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Photophysical and electrochemical studies of heteroleptic cyclometallated complexes of rhodium(III) containing 2-benzoylpyridine

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Abstract

Two heteroleptic cyclometallated complexes, *cis*-[Rh(bzpy)(bipy)Cl₂] (1) and *cis*-[Rh(bzpy)(phen)Cl₂] (2) (where bzpy = 2-(2-pyridylcarbonyl)phenyl, bipy = 2,2'-bipyridine and phen = 1,10-phenanthroline) have been synthesized and characterized. Based on IR and NMR data, it is evident that the coordinated bzpy ligand is *N*,*C* coordinated with Rh(III). Each complex shows high intensity bands in the UV region, assigned as spin-allowed π - π * transitions. The medium-intensity absorption band profile in the lower energy region can be explained by convolution of carbonyl n– π * and d–d* transitions. At low temperature (77 K), each complex shows a broad, symmetric and structureless red emission with a microsecond lifetime and, hence, is assigned as dd* phosphorescence. Voltammetric data have also been obtained for both complexes. There were two reduction peaks observed for each complex. The first reduction peak involves the transfer of two electrons and the elimination of two chlorides. The redox orbital involved in the second reduction is assigned to be the π * orbital localized on the carbonyl fragment of bzpy by examination of the influence on the reduction potentials in the presence of phenol.

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1. Introduction

The great interest in photophysical properties of cyclometallated metal complexes is becoming more intensive [1–3]. Ortho-metallated ligands, such as anionic ppy and thpy ligands (ppyH = 2-phenylpyridine, thpyH = 2-(2-thienyl)pyridine), exhibit higher ligand field strengths compared with that of 2,2'-bipyridine (bipy), due mainly to the strong-donor capability of carbon [3]. This moves both the d(t_{2g}) and d*(e_g) orbitals to higher energy. Since the latter are destabilized much more than the former, the ³d–d* excited state is expected to move to higher energy [3a]. The coordination chemistry of 2-benzoylpyridine (Hbzpy) has been constantly investigated for years [4–12]. It had been reported that this versatile ligand could coordinate in a variety of modes. It can act as a monodentate ligand (with coordination by either the nitrogen [4–6] or the oxygen [5] atom), as a neutral bidentate N,O ligand [6,8], and as a bridging N,O ligand [5] as well as an anionic bidentate N,C ligand [9–11].

By simply mixing $RhCl_3 \cdot 3H_2O$ with Hbzpy in 2-methoxyethanol for 4 days at room temperature, de Geest and Steel synthesized $Rh(Hbzpy)(bzpy)Cl_2$ (bzpy = 2-(2-pyridylcarbonyl)phenyl) [12]. They reported that the complex had a five-membered N,O metallacycle involving the chelating Hbzpy ligand and a six-membered N,C metallacycle involving the chelating bzpy ligand, on the basis of NMR chemical-shift analysis. However, this complex was found to be non-luminescent in our laboratory.

Hetero-bischelated Rh(III) complexes coordinated with anionic bzpy and a polypyridine ligand have not been

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reported to our best knowledge. In this article, we have obtained two heteroleptic cyclometallated Rh(III) complexes. Both the photophysical and electrochemical properties of the two complexes have been thoroughly examined to probe the bonding information of their coordination chemistry.

2. Experimental

2.1. Instrumentation

Recording of NMR, IR, mass and absorption spectra have been detailed elsewhere [13]. Low temperature (77 K) emission spectra were obtained with a SLM 8000[™] spectrofluorometer (SLM Instrument, Inc.) compact with photo-multiplier tubes which were used as detectors. An Xe-Hg lamp was utilized as the excitation source. Emission photoselection measurements of these complexes under study were obtained with the same instrument as the emission spectra, augmented with two additional sheets of polarizer placed in both the paths of the exciting light and emitting light. The luminescence lifetime was determined by a LN 3000 nitrogen laser with 337.1 nm pulses triggered and integrated by a SRS Model SR250 Gated Integrator (Standford Research Systems, Inc.) and Boxcar Average Module. Cyclic voltammetry (CV) and normal pulse voltammetry (NPV) experiments were carried out using a BAS-100B electrochemical analyzer (Bioanalytical Systems, Inc.) equipped with a three-electrode cell system. All experiments were conducted out under a N2 atmosphere. A Pt working electrode (BAS Model MF-2103, 1.6 mm dia.), a Pt wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used for voltammetric measurements. The ferrocenium/ferrocence redox couple was used as an internal standard, $E_{1/2}$ (Fc^{+/0}) = 0.40 V versus SCE. An H-type cell with a porous glass frit was used for controlled potential electrolysis (CPE) experiments using a Pt plate for the working and auxiliary electrodes.

2.2. Reagents

RhCl₃ · $3H_2O$ (Merck), 2,2'-bipyridine, 2-benzoylpyridine and 1,10-phenanthroline (Aldrich) were used as received. K[Rh(phen)Cl₄] was prepared according to the published procedure [14]. Me₂SO (Uvasol, Merck) was dried for spectroscopy. Et₄NClO₄ (TEAP), used as a base electrolyte, was obtained from Showa Chemical Co. and further purified by three recrystallizations from distilled H₂O. Laboratory grade solvents were used unless otherwise specified.

2.3. Synthesis

2.3.1. $[Rh(Hbzpy)(bzpy)Cl_2]$

 $[Rh(Hbzpy)(bzpy)Cl_2]$ was prepared according to the published procedure [12]. The orange-yellow product was

characterized by its ¹H NMR spectrum which was consistent with the literature data [12].

2.3.2. $cis-[Rh(bzpy)(bipy)Cl_2] \cdot 0.5H_2O(1)$

An intimate mixture of [Rh(Hbzpy)(bzpy)Cl₂] (0.324 g, 0.60 mmol) and bipy (0.562 g, 3.6 mmol) was placed in a ceramic boat (10 cm and 1.3 cm in length and width, respectively) and heated in an oven at 160 °C for 15 h. After cooling, the resulting reaction mixture was stirred for 2 h with 40 ml of methanol and then filtered. The precipitate was washed repeatedly with methanol and then dried under vacuum. 0.118 g (38%) of yellow crystalline product (1) was obtained. IR (cm⁻¹): v(C=O) 1674; v(Rh–Cl) 343, 324. δ_{H} (dmso d_6) 9.19 (1H, d, J = 5.6 Hz, $H_{b'6}$) (b' = bipy), 8.82 (1H, d, J = 8.4 Hz, $H_{b'3}$), 8.79–8.69 (3H, m, H_{b6} + $H_{b'6'} + H_{b3}$) (b = bzpy), 8.34 (1H, t, J = 7.6 Hz, $H_{b'4}$), 8.31 (1H, t, $H_{b'4'}$), 8.25 (1H, t, J = 7.6 Hz, H_{b5}), 8.15 $(1H, d, J = 7.6 \text{ Hz}, H_{b'3'}), 7.95 (1H, d, J = 8.0 \text{ Hz},$ $H_{b6'}$), 7.89–7.85 (2H, m, $H_{b'5} + H_{b'5'}$), 7.68 (1H, t, J = 6.8 Hz, H_{b4}), 7.66 (1H, d, J = 7.6, 1.2 Hz, H_{b3'}), 7.41 (1H, td, J = 7.6, 1.6 Hz, $H_{b5'}$), 7.25 (1H, t, $J = 7.2 \text{ Hz}, \text{ H}_{b4'}, \delta(\text{dmso-}d_6)$ 187.39 (CO), 163.75, 163.50, 157.37, 157.14, 154.54, 154.31, 153.29, 148.68, 140.77, 140.31, 139.84, 139.53, 129.65, 127.08, 126.93, 126.82, 126.27, 125.09, 123.86, 123.56, 123.47. Anal. Calc. for C₂₂H₁₇N₃O_{1.5}Cl₂Rh: C, 50.70; H, 3.29; N, 8.06; Cl, 13.60. Found: C, 50.62; H, 3.38; N, 8.17; Cl, 13.72%.

2.3.3. $cis-[Rh(bzpy)(phen)Cl_2] \cdot 0.5H_2O(2)$

An intimate mixture of K[Rh(phen)Cl₄] (0.464 g, 1.0 mmole) and Hbzpy (0.660 g, 3.6 mmole) was placed in a ceramic boat (10 and 1.3 cm in length and width, respectively) and heated in an oven at 210 °C for 15 h. After cooling, the resulting reaction mixture was stirred overnight with 50 ml of methanol/ H_2O (1:1, v/v) solution and then filtered. The yellow-brown filtrate was evaporated to dryness, followed by washing with dichloromethane. A deep yellow-green precipitate was obtained and washed repeatedly with acetone. After drying under vacuum, 0.169 g (31%) of yellow-green crystalline product (2) was obtained. IR (cm⁻¹): v(C=O) 1666; v(Rh–Cl) 342, 325. $\delta_{\rm H}$ (dmso- d_6) 9.97 (1H, d, J = 5.6 Hz, H_{b6}) (b = bzpy), 9.55 (1H, d, J = 4.8 Hz, H_{p2}) (p = phen), 9.00 (1H, d, J = 8.0 Hz, H_{p4}), 8.92 (1H, d, J = 8.0 Hz, H_{p5}), 8.44–8.29 (5H, m, $H_{b3} + H_{b4} + H_{p7} + H_{p8} + H_{p9}$), 8.16 (1H, dd, J = 8.0, 2.8 Hz, H_{p3}); 7.99–7.88 (2H, m, $H_{b5} + H_{p6}$), 7.67 (1H, d, J = 7.6 Hz, $H_{b6'}$), 6.94 (1H, t, $J = 7.2 \text{ Hz}, \text{ H}_{b5'}), 6.67 (1 \text{H}, \text{t}, J = 7.2 \text{ Hz}, \text{H}_{b4'}), 5.86$ (1H, d, J = 8.0 Hz, $H_{b3'}$), $\delta_{C}(\text{dmso-}d_6)$ 189.55 (CO), 156.44, 155.29, 154.99, 152.27, 151.13, 146.55, 140.30, 138.86, 138.76, 138.34, 137.91, 133.66, 130.90, 130.77, 129.21, 128.29, 127.86, 127.69, 126.93, 126.24, 126.13, 125.98, 124.02. Anal. Calc. for C₂₄H₁₇N₃O₁ ₅Cl₂Rh: C, 52.87; H, 3.14; N, 7.71; Cl, 13.01. Found: C, 52.76; H, 3.21; N, 7.84; Cl, 13.15%.

3. Results and discussion

3.1. Synthesis and assessment of structure

First [Rh(Hbzpy)(bzpy)Cl₂] was prepared according to published procedures [12] at this laboratory. Complex 1 was then prepared by heating the intimate mixture of [Rh(Hbzpy)(bzpy)Cl₂] and bipy in an oven at 160 °C for 15 h. Elimination of Hbzpy had been ascribed to the cleavage of the rather weak Rh-O bond, which led to a loss of stabilization due to the chelate effect [12]. Replacement of Hbzpy by phen under the same conditions, however, generated a mixture of at least two isomers, which we were unable to separate. The synthesis of complex 2 was accomplished by heating an intimate mixture of K[Rh(phen)Cl₄] and Hbzpy in an oven at 210 °C for 15 h. Attempts to get complex 1 by the latter procedure failed since a mixture of isomers was obtained again. The synthetic studies of the two different routes in connection with the stereochemistry of complexes 1 and 2 remain unknown to the authors to date.

The base peaks in the mass spectra of complexes 1 and 2 are m/z 512 and 536, corresponding to the molecular mass of *cis*-[Rh(bzpy)(bipy)Cl₂] and *cis*-[Rh(bzpy)(phen)Cl₂], respectively. The infrared spectra of the two complexes exhibit the v(C=O) stretching bands in the vicinity of 1666 cm⁻¹. On the basis that the v(C=O) stretching bands of complexes 1 and 2, as well as the free Hbzpy ligand (ca. 1668 cm⁻¹), are almost the same, it is evident that the chelated bzpy ligand forms a six-member *N*,*C* metallacycle, not a five-member *N*,*O* metallacycle. The stereochemistry of the RhCl₂ moiety in these complexes has been determined by IR data. Both complexes show two v(Rh-Cl)bands near 342 and 324 cm⁻¹, indicating that the two chlorides are *cis* to each other [15].

The proton peaks in the ^IH NMR spectrum of each complex show sixteen chemically different protons. From the ¹³C spectra, complexes **1** and **2** exhibit 22 and 24 carbons, respectively. In addition, the ¹³C DEPT of complexes

1 and 2 exhibit six and eight non-protonated carbon peaks, respectively. As a further confirmation of the double bond character of the C=O bond in the N,O ligands, δ_{CO} falls close to 200 ppm [8]. On the basis that δ_{CO} of complexes 1 and 2 relative to free Hbzpy ($\delta_{CO} = 193.5$ ppm) are almost the same, the NMR data are inconsistent with *N*,*O*-coordination of 2-benzoylpyridine. Due to the IR and NMR data, complexes 1 and 2 are consistent with the *N*,*C*-coordination of 2-benzoylpyridine. There are two possible isomers for [Rh(bzpy)(NN)Cl₂] (NN = bipy or phen) deduced from the hetero-bischelated complexes as displayed below.



In the cis- α conformation, $H_{b3'}$ of the phenyl moiety of the bzpy ligand is located above (or below) the pyridine of the bipy/phen ligand (see Fig. 1). For complex 1, the resonance position of $H_{h3'}$, $\delta = 7.66$, is somewhat deshielded compared to that of $H_{b4'}$, $\delta = 7.25$, as presented in Section 2. This is therefore inconsistent with the NMR chemical shift data since this hydrogen would indeed be more shielded due to the π -electron ring current of pyridine. In the $cis-\beta$ isomer, however, H_{b6} of the pyridyl moiety of the bzpy ligand is located below the plane of the pyridine of the bipy/phen ligand, which exhibit significant upfield shifts as expected due to the shielding effect of the ring current. For complex 1, the resonance position of H_{b6} , $\delta = 8.79$, is more shielded compared to $H_{b'6}$ in the plane of the pyridine of the bipy ligand, $\delta = 9.19$, as expected by the shielding effect of the ring current. Therefore, the NMR chemical shift data of complex 1 are consistent with



Fig. 1. The proposed structures of cis-[Rh(bzpy)LCl₂]: (A) $cis \beta$ -[Rh(bzpy)(bipy)Cl₂] (1); (B) $cis \alpha$ -[Rh(bzpy)(phen)Cl₂] (2).

the *cis*- β structure as illustrated in Fig. 1. The conformer of complex 1 is further evidenced by the NOESY experiment, available in the supplementary material. $H_{b'6}$ (b' = bipy) is spatially correlated with H_{b6} of pyridine in bzpy as demonstrated in the same figure.

For complex **2**, the chemical shift of $H_{b3'}$, $\delta = 5.86$, more upfield than that of $H_{b6'}$, $\delta = 7.67$, is due to the anisotropic effect resulting from the inductive ring current of the pyridyl ring. $H_{b3'}$ is located just above (or below) the pyridine of the phen ligand, and hence corresponds to the relative location of protons in space for the *cis*- α structure as illustrated in Fig. 1. The appearance of the chemical shift of $H_{b'6}$ for complex **1**, $\delta = 9.19$, more upfield than that of H_{p2} for complex **2**, $\delta = 9.55$, is due to the π -donor ability of the metallated phenyl ring, which is located *trans* to $H_{b'6}$, as demonstrated in the same figure.

Further assignments of the ¹H NMR spectra for complexes **1** and **2** have been done through ¹H COSY NMR experiments, available in the supplementary material.

3.2. Absorption spectra

The free Hbzpy ligand exhibits one intense $(\varepsilon \sim 10^4 \text{ cm}^{-1} \text{ M}^{-1})$ absorption at about $3.78 \times 10^4 \text{ cm}^{-1}$, arising from the spin-allowed $\pi - \pi^*$ transition. The weaker $(\varepsilon \sim 10^2 \text{ cm}^{-1} \text{ M}^{-1})$ absorption band observed at about 2.84×10^4 cm⁻¹ is assigned as the carbonyl n- π^* transition on the basis that the energy of this absorption peak exhibits a hypsochromic shift when the solvent polarity is increased [7]. The room temperature absorption spectra for complexes 1 and 2 are presented in Fig. 2A. Both shows an intense $(\varepsilon \sim 10^4 \text{ cm}^{-1} \text{ M}^{-1})$ absorption in the 3.1– 3.9×10^4 cm⁻¹ region which most likely arise from a spinallowed $\pi - \pi^*$ absorption of the coordinated ligands [7,16]. Each complex also exhibits an intermediate $(\varepsilon \sim 10^3 \text{ cm}^{-1} \text{ M}^{-1})$ absorption in the 3.0–2.7 × 10⁴ cm⁻¹ region. According to the absorption spectra of the related free ligands [7,16] and *cis*-[Rh(dpk)₂Cl₂]⁺ (dpk = di-2-pyridyl ketone) [17], this absorption can be assigned as a carbonyl n- π^* band [18], which was not observed for *cis*- $[Rh(bipy)_2Cl_2]^+$ and *cis*- $[Rh(phen)_2Cl_2]^+$ [19]. It is noted that the absorption band profile extended to lower energy (below $2.6 \times 10^4 \text{ cm}^{-1}$), which was not observed for the related ligands either. This might be the tail of the carbonyl $n-\pi^*$ band in combination with a rather weak dd^{*} absorption.

The excitation polarization spectrum of complex 1 is shown in Fig. 2B. The excitation polarization spectrum of complex 2 is very similar to that of complex 1. The symmetry of each complex is lower than C_{2V} and hence only a singly symmetric species is considered in the analysis of the electronic spectrum. In other words, the polarization limits pertaining to planar oscillators will not be pertinent here. The calculated limits are 0.5 and -0.33 [20], resulting from the combination of a linear absorption and a linear emission oscillator. The polarizations in the $\pi-\pi^*$ region of the two complexes are quite similar, showing little structure having minima (-10% for complex 1; -14% for complex 2) in the polarization spectra. These data also reveal that the absorption and emission are both linear oscillators [20]. Deviation of the polarization from -0.33 may be explained by the existence of other states having similar energies in the region [21].

The slightly structured shape and increased value for the excitation polarization spectrum in the $3.3-2.5 \times 10^4$ cm⁻¹ region suggest that there may be more than one absorption mode involved in this region, consistent with the carbonyl n- π^* transitions assignment. The polarization spectra increase sharply to about 0.20 in the lowest energy wavelength region (below 25×10^4 cm⁻¹) for both complexes. The magnitude that approaches the limit value 0.5 is expected for a linear absorber-linear emitter case [20]. Therefore, involvement other transitions is implied and one could reasonably conclude that the dd* absorption is buried in this low-energy region. Therefore, the carbonyl n- π^* transition must be involved and in which all spin-forbidden dd* transitions were likely buried, similar to that of *cis*-[Rh(dpk)₂Cl₂]⁺ [17].

3.3. Luminescence properties

Hbzpy shows a structural emission with a single vibrational progression of 1650 cm⁻¹, assigned as an $n-\pi^*$ transition [22]. The emission spectra recorded in ethanol/



Fig. 2. Absorption and excitation polarization spectra: (A) absorption spectra (room temperature): *cis* β -[Rh(bzpy)(bipy)Cl₂] (1) (——); *cis* α -[Rh(bzpy)(phen)Cl₂] (2) (—). (B) excitation polarization spectrum of *cis* β -[Rh(bzpy)(bipy)Cl₂] (1) (77 K, 689 nm emission).

methanol (9:1, v/v) at 77 K of complexes 1 and 2 are presented in Fig. 3. No emission behavior is observed at room temperature. Contained in Table 1 are the luminescent data of these complexes. The red emissions $(1.2-1.7 \times 10^4 \text{ cm}^{-1})$ recorded for complexes 1 and 2 are broad (with around 2.2×10^3 cm⁻¹ in half-width) and both are symmetric and structureless, as seen in Fig. 3. The lifetimes measured at the emission maximum are respectively 58 and 60 µs for complexes 1 and 2 (see Table 1). The energy of the emission peak is unaffected by changing the solvent from ethanol/ methanol to DMSO. In comparison with the band shape, lifetime and peak position studies performed on the cyclometallated Rh(III) complexes [3], the emission types of complexes 1 and 2 have excluded the possibilities of ³MLCT, ³SBLCT or ³ $\pi\pi^*$ emissions and hence are classified as a dd* phosphorescence [17,23].

The emission polarization spectra of both complexes, excited at 313 and 365 nm, are flat with a vanished slope. This observation indicates that the combination of absorber and emitter(s) gives the same polarization across the emission band. Therefore, it is reasonable to conclude that there is no other emission buried in the observed emission band. In other words, both complexes show a band of single emissions rather than multiple ones.



Fig. 3. Emission spectra of *cis* β -[Rh(bzpy)(bipy)Cl₂] (1) (----) and *cis* α -[Rh(bzpy)(phen)Cl₂] (2) (--) (77 K, 313 nm excitation).

Table 1
Phosphorescence data and lifetime (τ) for Rh(III) complexes at 77 K

Complex	Phosphorescence ^a		
	$v_{\rm max}~(\times 10^4~{\rm cm}^{-1})$	τ_{p} (µs)	
1	1.45	58	
2	1.49	60	
cis-[Rh(bipy) ₂ Cl ₂] ⁺	1.42 ^b	47 ^b	
cis-[Rh(phen) ₂ Cl ₂] ⁺	1.41 ^b	41 ^b	

^a In EtOH/MeOH (9:1).

^b Ref. [16].

No emission could be detected from [Rh(Hbzpy)-(bzpy)Cl₂] [12], but emission could be obtained from *cis*-[Rh(bzpy)(NN)Cl₂] (NN = bipy/phen). On one hand, it might be possible that the emission is occurring but is beyond the detection limits of our equipment [24]. On the other hand, it is possible that the phenyl ring of chelated Hbzpy can undergo rotation and then facilitate the non-radiative energy loss in this complex [25]. The bipyridyl-like ligands are more rigid than the *N*,*O*-coordinated Hbzpy ligand. When the N,O ligand (Hbzpy) is substituted by bipy/phen (a more rigid ligand), the emission could be observed. The latter reason at least is therefore supported by our results.

The metallated phenyl ring of bzpy is a weaker π -acceptor and a stronger-donor compared to bipy or phen. A strong-donor can move the metal d^{*}(e_g) orbitals to a higher energy, but a strong π -acceptor can lead to the lowering of the metal d(t_{2g}) orbitals. Therefore, the dd^{*} emission of complexes **1** and **2** were observed at a higher energy than that of *cis*-[Rh(bipy)₂Cl₂]⁺ and *cis*-[Rh(phen)₂Cl₂]⁺ (see Table 1) [16]. It is examined that the degree of raising of the metal d^{*}(e_g) orbitals for complexes **1** and **2** is more than the degree of lowering of the metal d(t_{2g}) orbitals for *cis*-[Rh(bipy)₂Cl₂]⁺ and *cis*-[Rh(phen)₂Cl₂]⁺, which results in the higher energy gap of the ³d–d^{*} excited state for complexes **1** and **2**. In other word, bzpy exhibits a higher ligand field strength compared with that of bipy or phen.

3.4. Electrochemical properties

Electrochemical studies were conducted in 0.10 M TEAP/DMSO solutions containing the corresponding Rh(III) complexes. Cyclic voltammetric data such as the peak potentials are collected in Table 2. No oxidation wave was observed when the potential was scanned from 0.0 to +2.0 V.

3.4.1. Electrochemistry of complexes 1 and 2

The cyclic voltammograms of complexes 1 and 2 have similar patterns, showing two reduction waves, c_{I} and c_{II} (see Table 2), and no corresponding oxidation wave appeared upon scan reversal with respect to c_{I} . The number

Table 2			
Cyclic voltammetric reduction	potentials for	Rh(III)	complexes ^a

Complex	v (V/s)	$(E_{\rm pc})_{\rm I}$	$(E_{\rm pc})_{\rm II}$
1	0.1	-1.19	-1.64
	2.0	-1.24	-1.67
2	0.1	-1.16	-1.65
	2.0	-1.22	-1.69
cis-[Rh(bipy)2Cl2] ⁺	0.1	-0.84^{b}	-1.46^{b}
cis-[Rh(phen) ₂ Cl ₂] ⁺	0.1	-0.85°	-1.46 ^c

^a Results for 1.2 mM samples in 0.10 M TEAP/DMSO solutions at a Pt electrode. E_{pc} in V vs. SCE.

^b Ref. [31].

^c Ref. [32].

of electrons transferred at the wave c_1 , estimated from controlled-potential electrolysis experiments at -1.20 and $-1.15 \text{ V} (E_{pc})_{I}$, were found to be 1.80 and 1.85 for complexes 1 and 2, respectively, indicating that wave c_1 for both complexes involved essentially a two-electron charge transfer process. An oxidation wave due to oxidation of the chloride ion was also observed at 1.07 V in the voltammograms obtained for the solutions after the electrolysis. For each complex, the ratio of the peak current of the chloride ion to that of wave c_{I} is close to one, indicating that two chlorides had been eliminated from the complex after electrolysis at wave c_1 . It has also been reported that electrochemical reduction of halide-coordinated complexes will generate products via dissociation of halide(s) [26-30]. As stated earlier, the emission of the two complexes is confirmed to be a dd* transition. The two-electron transfer reduction (wave c_{I}) results in higher electron density on the metal and, hence, destabilizes these complexes. This can rationalize the transfer of two electrons, in which the chemical reaction involves the loss of two chloride ions. and lead to the irreversible process at wave c_{I} .

The more negative values of $(E_{pc})_{I}$ obtained for complexes 1 and 2 compared to those reported for *cis*-[Rh-(bipy)₂Cl₂]⁺ and *cis*-[Rh(phen)₂Cl₂]⁺, as shown in Table 2, may be ascribed to the higher electron densities on the metal. This is well understood based on the nature of the negatively charged bzpy ligand, which is a better σ -donor but a poorer π -acceptor (vide supra). On the whole, reductions of the neutral species are more demanding than those for the cationic complexes.

Normal pulse voltammograms (NPV) were also recorded for the two complexes. Similar to the cyclic voltammograms, the NPV also exhibited reduction waves c_{I} and $c_{\rm II}$ for each complex. It was found that the ratio of the limiting current of waves c_{I} and c_{II} is 2:1. Furthermore, the ratio of the peak current of wave $c_{\rm I}$ to that of wave $c_{\rm II}$ is also close to two at relatively high scan rates. Because wave $c_{\rm I}$ is a two-electron charge transfer process, this result suggests that wave c_{II} is possibly a one-electron charge transfer process. When phenol was added into the solutions as the proton donor, no significant changes were observed for wave $c_{\rm I}$ in the cyclic voltammograms of the complexes, suggesting that wave $c_{\rm I}$ is due to the reduction at the metal-localized orbitals. On the other hand, the addition of phenol resulted in an evident potential shift and peak current increased for wave $c_{\rm II}$. Based on the influence of phenol, the reduction at wave c_{II} can be assigned to be localized at the carbonyl π^* orbital of bzpy. The same result was observed for the pik-coordinated or dpk-coordinated complexes of rhodium(III) [13,17].

4. Conclusions

In this study, two heteroleptic cyclometallated Rh(III) complexes, cis-[Rh(bzpy)(bipy)Cl₂] (1) and cis-[Rh(bzpy)-(phen)Cl₂] (2), have been synthesized and characterized. The anionic bzpy ligand is N,C coordinated to Rh(III)

based on IR and NMR data. Through analysis of NMR chemical shifts, structures of complexes 1 and 2 are consistent with $cis-\beta$ and $cis-\alpha$ conformers, respectively. Each complex shows high intensity bands in the UV region, assigned as spin-allowed $\pi - \pi^*$ transitions. The mediumintensity absorption band profile in the lower energy region can be explained by convolution of carbonyl $n-\pi^*$ and $d-d^*$ transitions. At 77 K, each complex shows a broad, symmetric and structureless red emission with microsecond lifetime, assigned as dd* phosphorescence. The electrochemical data also provide evidence in support of the assigned dd* emissions of the two complexes. The first two-electron reduction process occurs at the metal and is coupled with the elimination of two chlorides. Through examination of the influence of phenol on the reduction potentials, the redox orbital involved in the second reduction is assigned as the π^* orbital localized at the carbonyl fragment of bzpy.

5. Supplementary material

2D NMR for complexes 1 and 2 are available from the author on request. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or http:www.ccdc.cam.ac.uk.

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