

Mixed Ligand Ruthenium(II) Complexes: Synthesis, Structure, Electrochemical And Anion Sensing Studies

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Abstract: Ruthenium(II) complexes of compositions $[\text{Ru}(\text{bpy})_2(\text{L1})](\text{PF}_6)_2$ (1) and $[\text{Ru}(\text{bpy})_2(\text{L2})](\text{PF}_6)_2$ (2), where $\text{bpy}=2, 2'$ -bipyridine, $\text{L1}=4,5$ -bis[(E)-2-(4-methoxyphenyl)ethenyl]-1H,1'H-2,2'-biimidazole and $\text{L2}=4,5$ -bis[(E)-2-(4-bromophenyl)ethenyl]-1H,1'H-2,2'-biimidazole, have been synthesized and characterized by analytical and spectral methods. Both the complexes displayed a broad metal-to-ligand charge transfer band at ~ 475 nm in acetonitrile. Cyclic voltammetry studies showed that the Ru(II) complexes undergo fairly reversible one electron reductions involving the $\text{Ru}^{(II)}/\text{Ru}^{(III)}$ couple at the potentials between +1.042 - +1.089 V in acetonitrile. The anion-sensing activity of the present complexes was exhibited using absorption titration. The highly acidic nature of the N-H functions in biimidazole part can be easily deprotonated upon addition of tetrabutyl ammonium salts of various anions such as F^- , OAc^- , H_2PO_4^- , I^- , Br^- and HSO_4^- . It has been examined that all of the complexes have the ability to act as sensors for F^- and OAc^- ions and to some extent H_2PO_4^- .

Keywords: Anion-sensing, biimidazole, bipyridine, charge transfer, ruthenium(II), sensors, tetrabutyl.

1. INTRODUCTION

Since anions play a fundamental role in a wide range of biological, industrial, and environmental and chemical processes, numerous efforts have been devoted to the development of abiotic receptors for anionic species. Critical roles in the development of fluorescent sensors[1] and other electrochemical signaling devices[2] is played by suitably designed anion receptors[3]. In view of the fact that anions are ubiquitous in Nature, their detection using small and readily accessible assemblies appeals to the chemical community especially when the sensing event is visually appreciable without resorting to spectroscopic techniques and yields instant qualitative information, which is quantifiable using absorption spectroscopy[4]. Such sensing processes involve intrinsically weak interactions based upon the receptor design and quite often are challenged by the intervention of solvent molecules, which may interact more effectively with both the receptor and the guest[4]. Over the years, many receptors covalently attached or intermolecularly linked to chromophoric units and guests have been prepared and studied for various applications ranging from physiology and medical diagnostics[5]. Anions play significant roles in a range of biological processes and are implicated in a number of disease states, ranging from fluorosis to cystic fibrosis and are thus considered important targets in terms of receptor design[6]. A variety of molecular structures can be obtained by simple modification of chemical structures of organic materials. Amides[6], (thio)ureas[7], ammonium[8] and imidazole[9] are particularly effective in the reaction with anions through the formation of hydrogen bonds between the active N-H group and the anions, and there are many receptors of them with molecular clefts or cavities, which can recognize anions with different geometries[10]. Because of the presence of electron rich nitrogen atom, imidazole derivatives require protonation

and subsequently anion binding is accomplished by charged $\text{N}^+\text{---H}\cdots\text{X}$ -type hydrogen bonds with dominant electrostatic interactions. Attainment of the appropriate geometry can sometimes be problematic for proper host-guest interaction, with the purely organic hosts[11]. In recent times, polypyridine containing ruthenium(II) complexes whose luminescent properties can be tuned, are of particular interest as pH-induced sensitizers and luminescent sensors. A number of ruthenium(II) polypyridine based receptors have been designed as ion sensors[12-13], although such sensors for anions are relatively few. A quite a lot of properties have been attributed to the ruthenium complexes like antitumor activity [14] and antioxidant activity [15]. In this work, we have synthesized and studied the physicochemical properties of mixed-ligand ruthenium(II) complexes of the type $[\text{Ru}(\text{II})(\text{bpy})_2(\text{H}_2\text{Y-biim})]$ $\{\text{Y} = -\text{OMe}$ and $-\text{Br}$ groups $\}$ and their interactions with several anions, especially fluoride and acetate.

2. MATERIALS AND METHODS

Ruthenium chloride trihydrate, imidazole-2-carboxaldehyde, 4-methoxybenzaldehyde, 4-bromobenzaldehyde, biacetyl and piperidine were purchased from Sigma-Aldrich. Acetic acid, ammonium acetate, methanol, acetonitrile and ethanol were purchased from SD Fine chemicals. All the tetrabutylammonium salt of anions were received from Sigma-Aldrich and used as received. 1,4-bis(4-methoxyphenyl)butane-2,3-dione, 1,4-bis(4-bromophenyl)butane-2,3-dione were synthesized by adopting literature procedure[16]. Absorption spectra were recorded on Shimadzu UV-160A UV-Visible spectrophotometer. Cyclic (CV) and differential pulse voltammeteries (DPV) were performed by using CH instrument (USA) model CH-620 B electrochemical analyzer. A conventional three electrode system consisting of platinum disc as a working electrode, platinum wire as an auxiliary electrode and saturated calomel (SCE) as a reference electrode was used for the electrochemical measurements. 0.1 M tetrabutyl ammonium perchlorate (TBAP) was used as the supporting electrolyte for all the experiments. Positive ion electrospray ionization mass spectra of the complexes were obtained by using Thermo Finnigan LCQ 6000 advantage max ion trap mass spectrometer. Absorption titrations were carried out for each anion by adding

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various concentrations (up to 2 equivalents for tetrabutylammonium salts of anions) of additives to 20 μM solution of receptors in acetonitrile

2.1 Synthesis of Ligands

2.1.1 Synthesis of 4, 5-bis[(E)-2-(4-methoxyphenylethenyl)]-1H,1'H-2,2'-biimidazole (L1)

1, 4-bis(4-methoxyphenyl)butane-2,3-dione (0.2 g, 0.62 mmol), imidazole-2-carboxaldehyde (0.062 g, 0.65 mmol) and ammonium acetate (2 g, 25 mmol) were dissolved in 15 mL acetic acid and heated to reflux for 3 h. After cooling, cold water (10 mL) was added to the solution, during which orange precipitate was appeared. It was filtered and purified by column chromatography on silica using ethyl acetate: hexane (1:4) as an eluent. (Yield 0.12 g, 49 %). ESI MS: m/z (relative intensity): 399.3 (100, $\text{M}^+ + 1$). Anal. Calc. for $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_2$: C, 72.34; H, 14.71; N, 14.06. Found: C, 72.32; H, 14.63; N, 14.04.

2.1.2 Synthesis of 4, 5-bis[(E)-2-(4-bromophenylethenyl)]-1H,1'H-2,2'-biimidazole (L2)

An analogous synthetic procedure using 1,4-bis(4-bromophenyl)butane-2,3-dione instead of 1,4-bis(4-methoxyphenyl)butane-2,3-dione was used to prepare 4,5-bis[(E)-2-(4-bromophenylethenyl)]-1H,1'H-2,2'-biimidazole (Yield 0.17 g, 56 %). ESI MS: m/z (relative intensity): 495.2 (100, $\text{M}^+ - 1$). Anal. Calc. for $\text{C}_{22}\text{H}_{16}\text{Br}_2\text{N}_4$: C, 53.25; H, 3.25; N, 11.29. Found: C, 53.22; H, 3.21; N, 11.26.

2.2 Synthesis of Complexes

2.2.1 Synthesis of $[\text{Ru}(\text{bpy})_2(\text{L1})](\text{PF}_6)_2$ (1).

A mixture of $[\text{cis-Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (0.651 g, 1.25 mmol) and L1 (0.498 g, 1.25 mmol) was suspended in an ethanol/water solvent mixture (3/1, v/v). The mixture was refluxed under an inert atmosphere for 4 h while vigorous stirring was maintained. The reaction mixture was cooled to room temperature; the solvent was reduced under vacuum to one-third of its initial volume. A saturated aqueous solution of NH_4PF_6 was added to precipitate $[\text{Ru}(\text{bpy})_2(\text{L1})]^{2+}$ as its hexafluorophosphate salt. The product was filtered and washed with water (3×10 mL) and then purified by column chromatography on neutral alumina using acetonitrile/toluene (1.5/1, v/v) as an eluent. Yield: 1.27 g, 92 %. Anal. Calc. for $\text{C}_{44}\text{H}_{38}\text{F}_{12}\text{N}_8\text{P}_2\text{O}_2\text{Ru}$: C, 47.96; H, 4.03; N, 10.17. Found: C, 47.93; H, 4.01; N, 10.12. ESI-MS: m/z 811.33 ($\text{M} - 2\text{PF}_6$)⁺.

2.2.2 Synthesis of $[\text{Ru}(\text{bpy})_2(\text{L2})](\text{PF}_6)_2$ (2).

The synthesis and purification of compound 2 were similar to those of 1 using $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ (0.52 g, 1.0 mmol) and L2 (0.496 g, 1.0 mmol). Yield: 1.04 g, 87 %. Anal. Calc. for $\text{C}_{44}\text{H}_{38}\text{F}_{12}\text{N}_8\text{P}_2\text{Br}_2\text{Ru}$: C, 42.05; H, 2.69; N, 9.34. Found: C, 42.01; H, 2.66; N, 9.29; ESI-MS: m/z 909.13 ($\text{M} - 2\text{PF}_6$)⁺.

3. RESULTS

3.1 Synthesis and Characterisation

1,4-bis(4-methoxyphenyl)butane-2,3-dione and 1,4-bis(4-bromophenyl)butane-2,3-dione were condensed individually with imidazol-2-aldehyde in the presence of ammonium acetate. Ligands (L1 and L2) were obtained in moderate yield after column chromatography on silica gel using 1:4 ethylacetate : hexane as an eluent. Synthesized receptors

which were subjected to ESI mass spectrometry showed base peaks of protonated adduct at 399.3 and 495.2 for L1 and L2 respectively. The mixed ligand complexes $[\text{Ru}(\text{bpy})_2(\text{L})](\text{PF}_6)_2$ (1 and 2) have been isolated from ethanolic solution containing $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ as the starting material by reacting with substituted biimidazole derivatives under nitrogen atmosphere followed by precipitating the complexes as hexafluorophosphate salts. The analytical data obtained for the new complexes agree well with the proposed molecular formula. The ESI mass spectra of 1 and 2 displayed the molecular ion peaks at m/z 811.33 and 909.13 respectively. These peaks are reliable with the proposed molecular formula of the corresponding ruthenium(II) complexes. The structure of the complexes is revealed in Fig. 1.

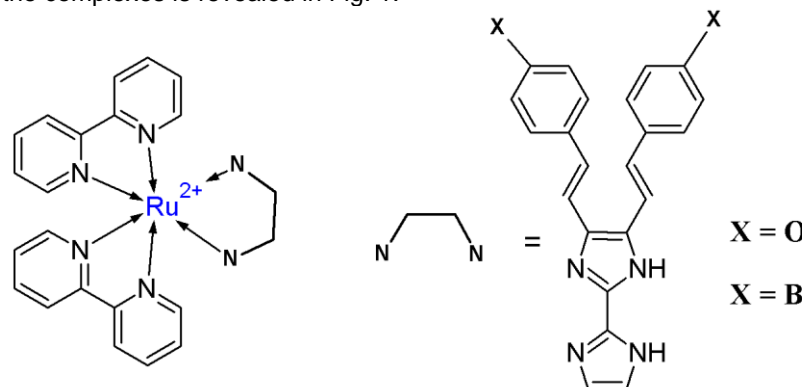


Fig. 1. Structure of Ruthenium(II) complexes

The absorption spectra of all the complexes are similar, showing two strong bands in the UV region and a broad band in the visible region. The complexes display a strong absorption band at 290 nm, which is attributed to the $\pi - \pi^*$ transition of bipyridine ligand. Bands appeared at 346 nm of 1 and 343 nm of 2 were attributed to the $\pi - \pi^*$ transition of ligands L1 and L2 respectively. Broad ¹MLCT absorption bands have been observed at 476 and 476.2 nm for complexes 1 and 2 respectively. The redox behavior of ruthenium complexes is studied with the help of cyclic voltammetry and differential pulse voltammetry. The cyclic and differential pulse voltammograms of the Ru(II) complexes show oxidation peaks at higher potentials thereby suggesting stable Ru(II) complexes. Electrochemical studies carried out for the present complexes are summarized in Table 1. The cyclic voltammograms of the complexes reveal a fairly reversible one electron redox process involving the $\text{Ru}^{(III)}/\text{Ru}^{(II)}$ couple, as judged from the peak potential separation of ~ 130 mV. Complex 1 gives an $E_{1/2}$ value of 1.097 V at 100 mVs^{-1} . Whereas complex 2 shows voltammetric response at 1.074 V. The $E_{1/2}$ values follow the order 2 > 1. Complex 2 showing a greater stabilization for the $\text{Ru}^{(III)}$ species could be related to the presence of methoxy group enhancing the π -acidity of the ligand.

3.2 Anion sensing studies

Absorption signaling

UV-Visible spectroscopy was employed to observe the spectral changes induced by the anion-metalloreceptor interaction in acetonitrile solutions. Upon the addition of 5 equivalents of Br^- , I^- and HSO_4^- ions to (2×10^{-5} μM) solutions of 1 and 2 individually, the MLCT peak at ~ 475 nm remains practically unchanged. Whereas, on addition of F^- , OAc^- and

H₂PO₄⁻ ions to 1 and 2, the above said MLCT band was shifted bathochromically to 473-499 nm. It clearly indicates the strong interaction of the anions with the receptors. These observations are in consistent with the visual changes as discussed above. It is believed that the red shift of the MLCT bands can be attributed to the second-sphere donor-acceptor interactions between metal coordinated biimidazole ligands (L1 and L2) and the anions. Such interactions may include either hydrogen bonding or proton transfer. These interactions increase the electron density at the metal centre thereby lowering the MLCT band energies.

Table 1 Spectroscopy and electro chemical data's for the complexes 1 and 2.

Complex	UV-Visible λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)	ESI-MS m/z	E _{1/2} (Ru ^(II) /Ru ^(III)) vs SCE	ΔE (mV)
[Ru(bpy) ₂ (L1)] (PF ₆) ₂ (1)	474.6(11500) 342.0(37450) 290.4(90350) 243.2(39400)	811.33 (M-2PF ₆) ⁺	+1.097 V	138
[Ru(bpy) ₂ (L2)] (PF ₆) ₂ (2)	478.0(9150) 344.3(29600) 290.2(72300) 244.4(43450)	909.13 (M-2PF ₆) ⁺	+1.074 V	133

4. DISCUSSION

Spectrophotometric titrations were carried out to observe the sensing property of 1 and 2 toward the F⁻, OAc⁻ and H₂PO₄⁻ ions. Absorption spectral changes for 1 and 2 over the 0-2 equiv range of anions are shown in Figures 3 and 4. With the incremental addition of TBAF to 1, gradual red shifts were observed in the successive absorption curves of MLCT band (Fig. 2). During this process, the absorption curves pass through the isosbestic points 361 and 488 nm, while in the case of 2, such changes occur through 357 and 484 nm. On the other hand, addition of other anions to the acetonitrile solutions of 1 and 2 did not induce any typical spectral changes. This clearly indicates that these anions are incapable to deprotonate the imidazole NH protons of the present complexes. Many scientists reported previously that deprotonation was observed in suitably substituted H-bond donor acceptor functionality in the presence of anions thereby leading to the classical Bronsted acid-base theory [18]. Titration experiment was also performed to examine the interaction of the present complexes (1 and 2) with acetate. Two isosbestic points were observed at 352 and 486 nm, on adding two equivalents of acetate to 1, and the MLCT band at 473 nm was red shifted to 499 nm. On adding acetate to 2, the MLCT band at 476 nm was shifted bathochromically to 489 nm along with two isosbestic points at 355 and 483 nm followed by change of color from yellow to orange. Color changes are most probably due to the deprotonation of NH protons by the anions.

5. CONCLUSION

Two new ruthenium(II) mixed ligand complexes were synthesized and characterized using various physico-chemical techniques. Both the complexes are able to sense fluoride and acetate ions greatly rather than other anions.

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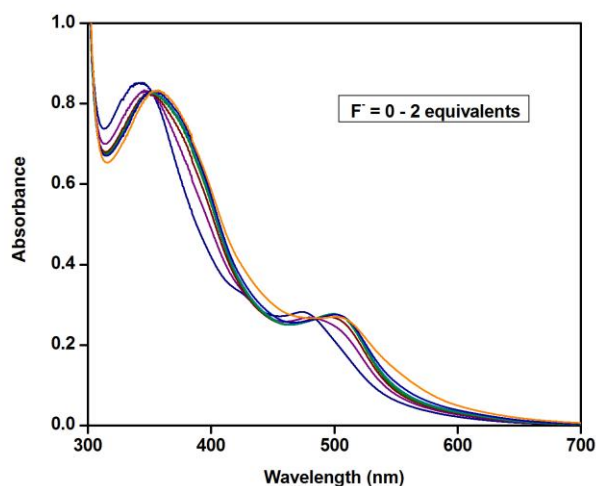


Fig. 2. UV-Vis titration of 1 ($20 \mu\text{M}$) in acetonitrile upon addition of fluoride ion (F^-)

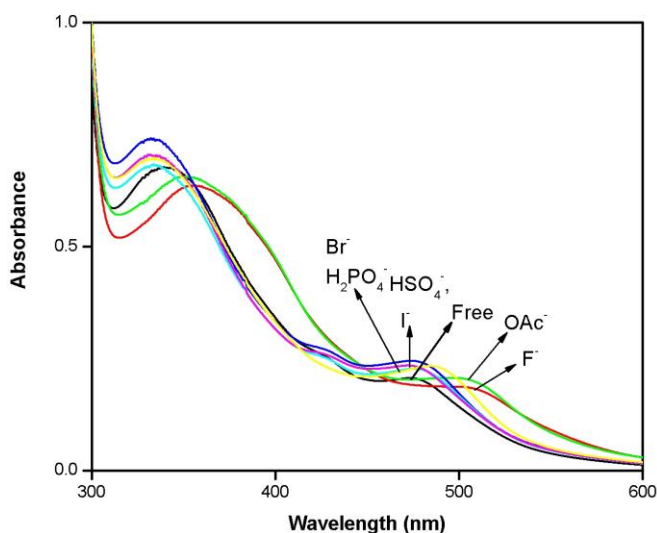


Fig. 3. Absorption spectral changes of 1 ($2 \times 10^{-5} \text{ mol dm}^{-3}$) in acetonitrile upon addition of 5 equivalent of different anions

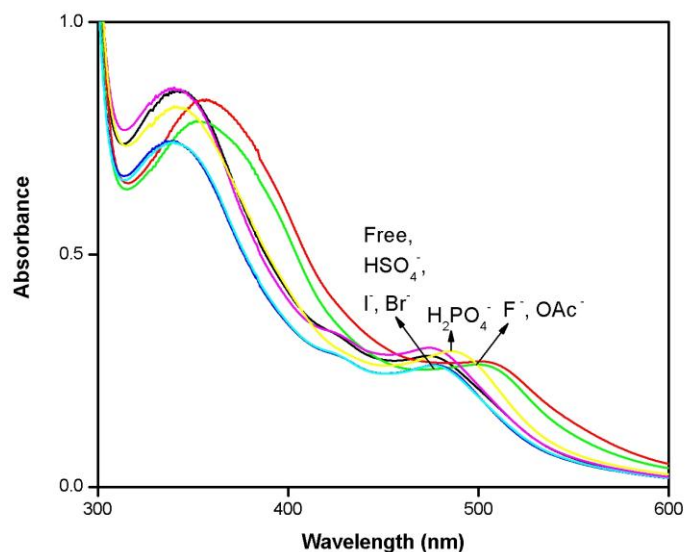


Fig. 4. Absorption spectral changes of 2 ($2 \times 10^{-5} \text{ mol dm}^{-3}$) in acetonitrile upon addition of 5 equivalent of different anions