

Synthesis and Spectroscopic Properties of Cationic *Bis*(bipyridine)-Phosphine Ruthenium Complexes

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The syntheses of heteroleptic *bis*-bipyridine ruthenium(II) complexes $[\text{Ru}(\text{R-bpy})(\text{R}'\text{-bpy})(\text{PPh}_3)\text{Cl}][\text{PF}_6]$ {(2) R-bpy = R'-bpy = 4,4'-dimethyl-2,2'-bipyridine and (3) R-bpy = 4,4'-dimethyl-2,2'-bipyridine, R'-bpy = 4,4'-dimethoxy-2,2'-bipyridine} were achieved by addition of ammonium hexafluorophosphate to a solution of equimolar amounts of *trans*, *cis*- $[\text{Ru}(\text{Me-bpy})(\text{PPh}_3)_2\text{Cl}_2]$ and R'-bpy on refluxing chloroform. The new complexes were characterized by NMR (^3P , ^1H), IR spectroscopy, mass spectrometry and elemental analysis. The structure of $[\text{Ru}(\text{Me-bpy})(\text{MeO-bpy})(\text{PPh}_3)\text{Cl}][\text{PF}_6]$ was identified by X-ray crystallography. Electronic absorption and emission spectra of the complexes were collected. Weak emissions in both complexes were highlighted at room temperature in the range 618-625 nm in methanol and acetonitrile. No emission were observed in chloroform solutions, suggesting that the rate of non-radiative decay (energy transfer) of the singlet metal-to-ligand charge transfer ($^1\text{MLCT}$) excited state is approaching or even faster than that of the inter-system crossing.

Keywords: Ruthenium, *Bis*(bipyridine), Heteroleptic, Luminescence.

INTRODUCTION

Ruthenium(II) diimine complexes with their extraordinary photophysical and photochemical properties have been a center of interest in the past four decades as such complexes characterized with strong absorbance in the visible domain due to the metal-to-ligand charge transfer “MLCT” as well as the long lifetimes for the triplet excited states that are resulted from the spin-orbit coupling. A wide range of ruthenium(II) diimine complexes are reported and their photophysical behaviours were characterized. Among the different possible ruthenium(II) diimine, homoleptic *bis*-diimine and *tris*-diimine ruthenium complexes extensively studied. They are obtainable by refluxing ruthenium(III) chloride hydrate or some other ruthenium(II) complexes with the right ratio of the ligand in alcohols or *N,N*-dimethylformamide (DMF) [1-5]. Synthesis of heteroleptic *bis*-diimine and *tris*-diimine ruthenium(II) complexes have also been reported, showing the possibility of adjusting the excited-state properties by the presence of different substituents on the diimine ligands [6-14]. Recent research in the area proved that the quantum yields of the luminescence in this class of complexes are affected by the presence of the competing non-radiative decay originated from thermal activation to the triplet metal-centered (^3MC) excited states. The decay from the ^3MC excited states facilitates the ligands dissociation; resulting possibly in decomposition or ligand substitution.

Introducing ligands with π -accepting character may lead to a greater splitting in the *d*-orbitals by the ligand strong field as a strategy to increase the luminescence quantum yield and life time of the emission by blocking the non-radiative decay pathway. In this paper, we report a synthetic route toward heteroleptic *bis*-diimine ruthenium(II) complexes with a general formula $[\text{Ru}(\text{R-bpy})(\text{R}'\text{-bpy})(\text{PPh}_3)\text{Cl}][\text{PF}_6]$. The spectroscopic features of the new complexes will be highlighted.

EXPERIMENTAL

All reactions were performed under a nitrogen atmosphere, using Schlenk techniques. Chloroform was dried over molecular sieves (3 Å); all other solvents were used as received. Ammonium hexafluorophosphate, 4,4'-dimethyl-2,2'-bipyridine (Me-bpy) (Aldrich) and 4,4'-dimethoxy-2,2'-bipyridine (MeO-bpy) (Aldrich) were purchased commercially and used as received. *Trans*, *cis*- $[\text{Ru}(\text{Me-bpy})(\text{PPh}_3)_2\text{Cl}_2]$ (**1**) was synthesized, following the literature reports [15].

Elemental analyses were conducted at King Abdulaziz University. UV-visible absorption spectra of 5×10^{-5} M solutions in 1 cm quartz cells were conducted with a Shimadzu UV-visible spectrophotometer UV-1650PC. UV-visible emission spectra were recorded for deaerated solutions (5×10^{-5} M) in 1 cm quartz cells using a Shimadzu UV-visible spectrofluorometer RF-5301PC. ^1H (850 MHz) NMR and ^3P NMR spectra

(344 MHz) were recorded using an Bruker Avance III HD NMR spectrometer. The spectra are referenced to residual chloroform (7.26, ^1H), or external H_3PO_4 (0.0 ppm, ^{31}P). High-resolution electrospray ionization (ESI) mass spectra were recorded using an Agilent Q-TOF 6520 instrument; all mass spectrometry are reported as m/z .

General procedure for synthesis of complexes 2 and 3: NH_4PF_6 and the ruthenium dichloride complex (**1**) were added to a flask containing 30 mL of CHCl_3 under a N_2 atmosphere followed by the addition of a stoichiometric amount of the R' -bpy (Me-bpy or MeO-bpy) ligand. The reaction mixture was stirred at reflux until the reaction mixture turned red (around 6 h). The reaction mixture was filtered to remove excess NH_4PF_6 and NH_4Cl . The filtrate was reduced in volume to about 10 mL and diethyl ether was added, forming an orange-red precipitate. The desired complex was collected by filtration and dried, affording the product as an orange-red powder.

[Ru(Me-bpy) $_2$ (PPh $_3$)Cl][PF $_6$] (2): Complex **1** (53 mg, 0.060 mmol), 4,4'-dimethyl-2,2'-bipyridine (15 mg, 0.081 mmol) and NH_4PF_6 (25 mg, 0.153 mmol) were reacted in 30 mL CHCl_3 , yielding **3** (46 mg, 84 %) as an orange-red powder. HR ESI MS $[\text{C}_{42}\text{H}_{39}^{35}\text{ClN}_4\text{P}^{102}\text{Ru}]^+$: calcd. 767.1644, found 767.1630 and $[\text{C}_{42}\text{H}_{39}^{37}\text{ClN}_4\text{P}^{102}\text{Ru}]^+$: calcd. 769.1655, found 769.1613. Anal. calcd. for $\text{C}_{42}\text{H}_{39}\text{ClF}_6\text{N}_4\text{P}_2\text{Ru}$: C, 55.30; H, 4.31; N, 6.14 %. Found: C, 54.94; H, 4.63; N, 6.49 %. ^1H NMR: 2.37, 2.44, 2.55, 2.61 (4 $\times$ s) [12H, 4 $\times$ -CH $_3$], 6.58 (dd, $^2J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HH}} = 1$ Hz) [1H, pyridine], 6.86 (d, $^2J_{\text{HH}} = 6.5$ Hz) [1H, pyridine], 6.89 (dd, $^2J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HH}} = 1$ Hz) [1H, pyridine], 7.02(s) [2H, pyridine], 7.08 (d, $^2J_{\text{HH}} = 5$ Hz) [1H, pyridine], 7.13(t, $^2J_{\text{HH}} = 8$ Hz) [12H, PPh], 7.23(m, $^2J_{\text{HH}} = 8$ Hz) [6H, PPh], 7.34(m) [12H, PPh], 8.00(s) [1H, pyridine], 8.04(s) [1H, pyridine], 8.09(s) [1H, pyridine], 8.13(s) [1H, pyridine], 8.97 (d, $^2J_{\text{HH}} = 6.5$ Hz) [1H, pyridine], 9.02 (d, $^2J_{\text{HH}} = 6.5$ Hz) [1H, pyridine]. ^{31}P NMR: 43.9(s, PPh $_3$), -144.7 (sep, $^1J_{\text{PF}} = 714$ Hz, PF $_6^-$).

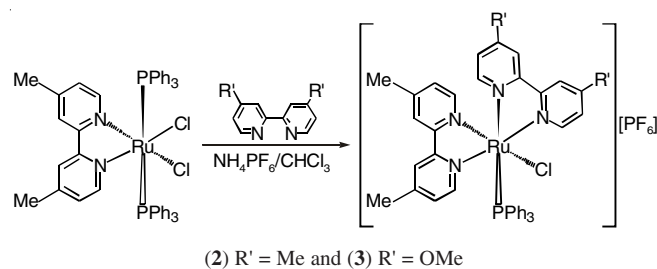
[Ru(Me-bpy)(MeO-bpy)(PPh $_3$)Cl][PF $_6$] (3): Complex **1** (211 mg, 0.240 mmol), 4,4'-dimethoxy-2,2'-bipyridine (51 mg, 0.236 mmol) and NH_4PF_6 (98 mg, 0.601 mmol) were reacted in 30 mL CHCl_3 , yielding **5** (196 mg, 86 %) as an orange-red powder. HR ESI MS $[\text{C}_{42}\text{H}_{39}^{35}\text{ClN}_4\text{O}_2\text{P}^{102}\text{Ru}]^+$: calcd. 799.1543, found 799.1513 and $[\text{C}_{42}\text{H}_{39}^{37}\text{ClN}_4\text{O}_2\text{P}^{102}\text{Ru}]^+$: calcd. 801.1553, found 801.1531. Anal. calcd. for $\text{C}_{42}\text{H}_{39}\text{F}_6\text{N}_4\text{O}_2\text{P}_2\text{Ru}$: C, 53.42; H, 4.16; N, 5.39 %. Found: C, 52.93; H, 4.63; N, 4.59 %. ^1H NMR: 2.37, 2.55(2 $\times$ s) [6H, 2 $\times$ -CH $_3$], 3.89, 4.06 (2 $\times$ s) [6H, 2 $\times$ -OCH $_3$], 6.59 (dd, $^2J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HH}} = 2$ Hz) [1H, pyridine], 6.75 (dd, $^2J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HH}} = 2$ Hz) [1H, pyridine], 6.81 (dd, $^2J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HH}} = 2$ Hz) [1H, pyridine], 6.88 (d, $^2J_{\text{HH}} = 6.5$ Hz) [1H, pyridine], 6.94 (d, $^2J_{\text{HH}} = 6.5$ Hz) [1H, pyridine], 6.96 (dd, $^2J_{\text{HH}} = 6.5$ Hz, $^3J_{\text{HH}} = 2$ Hz) [1H, pyridine], 7.14(t, $^2J_{\text{HH}} = 8$ Hz) [12H, PPh], 7.19(d, $^2J_{\text{HH}} = 7$ Hz) [1H, pyridine], 7.25(m) [6H, PPh], 7.34(m) [12H, PPh], 7.62 (d, $^3J_{\text{HH}} = 3$ Hz), 7.72 (d, $^3J_{\text{HH}} = 3$ Hz), 8.01(s) [1H, pyridine], 8.10(s) [1H, pyridine], 8.88 (d, $^2J_{\text{HH}} = 7$ Hz) [1H, pyridine], 9.02 (d, $^2J_{\text{HH}} = 6.5$ Hz) [1H, pyridine]. ^{31}P NMR: 45.1 (s, PPh $_3$), -144.5 (sep, $^1J_{\text{PF}} = 713$ Hz, PF $_6^-$).

Crystal data for [Ru(Me-bpy)(MeO-bpy)(PPh $_3$)Cl][PF $_6$] (3): Crystals of complex **3** was obtained from cooling a concentrated hot methanol solution. The sample was fixed on Agilent

Super Nova (Dual source) Agilent Technologies Diffractometer, equipped with graphite-monochromatic Cu/MoK $_{\alpha}$ radiation for data collection. Data collection at 296 K under the CuK $_{\alpha}$ radiation and reduction were carried out using CrysAlisPro software [16]. The structure and refinement was achieved using SHELXS-97 [17], in-built with X-Seed [18]. All non-hydrogen atoms were refined an isotropically by full-matrix least squares methods [17]. Aromatic and methyl hydrogen atoms, which were located geometrically and treated as riding atoms with [C-H = 0.93 Å with Uiso(H) = 1.2 Ueq(C)] and [C-H = 0.96 Å with Uiso(H) = 1.5 Ueq(C)], respectively.

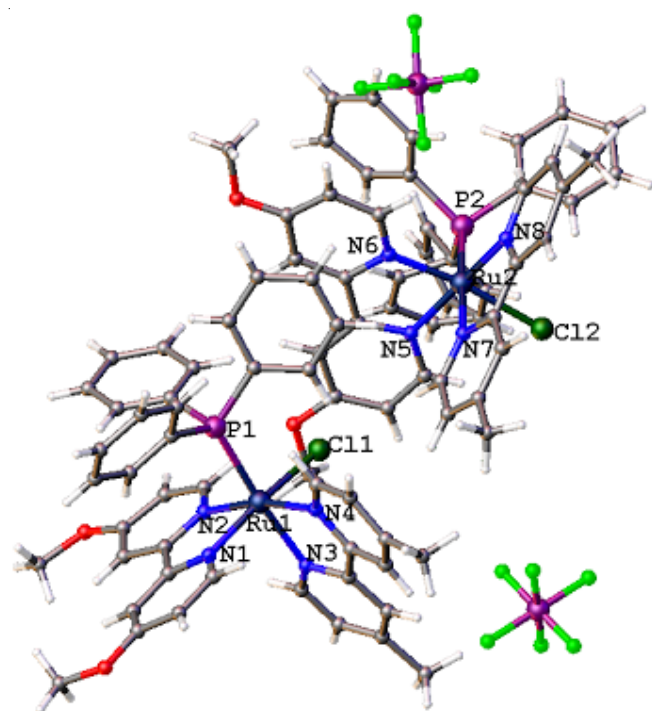
RESULTS AND DISCUSSION

The starting materials **1** was stirred in hot chloroform with excess amounts of NH_4PF_6 in the presence of the substituted bipyridine to afford complexes **2** and **3** (Scheme-I). Heating the reaction mixture was necessary to accelerate the rate of the reaction as the reaction was slow at room temperature (the reaction was incomplete after 18 h). The heating helps in increasing the dissociation rate of the triphenylphosphine ligand.



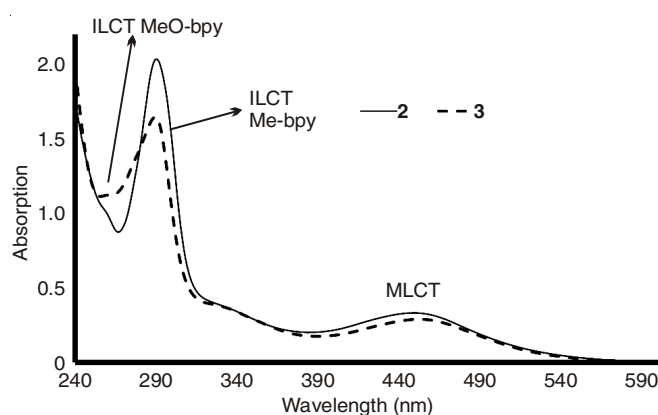
Scheme-I: Synthesis of complexes **2** and **3**

In general, all the complexes are soluble in chlorinated solvents, THF, acetone and moderately soluble in methanol and ethanol. The identities of the complexes were confirmed by ^1H NMR and ^{31}P NMR as well as elemental analysis. ^1H NMR spectra were affected by the asymmetric geometrical structures, causing all the methyl and pyridyl protons to show different signals. The integrations of the peaks of the methyl and/or methoxy substituents on the bipyridine (2.0-4.2 ppm) against each other in ^1H NMR are good indication of the complexes identities. ^{31}P NMR showed singlet peaks around 45 ppm for the complexes **2** and **3**. Single-crystal X-ray diffraction studies were carried out for complexes **3** (Fig. 1). For both Ru atoms coordination sphere, they consist of six atoms (for the second molecule N5, N6, N7, N8, P2 and Cl2), adopting a distorted octahedral geometry [trans angles for N2-Ru1-N4, N1-Ru1-Cl1 and N3-Ru1-P1 are $167.94(14)^\circ$, $169.08(11)^\circ$ and $174.94(11)^\circ$, respectively], while the phosphorus atom adopted a distorted tetrahedral geometry. The four ruthenium-nitrogen bonds' lengths are not identical, contributing to the geometrical distortion. Selected bond lengths and angles are provided in Table-1 and full details of the crystallographic data collection, structure solution and refinement can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif with deposition number CCDC 1404646 for complex **3**.

Fig. 1. Crystal structure of $[\text{Ru}(\text{MeO-bpy})(\text{MeO-bpy})(\text{PPh}_3)\text{Cl}][\text{PF}_6]$ (**3**)TABLE-1
BOND LENGTHS AND DIHEDRAL ANGLES FOR COMPLEX **3**

Atom	Atom	Length (Å)	Atom	Atom	Atom	Angle (°)
Ru1	P1	2.3299(13)	P1	Ru1	C11	92.78(5)
Ru1	C11	2.4191(13)	N1	Ru1	P1	95.38(11)
Ru1	N1	2.046(4)	N1	Ru1	C11	169.08(11)
Ru1	N2	2.072(3)	N1	Ru1	N2	78.59(14)
Ru1	N3	2.106(4)	N1	Ru1	N3	89.27(15)
Ru1	N4	2.084(4)	N1	Ru1	N4	93.39(14)
Ru2	P2	2.3310(14)	N2	Ru1	P1	90.77(11)
Ru2	C12	2.4234(14)	N2	Ru1	C11	94.09(11)
Ru2	N5	2.068(4)	N2	Ru1	N3	92.10(14)
Ru2	N6	2.052(4)	N2	Ru1	N4	167.94(14)
Ru2	N7	2.108(4)	N3	Ru1	P1	174.94(11)
Ru2	N8	2.093(4)	N3	Ru1	C11	82.86(11)

Absorption spectra: The UV-visible absorption and emission spectra of the complexes **2** and **3** were collected in different solvents (chloroform, methanol and MeCN) and those of the polar solvents summarized in Table-2. The collected absorption spectra of complexes **2** and **3** in methanol are overlaid in Fig. 2. The lowest-energy band has been assigned as metal-to-ligand charge transfer (MLCT) based on theoretical

Fig. 2. Absorption spectra of complexes **2** and **3** in methanol overlaid

calculations performed on similar complexes [19,20]. The energy bands appeared in the region between 265 and 300 nm are believed to be an intra-ligand charge transfer (ILCT) within the bipyridine ligands [19,20]. The introduction of second bipyridine ligand led to an increased intensity in the MLCT band accompanied with a shift in the absorption maxima controlled by the nature of functional groups of bipyridine. In acetonitrile solutions, MLCT and ILCT bands in the complexes **2** and **3** are almost identical to that of methanol solutions due to the similarity in dielectric constant for both solvents [21].

The emission spectra of complexes **2** and **3** were collected for methanol solutions at room temperature (Fig. 3) and very weak emissions were observed in the range 618–625 nm upon excitation at 510 nm. However, a slight increase in the emission intensity accompanied with weak blue shift in the emission maxima was observed as one unit of 4,4'-dimethyl-2,2'-bipyridine was replaced by 4,4'-dimethoxy-2,2'-bipyridine [22]. The emission spectra were recollected in acetonitrile solutions and a slight red shift or no significant shift in the emission maxima with no improvement in the intensities were observed. The original purpose for introducing the triphenylphosphine ligand was to increase the energy of the d_π orbital of the metal. The absence of any emission in chloroform suggested that the rate of non-radiative decay of the $^1\text{MLCT}$ excited state by energy transfer is faster than that of the intersystem crossing [23]. The polar solvents seem to affect the rate of energy transfer slightly and hence the weak emission was observed. More systematically varied complexes, accompanied with theoretical calculations, are needed in order to understand the electronic features of these complexes.

TABLE-2
ELECTRONIC SPECTRA OF COMPLEXES **2** AND **3**

Complex	Methanol			MeCN		
	λ_{max} (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Excitation	Emission	λ_{max} (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Excitation	Emission
$[\text{Ru}(\text{MeO-bpy})_2(\text{PPh}_3)\text{Cl}][\text{PF}_6]$ (2)	449 nm (6.62) sh 316 nm (9.18) 292 nm (40.16)	290 nm 510 nm	318 nm 621 nm	449 nm (6.62) sh 316 nm (9.18) 292 nm (40.16)	275 nm 510 nm	321 nm 625 nm
$[\text{Ru}(\text{MeO-bpy})(\text{MeO-bpy})(\text{PPh}_3)\text{Cl}][\text{PF}_6]$ (3)	452 nm (5.77) sh 316 nm (8.38) 289 nm (36.88) sh 264 nm (22.56)	275 nm 510 nm	311 nm 618 nm	452 nm (5.77) sh 316 nm (8.38) 289 nm (36.88) sh 264 nm (22.56)	275 nm 510 nm	319 nm 618 nm

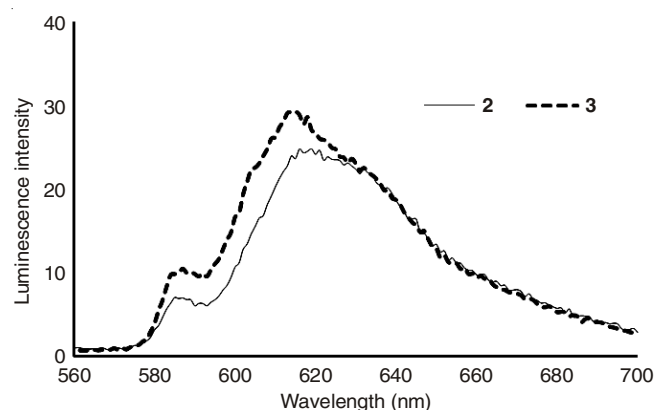


Fig. 3. Overlain emission spectra of 5×10^{-5} M solutions of complexes **2** and **3** in methanol

Conclusion

A synthetic route toward heteroleptic *bis*(substituted-bipyridine)ruthenium(II) complexes were reported using a new procedure and the spectroscopic data of the new complexes were collected. Weak emissions were observed in the new complexes at room temperature in the range 618-625 nm in methanol and acetonitrile. The low or no emission can be explained by the fast non-radiative decay (energy transfer) of the ¹MLCT excited state, competing the intersystem crossing that lead to less conversion of the singlet-excited state to the triplet-excited state. However, extensive spectroscopic studies accompanied with theoretical calculations for systematically varied series of complexes are ongoing to establish structure-luminescence property relationships.

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