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Emission switching of ferrocenyl Schiff bases and a representative ruthenium complex in alkaline DMSO: Absorption, electrochemical and microstructural studies

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Abstract

N,N′-Bis(4-ferrocenyl)-*p*-phenylene/octamethylene-diimines (L_1/L_2) and a representative Ru(II) complex $[Ru(DMSO)_2Cl_2L_1]\cdot 2H_2O$ were prepared and characterized which showed many fold enhancement in their luminescence in alkaline dimethylsulfoxide (DMSO) solution. Spectral and electrochemical properties of these compounds have been studied. Microstructure (SEM) of L_1 and its complex showed single-phase porous material of crystal size ~1 μm.

Keywords: Ferrocenyl Schiff bases; Emission switching; Absorption spectrum; Scanning electron micrographs

1. Introduction

Development of receptors capable of modifying the molecular properties (in terms of modulating the optical signals etc.), upon binding with specific substrate (guest) is an active area of modern research. In this context, ferrocene based receptors have been found to serve as attractive functional material [1]. Samuelson et al. and many others have prepared Schiff bases [2,3] on the skeleton of ferrocene and have studied them for their second-order nonlinear optics applications as well as in electrochemical sensing of cations. Based on theoretical studies made by Kanis et al. [4] it was found that it is enhanced delocalization in ferrocenyl complex which leads to second-order nonlinearity.

On the other hand, polyamines/imines are known to form stable complexes with transition metal ions [5–10] and these metallocene based complexes attributed to facile redox changes at metal centre and most importantly presented an extended π electron framework. Additionally, imine-functionalties constructed on the skeleton of ferrocene could be exploited as linker to some photoactive system like ruthenium as a component and several metallocene units have already been exploited as donor [11–16]. Hence binding of another metal center specially with ferrocenyl Schiff bases could provide an opportunity to study the transfer of electron/energy from delocalized metallocene unit to attached metal center.

Present article could be considered an addition to the knowledge in this area of research as luminescence, absorption spectra and electrochemical properties of these simple systems showed switching of both intraligand as well as metal–ligand charge–transfer transitions in alkaline DMSO solution.

2. Experimental

Starting materials were purchased from Sigma–Aldrich and used without further purification. Compounds were analyzed from Central Drug Research Institute, Lucknow, India whereas Emission Spectra were recorded on LS-45 Luminescence Spectrometer (Perkin-Elmer). Infrared and UV–vis spectra were recorded on JASCO FT/IR-5300 and Shimadzu UV-1601 spectrophotometer, respectively. ^{1}H NMR spectra were recorded on (JEOL AL 300 MHz). Electrochemical data were recorded on EG&G Instruments (Model-Versastat). Scanning electron micrographs were obtained using SEM-XL-20 (Philips) and a thin coating of the silver metal was done in vacuum (10^{-5} Torr) to improve the conductance of the samples.

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2.1. Synthesis of Schiff bases L_1 and L_2

Ferrocenyl Schiff bases (L_1 and L_2) were prepared using a general procedure by refluxing an ethanolic solution of ferrocene-4-carboxaldehyde (2.0 mmol) separately with ethanolic/methanolic solutions of *p*-phenylenediamine/1,8-diamino octane (1.0 mmol) on water bath for 8–9 h. Corresponding brown/dark-brown solids thus obtained were filtered and recrystallized from ethanol and dried *in vacuo*.

L_1, mp >310 °C. FAB mass (*m/z*); 501 (M^+). $C_{28}H_{26}N_2Fe_2$: Anal. Calcd. For: C, 66.9; H, 7.06; N, 5.21%. Found: C, 65.65; H, 7.13; N, 6.72%. IR ν_{max}(KBr) (cm^{-1}): $1618_{(CH=N)}$, $1491_{(ph)}$, $812_{(cp)}$, 507, $482_{(Fe\text{-}cp)}$. ^1H NMR in DMSO-d^6 (δ, ppm, 300 MHz, 298 K): 8.45 (2H, s, CH=N), 7.19 (4H, s, ArH), 4.82 (4H, s, C_5H_4), 4.69 (1H, s, C_5H_4), 4.54 (3H, s, C_5H_4), 4.31 and 4.28 (10H, s, C_5H_5). UV–vis λ_{max}(dmso) (nm): 451 (ε ($dm^3\ mol^{-1}\ cm^{-1}$) 800), 410 (2000).

L_2, mp >300 °C. FAB mass (*m/z*) 537 (M^+). $C_{30}H_{38}N_2Fe_2$ Anal. Calcd. For: C, 67.03; H, 7.07; N, 5.21%. Found: C, 66.48; H, 7.13; N, 6.0%. IR ν_{max}(KBr) (cm^{-1}): $1645_{(CH=N)}$, 823, $810_{(cp)}$. ^1H NMR in $CDCl_3$ (δ, ppm, 300 MHz, 298 K): 8.09 (2H, s, CH=N), 4.63 (4H, t, C_5H_4), 4.35 (4H, t, C_5H_4), 4.28 (10H, s, C_5H_5), 3.4 (4H, m, NCH_2), 1.79 (4H, s, –CH_2), 1.35 (8H, s, –CH_2). UV–vis λ_{max}(dmso) (nm): 396 (ε ($dm^3\ mol^{-1}\ cm^{-1}$) 1753), and 463 (1448).

2.2. Synthesis of metal complex

2.2.1. $[Ru^{II}(DMSO)_2Cl_2L_1]\cdot 2H_2O$; ($C_{32}H_{38}N_2Cl_2O_2S_2Fe_2Ru\cdot 2H_2O$)

Precursor complex *cis*-$[Ru^{II}Cl_2(DMSO)_4]$ was prepared by reported procedure [17]. To notice the changes in the spectral properties upon binding of Schiff bases with metal ion, one representative Schiff base L_1 was complexed with ruthenium by the addition of a solution of L_1 (0.05 g, 0.1 mmol) in ethanol (5 cm^3) to a solution of *cis*-$[Ru^{II}Cl_2(DMSO)_4]$ (0.10 g, 0.2 mmol) in DMSO while stirring up to 0.5 h, followed by reflux for 12 h under N_2 atmosphere. The microcrystalline dark brown solid thus obtained was filtered off and washed with distilled water, ethanol, diethylether and dried in vacuo. Mp >250 °C; FAB mass (*m/z*) 828. Anal. Calcd. for $C_{32}H_{38}N_2Cl_2O_2S_2Fe_2Ru\cdot 2H_2O$: C, 44.0; H, 4.9; N, 3.2%. Found: C, 44.5; H, 5.2; N, 3.1%. IR ν_{max}(KBr) (cm^{-1}): $1610_{(CH=N)}$, $1074_{(DMSO)}$, $1514_{(ph)}$, $835_{(cp)}$, $565_{(Fe\text{-}cp)}$, $424_{(Ru\text{-}Cl)}$. ^1H NMR in DMSO-d^6 (δ, ppm, 300 MHz, 298 K): 9.9 (2H, s, CH=N), 4.82 (4H, s, C_5H_4), 4.69 (4H, s, C_5H_4), 4.31 (10H, s, C_5H_5), 3.37 and 2.51 (DMSO overlapped with solvent DMSO). UV–vis λ_{max}(dmso) (nm): 574 (ε ($dm^3\ mol^{-1}\ cm^{-1}$) 575), 468 (1058) and 342 (2214).

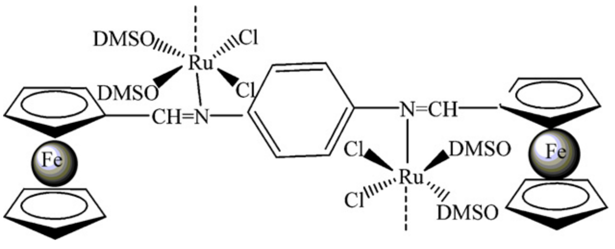

Fig. 1. Proposed structure of $[Ru(DMSO)_2Cl_2L_1]$.

3. Results and discussion

The analytical data supported the composition of Schiff bases and infrared spectral peaks were consistent with the earlier reports [18,19].

3.1. IR and ^1H NMR spectra

High resolution ^1H NMR spectral study of free Schiff base (L_1) gave three separate peaks (two for L_2) for protons of C_5H_4 rings attached to phenyl ring via imine bonds where as two very close singlets were observed for C_5H_5 rings (only one for L_2). This observation was considered in a way that delocalized electronic environment of C_5H_4 ring is disturbed hence showed different peak positions for protons attached to this ring and two singlets (for L_1) arising for protons of C_5H_5 ring indicated that both C_5H_5 rings are lying in little different plane which is also supported by its infrared spectrum showing two $\nu_{Fe\text{-}cp}$ vibrations. Thus one may consider that attachment of ferrocenyl groups through phenyl ring via imine linkage brought electronic perturbation in both cyclopentadienyl rings. This complex was found stable and showed non-electrolytic nature in DMSO (10^{-3} M).

As found from its infrared spectrum that only one peak at 565 cm^{-1} is observed for $\nu_{Fe\text{-}cp}$ vibration and it is supported by only one singlet observed at δ 4.31 ppm for protons of C_5H_5 rings in its ^1H NMR spectrum. These observations therefore support that both Fe-cp are now coplanar. Additionally, protons of C_5H_4 rings also experience almost delocalized electronic environment upon bonding with $[Ru(DMSO)_2Cl_2]$ unit as only two singlets were observed for their protons. Though two triplets for C_5H_4 protons like earlier reports [2] could not be observed may be because of poor resolution yet singlet observed for C_5H_5 protons is consistence with this report. The coordination of ruthenium with CH=N groups of ligand was considered due to lowering in position of $\nu_{CH=N}$ (1610 cm^{-1}) as compared to its position in the spectrum of free L_1 (1618 cm^{-1}) as well as due to deshielding of these protons (δ 9.9 ppm).

The composition of the complex as determined from its elemental analysis and mass indicated the presence of two coordinated DMSO molecules which are substantiated by its IR and ^1H NMR spectra showing peaks at 1074 cm^{-1} and δ 3.37 and 2.51 ppm respectively and is consistent with earlier reports [17,20]. High thermal stability and its solubility limited in DMSO only indicted that ligand preferred its coordination to metal ion in a polymeric frame (Fig. 1) which is supported by the mass spectrum showing peaks at mass higher than monomer unit.

3.2. Emission spectra

Emission data of L_1 recorded in DMSO indicated enhancement in its luminescence in alkaline medium (pH ~10.0) as compared to its behavior in the absence of NaOH (Fig. 2a).