Journal of Organometallic Chemistry 804 (2016) 101–107

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and photophysical properties of isocyano Ruthenium(II) quinoline-8-thiolate complexes with visible-light and near-infrared emission

Chi-Fai Leung [a, *], Chi-Chiu Ko [b, **]

[a] Department of Science and Environmental Studies, The Hong Kong Institute of Education, 10 Lo Ping Road, Tai Po, Hong Kong, China
[b] Department of Biology and Chemistry, City University of Hong Kong, Tat Che Avenue, Kowloon, Hong Kong, China

ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form
31 October 2015
Accepted 4 December 2015
Available online 24 December 2015

Keywords:
Photophysics
Cyclic voltammetry
Ruthenium
Isocyanide ligands

ABSTRACT

The reactions of $[Ru^{II}(SQ)_2(PPh_3)_2]$ (**SQ** = quinoline-8-thiolate) with different isocyanide ligands affords a series of emissive bis(quinoline-8-thiolate) ruthenium(II) complexes $[Ru^{II}(\mathbf{SQ})_2(PPh_3)(CNR)]$ (**1**–**6**). Two isomeric forms, i.e. *cis,trans* (**1a** – **6a**) and *cis,cis* (**1b** – **6b**) have been separated in these reactions. With the variation on the π-accepting ability of the isocyanide ligands, the CN stretches, lowest energy absorptions and the photoluminescence can be systematically modified.

1. Introduction

The development of tris(8-quinolinolate)aluminum (AlQ_3) based electroluminescent (EL) devices has aroused extensive investigation on metal 8-quinolinolates [1–7]. In contrast, emissive complexes of the sulfur analogues (quinoline-8-thiolate **SQ** derivatives) are less investigated. Most of the reports, so far, are confined to complexes of Pt(II), Pd(II) and other coinage metal centers, which were demonstrated to exhibit interesting luminescent and chemical properties [8–14]. As an extension of our recent work on the synthesis and photophysical properties of the luminescent isocyanide-containing bis(8-quinolinolate) ruthenium(II) complexes [15], we report herein the synthesis, crystal structures, electrochemical and photophysical properties of related bis(quinolin-8-thiolate) ruthenium(II) complexes $[Ru(SQ)_2(PPh_3)(CNR)]$ with isocyanide ligands of different electronic nature. Two different isomeric forms (*cis,trans*- and *cis,cis*-) were isolated and characterized. These complexes are found to show visible and NIR photoluminescence in room temperature solution, which may provide insights into the development of infrared emissive materials for the applications in various areas [16–23].

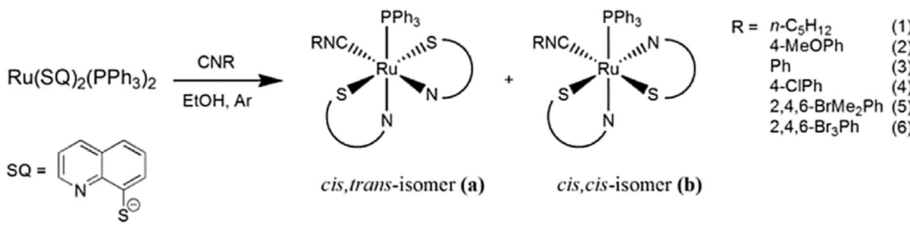
2. Results and discussion

2.1. Synthesis and characterizations

All of the target bis(quinoline-8-thiolato) ruthenium(II) complexes were synthesized from diphosphino bis(quinoline-8-thiolato) ruthenium(II) precursor complex $[Ru(SQ)_2(PPh_3)_2]$. The analytically pure synthetic precursor complex ($[Ru(SQ)_2(PPh_3)_2]$) can be obtained by the reaction of $Ru(PPh_3)_3Cl_2$ with 8-quinolinethiol hydrochloride (HSQ•HCl) in refluxing ethanol under an inert atmosphere of argon. The ligand substitution reaction of the precursor complex with 1.5 mol equivalent of isocyanide ligands (CNR) in refluxing ethanol under an inert atmosphere produces *cis,trans*- and *cis,cis*-isomeric mixtures of $[Ru(SQ)_2(PPh_3)(CNR)]$, where R = *n*-pentyl (**1**), *p*-methoxylphenyl (**2**), phenyl (**3**), *p*-chlorophenyl (**4**) and 4-bromo-2,6-dimethylphenyl (**5**) and 2,4,6-tribromophenyl (**6**) (Scheme 1) [24]. The two isomeric forms can be readily separated and obtained as analytically pure solid by column chromatography on silica gel. IR spectra of the isocyanide complexes show a strong ν_{CN} in the range of 1986–2103 cm^{-1} (KBr) and 2011–2108 cm^{-1} in CH_2Cl_2 (Table S1,

* Corresponding author.
** Corresponding author.
E-mail addresses: cfleung@ied.edu.hk (C.-F. Leung), vinccko@cityu.edu.hk (C.-C. Ko).

http://dx.doi.org/10.1016/j.jorganchem.2015.12.016
0022-328X/



Scheme 1. Synthetic route of $Ru(SQ)_2(PPh_3)(CNR)$ (**1**–**6**).

Supporting information). For the same geometrical isomers, the stretching frequencies ν(C≡N) of the isocyanide ligands are in the order of **6** < **5** < **4** ≤ **3** < **2** << **1**, which is in agreement with π-accepting ability of the corresponding isocyanide ligands ($CNPhBr_3$ > $CNPhBrMe_2$ > CNPhCl ≥ CNPh > CNPhOMe >> CNC_5). This confirmed the π-back-bonding interaction between the isocyanide ligands and the ruthenium(II) metal center with the extent of the interaction increases with the π-accepting ability of the ligands. The interaction not only lead to the weakening of the C≡N bond and the slight variation of the ligand structure, but also affect the electronic properties of these complexes as revealed in the trends of the lowest-energy absorption and emission energy.

2.2. X-ray crystal structure

Single crystals suitable for structural determinations with the X-ray crystallography were obtained by slow diffusion of *n*-pentane into dichloromethane solutions of **4a**, **5a** and **6b** at −14 °C. Perspective drawings of the complexes are shown in Figs. 1 and 2. Selected bonding parameters of these crystal structures are listed in Table 1. These complexes adopted a distorted octahedral geometry with the two quinoline-8-thiolato ligands coordinated in *cis*-geometrical arrangements, which can give rise to three different possible geometrical isomers (i.e. *cis*-N,*trans*-S; *trans*-N,*cis*-S; and *cis*,*cis*-isomers). As revealed from the crystal structures, **4a** and **5a** adopted a *cis*-N,*trans*-S (*cis,trans*) conformation with the two ancillary ligands *trans* to the nitrogen atoms of the two SQ ligand; whereas **6b** adopted a *cis*,*cis*-conformation with the phosphine ligand *trans* to the nitrogen atom of a SQ ligand and the isocyanide ligand *trans* to the sulfur atom of another SQ ligand. In view of the close resemblance of the spectroscopic properties among **1a** − **6a** as well as those among **1b** − **6b**, complexes **1a** − **6a** were assigned to adopt a similar *cis*,*trans*-configuration and **1b** − **6b** were assigned to adopt a similar *cis*,*cis*-configuration. Although the bonding parameters in all of these structures are in a typical ranges (e.g. Ru–C distances are in the range of 1.862–1.901 Å; C≡N distances are in the range of 1.166–1.182 Å; slightly bent isocyanide ligands with C≡N–C in the range of 162.5–165.4°; small bite angles of the chelating quinoline-8-thiolate in the range of 81.4–82.6°) compared to those of related ruthenium(II) complexes [15,25a,b–29]. The Ru-L bonds of the two SQ ligands in the crystal structures of the *cis*,*trans*-isomer (**4a** and **5a**) are much more symmetrical with similar Ru–S and Ru–N bond distances whereas the Ru–S and Ru–N bond distances of the two SQ ligands are significantly different in the *cis*,*cis*-isomer (**6b**). The non-linear

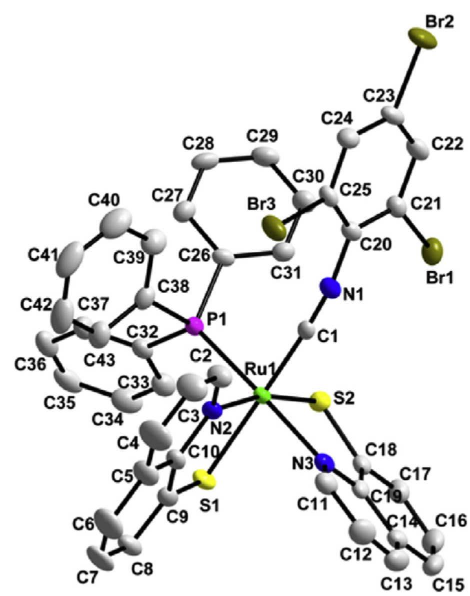


Fig. 2. ORTEP drawing of **6b** (thermal ellipsoids are drawn at the 50% probability; solvent of crystallization and hydrogen atoms are omitted for clarity).

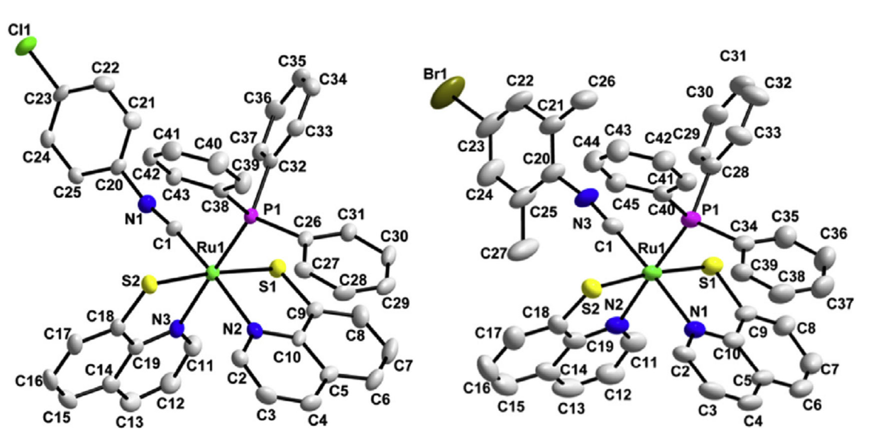


Fig. 1. ORTEP drawings of **4a** and **5a** (thermal ellipsoids are drawn at the 50% probability; solvent of crystallization and hydrogen atoms are omitted for clarity).