



Synthesis of a ruthenium(II) bipyridyl complex coordinated by a functionalized Schiff base ligand: Characterization, spectroscopic and isothermal titration calorimetry measurements of M^{2+} binding and sensing ($M^{2+} = Ca^{2+}, Mg^{2+}$)

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ABSTRACT

Bis-[methylsalicylidine-4'benzoic acid]-ethylene (LH_2) complexed with $cis-Ru(bpy)_2Cl_2 \cdot 2H_2O$ provides a complex of composition $[Ru(bpy)_2L] \cdot 2NH_4PF_6$ (**1**), which has been characterized spectroscopically. Its binding behaviour towards Mg^{2+} and Ca^{2+} ions is monitored using 1H NMR titration, isothermal titration calorimetry (ITC) and luminescence microscopy. The luminescent ruthenium complex binds Ca^{2+} in a more selective manner as compared to Mg^{2+} .

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1. Introduction

Supramolecular construction through non-covalent interactions like van der Waals force, hydrogen bonding, $CH-\pi$ interactions, π -stacking and hydrophobic effects for the study of molecular recognition have become the focal point of studies in the contemporary chemistry, biology and physiology [1–3]. The design and synthesis of artificial receptors that can achieve recognition at molecular level are demanding [4,5]. Polydentate ligands, such as Schiff bases, assisted by metal ions, provide highly organized supramolecular metal complexes. Such complexes possess binding sites and cavities for various cations, anions and organic molecules [6–10]. In this context, $Ru(bpy)_2^{2+}$ containing systems have been interesting owing to their involvement in efficient intramolecular electron or energy transfer processes [11]. The choice of such a building block is justified by its favorable excited states, redox properties as well as chemical properties. The advantage of molecular fluorescence for sensing and switching on/off is well documented in the literature [12–15]. In this backdrop, we set out to append a $Ru(bpy)_2^{2+}$ moiety to a Schiff base ligand (LH_2), as the luminescence property of such a system could then be exploited to monitor the binding of cations such as Mg^{2+} and Ca^{2+} , which are of biological

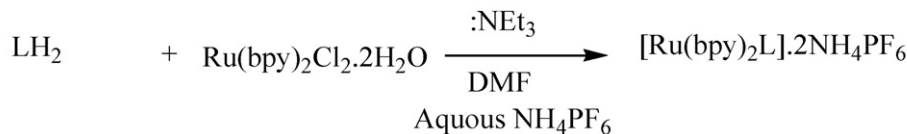
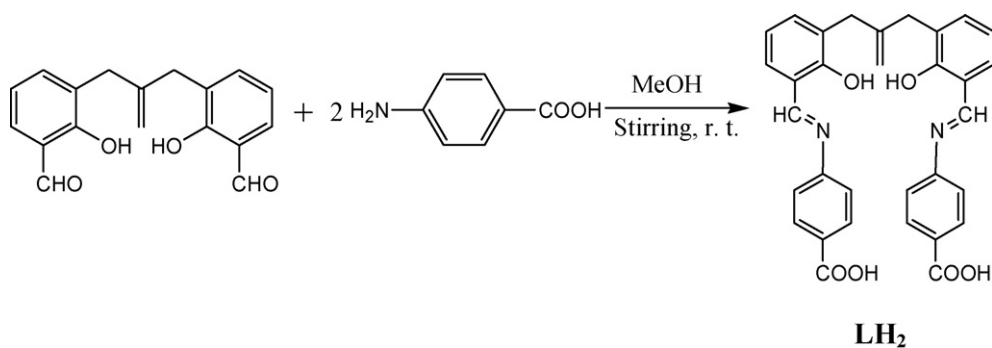
importance. Additionally, the selection of aldehydes has been made in view of its role in macrocyclisation [16] where as p-aminobenzoic acid is selected owing to its biological relevance besides its bifunctional nature [17].

2. Experimental

2.1. Materials and methods

Ruthenium(III)chloride, 2,2'-bipyridine and p-aminobenzoic acid were purchased from Sigma–Aldrich, while solvents were purchased from E. Merck and used without any further purification. The aldehyde was obtained as a gift sample from Dr. H. Hojou, IIS, Tokyo University, Japan. Elemental analysis and FAB mass measurements were carried on Carbo-Erba elemental analyzer 1108, JEOL SX-102 mass spectrometer respectively. IR spectra were recorded as KBr pellets on a JASCO FT-IR 5300 spectrometer whereas 1H NMR spectra were recorded on a JEOL AL 300 MHz spectrometer using $DMSO-d_6$ as solvents and TMS as internal references. However, 1H NMR spectra with the metal titration were recorded on an 800 MHz spectrometer. UV/visible and luminescence measurements are made in the range 200–700 nm on a Shimadzu UV-1601 spectrometer and Perkin Elmer LS-45 Luminescence spectrometer respectively. Time-resolved fluorescence measurements are carried out by time-correlated single-photon counting (TCSPC) method. A CW Nd: Vanadate (Millennia, Spectra Physics, USA) pumped mode-

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Scheme 1.

locked Ti-Sapphire laser with doubled tunable output was used for exciting the samples at 456 nm. Isothermal titration calorimetry (ITC) measurement was carried out using MicroCal VP-ITC titration micro-calorimeter at 25 °C.

2.2. Preparation of bis-[methylsalicylidine-4'-benzoic acid]-ethylene (LH₂)

Bis-[methylsalicylaldehyde]-ethylene (0.536 g, 1 mmol) was dissolved in methanol and added drop-wise to a methanolic solution of p-aminobenzoic acid (0.272 g, 2 mmol) with stirring. Stirring was continued for 2 h, resulting in formation of a yellow precipitate. This precipitate was filtered off and washed several times with methanol followed by washing with ether and dried in vacuo. Yield: 90%, M.P. > 250 °C, IR absorptions: $\nu_{\text{max}}/\text{cm}^{-1}$ 3076 (C=H); 2934 (–CH₂); 1680 (>=O); 1599 (CH=N); 1192 (–OH); 1577 and 1452 (C=C, Ar). ¹H NMR: δ_{H} (300 MHz, DMSO, Me₄Si); 13.37 (2H, s, –OH); 11.11 (2H, s, –COOH); 9.01 (2H, s, –N=CH); 8.01 (4H, m, Ar); 7.52 and 7.35 (8H, m, Ar); 6.97 (2H, m, Ar); 4.72 (2H, s, =CH₂); 2.5 (4H, s, –CH₂–). ¹³C NMR: δ_{C} (300 MHz, DMSO, Me₄Si) 166.833 (–COO); 165.77 (CH=N); 158.77 (C–OH); 151.43 (–CH–*C); 134.52 (N–C); 131.65 (COOH–*C); 131.20 (N–C=*CH), 128.92 (COOH–C=*CH); 121.54, 118.85 and 118.51 (Ar); 112.55 (*C=CH); 112.33 (=CH); 34.97 (–CH₂–) *assigned C atom, mass (*m/z*)⁺ 535 (molecular ion peak), elemental analysis (%): calculated for C₃₂H₂₆N₂O₆, C 71.9, H 4.8 and N 5.2; Found C 69.5, H 4.9 and N 4.7; UV absorptions: $\lambda_{\text{max}}(\text{DMSO})/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 280 (27,750), 298 (29,580), 403 (17,780).

2.3. Preparation of Ru^{II} Complex 1

LH₂ (0.536 g, 1 mmol) was dissolved in DMF and triethylamine (~2 mmol) was added to it with stirring followed by drop-wise addition of a solution of Ru(bpy)₂Cl₂·2H₂O (0.520 g, 1 mmol) in DMF. The reaction mixture was then refluxed on a sand bath for 26 h under N₂ atmosphere. After cooling, an aqueous solution of NH₄PF₆ was added slowly to it and the resulting solution was cooled in a refrigerator for 24 h. A dark colored solid appeared, which was then filtered and washed several times with water and dried in vacuo. The complex was further purified on alumina column using acetonitrile as eluent (Scheme 1). Yield: 40%, M. P. > 250 °C, IR absorptions: $\nu_{\text{max}}/\text{cm}^{-1}$ 3444^b (–OH+N–H from NH₄⁺); 2925 (–CH₂); 1602 (CH=N); 840.32 (PF₆[–]); 762 (pyridyl). ¹H NMR: δ_{H} (300 MHz,

DMSO, Me₄Si); 10.9 (2H, s, –OH); 9.6^{b,w}(N–H from ammonium ion); 9.2 (2H, s, –N=CH); 10.0 (2H, bpy); 8.7 (8H, m, Ar + bpy); 8.1 (11H, m, Ar + bpy); 7.2 (7H, m, Ar); 6.5 (2H, m, Ar); 4.2 (2H, =CH₂); 3.0 (4H, –CH₂–). ¹³C NMR: δ_{C} (300 MHz, DMSO, Me₄Si); 189.59, 187.50 (–C=O); 168.37, 167.43 (CH=N); 158.71, 158.40 (C–OH); 157.48, 157.26 153.25 (bpy); 152.88 (–CH–*C); 149.74, 149.51, 137.36, 137.12, 136.46 (bpy); 135.5 (N–C); 135.02 (COOH–*C); 135.0 (N–C=*CH); 133.52 (COOH–C=*CH); 131.88, 127.46, 126.25, 125.74, 125.27, 123.56, 123.276 and 119.559 (Ar); 113.757 (*C=CH); 110.897 (=CH); 34.225 (–CH₂–). b = broad, w = weak and * for C atom assigned; mass (*m/z*)⁺ 413 [Ru(bpy)₂]²⁺, 534 [L], 947 [Ru(bpy)₂L]. Elemental analysis (%): Calculated for [Ru(bpy)₂L]·2NH₄PF₆, C 49.0, H 3.9 and N 8.8; Found C 48.9, H 3.7 and N 8.4. UV absorptions: λ_{max} (acetonitrile)/nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 298 (38,500), 323 (11,200), 489 (9600), conductance: Λ_{M} (DMSO, 10^{–3} M) 133 ($\Omega^{-1} \text{cm}^2 \text{mole}^{-1}$). Emission: λ_{max} (acetonitrile)/nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 600.08 nm (9.3 a.u.).

3. Results and discussion

3.1. Characterization of ligand and complex

Complex 1 is found thermally stable and soluble in DMSO. Its composition has been assigned on the basis of its elemental analysis and spectral data. The repeated purification then elemental analyses measurements showed that complex contains two moles of NH₄PF₆. It also emphasizes that ligand is getting de-protonated during its complexation with metal ion. Though the possibility of isomeric complexes does exist but their separation could not be made at this stage of the study even using repeated column chromatography of the Complex 1.

IR spectrum of the free ligand shows major peaks at 1687 and 1599 cm^{–1} assigned to ν COOH and $\nu_{\text{CH=N}}$ vibrations respectively. These peaks shift to 1711 and 1602 cm^{–1} upon complexation. The significant change observed in case of carboxylate group vibration supports its coordination with the metal ion. Another peak observed at 841 cm^{–1} is assigned to ν PF₆[–] vibrations.

The above observations have further been supported by ¹H and ¹³C NMR spectra of the metal complex as compared to corresponding NMR spectra of free ligand. The peak observed at δ 13.3 ppm in the spectrum of free ligand is assigned to OH protons and is considered intramolecularly H–bonded with imine N in view of earlier report [16]. This peak shifts at δ 10.9 ppm in the spectrum of the

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