^{1}H NMR spectrum of **1**. The complex **1** upon crystallization with 1,4-diiodotetrafluorobenzene (DITFB) forms the halogen bonded complex **1a** (**1**·DITFB). The structural investigation shows that **1a** exhibits the halogen bonding interaction in which the non-coordinated pyridyl nitrogen acts as halogen bond acceptors by forming I···N interaction with iodine atom of DITFB. In addition iodine atom of complex **1** also acts as weak halogen bond acceptor.

Introduction

During the last two decades, the chemistry of halogen bond, alternative to hydrogen bond, represents an emerging area of research. It is termed as a non-covalent attractive interaction involving a nucleophile (halogen bond acceptor) and an electrophile containing halogen atom (halogen bond donor).[1] The halogen bond found applications in diverse areas such as crystal engineering, liquid crystal, luminescence, dye sensitized solar cell, etc.[2–10] Considering the importance, several nitrogen based ligands have been used as halogen bond acceptors.[2,5,10–13] Among the nitrogen based ligands, 2,2′:6′,2′′-terpyridines and 2,2′-bipyridines and their transition metal complexes possess interesting photophysical and electrochemical properties and used in self-assembled hydrogelation, luminescent chemosensors, mixed-valence chemistry, etc.[14–20] In particular, the study of platinum(IV) complexes of nitrogen ligands attracts considerable attention due to their intriguing dynamic behavior in solution and their involvement in Shilov-type chemistry.[21–27] Platinum(IV) complexes of 2,2′:6′,2′′-terpyridines also act as halogen bond acceptors.[28]

Herein we reported the synthesis and structural characterization of a new trimethylplatinum(IV) iodide complex of 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine ligand L, {$PtMe_3IL$} (**1**). The X-ray crystal structure shows that the terpyridine ligand L binds the platinum(IV) metal center in bidentate fashion which is in distorted octahedron environment with three methyl groups and an iodine atom. Furthermore, **1** upon crystallization with 1,4-diiodotetrafluorobenzene (DITFB) forms the halogen bonded complex **1a**. The structural investigation shows that **1a** exhibits the halogen bonding interaction in which the non-coordinated pyridyl nitrogen acts as halogen bond acceptors by forming I···N interaction with iodine atom of DITFB. In addition iodine atom of complex **1** also acts as weak halogen bond acceptor.

Experimental Section

General Methods and Materials: Trimethylplatinum(IV) iodide was purchased from Strem Chemicals. All other chemicals and solvents were of analytical reagent grade, purchased commercially, and used as received. The ligand 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine L was synthesized following a literature procedure,[29] whereas complex **1** was synthesized according to the literature method.[28] The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance DRX 400 and DRX 500 MHz spectrometer. The mass spectra were measured on a QSTAR Elite ESI-Q-TOF mass spectrometer equipped with an API 200 Turbo Ion Spray ESI source from AB Sciex (former MDS Sciex). Elemental analyses were performed with an Elementar Analysesysteme GmbH VarioIEL.

Synthesis of 4′-(4-Methoxyphenyl)-2,2′:6′,2′′-terpyridine (L): 2-Acetylpyridine (4.84 g, 40 mmol) was added to a solution of 4-methoxybenzaldehyde (2.72 g, 20 mmol) in methanol (100 mL). KOH pellets (3.4 g, 85 %) and aq. NH_3 (60 mL) were added to the stirred solution and the resulting mixture was refluxed for 36 hours. The precipitate was then filtered, washed several times with methanol (4 × 25 mL). The solid residue was then dissolved in dichloromethane (15 mL) and excess *n*-hexane added (60 mL). The resultant solid was filtered, washed with *n*-hexane (3 × 10 mL) and dried in air. Yield 35 %. **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C): δ = 8.7 (m, 4 H), 8.6 (d, 2 H, J = 8.0 Hz), 7.8 (m, 4 H), 7.3 (m, 2 H), 7.0 (d, 2 H, J = 8.7 Hz), 3.9 (s, 3 H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C): δ = 160.7, 156.5, 156.0, 150.0, 149.2, 137.0, 130.9, 128.7, 123.9, 121.5, 118.5, 114.5, 55.6 ppm. **MS**: m/z = 362.1237 ($[M + Na]^+$, calcd. 362.1264).

Synthesis of Complex [$PtMe_3IL$] (1): To a chloroform solution (4 mL) of trimethylplatinum(IV) iodide (150 mg, 0.41 mmol),

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139.0 mg (0.41 mmol) of L in chloroform (6 mL) was added and the reaction mixture was stirred at 50 °C for 12 h. The mixture was then concentrated after which an excess of *n*-hexane (30 mL) was added slowly. The resultant pale-yellow solid complex **1**, was filtered, washed with *n*-hexane, and dried in vacuo. Yield 84 %. Diffusing *n*-hexane into its chloroform solution at room temperature afforded pale-yellow crystals of **1**. **^{1}H NMR** (500 MHz, $CDCl_3$, –50 °C): δ = 9.1 (d, 1H, J 5.2 Hz), 8.8 (d, 1H, J = 7.8 Hz), 8.7 (d, 1H, J = 4.4 Hz), 8.4 (d, 1H, J = 8.1 Hz), 8.3 (br. s, 1H), 8.1 (m, 2H), 7.9 (td, 1H, J = 1.0, 7.7 Hz), 7.8 (d, 2H, J = 8.7 Hz), 7.6 (t, 1H, J = 6.0 Hz), 7.5 (m, 1H), 7.0 (d, 2H, J = 8.7 Hz), 3.9 (s, 3H, –OMe), 1.6 (s, 3H, Me,$^2J_{Pt–H}$: 73.3 Hz), 0.4 (s, 3H, Me, $^2J_{Pt–H}$: 72.1 Hz), 0.3 (s, 3H, Me, $^2J_{Pt–H}$: 70.3 Hz) ppm. **MS**: m/z = 579.1743 ($[PtMe_3(\mathbf{L})]^+$, calcd. 579.1720). Anal. calcd. for $C_{25}H_{26}IN_3OPt$ (706,48 g·mol^{-1}): C 42.50; H 3.71; N 5.95 %; found: C 42.45, H 3.75, N 5.83 %.

Crystallization of Halogen Bonded Complex 1a: 1,4-Diiodotetrafluorobenzene DITFB (25 mg, 0.063 mmol) was added to the solution of complex **1** (11 mg, 0.016 mmol) in chloroform (4 mL). The slow diffusion of *n*-hexane into the resulting solution at room temperature afforded deep-yellow crystals of XB complex **1a** (**1**·DITFB). Anal. Calcd. for $C_{31}H_{26}F_4I_3N_3OPt$ (1108.36 g·mol^{-1}): C 33.59; H 2.36; N 3.79 %; found: C 33.36, H 2.19, N 3.58 %.

X-ray Crystallographic Studies: Diffraction data for **1** was collected using Agilent Supernova single source diffractometer (with Mo-K_α radiation; λ = 0.71073 Å) equipped with an Atlas detector. Data acquisition, reduction and analytical face-index based absorption correction for all these complexes were made using program CrysAlisPro.[30] X-ray diffraction data for single crystal of **1a** was collected using a Bruker-Nonius Kappa CCD diffractometer equipped with an APEX II detector with graphite-monochromatized Mo-K_α (λ = 0.71073 Å) radiation at 123 K. Collect software was used for data collection[31] and DENZO-SMN for its processing.[32] Absorption correction was applied with the multi-scan SADABS program.[33] The structures were solved with the program Superflip[34] and refined by full-matrix least-squares on F^2 using the WinGX[35] software equipped with SHELXL-2015 program.[36] Anisotropical displacement parameters were introduced for all atoms except hydrogen atoms which were calculated into their ideal positions using isotropic displacement parameters 1.2–1.5 times of the host atom. The figures were made using Mercury[37] program. X-ray crystallographic data and structural refinement parameters for the complexes are reported in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1947524 and CCDC-1947525. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

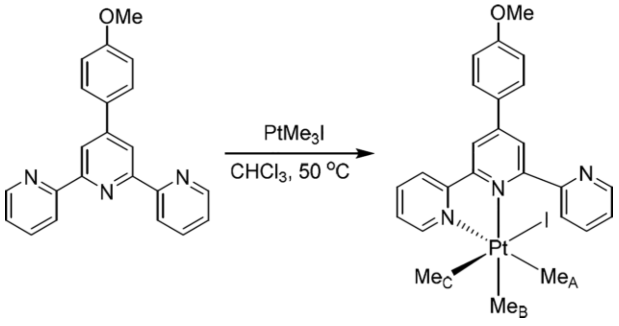
Supporting Information (see footnote on the first page of this article): NMR Spectra of ligand 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine L and mass spectrum of complex **1** given in supporting information.

Results and Discussion

The trimethylplatinum(IV) complex **1** was synthesized by the reaction between trimethylplatinum(IV) iodide and terpyridine ligand 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine **L** in chloroform in equimolar ratio (Scheme 1 and Experimental Section). Complex **1** was characterized by ^{1}H NMR spectroscopy, ESI-Mass spectroscopy, CHN analysis, and single crystal X-ray diffraction study. The electrospray ionization mass spectrometry (ESI-MS) analysis of **1** showed the presence of $[PtMe_3L]^+$, generated due to the loss o iodide. In addition, the isotope patterns consistent with those calculated for the formulated species (Figure 1).

Table 1. Crystallographic data for the complex **1** and its halogen bonded complex **1a**.

	1	**1a**
Empirical formula	$C_{25}H_{26}IN_3OPt$	$C_{30.5}H_{24.5}Cl_{0.5}F_4I_3N_3OPt$
M_w /g	706.48	1118.55
T /K	173(2)	123.01(10)
λ /Å	0.71073	0.71073
Crystal color, shape	pale-yellow, block	yellow, needle
Crystal size /mm^3	0.38 × 0.25 × 0.10	0.25 × 0.16 × 0.07
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a /Å	8.7230(3)	8.4383(2)
b /Å	9.3072(3)	13.5776(5)
c /Å	15.2454(9)	15.9896(6)
α /°	91.408(4)	114.7780(10)
β /°	98.703(3)	99.276(2)
γ /°	102.898(3)	95.599(2)
V /Å^3	1190.41(9)	1613.44(9)
Z	2	2
ρ_c /g·cm^{-3}	1.971	2.302
μ /mm^{-1}	7.212	7.313
F(000)	672	1036
θ range /°	2.25 to 25.00	2.488 to 24.997
Completeness to θ_{full}	99.9 %	99.2 %
Reflections collected	7500	9238
Independent reflections	4192 [R(int) = 0.0240]	5620 [R(int) = 0.0261]
Data / restraints / parameters	4192 / 0 / 284	5620 / 0 / 395
Goodness-of-fit on F^2	1.081	1.189
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0251, wR_2 = 0.0581	R_1 = 0.0327, wR_2 = 0.0735
R indices (all data)	R_1 = 0.0280, wR_2 = 0.0606	R_1 = 0.0354, wR_2 = 0.0750
Largest diff. peak and hole /e·Å^{-3}	0.647 and –0.934	2.578 and –1.816



Scheme 1. Synthesis of complex **1**.

^{1}H NMR Spectroscopy

The ^{1}H NMR spectrum of complex **1** was measured in $CDCl_3$ at low temperature (–50 °C) as room temperature ^{1}H NMR spectrum showed severe broadening. The ^{1}H NMR spec-

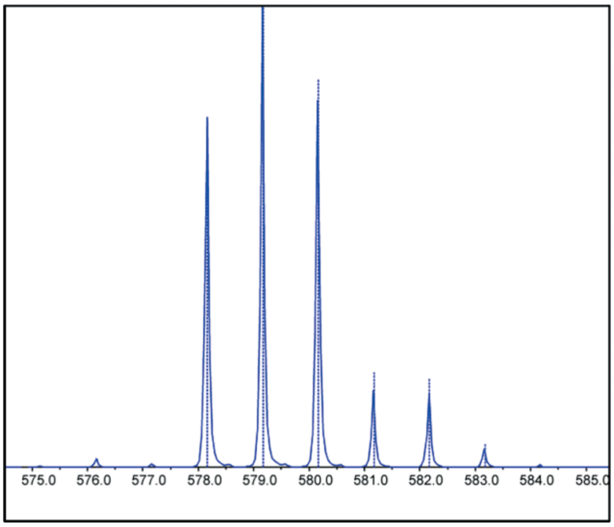


Figure 1. ESI-Q-TOF mass spectrum of complex **1**, showing experimental (solid line) and theoretical (dotted line) isotopic distributions of platinum metal.

trum of **1** is closely analogous to the spectra of reported Pt^{IV}-terpyridine complexes.[17,28,38] The presence of three platinum-methyl signals with satellites, due to ^{195}Pt-H scalar coupling, revealed the presence of three non-equivalent methyl groups (two equatorial methyl groups designated as Me_A and Me_B and one axial methyl group Me_C) in complex **1** (Figure 2). The above observation gives an indication that **L** binds the platinum metal center in bidentate fashion, which is further confirmed by the presence of ten signals for the hydrogen nuclei of terpyridine core.

X-ray Crystallographic Study

X-ray Structure of Complex 1

In order to firmly establish the bidentate binding nature of the terpyridine ligand **L** in the complex 1, crystallization of the complex **1** was carried out. The Pale-yellow colored single crystals of **1** were obtained by diffusing *n*-hexane into its chloroform solution at room temperature. The complex **1** crystallizes in triclinic $P\bar{1}$ space group. The crystal structure shows that the platinum metal center is in a distorted octahedral coordination environment with three methyl groups in *fac* geometry, two nitrogen atoms from the pyridyl groups of the terpyridine ligand and an iodine atom (Figure 3). Similar coordination geometry of the platinum metal core has also been observed in previously reported bidentate Pt^{IV}-terpyridine complexes.[17,28,38]

The deviation from ideal octahedral arrangement mostly originates from geometric constrains imposed by the constrained bite angle of the terpyridine ligands in the complex [N1–Pt1–N2 angle is 75.9(2)° (caption in Figure 3). The Pt–N bond length to the central pyridine ring [2.263(3) Å] is significantly longer than the corresponding Pt–N bond involving terminal pyridine ring (2.137(4) Å]. The Pt–N bond lengths in complex **1** are found to be similar to the Pt–N bond lengths

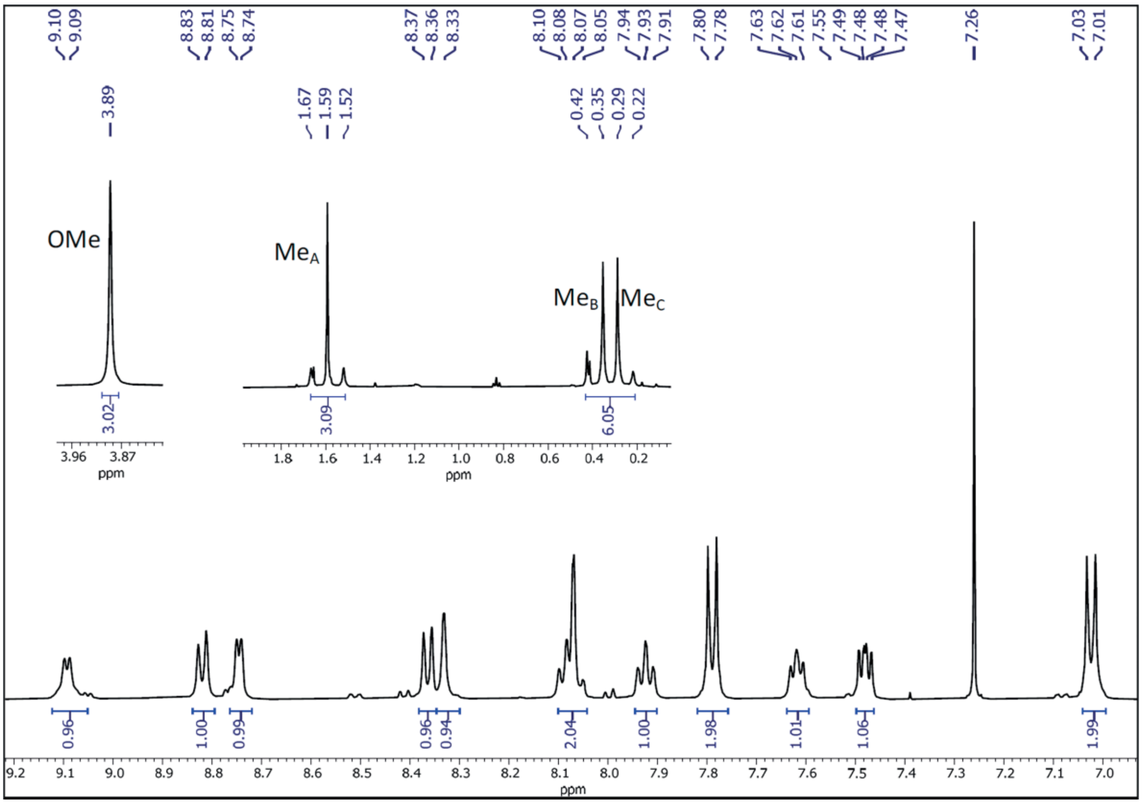


Figure 2. 500 MHz ^{1}H NMR spectrum of complex **1** in $CDCl_3$ at –50 °C. Inset showing the satellite signals (due to ^{195}Pt-H coupling) for the methyl groups. For labeling, see Scheme 1.

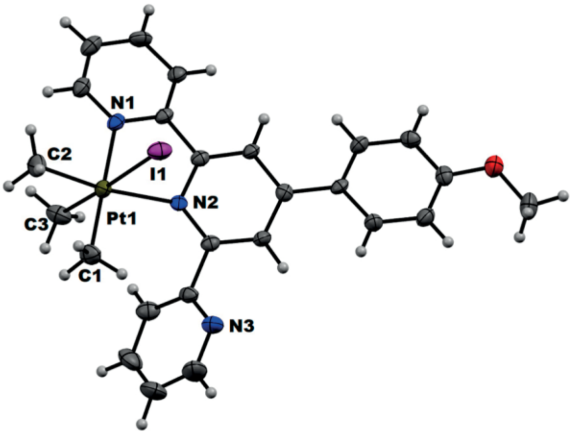


Figure 3. Molecular structure of complex **1**. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths and angles: Pt1–N1 = 2.137(4) Å, Pt1–N2 = 2.263(3) Å, Pt1–I1 = 2.7957(4) Å, Pt1–C1 = 2.058(5) Å, Pt1–C2 = 2.049(4) Å, Pt1–C3 = 2.090(5) Å, N1–Pt1–N2 = 75.9(2)°, C1–Pt1–N1 = 178.2(2)°, C2–Pt1–N2 = 171.9(2)°, C3–Pt1–I1 = 177.7(2)°, C1–Pt1–N2 = 103.3(2)°.

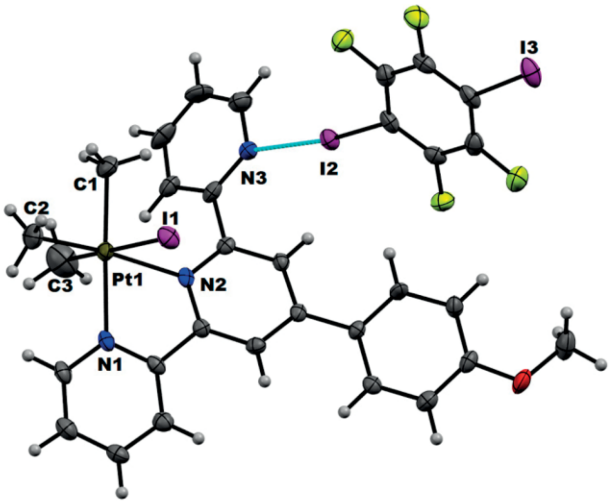


Figure 4. Molecular structure of complex **1a** (**1**·DITFB). Thermal ellipsoids are drawn at the 50 % probability level. XB interaction between N3 and I2 is shown in dotted bond (indigo color). Selected bond lengths and angles: Pt1–N1 = 2.168(5) Å, Pt1–N2 = 2.247(5) Å, Pt1–I1 = 2.7651(5) Å, Pt1–C1 = 2.057(7) Å, Pt1–C2 = 2.040(7) Å, Pt1–C3 = 2.07(4) Å, N1–Pt1–N2 = 75.6(2)°, C1–Pt1–N1 = 177.9(2)°, C2–Pt1–N2 = 172.8(3)°, C3–Pt1–I1 = 176.6(2)°, C1–Pt1–N2 = 102.3(2)°. I2···N3 = 2.866(6) Å.

found in $PtMe_3IL$ complexes [2.143(3) and 2.250(4) Å, when L is 4′-(4-cyanophenyl)-2,2′:6′,2′′-terpyridine;[28] 2.145(3) and 2.263(4) when L is 4′-(4-tolyl)-2,2′:6′,2′′-terpyridine].[28] Like Pt–N bond lengths, the N–Pt–N bond angles also follows the similar trend: 75.8(2)° in $PtMe_3IL$ [L is 4′-(4-cyanophenyl)-2,2′:6′,2′′-terpyridine], and 75.4(2)° in $PtMe_3IL$ where L is 4′-(4-tolyl)-2,2′:6′,2′′-terpyridine. All other bond lengths and angles of **1** are analogous to that of previously reported Pt^{IV}-terpyridine complexes.[17,28,38] The structural study also showed that the pyridyl groups are having *cis*,*trans* configuration in **1**. Similar feature is also observed in reported bidentate metal-terpyridine complexes.[17,28,38–41]

Halogen Bonded Complexes 1a

The yellow colored crystals of the XB complex **1a** were obtained by slow diffusion of *n*-hexane into a mixture of an excess of 1,4-diiodotetrafluorobenzene DITFB and platinum(IV) complex **1** in chloroform at room temperature. The complex **1a** crystallizes in the triclinic *P-1* space group. The crystal structure of **1a** is shown in Figure 4. The crystal structure shows that the asymmetric unit of **1a** contains a molecule of **1** along with DITFB. Like complex **1**, in complex **1a**, the platinum metal center is also coordinated by three methyl groups, two nitrogen atoms of the terpyridine ligand L and an iodine atom. It is to be noted that that coordination sphere of platinum(IV) is also occupied by small amount of chlorine atom. The presence of chlorine atom could be due to the trace amount of HCl molecule present in $CHCl_3$ which is used as crystallization solvent.

In halogen bonded complex **1a** the nitrogen atom of the non-coordinated pyridyl group acts as XB acceptor by forming relatively short distanced I···N interaction with iodine atom of DITFB [I···N distance 2.866(6) Å with C–I···N angle of 173.5(2)°] with XB interaction ratio R_{XB} 0.81 [$R_{XB} = d_{XB}/(X_{vdw} + B_{vdw})$].[42] The R_{XB} value for I···N interaction between iodine atom of DITFB and non-coordinated pyridine N atom of terpyridine moiety was found to be 0.83 [I···N distance 2.934(5) Å and C–I···N angle 172.7(2)°] in the XB complex $2PtMe_3IL \cdot DITFB \cdot 2CHCl_3$, where L is 4′-chloro-2,2′:6′,2′′-terpyridine,[28] whereas R_{XB} value for similar I···N interaction found to be 0.81 [I···N distance 2.848(6) Å and C–I···N angle 176.5(3)°] in $PtMe_3IL \cdot 2IPFB$ (L is 4′-chloro-2,2′:6′,2′′-terpyridine), 0.82 [I···N distance 2.886(7) Å and C–I···N angle 176.4(2)°] in $PtMe_3IL \cdot IPFB$ [L is 4′-(4-cyanophenyl)-2,2′:6′,2′′-terpyridine], and 0.79 in $PtMe_3IL \cdot 2IPFB$ [L is 4′-(4-tolyl)-2,2′:6′,2′′-terpyridine with I···N distance 2.785(9) Å and C–I···N angle 175.4(3)°].[28]The above data of R_{XB} indicates relatively strong XB acceptor character of the non-coordinated pyridyl group; however, the observed R_{XB} value in complex **1a** is higher in comparison to the R_{XB} value found in *N*,*N*-dimethylpyridin-4-amine-1-fluoro-4-(iodoethynyl)-benzene (R_{XB} = 0.74),[12] in which pyridyl nitrogen atoms involved in halogen bonding with C–I type donors, iodosaccharine and iodosuccinimide (R_{XB} = 0.65).[13] In addition, platinum(IV) bound iodine atom also involved in weaker XB interaction with iodine atom of DITFB (I1···I2 distance 3.5009(8) Å with R_{XB} 0.88). The above data clearly indicates weak XB acceptor character of the platinum(IV) bound iodine atom (Figure 5). Similar type of Pt-I···I interaction in which platinum bound iodine atom also acts as weak XB acceptor also observed in $PtMe_3IL \cdot 2IPFB$, where L is 4′-chloro-2,2′:6′,2′′-terpyridine [I···I distance 3.5711(8) Å, R_{XB} 0.90], $PtMe_3IL \cdot IPFB$, where L is 4′-(4-cyanophenyl)-2,2′:6′,2′′-terpyridine [I···I distance 3.4955(7) Å, R_{XB} 0.88] and $PtMe_3IL \cdot 2IPFB$, where L is 4′-(4-tolyl)-2,2′:6′,2′′-terpyridine [I···I distance 3.4179(11) Å, R_{XB} 0.86].[28]

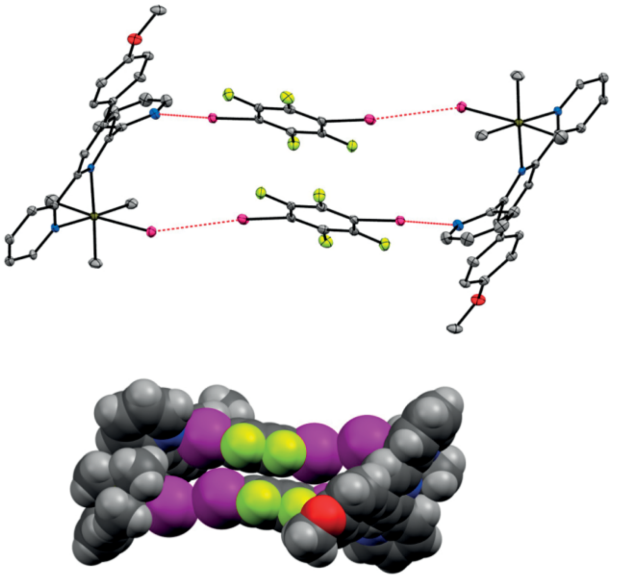


Figure 5. The molecular structure of XB complex **1a** with thermal ellipsoids at 50 % probability level (top) and with CPK view (bottom), showing I···N and I···I interactions. The hydrogen atoms are omitted for clarity. I···I distance 3.5009(8) Å with C–I···I angle 159.5(2)°; I···N distances 2.866(6) Å with C–I···N angles of 173.5(2)°.

In the crystal packing of **1a**, the platinum(IV) centers are connected to each other by DITFB with the help of I···N and I···I interactions (Figure 5). Furthermore, phenyl ring of terpyridine ligand in **1a** also exhibits weak π···π interaction with one of the pyridine rings of terpyridine moieties of adjacent molecules of **1a**. Moreover, oxygen atom of methoxy group exhibits weak C-H···O interactions with methyl group of adjacent molecule of complex **1a**. In addition, iodine atom also experienced weak halogen···C–H interaction with phenyl ring hydrogen atoms (Figure 6).

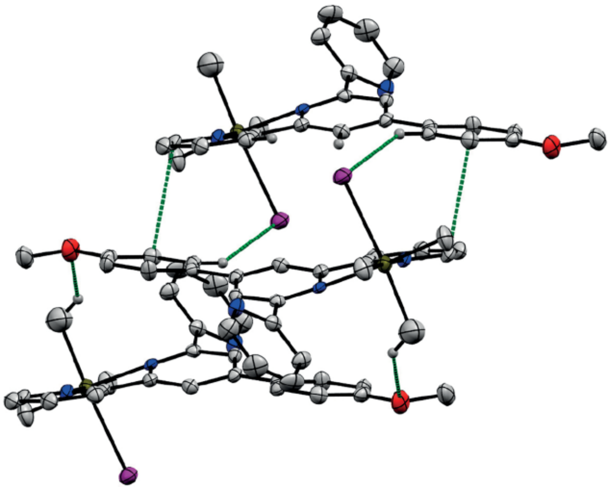


Figure 6. Crystal packing of **1a** showing π···π, C–H···I and C–H···O interactions (shown in dotted green color). All the hydrogen atoms except involved in weak interactions are omitted for clarity.

Conclusions

We herein reported the synthesis and structural characterization of a new trimethylplatinum(IV) iodide complex of 4′-(4-methoxyphenyl)-2,2′:6′,2′′-terpyridine ligand L, {$PtMe_3IL$} (**1**). The complex **1** was synthesized by the reaction between trimethylplatinum(IV) iodide and ligand L in equimolar ratio in chloroform and characterized by ^1H NMR spectroscopy, CHN analysis, Mass spectrometry and single-crystal X-ray diffraction study. ^1H NMR spectrum of **1** shows the presence of three chemically non-equivalent methyl groups in the complex. In addition, presence of ten signals for the hydrogen nuclei of terpyridine core also revealed bidentate nature of the ligand L, which is further confirmed by the crystal structure of **1**. The crystal structure of **1** shows that platinum metal is in distorted octahedron environment being coordinated by three methyl groups, one iodine atom and two nitrogen atoms from the terpyridine ligand (bidentate ligand). Furthermore, complex **1** upon crystallization with 1,4-diiodotetrafluorobenzene from the halogen bonded complex **1a**. The structural investigation shows that **1a** exhibits the halogen bonding interaction in which the non-coordinated pyridyl nitrogen acts as halogen bond acceptor by forming I···N interaction with iodine atom of DITFB. In addition iodine atom of complex **1** also acts as weak halogen bond acceptor.

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Keywords: Halogen bond; Trimethylplatinum(IV); Terpyridine; 1,4-Diiodotetrafluorobenzene (DITFB) / X-ray diffraction

References

[1] G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati, K. Rissanen, *Pure Appl. Chem.* **2013**, *85*, 1711.
[2] R. W. Troff, T. Mäkelä, F. Topić, A. Valkonen, K. Raatikainen, K. Rissanen, *Eur. J. Org. Chem.* **2013**, 1617.
[3] L. Brammer, G. M. Espallargas, S. Libri, *CrystEngComm* **2008**, *10*, 1712.
[4] K. Rissanen, *CrystEngComm* **2008**, *10*, 1107.
[5] K. Raatikainen, K. Rissanen, *CrystEngComm* **2011**, *13*, 6972.
[6] K. Raatikainen, K. Rissanen, *Chem. Sci.* **2012**, *3*, 1235.
[7] N. K. Beyeh, M. Cetina, K. Rissanen, *Chem. Commun.* **2014**, *50*, 1959.
[8] A. Valkonen, M. Chukhlieb, J. Moilanen, H. M. Tuononen, K. Rissanen, *Cryst. Growth Des.* **2013**, *13*, 4769.
[9] V. V. Sivchik, A. I. Solomatina, Y.-T. Chen, A. J. Karttunen, S. P. Tunik, P.-T. Chou, I. O. Koshevoy, *Angew. Chem. Int. Ed.* **2015**, *54*, 14057.
[10] H. L. Nguyen, P. N. Horton, M. B. Hursthouse, A. C. Legon, D. W. Bruce, *J. Am. Chem. Soc.* **2004**, *126*, 16.
[11] C. Präsang, A. C. Whitwood, D. W. Bruce, *Chem. Commun.* **2008**, 2137.
[12] E. Bosch, *Cryst. Growth Des.* **2014**, *14*, 126.
[13] O. Makhotkina, J. Lieffrig, O. Jeannin, M. Fourmigue, E. Aubert, E. Espinosa, *Cryst. Growth Des.* **2015**, *15*, 3464.

[14] B. N. Ghosh, S. Bhowmik, P. Mal, K. Rissanen, *Chem. Commun.* **2014**, *50*, 734.
[15] S. Bhowmik, B. N. Ghosh, K. Rissanen, *Org. Biomol. Chem.* **2014**, *12*, 8836.
[16] S. Bhowmik, B. N. Ghosh, V. Marjomäki, K. Rissanen, *J. Am. Chem. Soc.* **2014**, *136*, 5543.
[17] B. N. Ghosh, F. Topić, P. K. Sahoo, P. Mal, J. Linnera, E. Kalenius, H. M. Tuononen, K. Rissanen, *Dalton Trans.* **2015**, *44*, 254.
[18] W. Kaim, G. K. Lahiri, *Angew. Chem. Int. Ed.* **2007**, *46*, 1778.
[19] C.-J. Yao, Y.-W. Zhong, J. Yao, *J. Am. Chem. Soc.* **2011**, *133*, 15697.
[20] R. C. Evans, P. Douglas, C. J. Winscom, *Coord. Chem. Rev.* **2006**, *250*, 2093.
[21] B. N. Ghosh, H. Hausmann, M. Serafin, D. Lentz, S. Schlecht, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2202.
[22] B. N. Ghosh, D. Lentz, S. Schlecht, *New J. Chem.* **2015**, *39*, 3536.
[23] B. N. Ghosh, S. Schlecht, A. Bauzá, A. Frontera, *New J. Chem.* **2017**, *41*, 3498.
[24] B. N. Ghosh, S. Schlecht, *RSC Adv.* **2015**, *5*, 101900.
[25] A. S. Goldman, K. I. Goldberg, *Activation and Functionalization of C–H Bonds*, Am. Chem. Soc., Washington, DC, **2004**.
[26] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507.
[27] M. Lersch, M. Tilset, *Chem. Rev.* **2005**, *105*, 2471–2526.
[28] B. N. Ghosh, M. Lahtinen, E. Kalenius, P. Mal, K. Rissanen, *Cryst. Growth Des.* **2016**, *16*, 2527.
[29] J. Wang, G. S. Hanan, *Synlett* **2005**, 1251.
[30] Rigaku Oxford Diffraction **2018**, CrysAlisPro Version 38.46.
[31] R. W. Hooft, in *COLLECT*, Nonius BV, Delft, The Netherlands, **1998**.
[32] Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307.
[33] G. M. Sheldrick, SADABS, Bruker Analytical X-ray system, Inc., Madison, Wisconsin, **2008**.
[34] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.
[35] L. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.
[36] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2015**, *71*, 3; b) G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3.
[37] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* **2008**, *41*, 466.
[38] E. W. Abel, V. S. Dimitrov, N. J. Long, K. G. Orrell, A. G. Osborne, V. Šik, M. B. Hursthouse, M. A. Mazid, *J. Chem. Soc., Dalton Trans.* **1993**, 291.
[39] D. H. Gibson, J. G. Andino, M. S. Mashuta, *Organometallics* **2005**, *24*, 5067.
[40] E. R. Civitello, P. S. Dragovich, T. B. Karpishin, S. G. Novick, G. Bierach, J. F. O'Connell, T. D. Westmoreland, *Inorg. Chem.* **1993**, *32*, 237.
[41] E. W. Abel, K. G. Orrell, A. G. Osborne, H. M. Pain, V. Šik, M. B. Hursthouse, K. M. A. Malik, *J. Chem. Soc., Dalton Trans.* **1994**, 3441.
[42] J. P. M. Lommerse, A. J. Stone, R. Taylor, F. H. Allen, *J. Am. Chem. Soc.* **1996**, *118*, 3108.

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