

# Synthesis, characterization and crystal structure of a new ruthenium polypyridyl complex [Ru(phen)<sub>2</sub>(4,4'-dicarboxy-2,2'-bipyridine)]PF<sub>6</sub>

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**Abstract:** A new Ru(II) polypyridyl complex, [Ru(phen)<sub>2</sub>(4,4'-dicarboxy-2,2'-bipyridine)]PF<sub>6</sub>·1.5H<sub>2</sub>O, was synthesized and characterized by single crystal X-ray diffraction, elemental analyses, electrospray ionization mass spectrometry, infrared spectra, ultraviolet (UV) spectra, and emission spectra. The structure of the cation [Ru(phen)<sub>2</sub>(4,4'-(COO<sup>-</sup>), (COOH)-2,2'-bpy)]<sup>+</sup> consists of a six-coordinated ruthenium atom chelated by two phen ligands and one 4,4'-dicarboxy-2,2'-bipyridine ligand. The absorption spectrum of the Ru(II) complex is characterized by two intense ligand-centered transitions in the UV region and one metal to ligand charge transfer in the visible region. Moreover, the complex can display luminescence in water at room temperature, with maximum emission at 623 nm.

**Supporting information:** Cif file

**Keywords:** Ru(II) complex; Polypyridyl ligand; Spectra and Structure.

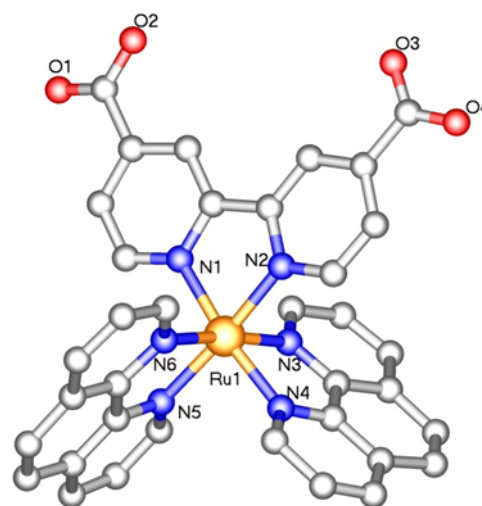
## 1. INTRODUCTION

Ruthenium polypyridyl complexes have been subjected to a number of studies concerning their excellent chemical stability, facile electron transfer, strong luminescent emission, and potential roles in medical applications [1–6]. Particular emphasis has been given to the examination of the antineoplastic properties of ruthenium complexes with a number of ligands of biological interest [7]. Geometry is a very important factor in studying the properties of ruthenium polypyridyl complexes. Ligands derived from various modifications of 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) have been employed to address different issues [8]. Modifying the polypyridyl ligands or changing the substituents on the ligands can result in interesting differences in the spatial configurations and electronic structures of Ru(II)-polypyridyl complexes [9–12]. This study reports the synthesis, crystal structure, and properties of a new Ru(II) polypyridyl complex called [Ru(phen)<sub>2</sub>(4,4'-(COO<sup>-</sup>), (COOH)-2,2'-bpy)]PF<sub>6</sub>·1.5H<sub>2</sub>O.

## 2. EXPERIMENTAL

### 2.1 Analyses and Physical Measurements

Elemental analyses of C, H, and N were carried out using a Perkin–Elmer 240C elemental analyzer (Germany). Electrospray



**Figure 1.** X-ray crystal structure of [Ru(phen)<sub>2</sub>(4,4'-(COO<sup>-</sup>), (COOH)-2,2'-bpy)]PF<sub>6</sub>·1.5H<sub>2</sub>O. All hydrogen atoms are omitted for clarity.

pray ionization mass spectrometry (ESI–MS) was recorded on an LQC system (Finnigan MAT, USA) using CH<sub>3</sub>CN as the mobile phase. Infrared (IR) spectra were recorded on a Nicolet Avatar 170 Fourier transform-IR spectrophotometer (USA) scanning from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> as KBr pellets. UV–Vis spectrum was measured on a Shimadzu UV-3150 spectrophotometer (Japan). Luminescence spectrum was measured on a Perkin–Elmer Ls55 spectrofluorophotometer (USA).

### 2.2 X-Ray Single Crystal Structure Determination

A monoclinic red crystal with approximate dimensions of 0.40 mm × 0.24 mm × 0.04 mm was placed on a Bruker Smart Apex CCD area detector. Intensity data were collected with a graphite-monochromator under Cu Kα radiation (λ = 1.54178 Å) at 153(2) K. The structure was analyzed by direct methods. All non-hydrogen atoms were refined anisotropically by least-squares on F<sup>2</sup> using the SHELXTL program [13]. The atoms were first refined isotropically, and then anisotropically. The hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters. The structure factors in the calculations were included in the final stage of full-matrix least-square refinement. The final refinements converged

at  $R_1 = 0.0452$  and  $\omega R_2 = 0.2619$ , with  $\omega = 1/[\sigma^2(F_o^2) + (0.1778P)^2 + 66.9701P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . Crystal data and collection parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

### 2.3 Preparation of

#### [Ru(phen)<sub>2</sub>(4,4'-(COO)<sup>-</sup>, (COOH)-2,2'-bpy)]PF<sub>6</sub>·1.5H<sub>2</sub>O

4,4'-Dimethyl-2,2'-dipyridyl was purchased from Aldrich Chemical Co. 4,4'-Dicarboxy-2,2'-bipyridine and *cis*-[Ru(phen)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O were prepared and characterized according to previously described methods [14, 15].

A mixture of *cis*-[Ru(phen)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O (0.28 g, 0.5 mmol), 4,4'-dicarboxy-2,2'-bipyridine (0.12 g, 0.5 mmol), and ethylene glycol (30.0 mL) was heated at 120 °C under the protection of argon for 6 h, during which the solution turned red. The solution was then cooled to room temperature. After filtration, saturated NH<sub>4</sub>PF<sub>6</sub> was added dropwise, resulting in a red-orange precipitate which was filtered and recrystallized with CH<sub>3</sub>CN/CH<sub>3</sub>CH<sub>2</sub>OH (1:1, v/v). Dark red single crystals were obtained. Yield: 0.30 g (68.6%). Anal. Calcd for C<sub>36</sub>H<sub>26</sub>F<sub>6</sub>N<sub>6</sub>O<sub>5.5</sub>PRu (876.67): C, 49.32; H, 2.99; N, 9.59. Found: C, 49.43; H, 2.87; N, 9.80. ESI-MS:  $m/z = 850.9$  [M]<sup>+</sup> (28), 353.3 [M-PF<sub>6</sub>]<sup>2+</sup> (100), IR  $\nu$  (cm<sup>-1</sup>) (KBr pellet): 3395, 3080, 1714, 1613, 1544, 1368, 1233, 843, and 772. UV  $\lambda$  (nm): 263, 292, and 451.

**Table 1.** Crystallographic Data of [Ru(phen)<sub>2</sub>(4,4'-(COO)<sup>-</sup>, (COOH)-2,2'-bpy)]PF<sub>6</sub>·1.5H<sub>2</sub>O

Complex [Ru(phen) <sub>2</sub> (4,4'-(COO) <sup>-</sup> , (COOH)-2,2'-bpy)]PF <sub>6</sub> ·1.5H <sub>2</sub> O	
Empirical formula	C <sub>36</sub> H <sub>26</sub> F <sub>6</sub> N <sub>6</sub> O <sub>5.5</sub> PRu
Formula weight	876.67
Temperature (K)	153(2)
Wavelength (Å)	1.54178
Crystal system, Space group	Monoclinic, C2/c
<i>a</i> (Å)	17.7392(4)
<i>b</i> (Å)	21.3783(6)
<i>c</i> (Å)	21.3986(5)
$\alpha$ /°	90
$\beta$ (°)	96.020(2)
$\gamma$ /°	90
Volume (Å <sup>3</sup> )	8070.3(3)
<i>Z</i>	8
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.443
<i>F</i> (000)	3528
Crystal size (mm)	0.40 × 0.24 × 0.04
<i>q</i> range for data collection (°)	3.248 to 65.769
Limiting indices	-19 ≤ <i>h</i> ≤ 20, -23 ≤ <i>k</i> ≤ 25, -24 ≤ <i>l</i> ≤ 24
Reflections collected	6681
Independent reflections	5233 ( <i>R</i> <sub>int</sub> = 0.0452)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.060
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 <i>s</i> ( <i>I</i> )] <sup>a</sup>	0.1017 / 0.2825
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0873 / 0.2619
Largest diff. peak (eÅ <sup>-3</sup> )	2.933 / -1.165

## 3. RESULTS AND DISCUSSION

### 3.1 Structure Description

The title complex contains a six-coordinated ruthenium atom chelated by two phen ligands and one 4,4'-dicarboxy-2,2'-bipyridine ligand (Figure 1). One of two carboxy groups of 4,4'-dicarboxy-2,2'-bipyridine is deprotonated. The coordination geometry about the ruthenium atom is a distorted octahedron. The bite angles between the two phen, the 4,4'-dicarboxy-2,2'-bipyridine chelate rings, and the ruthenium atom are 79.4(3)°, 80.1(3)°, and 79.0(2)°, respectively. The observed deviation from the ideal octahedral geometry is due to the customary narrow bite angles of bipyridine moieties, which are also observed in some other ruthenium complexes [16]. The Ru-N bond distances for the title complex [2.047(6) Å to 2.073(6) Å] agree with previously reported values [17, 18]. The torsion angle between 4,4'-dicarboxy-2,2'-bipyridine is 5.0°.

The Ru-N bond distances are significantly shorter than those of Ru-N for Ru(NH<sub>3</sub>)<sub>6</sub>I<sub>2</sub> (2.144 Å) [19]. In contrast to polypyridyl which coordinates to Ru(II) through  $\sigma$  bonding and weak  $\pi$  bonding, the ammonia coordinates to Ru(II) through  $\sigma$  bonding only. The bond distances of Ru-N (phen) and Ru-N (4,4'-dicarboxy-2,2'-bipyridine) are essentially identical and within the experimental error, showing that the  $\pi$  back-bonding interactions statistically involve each of the ligands present in the coordination sphere [16].

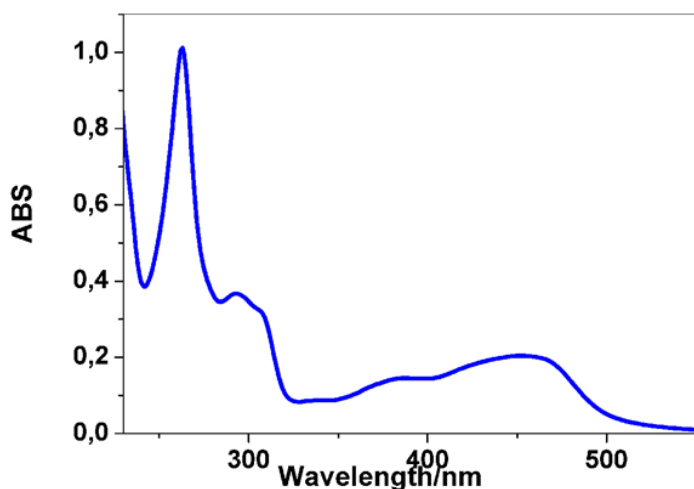
### 3.2 Electronic Spectra

The absorption spectrum of the Ru(II) complex is characterized by two intense ligand-centered transitions (LC) in the UV region at 263 and 292 nm, and a metal to ligand charge in the visible region at 451 nm (Figure 2). The visible bands around 451 nm arise from the metal (*d<sub>n</sub>*) to ligand ( $\pi^*$ ) charge transfer transitions. The ultraviolet bands at 263 and 292 nm belong to the  $\pi \rightarrow \pi^*$  transitions of the ligands [17].

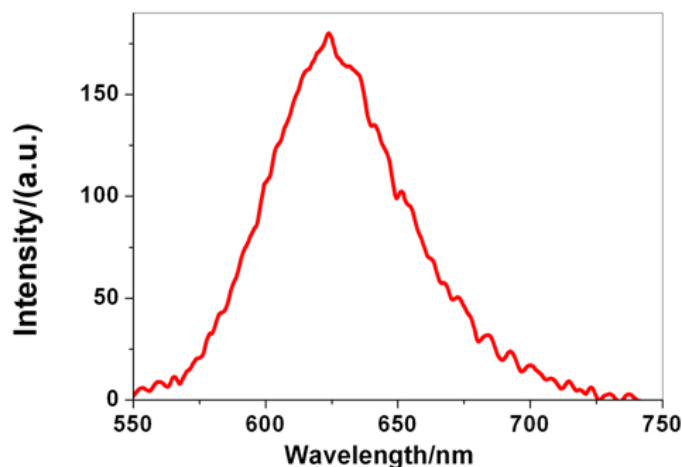
Upon excitation of the complex using a wavelength of 451 nm, it fluoresces with a maximum wavelength of about 623 nm (Figure 3), which is typical for this type of Ru(II) complex [20].

**Table 2.** Selected bond lengths (Å) and angles (°) for metal environments of [Ru(phen)<sub>2</sub>(4,4'-(COO)<sup>-</sup>, (COOH)-2,2'-bpy)]PF<sub>6</sub>·1.5H<sub>2</sub>O.

Ru(1)-N(1)	2.047(6)	Ru(1)-N(2)	2.050(7)
Ru(1)-N(3)	2.073(6)	Ru(1)-N(4)	2.066(6)
Ru(1)-N(5)	2.069(6)	Ru(1)-N(6)	2.051(7)
N(1)-Ru(1)-N(2)	79.0(2)	N(1)-Ru(1)-N(3)	94.8(2)
N(1)-Ru(1)-N(4)	172.1(3)	N(1)-Ru(1)-N(5)	97.0(2)
N(1)-Ru(1)-N(6)	91.5(2)	N(2)-Ru(1)-N(3)	84.8(2)
N(2)-Ru(1)-N(4)	95.1(3)	N(2)-Ru(1)-N(5)	175.4(2)
N(2)-Ru(1)-N(6)	97.8(3)	N(3)-Ru(1)-N(4)	79.4(3)
N(3)-Ru(1)-N(5)	97.8(2)	N(3)-Ru(1)-N(6)	173.6(2)
N(4)-Ru(1)-N(5)	89.1(3)	N(4)-Ru(1)-N(6)	94.5(3)
N(5)-Ru(1)-N(6)	80.1(3)		



**Figure 2.** Absorption spectra of  $[\text{Ru}(\text{phen})_2(4,4'-(\text{COO})-(\text{COOH})-2,2'\text{-bpy})]\text{PF}_6 \cdot 1.5\text{H}_2\text{O}$  in water.



**Figure 3.** Emission spectra of  $[\text{Ru}(\text{phen})_2(4,4'-(\text{COO})-(\text{COOH})-2,2'\text{-bpy})]\text{PF}_6 \cdot 1.5\text{H}_2\text{O}$  in water at the excitation wavelength of 451 nm.

### Supplementary Data

CCDC 945568 contains the supplementary crystallographic data for  $[\text{Ru}(\text{phen})_2(4,4'-(\text{COO})-(\text{COOH})-2,2'\text{-bpy})]\text{PF}_6 \cdot 1.5\text{H}_2\text{O}$ . These data are free via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre. The contact information of the centre is: 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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