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Original Article

Platinum(II) Complex of Benzimidazole-Derived N-Heterocyclic Carbene: Synthesis, Characterization, and Photophysical Properties

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Abstract: Platinum(II) complex of benzimidazole-derived N-heterocyclic carbene with formula [$PtCl_2$(DMSO)(bimy)] was successfully synthesized via one pot reaction between 1,3-diisopropyl benzimidazolium (bimy·HBr), Ag_2O and [$PtCl_2$(DMSO)] (DMSO = dimethyl sulfoxide). The complex was characterized by means of multinuclear (^1H and $^{13}C\{^1H\}$) magnetic resonance and single crystal X-ray diffraction (XRD). The UV-Vis absorption spectra of the compound show an absorption shoulder above 300 nm. Under excitation by 285 nm UV lamp, solution of the compound in DCM is highly emissive showing emission maxima at around 410 nm. DFT calculations were also carried out for the complex to gain insight on its electronic structure and the nature of electronic transition involved in the absorption/emission process.

Keywords: Platinum(II) complex, N-heterocyclic carbene, luminescent complex.

1. Introduction

Platinum(II) complexes have received great deals of attention due to their potential application in various fields, especially catalysis [1-5], bioactive compound and drug development [6-9] and especially in luminescent materials [10-12]. Reported luminescent platinum(II) complexes normally bearing classical Werner's types donor ligands such as diimines or polypyridines. Some organometallic ligand systems, including cyclometalated carbanions and acetylides have also been explored.

In parallel, N-heterocylic carbenes (NHCs) have recently emerged as one of the most powerful class of ligands for organometallic chemistry [13-15]. Tremendous successes in the field of catalysis has been achieved for transition metal complexes of NHCs due to their excellent turnability in electronic structure. Nonetheless, extending NHC complexes to the fields of luminescent materials remain relatively limited. The reported luminescent platinum(II) NHCs complexes largely focus on the chelating triazole derived NHCs [16].

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In this work, we report the synthesis of blue-light-emitting platinum(II) complex which feature simple benzimidazole-derived carbene.

2. Experimental section

All syntheses were carried out without precautions to exclude air and moisture unless otherwise stated. Benzimidazole, 2-bromopropane were purchased from Macklin Chemicals while silver(I) oxide and potassium tetrachloroplatinate(II) were provided by Aladdin. Solvents for syntheses and spectroscopic measurements were used as received. ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy were measured on a Bruker-500 MHz instrument at 300 K. UV-vis spectrum was recorded on a Jasco V-730 instrument whereas luminescent spectrum was obtained using a Hitachi F-4500 instrument.

2.1. Synthesis of 1,3-diisopropyl benzimidazolium bromide (bimy·HBr)

The salt was synthesized following reported procedure. In a Schlenk tube, a mixture of benzimidazole (120 mg, 1 mmol) and K_2CO_3 (155 mg, 1.1 mmol) in acetonitrile (3 mL) was stirred for 1 h. Isopropyl bromide (0.3 mL, 2 mmol) was added and the mixture was stirred under reflux for 24 h. Two other portions of isopropyl bromide (0.5 mL, 2 mmol) were added separated by 12 h. The volatiles were then removed under reduced pressure. Dichloromethane (20 mL) was then added to dissolve the product. Solution of the salt was then pumped dry and ethyl acetate was subsequently added to precipitate out the product as white solid (Yield: 75%). Identity of the salt was confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The spectroscopic data agree well with reported in literature [17].

2.2. Synthesis of cis-[$PtCl_2$(DMSO)(bimy)]

In the first round bottom flask, a mixture of bimy·HBr (142 mg, 0.5 mmol) and Ag_2O (60 mg, 0.26 mmol) in dichloromethane (20 mL) was stirred for 12 h. In the second flask, K_2PtCl_4 (207 mg, 0.5 mmol) in dimethylsulfoxide (DMSO, 2 mL) were stirred for 5 h. After that, the reaction mixture from the first flask was transferred to the second flask, and stirred for an additional 24 h. The precipitate was then removed and the volatiles were removed under reduced pressure. Water (20 mL) was then added to precipitate out the compounds from the DMSO solution. Filtration was carried out to obtained the crude product, which was then subjected to silica gel chromatography purification. The titled complex was isolated as white solid (Yield: 161 mg, 59%).

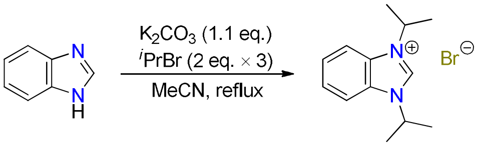
2.3 DFT calculation

DFT calculations for the complex were performed using Gaussian software. B3PW91 functional was employed together with SDD basis set for Pt and 6-31G* basis set for all the lighter atoms. The gas-phase structure was first optimized and frequency calculation was performed to confirm the stationary point obtained was minimal. Electronic structure of the complex was studied using the optimized geometry.

3. Results and discussion

3.1. Synthesis of 1,3-diisoproyl benzimidazolium bromide (bimy·HBr) and the platinum(II) cis-[$PtCl_2$(DMSO)(bimy)] complex.

The salt was synthesized by nucleophilic substitution reaction between benzimidazole and isopropyl bromide (**Error! Reference source not found.**).



Scheme 1. Synthesis of bimy·HBr salt

The salt was obtained as a white solid, which is soluble in dichloromethane, chloroform, methanol and acetonitrile. It is however not soluble in diethyl ether, hexane or ethyl acetate.

Scheme 1. Synthesis of cis-[$PtCl_2$(DMSO)(bimy)]

Complex cis-[$PtCl_2$(DMSO)(bimy)] was synthesized via silver carbene transfer pathway. The salt was first stirred with silver(I) oxide to form the silver(I) benzimidazolin-2-lidene complex, which was then react with [$PtCl_2(DMSO)_2$] to form the expected complex (Scheme 1).

The complex was purified using silica gel chromatoghraphy with dichloromethane as eluent. The complex displays good solubility in dimethyl sulfoxide, dichloromethane or chloroform but it is not soluble in diethyl ether, hexane.

3.2. Characterization of the platinum(II) cis-[PtCl$_2$(DMSO)(bimy)] complex.

Identity of the complex was characterized by means of multinuclear (^{1}H, ^{13}C{^{1}H} NMR) spectroscopy and single crystal X-ray diffraction. ^{1}H and ^{13}C{^{1}H} spectra of the complex are presented in Figure 1 and Figure 2. Formation of the complex was first indicated by the absence of low field signal (10 -12 ppm), characteristic for the acidic proton of the benzimidazolium salt. In addition, all the protons in the heterocyclic ring give signals with splitting as expected, suggesting the presence of benzimidazolin-2-yidene ligand. Two CH(CH$_3$)$_2$ isopropyl protons are equivalent and appear as a septet at 6.29 ppm. Protons in methyl groups of isopropyl substituents give one duplet signal at 1.75 ppm. Notably, the singlet at 3.55 ppm are assigned to protons in DMSO methyl groups, confirming the presence of coordinated dimethylsulfoxide in the complex.

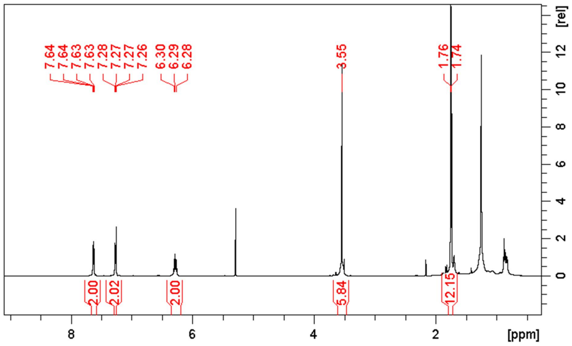


Figure 1. ^{1}H NMR spectrum of the complex.

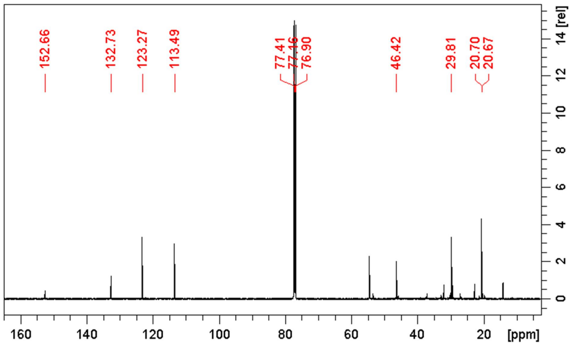


Figure 2. ^{13}C{^{1}H} NMR spectrum of the complex.

In the ^{13}C{^{1}H} spectrum of the complex, signals are observed for all the carbon in the complex. Signal for aliphatic carbons are observed in the 20-60 ppm range, whereas aromatic carbons give signals in the 110-140 ppm region. Notably, the less intense resonance at 152.7 ppm can be assigned to carbene carbon of the NHC. Chemical shift for carbene carbon in [PtCl$_2$(DMSO)(bimy)] is similar to reported value for platinum(II) NHC complexes [4, 18].

3.3. Molecular structure of the complex.

Identity of the complex was unambiguously confirmed by single crystal X-ray diffraction. Single crystals of the complex were obtained by slow evaporation of their solution in chloroform/hexane solvent mixture at ambient temperature. The compound crystalized in $P_{2_1 2_1 2_1}$ space group with orthorhombic crystal system. The asymmetric unit contains one complex molecule. The crystallographic data are summarized in Table 1.

Table 1. Crystallographic data of the complex.

parameter	value
Empirical formula	$C_{16}H_{26}Cl_4N_2OPtS$
Formula weight	315.67
Crystal system	orthorhombic
Space group	$P_{2_1 2_1 2_1}$
a/Å	9.4725(6)
b/Å	10.3423(6)
c/Å	23.7611(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2327.8(2)
Z	1
2θ/°	5.22–52.96
hkl	$-11 \le h \le 8$ $-12 \le k \le 12$ $-29 \le l \le 29$
Reflections collected	19280
Independent reflections	4788
Data/restraints/parameters	4788/0/232
Goodness-of-fit	1.076
R [I>=2σ (I)]	$R_1 = 0.038$ $wR_2 = 0.090$

Its molecular structure is presented in Figure 3 and selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths (Å) and bond angle (°)

bond	length (Å)	bond	angle (°)

Pt–C(2)	1.973(8)	C(2)PtCl(1)	177.9(3)
Pt–Cl(1)	2.367(2)	C(2)PtCl(2)	87.4(3)
Pt–Cl(2)	2.325(2)	C(2)PtS	90.5(3)
Pt–S	2.201(2)	SPtCl(2)	177.6(1)

The molecular shows the complex is essentially in square planar geometry with the Pt(II) center coordinated by two chlorido, a κ-S dimethylsulfido, and a benzimidazole-derived NHC ligands. The NHC and the DMSO ligands are in trans configuration. Noted that the heterocycle plane is nearly perpendicular to the coordination plane, forming a dihedral angle of 84.85°. The crystal packing is supported by CH-X interaction between hydrogen in CH_3/phenyl group and the chlorido ligand of the oxygen atom of the DMSO moiety (Figure 4. Short contact interaction in the crystal of the complex).

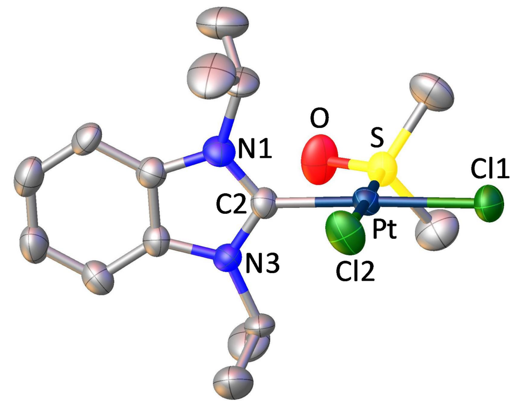


Figure 3. molecular structure of the complex. Thermal ellipsoids were plotted at 50% probability. Hydrogen atoms were omitted for clarity.

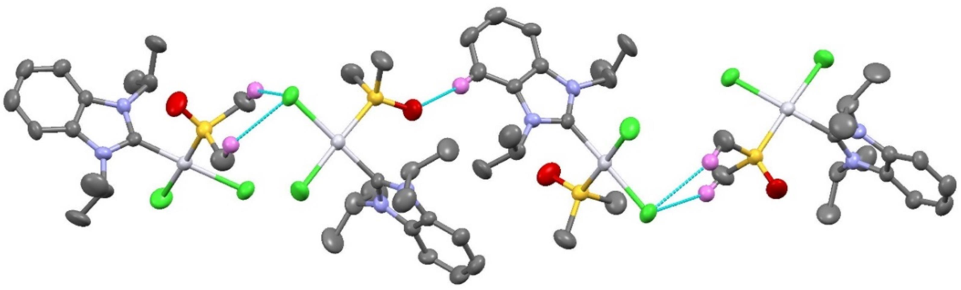


Figure 4. Short contact interaction in the crystal of the complex are shown as dashed light blue lines

3.4. Absorption and emission spectroscopy

Absorption and emission spectra of the complex are presented in Figure 5 and Figure 6. UV-Vis absorption and emission spectra of the complex Its absorption spectrum shows no peak above 400 nm, indicating that the compound does not absorb visible light, which is in agreement with the colorless nature of its solution in dichloromethane.

Figure 5. UV-Vis absorption and emission spectra of the complex (inset: a zoom into 250-300 nm region)

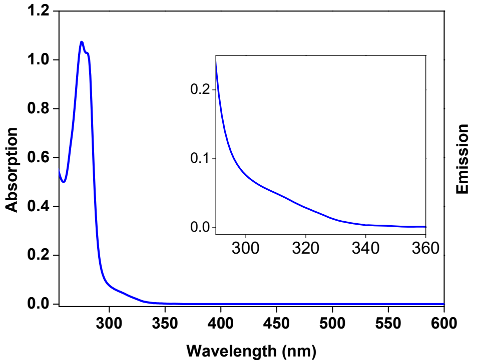


Figure 6. UV-Vis absorption and emission spectra of the complex

Notably, an absorption shoulder is observed in the range from 300-350 nm, which can be tentatively assigned to d-d transition in nature. In addition, intense absorption band peaked at 274 nm can be attributed to π-π^* transition of the benzimidazolin-2-ylidene moiety.

In the emission spectrum, a vibronic structured emission peak maxima at 410 nm is observed, which is in line with the fact that the compound emits blue light under UV light irradiation.

3.5. Electronic structure of the complex.

To gain insights on electronic structure and the nature of electronic transitions involved in the absorption and emission spectra of the complex, density function theory (DFT) calculations were performed. Optimized structure of the complex is presented in Figure 7 along with Cartesian coordinates definition. Selected bond lengths and angles are listed in Table 3. The structural parameters agree well with experimentally determined data, suggesting the suitability of functional and basis sets used.

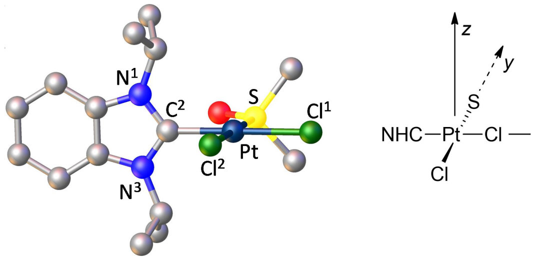
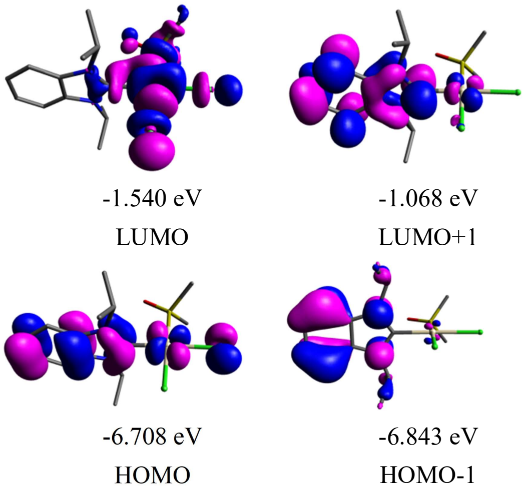


Figure 7. Optimized geometry of the complex and Cartesian coordinates definition.

Table 3. Selected bond lengths and angles in optimized structure of the complex

bond	length (Å)	bond	angle (°)
Pt–C(2)	1.992	C(2)PtCl(1)	177.3
Pt–Cl(1)	2.386	C(2)PtCl(2)	85.6
Pt–Cl(2)	2.337	C(2)PtS	93.9
Pt–S	2.259	SPtCl(2)	179.6

Surface of frontier orbitals of the complex and their respective energy are presented in Figure 8. Basically, the LUMO+1 orbital is the π^* orbitals of the benzimidazolin-2-ylidene with small contribution from d_{xy} orbital of Pt(II). In addition, LUMO is a combination of platinum(II) $d_{x^2-y^2}$ and p orbital of chlorido ligand. On the other hand, HOMO is basically a combination of chlorido p orbital with platinum(II) d_{xy} and π system of benzimidazole ring. The HOMO-1 largely delocalized on the benzimidazole ring with negligible contribution from platinum(II) center.


-1.540 eV LUMO

-1.068 eV LUMO+1

-6.708 eV HOMO

-6.843 eV HOMO-1

Figure 8. Frontier orbital surfaces and energy.

Table 4. Calculated vertical singlet excitation energies of the complex

No	Energy (f)	Transition (%)	Assignment
1	315 (0.0122)	H-3→L (97%)	$d_{z^2} \rightarrow d_{x^2-y^2} + p_x$
2	303 (0.007)	H→L (70%)	$d_{xy} + \pi_{bimy} \rightarrow d_{x^2-y^2} + p_x$
		H-5→L (13%)	$d_{z^2} \rightarrow d_{x^2-y^2} + p_x$

In summary, the d-d transition of the metal center with small contribution from π of the benzimidazolin-2-ylidene and chlorido ligands are essential for the absorption and emission characteristic of the complex.

TD-DFT calculation results are summarized in Table 4. The calculations suggested that the absorption shoulder above 300 nm is originated from H-3→L electronic transition, which is basically $d_{z^2} \rightarrow d_{x^2-y^2} + p_x$ transition. In addition, a small contribution comes from a mixture of H→L transition, which are in fact $d_{xy} + \pi_{bimy} \rightarrow d_{x^2-y^2} + p_x$ transition. The calculation also suggests the intense absorption below 300 nm is intraligand charge transfer (ILCT) in nature.

4. Conclusion

Platinum(II) complex of benizmidazole-derived NHC with formula *cis*-[$PtCl_2$(DMSO)(bimy)] has been successfully synthesized. The complex has been characterized by means of multinuclear (^{1}H và $^{13}C\{^1H\}$) NMR and single crystal X-ray diffraction. The complex in both solid or solution state is highly emissive, emitting blue light under UV irradiation. DFT calculations suggest that lowest energy absorption and emission are largely contributed by the *d-d* transitions perturbed by π conjugation of benzimidazolin-2-ylidene and *p* orbital of the chlorido ligand.

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