



Synthesis, characterization, X-ray crystal structure, luminescence, electrochemical and solvatochromism studies of new dimer of nickel and palladium complexes containing ferrocenyl imine ligand



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ABSTRACT

The synthesis of a new Schiff base ligand was investigated by the reaction of ferrocenecarboxaldehyde, $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{CHO})]$, with 2-aminoethanethiol at room temperature. For this product, ring closure was also observed in the crystalline form which thiazolidine was obtained. Furthermore, new homobimetallic complexes of nickel(II) and palladium(II) were synthesized by the reaction of the new Schiff base ligand with nickel chloride and palladium chloride in 1:1 M ratio. In nickel and also palladium complexes the ligands were coordinated to the metals via the imine N atoms and the chlorido-bridged unit for the reported complexes was suggested. The complexes have been found to possess 1:1 metals to ligands stoichiometry. The emission and absorption spectra of the ligand and its complexes were studied in methanol solvent. Electrochemical properties of the ligand and its metal complexes were investigated in CH_3CN solvent at the 100 mVs^{-1} scan rate. The Schiff base ligand and its metal complexes showed both reversible and irreversible processes at this scan rate. These compounds have been characterized by IR, ^1H NMR, UV/Vis and elemental analysis. The crystal structure of the thiazolidine has been determined by single crystal X-ray diffraction.

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1. Introduction

Ferrocenecarboxaldehyde is one of the most useful starting materials for the synthesis of many ferrocene derivatives. Ferrocene-containing compounds are currently receiving much attention due to their increasing role in the rapidly growing area of materials science. The study of Schiff bases containing ferrocenyl units ($\text{Cp} = [(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-})]$) has been the subject of intense interest during the last years due to their noteworthy applications in several areas such as homogeneous catalysts for various processes [1], molecular sensors [2], molecular magnetic [3] and nonlinear optical materials [4]. Furthermore, the synthesis of ferrocene-derivatives compounds thus allows the opening of a potential area of research in designing and synthesizing multi-functional drugs against several types of cancers [5–10]. Moreover, ferrocene represents a fundamental compound in the recent developments of organometallic chemistry [11]. Studying of Schiff

bases derived from ferrocene carboxyaldehyde and their metal complexes is a quite attractive subject. Ferrocene-containing metal chelate complexes can be regarded as multi-nuclear molecules possessing both the features of organometallics and coordination chemistry [12]. Many studies on this class of ferrocene containing molecules have been reported recently. Syntheses of imines have been achieved by using several reagents such as zinc chloride, titanium chloride, molecular sieves or alumina [13–15].

Schiff base ligands with sulphur and nitrogen donor atoms in their structures, act as good chelating agents for the transition metal ions, because of the presence of both hard nitrogen and soft sulphur donor atoms in the backbones of these ligands [16]. These ligands readily coordinate with a wide range of transition metal ions yielding stable and intensely colored metal complexes [17]. Also, Schiff bases with donors (N, S, etc.) have structure similarities with neutral biological systems and also due to the presence of imine groups, they have been utilized in elucidating the mechanism of transformation of rasemination reaction in biological systems [18–21].

We have recently reported the synthesis of Schiff base ligands containing 2-mercaptoethylamine and their monomeric and

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dimeric metal complexes [22,23]. In this paper, we expand upon our preliminary report by describing the synthesis of new Schiff base ligand containing ferrocene group and its homobimetallic nickel and palladium complexes. For the ferrocenyl imine, ring closure was observed in the crystalline form and thiazolidine was obtained. The new dimeric complexes were synthesized by the reaction of the new Schiff base ligand with nickel chloride hexahydrate and also palladium chloride in 1:1 M ratio. These types of complexes have received considerable attention because the synthesis of such ferrocene-derived compounds thus allows the opening up of a potential area of research in designing and synthesizing multifunctional drugs. The Schiff base ligand, its complexes and thiazolidine were characterized by FT-IR, ¹H NMR, UV–Vis spectroscopies, elemental analysis, molar conductance and X-ray crystallography. Electrochemical and emission behavior of the Schiff base and its metal complexes were also studied by cyclic voltammetry and fluorescence spectroscopy, respectively.

2. Experimental section

2.1. Materials and physical measurements

All chemicals were reagent grade quality purchased from commercial sources and used as received. UV–Vis and fluorescence spectra were recorded on an Analytik Jena Specord 205 spectrophotometer and FP-6200 spectrofluorometer, respectively. FT-IR spectra were obtained as KBr pellets on a Perkin–Elmer spectrum RXI FT-IR spectrophotometer. ¹H NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrophotometer, using TMS as an internal standard. The elemental analyses were performed using a Perkin–Elmer 2400 series II. Melting points were determined on a Barnstead Electrothermal 9100. Conductivity was measured in DMSO solution (3×10^{-4} M) using a 712 conductometer (Metrohm).

Cyclic voltammograms were performed using a Metrohm Autolab/PGSTAT302N system equipped with a three-compartment cell and a personal computer for data storage and processing. An Ag/AgCl (saturated KCl) reference electrode (Metrohm), a Pt-rod as counter electrode and a platinum disk electrode (i.d. = 3 mm) as working electrode (Metrohm Pt-disk) were employed for the electrochemical studies. Voltammetric measurements were performed at room temperature in CH₃CN solution with 0.2 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.

2.2. Syntheses

2.2.1. Synthesis of the ferrocenyl imine ligand, **1**

2-aminoethanethiol (0.070 g, 0.907 mmol) in methanol (5 mL) was added to a solution of ferrocenecarboxaldehyde (0.194 g, 0.907 mmol) in methanol (30 mL). The red solution was stirred for 1 h at room temperature. Then, the solvent was evaporated and the oily solid residue dissolved in hot n-hexane to give a pure product as pale pink powder. This product was dried in vacuo at room temperature. (yield: 43%), pale pink, m.p: 86 °C, Anal. Calc. for [C₁₃H₁₅FeNS] (**1**): (M.W: 273.18), C, 57.16; H, 5.53; N, 5.13%. Found: C, 56.98; H, 5.49; N 5.02%; IR (KBr, ν/cm^{-1}): 1641 $\nu(\text{CN})$, 3084 $\nu(\text{CH})$, 1324–1443 $\nu(\text{C}=\text{C})$ (aromatic), 820 $\nu(\text{CS})$, 826, 1027, 1103 $\nu(\text{Fe}-\text{Cp})$. ¹H NMR (400 MHz; DMSO-*d*₆, δ/ppm): 8.18 (1H, s, CH=N), 3.03 (2H, t, S–CH₂), 3.80 (2H, t, N–CH₂), 4.39 (2H, t, Cp), 4.65 (2H, t, Cp), 4.23 (5H, s, Cp).

2.2.2. Synthesis of the nickel complex, **2**

A methanolic solution (5 mL) containing NiCl₂·6H₂O (0.216 g, 0.908 mmol) was added slowly to a solution (5 mL) of ferrocenyl imine **1** (0.248 g, 0.908 mmol) and the mixture was stirred and

heated on a water bath at 70 °C for 7 h. The brown solution of complex was left to stand for a night. The oily brown precipitate was washed with petroleum ether and then dried in vacuum. (yield: 57%), brown, m.p: >400 °C, Anal. Calc. for [C₂₆H₂₈N₂S₂Ni₂Cl₄Fe₂].6H₂O (**2**): (M.W: 911.57), C, 34.26; H, 4.42; N, 3.07%. Found: C, 34.06; H, 4.26; N, 3.17%; IR (KBr, ν/cm^{-1}): 1620 $\nu(\text{CN})$ (imine), 1456, $\nu(\text{C}=\text{C})$ (aromatic), 826 $\nu(\text{CS})$, 492 $\nu(\text{Ni}-\text{N})$.

2.2.3. Synthesis of palladium complex, **3**

The synthetic procedure was analogous to that of nickel complex **2**, except that an ethanolic solution of PdCl₂ (0.161 g, 0.907 mmol) was used instead of NiCl₂·6H₂O and heated on a water bath at 70 °C for 7 h. A brown precipitate was obtained and washed with petroleum ether, then dried in vacuum. (yield: 94%), brown, m.p: >400 °C, Anal. Calc. for [C₂₆H₂₈N₂S₂Pd₂Cl₄Fe₂] (**3**): (M.W: 898.98), C, 34.74; H, 3.14; N, 3.12%. Found: C, 34.43; H, 2.93; N, 3.89%. IR (KBr, ν/cm^{-1}): 1626 $\nu(\text{CN})$ (imine), 1455 $\nu(\text{C}=\text{C})$ (aromatic), 829 $\nu(\text{CS})$, 502 $\nu(\text{Pd}-\text{N})$.

3. Results and discussion

3.1. Synthesis and characterization of the compounds

When ferrocenecarboxaldehyde reacted with 2-aminoethanethiol in MeOH with 1:1 M ratio and the mixture was stirred in the air at room temperature for 1 h, a ferrocenyl imine ligand was formed. In the crystalline form, cyclization reaction was occurred and the thiazolidine was obtained in competition with the ferrocenyl imine ligand of the corresponding type (Scheme 1). In Scheme 1, the evidence for the existence of form **I** (Schiff base) and **II** (thiazolidine) was proved by the spectroscopic and single crystal X-ray diffraction data. It can be suggested that the ring closure can occur in the Schiff base to form the thiazolidine in the crystalline structure.

The single crystal of thiazolidine was grown in n-hexane by slow cooling during 2 day at 2 °C and its structure was determined by X-ray crystallography, whereas suitable single crystals could not be grown for nickel and palladium complexes by different methods. Based on the X-ray crystallography data a ring closure was suggested for the Schiff base ligand.

The homobinuclear complexes of nickel and palladium containing N donor atoms were synthesized by the reaction of the Schiff base ligand with nickel chloride hexahydrate and also palladium chloride in 1:1 M ratio in methanol (Scheme 2). In these homobimetallic complexes NiNi and PdPd metal centers were bridged by the chloride atoms as bridging ligands and formed dichlorido-bridged nickel(II) and palladium(II) dimer complexes [24]. In suggested structure, the Schiff base ligand was coordinated to the nickel and palladium via the imine N atom [25–29]. Furthermore, based on the spectroscopy data, tetrahedral structure was suggested for these compounds.

3.2. Crystal structure determination and refinement

The X-ray diffraction measurements were made on an STOE IPDS-2T diffractometer with graphite monochromated Mo-K α radiation. For compound **II**, yellow needle shape crystal was chosen using a polarizing microscope and was mounted on a glass fiber which was used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data from 3105 unique reflections. Data were collected to a maximum 2θ value of 58.32° in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [30] software package. A numerical absorption correction was applied using X-RED [31] and X-SHAPE [32] software. The data were

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