



Differently-charged tautomeric forms of three related hexacoordinated complex compounds of Fe(II)

Research article

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Abstract

This paper presents the results of the elemental analysis, followed by a physical-chemical study for three Fe(II) complexes, each of them containing – besides two bidentate ligands represented by two 2,2'-dipyridyl molecules – another bidentate ligand which is either a pyridine imine or a benzo[*d*]imidazole derivative. The results thus gathered (combined with the results of a quantum-mechanical study that will be reported in a further paper) lead to the deduction that all the complex compounds exhibit an octahedral geometry, having three (N, N) bidentate ligands.

Keywords: complex compounds, tautomeric forms, heterocyclic (N, N) ligands, Fe(II) complex compounds, spectral analysis

1. INTRODUCTION

Coordination chemistry has been significantly enriched due to the synthesis and characterization of a large number of six-coordinate octahedral complexes of the transition elements.

In many of them, the metal is coordinated by nitrogen atoms. Particular attention has been given to the complex compounds formed by transition metals with heterocycles that act as bidentate ligands, using two nitrogen atoms as electron donors [1-4].

Within this area, three Fe(II) complexes will be described here – containing a pyridine imine, 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole, and two of its derivatives beside two 2,2'-dipyridyl molecules: 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid and prop-2-yn-1-yl-2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinate.

These complexes have been synthesized and then structurally investigated by usual physical-chemical analysis (molar conductivity measurements, mass spectrometry and electronic spectroscopy), preceded by elemental analysis.

All the data thus gathered (joint with the results of a quantum-mechanical study that will be reported in a further paper) have led to the conclusion that all the complex compounds exhibit an octahedral geometry, the chemical bond obviously involving only nitrogen atoms as electron donors.

2. MATERIALS AND METHODS

2.1. *Materials and instruments*

The following reagents (Aldrich) were used in obtaining the three Fe(II) complex compounds presented within this study: ethanol, pyridine-2-carbaldehyde, 3,4-diaminobenzoic acid, copper acetate, sodium sulfide nonahydrate, hydrochloric acid, potassium hydroxide, dichloromethane, thionyl chloride, dimethylformamide, propargyl alcohol, triethylamine, potassium nitrate.

The elemental analysis was performed on a Perkin Elmer 2380 analyzer.

The molar conductivities were found in chloroform by using an OK-102 conductivity-meter at 300 K.

The mass spectra were obtained on a Mass Spectrometer Micromass LCT-type, by applying the ElectroSpray Ionization (ESI) technique.

The electronic spectra were performed in 10^{-4} M ethanolic solutions, with an Ocean Optics spectrophotometer.

2.2. Methods

The first ligand, 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole, denoted as L, was synthesized by an already published procedure, firstly obtaining its dihydrochloride and then recovering the ligand itself.

In order to obtain the second ligand, 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid, denoted as L', 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid dihydrochloride was formerly obtained: 12.82 g of pyridine-2-carbaldehyde were added to a mixture of a solution of 16.31 g of 3,4-diaminobenzoic acid in 150 mL of ethanol with a solution of 21.82 g of copper acetate in 250 mL of water, then the reaction mixture was heated for three hours on a boiling water bath. The redish-brown precipitate of the formed copper complex compound was filtered off and then dispersed in 150 mL of ethanol.

To decompose this complex, 51.58 g of Na₂S·9H₂O was put in the suspension, then the mixture was heated for two hours on the water bath, copper sulfide was filtered off from the hot solution and washed with hot water on the filter. The two filtrates were combined and highly acidified with hydrochloric acid. H₂S was removed from the solution by heating the water bath. On cooling the precipitated 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid dihydrochloride was filtered off to recrystallize it from the solvent.

The ligand itself, 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid (L') was obtained by mixing its dihydrochloride with an equivalent quantity of KOH in ethanol, the precipitated KCl was filtered off and finally the ethanol was distilled off.

In order to obtain the third ligand, namely prop-2-yn-1-yl-2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinate, denoted as L'', previously prop-2-

yn-1-yl-2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinate dihydrochloride was obtained: 1 g of SOCl₂ and one drop of DMF were added to a dispersion of 1 g of 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid dihydrochloride in 20 mL of dichloromethane; this mixture was heated for one hour on a water bath, the solvent was vacuum distilled, and 5 g of propargyl alcohol together with 0.9 g of triethylamine were added to the mixture in order to cool it; the reaction mixture was heated at the same time, continuously stirring for another hour on the water bath, then it was cooled, and poured into water.

The precipitate was filtered off, washed with water, and recrystallized from concentrated hydrochloric acid.

The ligand itself, prop-2-yn-1-yl-2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinate, (L'') was recovered from its dihydrochloride by mixing it with an equivalent quantity of KOH in ethanol; the precipitated KCl was filtered off, and the ethanol was finally distilled off.

Iron complex compound [Fe(dpy)₂Cl₂] \cdot 2H₂O (dpy standing for 2,2'-dipyridyl) was synthesized by an already published method.⁵

To synthesize the three complex compounds, in each case, to an amount of 0,098 g of the crystalline complex [Fe(dpy)₂Cl₂] \cdot 2H₂O were added 0.2 mmol ligand (L, L' or L'') and then 10 mL of ethanol, thus obtaining a dark-purple solution.

The reaction mixture was boiled for three hours, while the solution turned redish-brown. The solvent was removed on a rotary evaporator, the oily residue was extracted with water, this solution being added to a saturated solution of potassium nitrate.

The isolated fine crystalline precipitate was finally filtered off, washed with diethyl ether and air dried.

3. RESULTS AND DISCUSSION

3.1. Results and discussion

The results obtained by elemental analysis for the three ligands involved in this study are the following:

L: 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole dihydrochloride

Procentual formula found: %C 53.76; %H 4.15 %N 15.64; %Cl 26.45.

Procentual formula calcd.: %C 53.73; %H 4.11 %N 15.67; %Cl 26.49.

Molecular weight: 268

Molecular formula: C₁₂H₁₁N₃Cl₂

2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole

Procentual formula found: %C 73.90; %H 4.57; %N 21.53.

Procentual formula calcd.: %C 73.85; %H 4.61; %N 21.54.

Molecular weight: 195

Molecular formula: C₁₂H₉N₃

L': 2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid dihydrochloride

Procentual formula found: %C 50; %H 3.5; %O 10.27; %N 13.5; %Cl 22.73.

Procentual formula calcd.: %C 50; %H 3.53; %O 10.26; %N 13.46; %Cl 22.75.

Molecular weight: 312

Molecular formula: C₁₃H₁₁O₂N₃Cl₂

2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid

Procentual formula found: %C 65.23; %H 3.83; %O 13.38; %N 17.56.

Procentual formula calcd.: %C 65.27; %H 3.77; %O 13.39; %N 17.57.

Molecular weight: 239

Molecular formula: C₁₃H₉O₂N₃

L'': prop-2-yn-1-yl-2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinate dihydrochloride

Procentual formula found: %C 54.9; %H 3.7; %O 9.2; %N 11.96; %Cl 20.27.

Procentual formula calcd.: %C 54.86; %H 3.71; %O 9.14; %N 12; %Cl 20.29.

Molecular weight: 350

Molecular formula: C₁₆H₁₃O₂N₃Cl₂

prop-2-yn-1-yl-2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinate

2-(1*H*-benzo[*d*]imidazol-2-yl) isonicotinic acid

Procentual formula found: %C 69.35; %H 3.98; %O 11.53; %N 15.14.

Procentual formula calcd.: %C 69.32; %H 3.97; %O 11.55; %N 15.16.

Molecular weight: 277

Molecular formula: C₁₆H₁₁O₂N₃

The composition of the complex compounds thus obtained, $[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$, $[\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$ and $[\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$ was found from the results of mass spectrometry measurements.

By using the ElectroSpray Ionization (ESI) technique, in the mass spectrum of the complex compound $[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$, molecular ion peaks were detected corresponding to double-charged and mono-charged forms of the complex.

The existence of these two forms originated from the possibility of deprotonation of the benzimidazole fragment in the ligand L, resulting in decrease by one unit of the charge and mass of the species.

In the mass spectra of the complex compounds $[\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$ and $[\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$, as in that of complex $[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$, two signals from molecular cations of each compound exhibited, corresponding to species with one and two positive charges.

In all these cases, the isotopic distribution within the molecular ions signals entirely corresponded to the theoretically calculated form of peaks for the presumed compositions of the complex compounds.

The results obtained by mass spectrometry measurements (ElectroSpray Ionization – EIS method) and molar conductivity measurements for the three complex compounds involved in this study are the following:

$[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$:

Mass spectrum, m/Z: 609.0, 305.5.

Molar conductivity: $1.89 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (it acts as an electrolyte).

$[\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$:

Mass spectrum, m/Z: 653.0, 327.8.

Molar conductivity: $1.93 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (it acts as an electrolyte).

$[\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$:

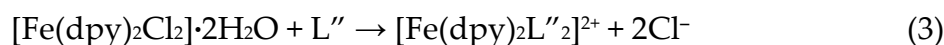
Mass spectrum, m/Z: 689.0, 342.3.

Molar conductivity: $1.97 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ (it acts as an electrolyte).

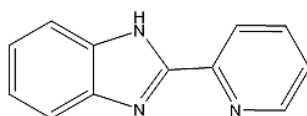
3.2. Discussion

In the reaction of the neutral complex $[\text{Fe}(\text{dpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ with these three bidentate ligands of pyridylbenzimidazole series, a substitution occurs, specifically the one of the two chloroligands, leading to the formation of a double-charged cation in each case, thus resulting, $[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$, $[\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$ and $[\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$.

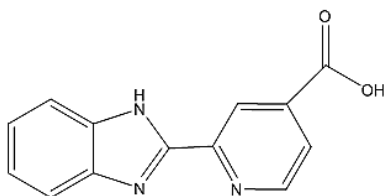
The substitution reactions may be written as follows, in the three cases taken for the present study:



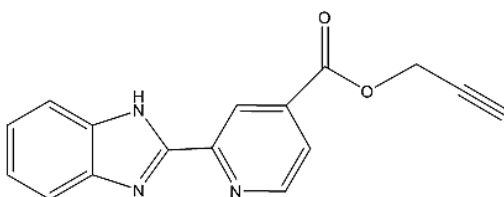
The structural formulae of all the three investigated ligands are shown in what follows.



2-(pyridin-2-yl)-1H-benzo[d]imidazole (referred to as L)



2-(1H-benzo[d]imidazol-2-yl) isonicotinic acid (referred to as L')



prop-2-yn-1-yl-2-(1H-benzo[d]imidazol-2-yl) isonicotinate (referred to as L'')

As far as the electronic spectra are concerned, it was presumed that the introduction of these ligands into the composition of the complex compounds $[\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$, $[\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$ and $[\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$ might lead to a shift of the absorption band in the visible region.

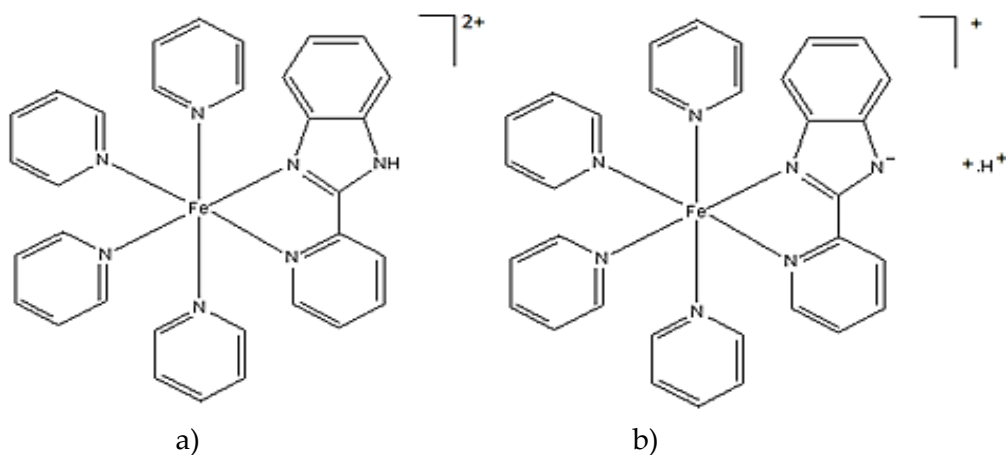
Indeed, due to the potential opportunity of the application of the Fe(II) dipyriddy complexes for sunlight conversion, the visible part of the electronic spectra of these compounds is the most interesting.

All the three electronic spectra are characterized by a wide band having a maximum at about 460 nm (the extinction coefficient was about $3000 \text{ L}\cdot\text{mol}^{-1}\text{cm}^{-1}$, indicating that the presence of a substituent at the benzo[*d*]imidazole fragment of the first ligand (either $-\text{COOH}$ or $-\text{COO}-\text{CH}_2-\text{C}\equiv\text{CH}$) doesn't mainly influence the absorption in the visible range.

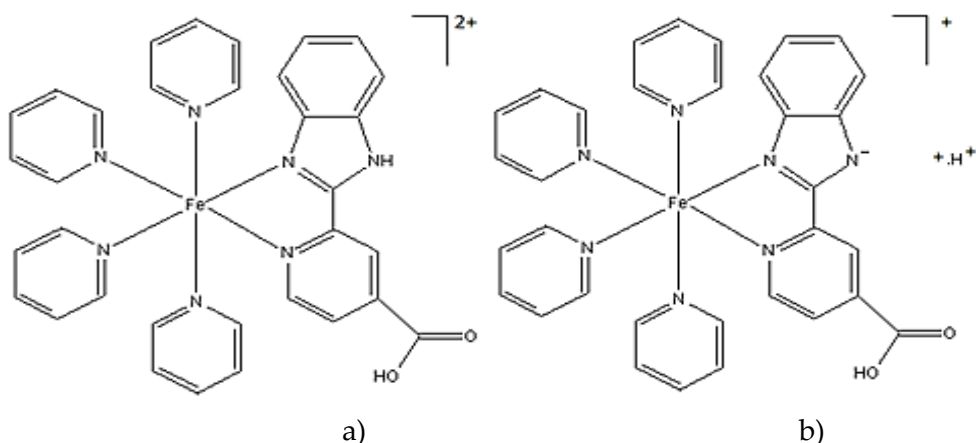
As compared to the Fe(II) tris-dipyriddy complex, this band suffered a red shift by almost 10 nm, but its intensity in the absorption maximum is several times less than for the corresponding band of $[\text{Fe}(\text{dpy})_3]^{2+}$.

3.3. Proposed structural formulae for the complex compounds

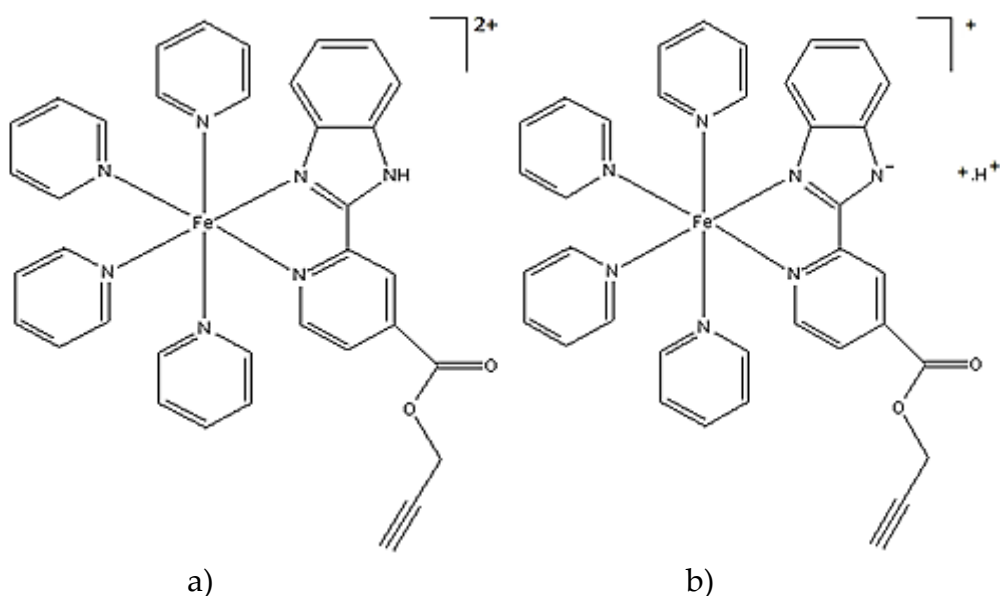
The proposed structural formulae for the three complexes are shown in what follows.



$\text{Fe}(\text{dpy})_2\text{L}_2]^{2+}$: a) double-charged form; b) mono-charged form



$\text{Fe}(\text{dpy})_2\text{L}'_2]^{2+}$: a) double-charged form; b) mono-charged form



$\text{Fe}(\text{dpy})_2\text{L}''_2]^{2+}$: a) double-charged form; b) mono-charged form

4. CONCLUSIONS

About the complex compounds that this work dealt with, the first results (obtained by gathering information from their elemental composition, conductometric behavior, mass spectrometry and electronic

spectroscopy) suggest that they all exhibit an octahedral geometry, two forms co-existing for them: a double-charged form and a mono-charged one, acting as electrolytes in both cases. As stated earlier, a quantum-mechanical study (confirming these conclusions) will be reported in a further paper.

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