Structural, electronic and optical properties of Fe(III) complex with pyridine-2,6-dicarboxylic acid: A combined experimental and theoretical study

Felipe A. La Porta [a,b,*], Paulize H. Ramos [c], Eliane C. de Resende [c], Mario C. Guerreiro [c], Juliana O.S. Giacoppo [c], Teodorico C. Ramalho [c], Julio R. Sambrano [d], Juan Andrés [b], Elson Longo [a]

[a] Instituto de Química, Universidade Estadual Paulista (UNESP), PO Box 355, 14801-970 Araraquara, SP, Brazil
[b] Department of Analytical and Physical Chemistry, Univ Jaume I, Castelló de la Plana 12071, Spain
[c] Departamento de Química, Universidade Federal de Lavras, CEP 37200-000 Lavras, MG, Brazil
[d] Laboratório de Simulação Molecular, UNESP, PO Box 473, 17033-360 Bauru, SP, Brazil

ARTICLE INFO

ABSTRACT

This paper describes the synthesis, as well the structural, electronic and optical properties of a novel complex of Fe(III) with pyridine-2,6-dicarboxylic acid (DPA). The complex was characterized by Fourier transform infrared (FT-IR) spectroscopy, Fourier transform Raman spectroscopy (FT-Raman), field emission scanning electron microscopy (FE-SEM), UV–Vis absorption spectroscopy and photoluminescence (PL) measurements. The chemical compositions were examined with an energy dispersive X-ray spectrometer (EDXS) analysis. First principle calculations at density functional theory (DFT) level have been carried out in order to understand the effects caused by structural distortions. The synthesized iron complex shows a molar ratio of 1:2 metal/ligand with an approximate octahedral configuration. Theoretical results derived from the analysis of molecular orbitals (MOs) and the electron density obtained from Quantum Theory of Atoms in Molecules (QTAIM) point out that the chemical bonds between oxygen and the iron atom in the Fe–DPA complex is predominantly electrostatic. In order to modeling the PL emissions, an energy profile associated to the variation of the dihedral angle (C–N–N–C) of the Fe–DPA complex, connecting the ground and excited electronic states, allows us to find a relationship between structural order–disorder effects with PL emissions.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The rational design and synthesis of novel coordination compounds is an active topic of investigation, because it expands the range of new complexes with preselected physical and chemical properties. In the last decades, an increasing interest in transition metal coordination compounds with conjugated organic ligands bearing functional groups can be observed [1–10]. Metal coordination-induced alteration in photophysical or electrophysical properties is essential for the related applications, and stable luminescent complexes with a wide range of colors (green, blue and red) can be useful for electro luminescent displays [11,12], but they are still rare and very challenging to prepare [13,14]. In particular, the design and synthesis of a blue luminescent Fe(III) complex has

become a very active area of research as a result of the demand for more sensitive and selective chemosensors for in vivo and in vitro purposes [15–17].

The complexation of metallic ions with the pyridine-2,6-dicarboxylic acid (DPA) has been extensively studied [18–22]. DPA shows important characteristics, such as low toxicity and its diversified biological activity being present in many natural products such as oxidative degradation product of vitamins, coenzymes, alkaloids and the reactivity of this ligand has been reported [23,24]. However, to the best of our knowledge, few systematic investigations on this ligand with Fe(III) have been carried out to date [22], and in previous studies [25,26], we have used a theoretical model to describe the parallel proton transfer pathways in acid–base reactions.

This article presents the synthesis of an iron(III) complex with DPA. This complex was characterized by Fourier transform infrared (FT-IR) spectroscopy, Fourier transform Raman spectroscopy (FT-Raman), field emission scanning electron microscopy

* Corresponding author at: Instituto de Química, Universidade Estadual Paulista (UNESP), PO Box 355, 14801-970 Araraquara, SP, Brazil. Tel.: +55 16 3301 9892; fax: +55 16 3301 9691.
E-mail address: felipe_laporta@yahoo.com.br (F.A. La Porta).

(FE-SEM), UV–Vis absorption spectroscopy and PL measurements. The chemical compositions were examined with an energy dispersive X-ray spectrometer (EDXS) analysis. To complement experimental results, the subtle balance between the structural parameters, electronic and optical properties has been addressed by first principles calculations at the density functional theory (DFT) level. In addition, analysis based on molecular orbitals (MOs) and Quantum Theory of Atoms in Molecules (QTAIM) method [27,28] has been carried out in order to understand the effects caused by structural distortions.

2. Methodology

2.1. Materials

Ferric nitrate ($Fe(NO_3)_3 \cdot 6H_2O$) were supplied by Vetec, the pyridine-2,6-dicarboxylic acid was obtained from Fluka and used without additional treatment.

2.2. Synthesis

The synthesis of the complex was conducted based on the methodology proposed by Sanyal et al. [29]. The ferric nitrate (0.6 mM) was dissolved in a solution of DPA (120 mM) at the molar proportion of 1:2 iron/DPA. The mixture was left under agitation at room temperature (25 ± 2 °C) until the complete solubilization of the salt, soon afterwards the mixture was left to rest for 48 h for formation of the light green colored crystals. It is clear that the protons liberated from the two ligand molecules during the complex formation process are going to solution. In fact, an acidification of the solution is observed and a pH around 4.5 is reached.

2.3. Characterizations

The complex obtained was structurally characterized by FTIR spectroscopy in a Bruker-Equinox 55 (Germany), using a 30° specular reflectance accessory. The FT-Raman spectroscopy was recorded in the range from 50 cm^{-1} to 3500 cm^{-1} with a RFS100 spectrophotometer (Bruker, Germany). The spectra were obtained using a Nd:YAG laser (λ = 1064 nm), keeping its maximum output power at 100 mW. The morphologies of the new Fe(III) complex with pyridine-2,6-dicarboxylic acid powder were observed by field emission scanning electron microscopy (FE-SEM) using FEG-VP JEOL. The compositional analysis as well as the mapping of the ele-

ments in the samples have been performed by means of energy dispersive X-ray spectroscopy (EDXS). Elemental analysis of C, H, and N atoms was performed by model Thermo FLASH EA 1112 Series. The UV–Vis spectra were taken using a Cary 5G spectrophotometer (Varian, USA) in diffuse reflection mode. PL spectra were collected with a Thermal Jarrel-Ash Monospec monochromator and a Hamamatsu R446 Photomultiplier. The 350.7 nm (2.57 eV) exciting wavelength of a krypton ion laser (Coherent Innova) was used with the output of the laser kept at 200 mW. All measurements were performed at room temperature.

2.4. Computational details

DFT method [30,31] has emerged as an alternative to traditional *ab initio* methods in the study of structure and reactivity of chemical systems [25]. In this work, all calculations were carried out with the GAUSSIAN09 package [32]. The energy minima were identified at the B3LYP functional [33,34], with basis set 6-31+G(d,p) was used for the C, N, O and H atmos and the 8s6p4d1f basis set was used for the Fe atom. This theoretical level was also used for the frequency calculations. The complex Fe–DPA have been confirmed as minima on the potential energy surface, i.e. all vibrational modes present positive values.

QTAIM proposed by Bader [27,28,35–40] enables us to analyze, evaluate, and classify the nature of chemical interactions. The figures of molecular orbitals (MOs) were prepared using the Gauss View 2.1 package with a contour value of 0.020. This computational procedure has been used previously in similar systems with success [22,41]. All calculations of the structures of this work were carried out in gas phase and the effect of the solvent was not considered. QTAIM calculations were performed using the resulting wave functions obtained from the single point energy calculations were performed using 6-311+G(d,p) basis set. QTAIM topological analyses, and the evaluation of the local properties and integral properties over the atomic basins (Ω), were carried out with the AIMALL program [42].

3. Result and discussions

3.1. Characterization

The complex was characterized by different techniques for a better understanding of the physicochemical properties of this new material. The FTIR and Raman analyses (Fig. 1) showed bands
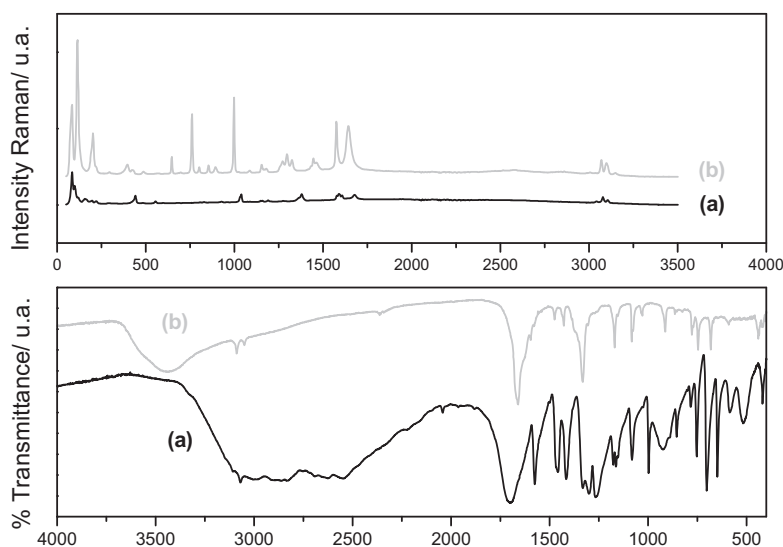

Fig. 1. FT-Raman spectrum (upper) and FTIR spectrum (below) (a) the free ligand and (b) Fe–DPA complex.