



A new cycloruthenated complex: Synthesis, characterization and colorimetric detection of bisulphite in water

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ABSTRACT

A new hydrophilic cyclometallated ruthenium complex **1** ($\text{Ru}(\text{pba})(\text{bpy})_2^+$, $\text{Hpba} = 4\text{-(2-pyridyl)benzaldehyde}$, $\text{bpy} = 2,2'\text{-bipyridine}$) was successfully synthesized. The as-prepared complex exhibited typical MLCT absorptions centered at 536 nm, which are assigned to Ru-bpy CT transitions and noticeably red-shifted relative to $\text{Ru}(\text{bpy})_3^{2+}$ derivatives because of the formation of Ru–C bond. In view of a possible adduct of aldehyde and bisulphite, its performance to recognize HSO_3^- ions was investigated in details. Upon addition of bisulphite, the maximum of MLCT absorptions was blue-shifted to 400 nm, accompanied with an apparent color change from red to yellowish. However, there were no obvious changes observed in MLCT bands upon addition of other common anions, cysteine and homocysteine. The results showed that this cycloruthenated complex displayed high selectivity to bisulphite, which can be detected with the naked-eye. The detection limit of the chemo-sensor for bisulphite reached $2.73 \mu\text{mol/L}$.

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Introduction

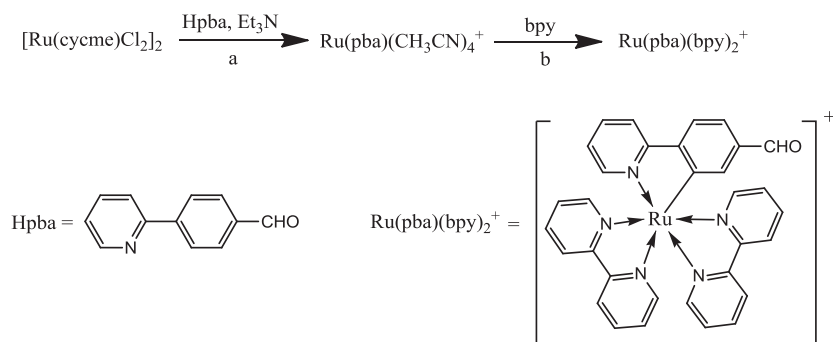
Recently, much attention have been drawn to the cyclometallated polypyridine ruthenium(II) complexes because of their distinguished photophysical properties [1–4]. Different from conventional ruthenium oligopyridyl complex ($[\text{Ru}^{\text{II}}(\text{N}^{\text{N}})_2(\text{N}^{\text{N}})]^{2+}$), cyclometallated ruthenium(II) complex ($[\text{Ru}^{\text{II}}(\text{N}^{\text{N}})_2(\text{C}^{\text{N}})]^+$) has an anionic carbon center by the replacement of a nitrogen atom in bipyridine. The formation of the Ru–C bond dramatically changes the electronic properties of the ligands and facilitates the MLCT absorption shifting to long-wavelength range [2–4]. Up to now, these complexes have been used as energy acceptors [5], electron transfer sensitizers in dyads [6], and sensitizers for dye-sensitized solar cells [7–9]. To the best of our knowledge, there are only a few examples of such complexes that were used as chemo-sensors [10–13]. A cyclometallated ruthenium complex with a triarylborane at the outer rim as cyanide chemo-sensor was first reported by Gabbaï [10]. Then, several cyclometallated ruthenium complexes with 2-(2-thienyl)pyridine derivatives were synthesized and used as Hg^{2+} chemo-sensor [11–13]. All these complexes demonstrated

good absorptions at long-wavelength to realize visualization quite readily, which makes cyclometallated ruthenium complexes promising chemo-sensors.

Bisulfite, as an important additive in foodstuffs, is one of the most widely distributed environmental pollutants [14–17]. The excessive intake of bisulphite may cause asthmatic attacks and allergic reactions [18]. So the development of selective and sensitive signaling chemo-sensors for the determination and visualization of bisulphite is a very attractive research topic. Compared with conventional analytical techniques including spectrophotometry [19], spectrofluorimetry [20], chemiluminescence [21], chromatography [22] and enzymatic techniques [23], optical sensors have drawn significant attentions because of their simplicity, sensitivity and virtues in real-time observation and visualization. More and more organic dye-based optical sensors have been designed such as coumarin derivatives [24–26], benzo[e]indolium derivatives [27,28], rhodamine derivatives [29], naphthalimide derivatives [30,31] and dipyrromethene derivatives [32]. However, few bisulphite optical sensors are based on heavy-metal complexes, which have more advantages over organic dyes with low-lying excited states or long-wavelength emission [33–35]. Therefore, we were intrigued by the possibility of equipping cyclometallated ruthenium complex with sensitive group to bisulphite. Herein, a new hydrophilic cyclometallated ruthenium complex $\text{Ru}(\text{pba})(\text{bpy})_2^+$ (**1**,

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Scheme 1. Synthetic routes of $\text{Ru}(\text{pba})(\text{bpy})_2^+$ (**1**). a). KPF_6 , CH_3CN , 50°C , b). CH_3OH , reflux for 3 h.

Hpba = 4-(2-pyridyl)benzaldehyde, bpy = 2,2'-bipyridine) was successfully synthesized. The transformation of the aldehyde into bisulphite adducts leads to a change in the electron acceptor strength [36–38], which resulted in an apparent color change from red to yellowish. Therefore, it can be used as a colorimetric chemosensor for HSO_3^- in water.

Results and discussion

Synthesis and characterization of $\text{Ru}(\text{pba})(\text{bpy})_2^+$

Synthesis of $\text{Ru}(\text{pba})(\text{bpy})_2^+$ is presented in Scheme 1. As it is well known that aldehyde is somewhat unstable under strong basic conditions. Thus the common deprotonation reagent NaOH cannot be used in cycloruthenation of 4-(2-pyridyl)benzaldehyde (Hpba) in acetonitrile [1]. Herein, triethylamine was chosen as deprotonation reagent in the cycloruthenation reaction of Hpba and $[\text{Ru}(\text{cycme})\text{Cl}_2]_2$ in acetonitrile. Without further purification, 2,2'-bipyridine was then added in the following reaction to obtain $\text{Ru}(\text{pba})(\text{bpy})_2^+$ with high overall yield of 86%.

The identity of this complex was verified by NMR, MS, element analysis and X-ray crystallographic analysis. ^1H NMR spectroscopy is provided in Fig. S1. Upon cyclometallation, there were significant upfield shifts for all aromatic cyclometallating ligand proton signals

because cyclometallation resulted in a significant increase in electron density on the ligand [39,40]. For example, the singlet assigned to hydrogen signal of aldehyde shifted from δ 10.09 to 9.72 ppm. In ^{13}C NMR spectra (Fig. S1), the signal for carbon of **1** which was coordinated to the ruthenium center directly was observed at δ 193.78 ppm, being accordance with those of $[\text{RuL}(\text{bpy})_2]\text{PF}_6$. The MS spectrum of **1** showed the parent peak of $\text{Ru}(\text{pba})(\text{bpy})_2^+$ at $m/z = 596.05$ (Fig. S3), which corresponded to the loss of one counter ion. All these spectra and elemental analysis data provided powerful illustration for the next X-ray crystallographic analysis.

Fig. 1 showed the molecular structure of **1** determined by X-ray crystallographic study. Further details of the crystal data, data collection, structure solution, and refinement parameters are summarized in Table 1. Selected bond distances and angles are collected in Table 2. Herein, **1** adopts a triclinic, distorted octahedral coordination around the $\text{Ru}(\text{II})$ center with two chelating bpy and the (N,C) -bidentate ligand. The $\text{Ru}-\text{C}(31)$ bond was measured to be $2.075(3)$ Å, in the range of $\text{Ru}-\text{C}$ distances observed for similar complexes [40–42]. With respect to the average $\text{Ru}-\text{N}$ distance $2.043(8)$ Å observed for the bipyridine $\text{N}(3)$, $\text{N}(4)$ atoms, the $\text{Ru}-\text{N}(1)$ bond trans to the $\text{Ru}(1)-\text{C}(31)$ bond is somewhat elongated ($2.078(3)$ Å) because of the strong trans effect of the

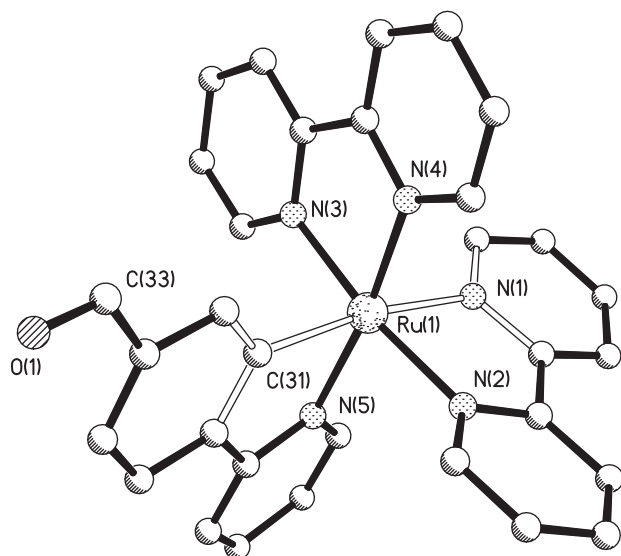


Fig. 1. ORTEP representation of the X-ray structure of $[\text{1}]\text{PF}_6$. The hydrogen atoms and counterion are omitted for clarity.

Table 1
Crystal data and structure refinement for **1**.

Empirical formula	$\text{C}_{32}\text{H}_{24}\text{F}_6\text{N}_5\text{O P Ru}$	
Formula weight	740.60	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 10.8703(4)$ Å	$\alpha = 116.118(2)^\circ$
	$b = 13.7645(4)$ Å	$\beta = 109.379(2)^\circ$
	$c = 14.2345(8)$ Å	$\gamma = 95.964(2)^\circ$
Volume (Å ³)	1723.65(13)	
Z	2	
Density (mg/m ³ , calculated)	1.423	
Absorption coefficient (mm ⁻¹)	0.565	
F(000)	740	
Theta range for data collection (°)	2.28–27.00	
Index ranges	$-13 \leq h \leq 13$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$	
Reflections collected	38,688	
Independent reflections [R_{int}]	7475 [0.0369]	
Completeness to theta = 27.00°	99.2%	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters,	7475/0/404	
Goodness-of-fit on F^2	1.070	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0514$, $wR_2 = 0.1406$	
R indices (all data)	$R_1 = 0.0632$, $wR_2 = 0.1488$	
Largest diff. peak and hole ($e \text{ Å}^{-3}$),	1.078 and -0.738	

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