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Synthesis, structure and electrochemical properties of the cationic complex tris-(imidazolidine-1,10-phenanthroline)iron(II)

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ABSTRACT

The complex $[Fe^{II}(Imz\text{-}phen)_3](PF_6)_2$, (Imz-phen = imidazolidine-[4,5-f]-1,10-phenanthroline) has been prepared and characterized using X-ray diffraction, UV–vis and IR spectroscopy, elemental analysis, fast atomic bombardment (FAB) mass spectrometry, and cyclic voltammetry. Its crystal lattice includes acetonitrile (π–π bound to phenanthroline), methanol, and water molecules. Scanning continuously between 1000 mV and 1650 mV in CH_3CN, a modified electrode that includes the iron (II) complex is obtained; after the 25th continuous cycle a stable film is formed that is electrocatalytically active in the reduction of sulfur oxoanions. When the electrocatalytic properties are evaluated in ethanol/water solution, the current achieved from the electroreduction of these sulfur species is linearly dependent on the respective concentrations, suggesting potential application in sulfite determination.

The synthesis of new complexes with polypyridyl ligands containing transition metals with imidazo derivatives has been of great interest because the imidazole moiety can be intercalated with DNA [1]. The luminescence properties of these kinds of coordination compounds have also been reported [2]. Also, several iron(II) phenanthroline derivatives generate polymer films by electrochemical methods. Depending on the substituents in the polypyridine ligand, the oxidation of these functional groups [3] to their cation radicals causes polymer film growth on the electrode surface [3–9]. The most widely used technique to generate these modified electrodes is repetitive cyclic voltammetry, because this technique forms stable, ordered, and highly covered surfaces [3–9]. The characteristics and properties of these polymer films are of interest for analytical purposes and in other related areas [10]. The main reactions studied with these modified electrodes are the reduction of CO_2 [11,12] and H_2O_2 [3], and the oxidation of glucose [13] and SO_3^{2-} [5,7].

On the other hand, the HSO_3^- sulfur oxoanion is used intensively in food and beverage industries as an antioxidant and antiseptic agent whose active species is SO_2 as a consequence of several acid–base equilibria. Surprisingly, many of the determinations of these S(IV) oxoanions are still made by classical analytical methods [14]. Therefore, the development of new coordination compounds able to sense S(IV) oxoanions is relevant [10].

In this paper we present the synthesis and characterization of a polypyridyl iron(II) complex containing an imidazolidine substituted phenanthroline. The preparation of this complex was unexpected and surprising (see experimental part) because the original ideas was to modify the electrode with the Fe(II) complex of the ligand 5,6 diamine phenanthroline, since an enhanced electropolymerization compared to the Fe(II) phenanthroline derivatives already in the literature [4–9] was expected. However, the resulting complex was able to generate a film on a glassy carbon surface, and the corresponding modified electrode presents electrocatalytic properties by the reduction of S(IV) oxoanions in ethanol/water solution [15].

IR data were collected using a Perkin–Elmer Lambda-11 spectrophotometer and a Perkin–Elmer series 2000 FTIR/Raman spectrometer. Elemental analysis was carried out on an EAGER 200 instrument. Mass spectrometry was performed on a Termo Finingan MAT 95XP spectrometer. The fast atomic bombardment (FAB) mass spectrometry was operated in the positive mode, applying 30 keV and registered in 3-nitrobenzyl alcohol. X-ray diffraction was performed on a Bruker SMART APEX II CCD X-ray diffractometer. All electrochemical measurements were carried out with a CHI 620-b electrochemical analyzer. In aprotic media, a three-electrode system was used with glassy carbon (GCE) (CH

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Instrument, 3 mm diameter) as the working electrode, the reference electrode was Ag/AgCl (3M KCl) connected to working electrode by a modified Pt-bridge Luggin capillary, a platinum wire was used as an auxiliary electrode. In our experimental conditions in acetonitrile (ACN), the couple ferrocene/ferrocenium has a potential of 422 mV versus Ag/AgCl.

In aqueous solution, the conditions were the usual and the reference electrode was a conventional Ag/AgCl (3M KCl).

The $[Fe(Imz\text{-}phen)_3]^{2+}$ complex was prepared from 3/1 ratio between 5,6-diamine-1,10-phenanthroline [16] and iron(II) acetate as follows: one equivalent of iron(II) acetate was refluxed in 15 mL ACN in argon atmosphere, then three equivalents of 5,6-diamine-1,10-phenanthroline was added quickly, and the solution was refluxed for 15 min. The hot solution was cooled at room temperature and the solvent was evaporated under reduced pressure. The solid product was dissolved in acetone and purified in a neutral alumina column, using toluene/acetonitrile 2:8 as the eluent.

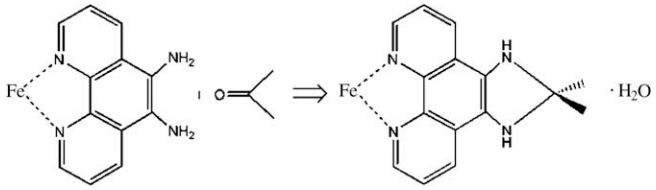
The larger dark red fraction was evaporated under reduced pressure, and the solid obtained was dissolved in deionized water to which two equivalents of aqueous NH_4PF_6 solution were added. The red solid obtained was filtered and dried under vacuum at 120 °C. Yield: 20%.

Anal. Found (%): C, 47.63; H, 3.65; N, 14.43; a related discussion is provided in the X-ray section. FAB mass spectrometry: (984.8 m/z: $M–PF_6^- –H_2O$); (944.2 m/z: $M–PF_6^- –3H_2O$); 800.7 m/z: $M–2PF_6^- –3H_2O$). IR [(KBr) υ_{max} (cm^{-1})]: 564, 847 (PF_6 counter-anion), 729, 811 (C–H aromatic bending), 1547, 1570, 1588 (C–N phenanthroline), 1611, 1629, 1694 (imine group), 2923, 2994, 3047 (C–H aromatic stretching), 3447 (water crystal lattice). UV–vis: [CH_3CN, λ_{max} (nm)] 244 nm, 82,924 M^{-1} cm^{-1}; 315 nm, 26,818 M^{-1} cm^{-1}; 325 nm, 22,558 M^{-1} cm^{-1}; 381 nm, 5,925 M^{-1} cm^{-1}; 536 nm, 4,418 M^{-1} cm^{-1}.

X-ray crystal structure

Crystals were obtained by slow diffusion of ether in a saturated acetonitrile solution of the complex. The iron compound is octahedral with a 2-fold axis passing over the metal and C22, as seen in Fig. 1a. Surprisingly, the expected 5,6-diamine-1,10-phenanthroline ligand appears modified, as its two NH_2 moieties form a 5-membered ring. Apparently, acetone in the chromatographic alumina column reacted with the original ligand establishing a semi-Schiff reaction, see Scheme 1.

The range of the Fe–N bond distances, 1.966(3)–1.977(3) Å, compares well with related values in the literature [17]. However, the title compound displays a complex pattern of included species: (1) two PF_6 counter-anions located so that their F3 atom establish short interactions with the ring C4–C5–C6–C7–C11–C12, with separations in the range of F3-C = 3.09–3.18 Å, Fig. 1b; (2) two acetonitriles located between two complexes (Fig. 1c) showing several



Scheme 1.

π–π interactions so that each acetonitrile interacts with one ligand (N7–C16 = 3.422 Å, C25–C17 = 3.459 Å), with a second acetonitrile (C25–C25 = 3.483 Å, C24–N7 = 3.486 Å), and each N(acetonitrile) interacting with a neighbor C atom of another ligand (N7–C11 = 3.490 Å, N7–C7 = 3.341 Å); (3) methanol and water molecules are also included in the crystal, but their location is "outside" the complex coordination sphere, as seen in Figure S1, deposited. Since the acetonitrile C24 atom belongs to a methyl group, its separation from N7 (3.486 Å), almost equal to that of graphite, suggests a potential isonitrile nature. The crystal structure suggests an explanation for the observed disagreement in the elemental analysis. The expected C, H, N percentages are 47.79, 4.32, 15.30, while the experimental values are 47.63, 3.64, and 14.43, respectively. A partial mass loss of acetonitrile, water and methanol explains the lower C, H and N content found. This methanol molecule could arise from acetone impurity. Among the iron-phenanthroline complexes containing included acetonitrile, bis(μ3-oxo)-heptakis(μ2-benzoato)-bis(1,10-phenanthroline)-tetra-iron(III) perchlorate acetonitrile solvate [18] contains two acetonitrile molecules with π–π C–N and C–C separations in the range 3.11–3.34 Å, plus a π–π C(acetonitrile)-C(phenanthroline) separation of 3.28 Å; bis(μ3-oxo)-hexakis(μ2-acetato)-bis(azido)-bis(1,10-phenanthroline)-tetra-iron(III) acetonitrile solvate [19] shows only a π–π C(acetonitrile)–C(phenanthroline) interaction of 3.31 Å, and, thus, the title compound π–π interactions involving acetonitrile and phenanthroline atoms are more marked.

Therefore, the complex arrangement of the title compound displays (1) great ability to form π–π bonds through F-aromatic, acetonitrile-acetonitrile, and acetonitrile-aromatic moieties; (2) large hydrophilic areas, shown by water and methanol inclusion, suggesting varied options for potential reactivity. In this context the use of an electrode having this deposited iron complex is shown below.

Fig. 2 displays the cyclic voltammogram starting from 0 mV to positive potentials, of a 1 mM solution of $[Fe\ (Imz\text{-}phen)_3]^{2+}$ in ACN with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. At negative potentials the $[Fe(Imz\text{-}phen)_3]^{2+}$ complex shows three quasi-reversible electrochemical processes with an $E_{1/2}$ value centered at −1000 mV (ΔE_p = 152 mV), −1350 mV (ΔE_p = 112 mV) and −1730 mV

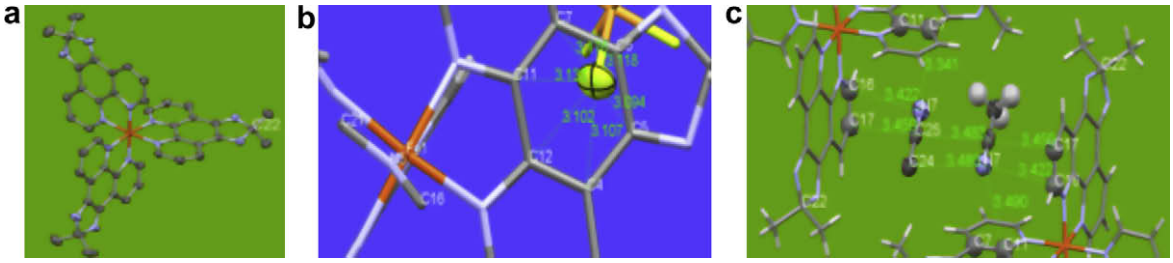


Fig. 1. (a) Ortep drawing of the cationic iron complex, excluding anions, acetonitrile, water, and methanol molecules. A crystallographic 2-fold axis passes over Fe and C22; (b) F3 interaction with the ring C4–C5–C6–C7–C11, C12; (c) acetonitrile molecules displayed between two iron complexes showing π–π interactions. The molecule is formally $[Fe(C_{15}H_{12}N_4)_3](PF_6)_2(CH_3OH)_2(CH_3CN)_2(H_2O)_{2.5}$, $C_{51}H_{55}F_{12}FeN_{14}O_{4.5}P_2$, a = 16.7078(13) Å, b = 17.4880(13) Å, c = 18.8976(14) Å, β = 93.434(1), V = 5511.7(1.2) $Å^3$, monoclinic C 2/c. Data taken at low temperature (125 K) and refined on F, Rf = 0.058, Rw = 0.083.

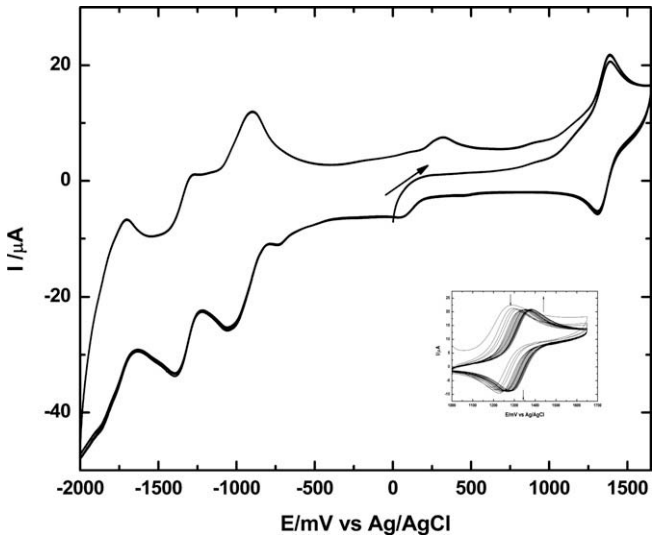


Fig. 2. Cyclic voltammogram of 1 mM [Fe (Imz phen)$_3$][PF$_6$]$_2$ in ACN. Supporting electrolyte 0.1 M TBAPF$_6$. Scan rate 100 mV/s. Inset: Modification of GC by cycling potential of 1 mM [Fe (Imz phen)$_3$][PF$_6$]$_2$ in ACN, 25 scans. 0.1 M TBAPF$_6$. Scan rate 100 mV/s.

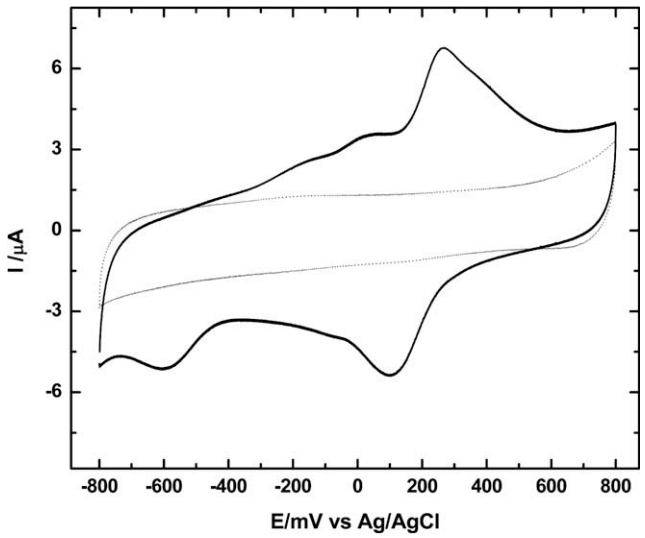


Fig. 3. Cyclic voltammogram of film derived from [Fe (Imz phen)$_3$]$^{2+}$ in the absence of complex (solid line), and bare GC (dotted line) in ethanol/water solution, pH = 3.5. Scan rate 100 mV/s.

(ΔE_p = 144 mV) that would be associated with electron transfers of the aromatic system of the ligand [20,21]. On the other hand, at positive potentials a quasi-reversible process with an $E_{1/2}$ value of 1350 mV (ΔE_p = 78 mV) that could be assigned to the Fe(II)/Fe(III) redox couple [4] is seen.

An electrochemical quasi-reversible process at $E_{1/2}$ value of 180 mV is seen. This process is not observed when the experiment is performed between 250 mV and −250 mV, but it appears when the scan goes from 1650 mV to −2000 mV. Also, the process appears in the second scan when the cyclic voltammetry is carried out from 250 mV to −2000 mV. Probably this process has a ligand centered nature since it has been observed when cyclic voltammetry experiments are performed with 5, 6 diamine phenanthroline ligand where a redox process appears at the same potential. See Supporting information (Figure S2).

When the electrode is continuously scanned between 1000 mV and 1650 mV (see the inset in Fig. 2) an increase in the current with a positive shift of the potential of the Fe(II)/Fe(III) redox couple is observed: this behavior is typical of a growing film. The *N*-substituted amino group could be responsible for the film formation, like the cases of *N*-substituted anilines reported in the literature [23,24]. When the modified electrode [25] is cycled in ethanol/water solution [15,22,26] (see Fig. 3), the generated film presents an electrochemical quasi-reversible process with an $E_{1/2}$ of 190 mV and an irreversible wave with an E_{pc} = −600 mV. These waves are independent, since when the modified electrode was scanned between 0 mV and −800 mV, starting at 0 mV, the only wave that appeared was the process centered at −600 mV. The same behavior is seen when the potential is scanned between 0 mV and 800 mV, starting at 0 mV, and the electrochemical quasi-reversible couple is independent of the other processes. These two waves are currently under investigation by spectroelectrochemical methods, since there is no agreement in the literature on the assignment of the related electrochemical processes.

It is not possible to decide if the redox couple appearing at 180 mV in Fig. 2 corresponds to the redox couple appearing at 190 mV in Fig. 3. What is certain, however, is that in both cases it is a ligand process.

Fig. 4 shows the voltammetric behavior of the modified electrode in the ethanol/water solution, with increasing concentrations of HSO_3^-. It is possible to see an enhancement of the cathodic current for the modified electrode compared to the bare glassy carbon and also a shift at the beginning of the potential wave. In the case of the modified electrode, the current increases and the potential wave shifts to more positive potentials showing the electrocatalytic character of this film toward this compound. It should be noted that when the HSO_3^- concentration increases, a shift of E_{pc} values occurs. This fact produces a 174 mV displacement when the concentration varies from 1 mM to 28 mM; this is characteristic for an electrochemical irreversible process [27].

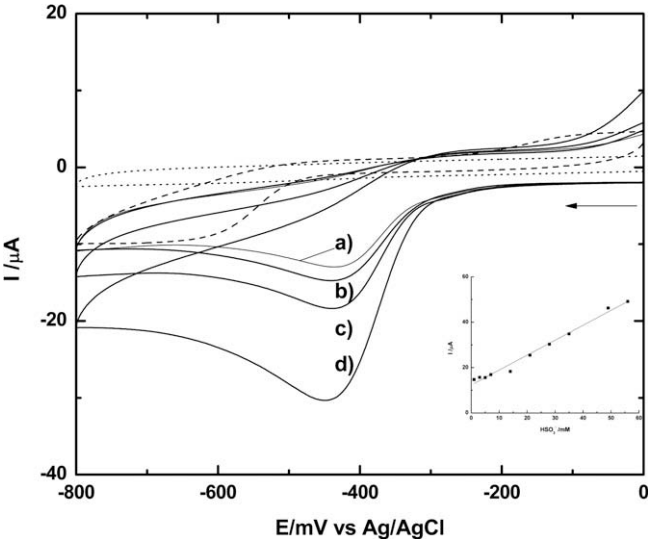


Fig. 4. Electrocatalysis for reduction of HSO_3^- in ethanol/water solution, pH 3.5 on glassy carbon electrode modified with a film derived from [Fe (Imz phen)$_3$]$^{2+}$. Scan rate 100 mV/s. GC (dotted line), GC in the presence of 1 mM HSO_3^- (dashed line), CV Fe (Imz phen)$_3$]$^{2+}$ film in the presence of HSO_3^- (solid lines) (a) 1 mM, (b) 7 mM, (c) 14 mM, (d) 28 mM. Inset: Calibration curve for reductive electrocatalysis of HSO_3^- in ethanol/water solution at pH 3.5 with modified electrode with film derived from [Fe (Imz phen)$_3$]$^{2+}$complex.

Since a shift of I_{pc} with concentration was seen, the current response centered at −440 mV may be used for analytical purposes. The inset in the Fig. 4 shows a linear relationship between the current at fixed potential and the concentration of HSO_3^- for the modified electrode. Although some analytical parameters [28] such as

limit of detection (8.20×10^{-4} M) and limit of quantification (1.43×10^{-3} M) are somewhat high, designing an improved separation method and with the choice of a more sensitive electroanalytical technique, this modified electrode should be considered as a potential sensor.

In conclusion, in this work a new and easily prepared Fe(II) complex of an imidazo derivative from 5,6 diamine-1,10-phenanthroline was obtained. The complex is able to form stable films that can be used for the determination of HSO_3^- in ethanol/water solutions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.02.017.

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[25] To discriminate the nature of the film formed, we modified the glassy carbon electrode with the drop coating and dip coating methods with a ACN solution 1 mM of the complex in 0.1 M $TBAPF_6$. When the drop coating method was used the surface was modified with 2 μL drop, the electrode was dried at room temperature and rinsed with ACN. When the dip coating method was used the electrode was immersed 15 min in the complex solution and then rinsed with ACN. The modified electrodes obtained where tested by cyclic voltammetry in a 0.1 M $NaClO_4$ solution (free of complex). The comparison among the three modified electrodes show different potentiodinamic responses indicating a dissimilar nature of adsorbed species being the modified electrode with the potentiodinamic scan method the most active in terms of coverage surface (see S3).
[26] A 12% v/v ethanol:H_2O solution, 5×10^{-2} M tartaric acid, 0.1 M $NaClO_4$, was used to model a wine matrix. Tartaric acid was added to the solution because it is the main acid component of red wines.
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