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Synthesis, characterization and crystal structure of the tridentate metalloligand formed from mono-condensation of ferrocenoylacetone and 1,2-phenylenediamine

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Abstract

Reaction of the ferrocenoylacetone **1** with *o*-phenylenediamine in refluxing dry toluene affords the new air and thermally stable organometallic tridentate compound ("half unit") **2**, which was isolated and characterized by elemental analysis, IR, UV–visible, ^{1}H and ^{13}C NMR spectroscopy and, in addition, authenticated by a single crystal X-ray diffraction analysis. In solution, the metalloligand **2** exists as a mixture of two tautomeric isomers: a keto-amine or enaminone form (60%), $CpFe(\eta^5\text{-}C_5H_4)\text{–}C(O)CH{=}C(CH_3)N(H)\text{-}o\text{-}C_6H_4NH_2$ ($Cp = \eta^5\text{-}C_5H_5$), and a keto-imine or iminone form (40%), $CpFe(\eta^5\text{-}C_5H_4)\text{–}C(O)CH_2C(CH_3)N\text{-}o\text{-}C_6H_4NH_2$, whereas only the enaminone form is found in the solid state. The structure of **2** is stabilized by a network of intra- and intermolecular hydrogen bonds involving N–H, NH_2 and C=O groups.

Keywords: Ferrocenoyl ketoamine; Half unit; Hemi-Schiff base; Tridentate ligand; Crystal structure

1. Introduction

Tridentate ligands, synthesized by a single condensation reaction of a carbonyl function of a β-diketone with only one amine group of an aliphatic 1,2-diamine, are well documented in the literature [1], and are considered as the most effective intermediates in the synthesis of tetradentate unsymmetrical Schiff bases when they are reacted with appropriate carbonyl compounds [2]. These ligands referred to as "half units" [1a,1b,3] can exist, in solution, as a tautomeric mixture of the keto-amine (enaminone) and keto-imine (iminone) forms [1]. In general, the synthesis of these condensation products requires a careful control of the reaction conditions, *e.g.*, (i) slow addition of the carbonyl compound to an excess of the 1,2-diamine [4], (ii) utilization of equimolar amounts of the carbonyl compound and of the 1,2-diamine in highly diluted solutions [5], (iii) partial hydrolysis of a symmetrical 2:1 tetradentate Schiff base [6], etc. On the other hand, only few examples of similar tridentate ligands derived from aromatic 1,2-diamines and β-diketones have been reported in the literature [7]. In this work, we report on (i) the synthesis of a new tridentate ferrocenoyl keto-amine ligand **2**, successfully prepared by a classical direct mono-condensation reaction between the ferrocene-based precursor ferrocenoylacetone **1** and *o*-phenylenediamine (see Scheme 1 for the formulae of compounds), (ii) the full characterization (IR, UV–visible, ^{1}H and ^{13}C NMR), (iii) the electrochemical behavior, and (iv) the crystalline and molecular structure solved by X-ray diffraction analysis.

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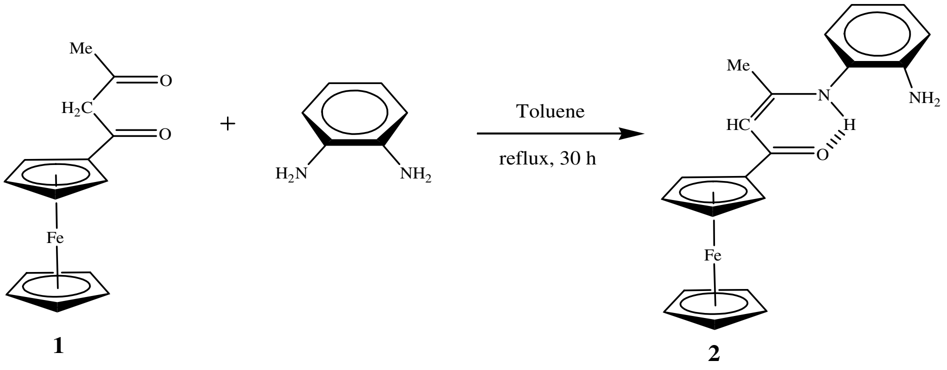

Scheme 1.

2. Experimental

2.1. Materials and physical measurements

Solvents were dried and distilled under dinitrogen by standard methods prior to use. Reagents were purchased from commercial suppliers and used without further purification. Ferrocenoylacetone **1** was synthesized according to published procedure [8]. Microanalytical data were obtained on a Perkin Elmer model 2400 elemental analyzer. IR spectra were obtained as KBr disks on a Bruker IFS28 FT spectrophotometer, in the range 4000–400 cm^{-1}. Electronic spectra were recorded in CH_2Cl_2 solutions with a Spectronic, Genesys 2, spectrophotometer. ^1H and ^{13}C NMR spectra were acquired at 297 K on a multinuclear Bruker Advance 500 spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, using the residual solvent resonances as internal references. Coupling constants (J) are reported in Hertz (Hz), and integrations are reported as number of protons. The following abbreviations are used to describe peak patterns: br, broad; s, singlet; d, doublet; t, triplet. ^1H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^1H–^1H COSY, ^1H–^{13}C HMQC, and ^1H–^{13}C HMBC NMR experiments, and are given according to the numbering scheme of Fig. 1. Electrochemical measurements were performed using a Radiometer Analytical model PGZ 100 all-in one potentiostat, using a standard three-electrode setup with a vitreous carbon working electrode, platinum wire auxiliary electrode and Ag/Ag^+ as the reference electrode. Acetonitrile solutions were 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte n-$Bu_4N^+PF_6^-$ with the voltage scan rate = 100 mV s^{-1}. Under these experimental conditions, the $E_{1/2}$ for $Cp_2Fe^{0/+}$ couple was located at 0.089 V ($\Delta E_p = 70$ mV). $E_{1/2}$ is defined as equal to $(E_{pa} + E_{pc})/2$, were E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. Melting points were determined in evacuated capillaries and were not corrected.

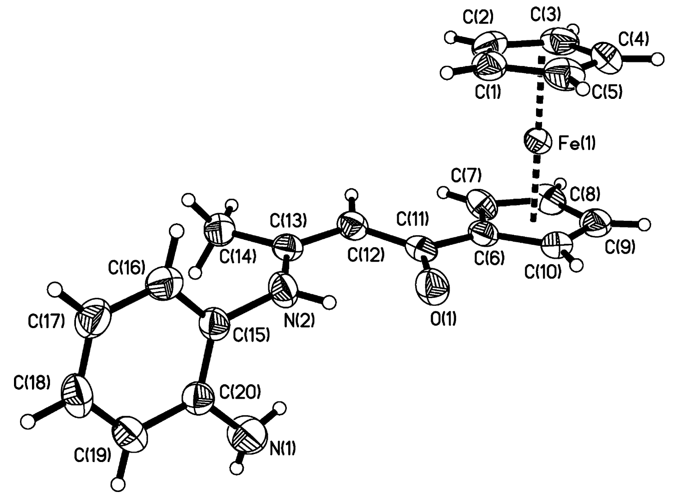

Fig. 1. Molecular structure of complex **2** showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

2.2. Synthesis of the organometallic "half unit" **2** [9]

A three necked round bottom flask equipped with a Dean–Stark apparatus was loaded with a magnetic stir bar, ferrocenoylacetone **1** (600 mg, 2.20 mmol), 1,2-phenylenediamine (242 mg, 2.20 mmol) and toluene (80 mL). The reaction mixture was refluxed for 15 h. After cooling, the reaction was monitored by TLC, hexane–diethyl ether mixture (1:1), on aluminum plates coated with neutral silica gel (60 F_{254}, Merck). As ferrocenoylacetone was still present, 65 mg (0.6 mmol) of 1,2-phenylenediamine were added to the reaction mixture that was heated to reflux for additional 15 h. After cooling, the solvent was removed under vacuum. The solid residue was dissolved in diethyl ether and adsorbed on a column packed with silica gel. Elution with diethyl ether produce the release of an orange band, which was collected. The solvent was evaporated under reduced pressure and the product was recrystallized from CH_2Cl_2–hexane mixture (1:1), affording 505 mg (64%) of orange microcrystals. A crystal from this crop was used for a X-ray structure determination. M.p. 136–138 °C.