



Novel Pentacyanoferrate Complexes with Dinitrile Ligands (Malononitrile and Succinonitrile)

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Abstract In the present work the complexes $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NC}(\text{CH}_2)_n\text{CN})]$ ($n = 1 =$ malononitrile and $n = 2 =$ succinonitrile) have been isolated and characterized by cyclic voltammetry, Uv-vis and FTIR spectroscopies. A metal to ligand charge-transfer transition was observed only for $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NCCH}_2\text{CN})]$ complex (316 nm, $3,57 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). The succinonitrile complex of pentacyanoferrate(II) exhibits a band maximum at 370 nm, which was assigned to ligand field transition. The half wave potentials, $E_{1/2}$, for $[\text{Fe}(\text{CN})_5(\text{C}_3\text{H}_2\text{N}_2)]^{3-/2-}$, $[\text{Fe}(\text{CN})_5(\text{C}_4\text{H}_4\text{N}_2)]^{3-/2-}$ and $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-/2-}$ were measured as 341, 350 and $126 \pm 5 \text{ mV}$ (vs ECS), respectively. That is, in comparison with $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$, MN and SN, stabilize the Fe(II) ion by 215 and 224 mV, respectively.

Keywords Malononitrile, succinonitrile, pentacyanoferrate, voltammetry, electron transfer

Introduction

Although the chemistry of the pentacyanoferrates have been extensively studied and characterized over the years [1-9], special attention remains on this class of compounds. Like the pentaammineruthenium complexes, pentacyanoferrate(II, III) probe is inert with respect to substitution reaction, providing a simplified and safety way of studying the systematic effect of the ligand moiety on the metal ion properties [3,10,11]. This makes it a suitable system for comparative study, which is relevant specially regarding ligands of biological significance. In addition, the effect of the radial extension of the orbital (compared to Ru 4d orbitals, for example), as well as the presence of a good π -acid ligand, CN^- (instead the innocent NH_3 ligand in the ammineruthenium complexes), which promote changes on the metal ion behaviour, can also be evaluated. Another feature of the pentacyanoferrate (II, III) system is that it does not allow the formation of chelates, what can be useful to evaluate the isolated characteristics of the coordinating groups, as well as to discriminate electronic, steric or chemical effects on such molecules.

In order to overcome the difficulties involved in following chemical reactions in biological systems, many coordination compounds have been employed as models (in an attempt to study metal-biological ligands binding), from both, theoretical and experimental points of view [12] to study the electron transfer process in iron complexes [13,14]. In this sense, dinitriles are also interesting ligands for studying the interaction between Fe and N-compounds. They can act as monodentate (Fig. 1A, B) or as bridging bidentate ligands (Fig. 1C, D), such as many biological N-systems. [15,16].



The present work is inserted in the previously mentioned context, and is dedicated to report the synthesis, characterization and electron transfer studies of the complexes $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}]$ ($\text{L} = \text{malononitrile}, \text{C}_3\text{H}_2\text{N}_2$; succinonitrile, $\text{C}_4\text{H}_4\text{N}_2$).

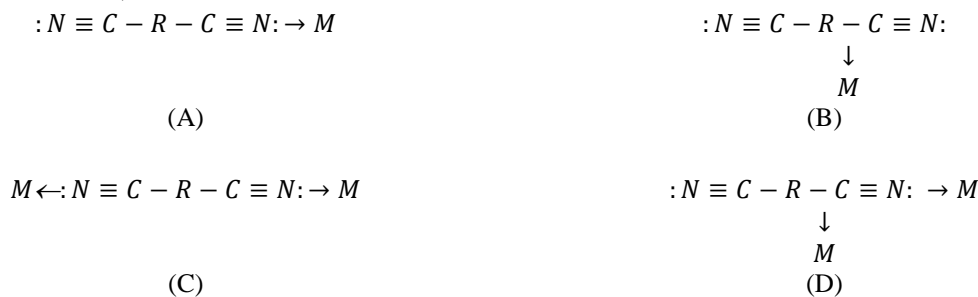


Figure 1: Coordination modes of dinitrile ligands: (A) end-on; (B) side-on; (C, D) bridging modes

Experimental

Materials

All the chemicals were of analytical grade and were used directly as supplied. $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$, propanedinitrile (malononitrile, MN) and butanedinitrile (succinonitrile, SN) were purchased from Merck Chemical Company. All solutions were prepared using purified water (specific resistivity > 18.2 MΩ cm at 25 °C). The ethanol employed were freshly distilled before use.

All preparations were carried out under argon (white Martins S.A.) and purified using CrCl_2 (HCl 1.0 mol L⁻¹) solutions and zinc amalgam.

Apparatus and techniques

Elemental analysis were performed in a EA 1110 CHNS-O CE equipment.

The UV-Vis spectra were obtained in a Cary 50 apparatus. The FT-IR spectra were recorded in a Nicolet Nexus 470 equipment in KBr discs.

The cyclic and pulse voltamograms were obtained in a voltametric analyser BAS model CV-500 W. Pyrolytic graphite and Pt were employed as work and auxiliary electrodes, respectively. The experimental conditions were as follows: K_2SO_4 , $\mu = 1.25 \text{ mol L}^{-1}$, pH = 9.3, T = 26.0 ± 0.1 °C.

Synthesis of pentacyanoferrate compounds

The complex $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ was employed to prepare $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$, as described elsewhere and recrystallized from concentrated ammonia [3,17].

The complex $\text{Na}_3[\text{Fe}(\text{CN})_5\text{C}_3\text{H}_2\text{N}_2]$ was prepared as follows: 1.10 g of malonitrile was dissolved in 20 cm³ of water. After that, 110 mg of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$ were added to the system. The mixture was under argon atmosphere and was magnetically stirred for 6 h. Then, 100 cm³ of cold ethanol was added, provoking the precipitation of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{C}_3\text{H}_2\text{N}_2]$, which was filtered off, washed with absolute and freshly distilled ethanol and stored under vacuum atmosphere in the absence of light.

The complex $\text{Na}_3[\text{Fe}(\text{CN})_5\text{C}_4\text{H}_4\text{N}_2]$ was prepared as follows: 1.71 g of succinonitrile and 0.18 g of sodium acetate were added to 10 cm³ of water. After that, 400 mg of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$ were added. The mixture was under argon atmosphere and was magnetically stirred for 6 h. Then, 100 ml of a cold mixture of 1:1 (v:v) acetone:2-butanol were added to the system, precipitating $\text{Na}_3[\text{Fe}(\text{CN})_5\text{C}_4\text{H}_4\text{N}_2]$, which was filtered off and washed with absolute and freshly distilled ethanol and stored under vacuum atmosphere in the absence of light.

Results and Discussion

The UV-Vis spectra data are summarized in Table 1. To the prepared complexes, ligand field (LF), inner ligand (IL) and metal to ligand (MLCT) bands are verified in accordance with the literature for similar complexes [3].



The main infrared bands for malononitrile, succionitrile and their respective complexes are summarized in Tables 2 and 3. To $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{C}_3\text{H}_2\text{N}_2)]$, the ligand coordination is confirmed by the lowering (free ligand *versus* complex) of the $\nu(\text{C}\equiv\text{N})$ bands. On the other hand, to $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{C}_4\text{H}_4\text{N}_2)]$ an increase in the $\nu(\text{C}\equiv\text{N})$ bands (free ligand *versus* complex) is observed.

For both complexes, the equatorial $\nu(\text{C}\equiv\text{N})$ band are located at higher frequencies, in comparison with $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$. Such fact shown that the π -bonds of the nitriles are stronger than the π -bonds in the CN^- group, that is, the nitriles are effective π acid ligands.

The cyclic voltametric data are summarized in Table 4. The cyclic voltamograms for $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{C}_3\text{H}_2\text{N}_2)]$ and $[\text{Fe}(\text{CN})_5(\text{C}_4\text{H}_4\text{N}_2)]$ are shown in Figures 2 and 3, respectively.

The half wave potentials, $E_{1/2}$, for $[\text{Fe}(\text{CN})_5(\text{C}_3\text{H}_2\text{N}_2)]^{3-/2-}$, $[\text{Fe}(\text{CN})_5(\text{C}_4\text{H}_4\text{N}_2)]^{3-/2-}$ and $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ were measured as 341, 350 and 126 ± 5 mV (vs ECS), respectively. That is, in comparison with $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$, MN and SN, stabilize the Fe(II) ion by 215 and 224 mV, respectively. Furthermore, based on the obtained cyclic voltamograms, can be concluded that the redox processes are reversible.

Table 1: UV-Vis bands for the prepared complexes

Complex	IL		LF		MLCT	
	$\lambda(\text{nm})$	$\epsilon (\text{L mol}^{-1}\text{cm}^{-1})$	$\lambda(\text{nm})$	$\epsilon (\text{L mol}^{-1}\text{cm}^{-1})$	$\lambda(\text{nm})$	$\epsilon (\text{L mol}^{-1}\text{cm}^{-1})$
$[\text{Fe}(\text{CN})_5\text{C}_3\text{H}_2\text{N}_2]^{3-}$	192	$1,38 \times 10^4$			3163,57 $\times 10^3$	
	240	$2,16 \times 10^4$				
$[\text{Fe}(\text{CN})_5\text{C}_4\text{H}_4\text{N}_2]^{3-}$	220	$9,02 \times 10^3$		$3702,17 \times 10^2$		

Table 2: Main infrared bands for malononitrile and its complex

$\text{C}_3\text{H}_2\text{N}_2$	$\text{Na}_3[\text{Fe}(\text{CN})_5(\text{C}_3\text{H}_2\text{N}_2)]$	Attribution
2966	2918	$\nu^{\text{as}}(\text{CH})$
2933	2856	$\nu^{\text{s}}(\text{CH})$
2274	2260	$\nu(\text{CN})$
1394	1402	$\delta(\text{CH}_2)$
	1329	$\delta(\text{CH}_2)$
	1294	$\delta(\text{NH}_3)$
1223	1083	$\delta(\text{CH}_2)$
937	934	$\nu(\text{C-CN})$
893	918	$\delta(\text{CC})$
733	780	$\rho(\text{CH}_2)$
584	540	$\delta(\text{CC})$
418	419	$\delta(\text{CCN})$

Table 3: Main infrared bands for succionitrile and its complex

$\text{C}_4\text{H}_4\text{N}_2$	$\text{Na}_3[\text{Fe}(\text{CN})_5(\text{C}_4\text{H}_4\text{N}_2)]$	Attribution
2989	2997	$\nu(\text{CH})$
2950	2920	$\nu(\text{CH})$
2254	2255	$\nu(\text{CN})$
	2114	$\nu(\text{CN})$
	2058	$\nu(\text{CN})$
	1638	$\delta(\text{NH}_3)$
1560	1566	$\nu(\text{CC})$
	1555	$\nu(\text{CC})$
1425	1414	$\delta(\text{CH}_2)$
1336	1345	$\delta(\text{CH}_2)$

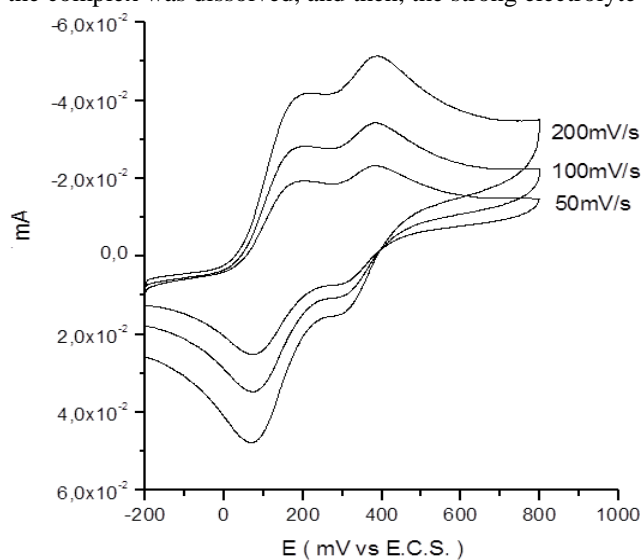
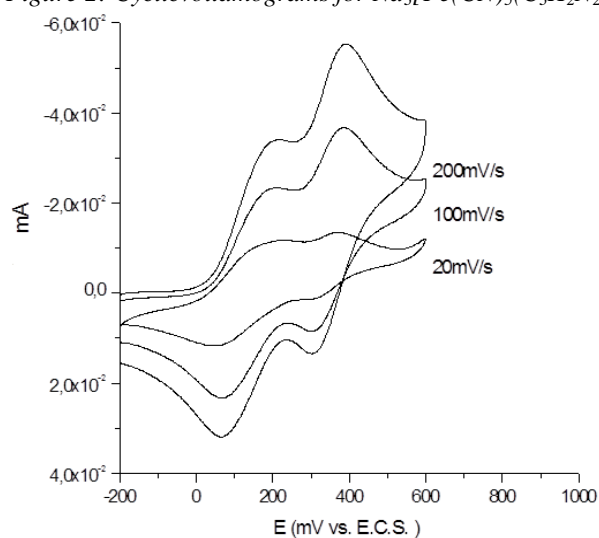


1232	1223	□ (CH ₂)
1200	1200	□ (CH ₂)
1003	1021	□ (CH ₂)
962	963	δ(CH ₂)
918	929	v(C-CN)
418 ^(f)	419	δ(CCN)

Table 4: Cyclic voltametric data for the prepared complexes

Group	1 ^o E _{1/2} (mV) vs. E.C.S.	2 ^o E _{1/2} (mV) vs. E.C.S.
[Fe(CN) ₅ MN] ^{3-/2-}	135 ^(a)	341
[Fe(CN) ₅ SN] ^{3-/2-}	139 ^(a)	350
[Fe(CN) ₅ SN] ^{3-/2-}	136 ^(b)	346
[Fe(CN) ₅ H ₂ O] ^{3-/2-}	126 ^(a)	

^aAqueous media, K₂SO₄, μ = 1.25, pH = 9.3; 26.0 ± 0.1 °C; ^bAqueous media, K₂SO₄, μ = 1.25; pH = 9.3; 26.0 ± 0.1°C (in this measurement, the complex was dissolved, and then, the strong electrolyte was added).

**Figure 2:** Cyclic voltammograms for Na₃[Fe(CN)₅(C₃H₂N₂)]**Figure 3:** Cyclic voltammograms for Na₃[Fe(CN)₅(C₄H₄N₂)]

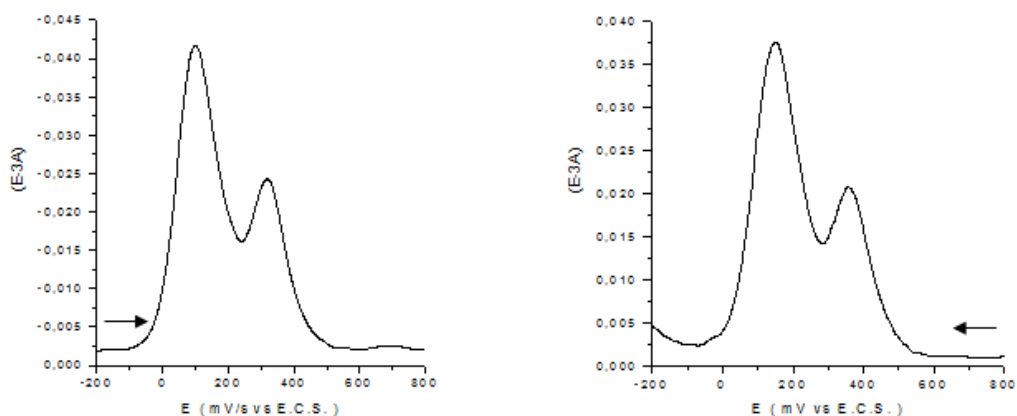


Figure 4: Differential pulse voltammograms for $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{C}_3\text{H}_2\text{N}_2)]$ ($[\text{Fe}(\text{II})] = 2.4 \times 10^{-3} \text{ mol L}^{-1}$)

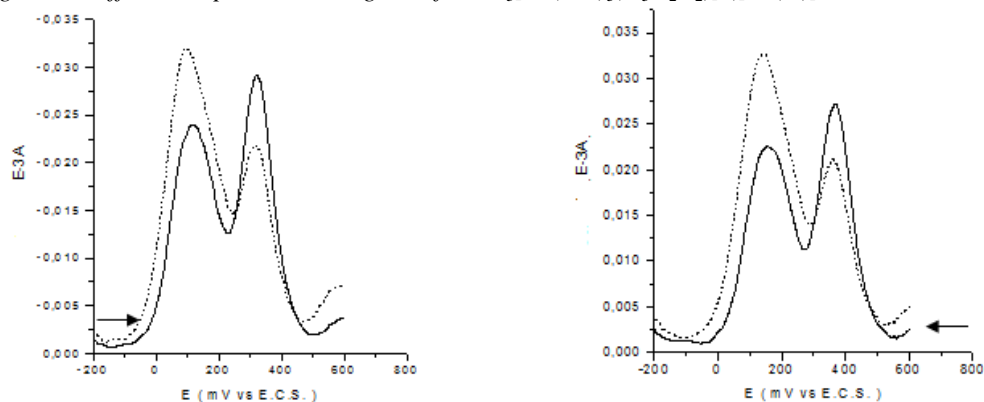


Figure 5: Differential pulse voltammograms for $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{C}_4\text{H}_4\text{N}_2)]$. Dashed line: firstly, the compound was dissolved in water, and then, the strong electrolyte was added.

The differential pulse voltametric data are summarized in Table 5. The obtained differential pulse voltammograms are shown in Figures 3 and 4. The presence of two peaks in such voltammograms, is in agreement with the following proposed scheme:

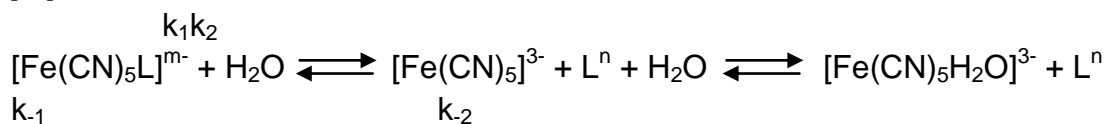


Table 5: Differential pulse voltametric data for the prepared complexes

Complex	$1^{\circ}E_{pa}$ (mV vs E.C.S)	$2^{\circ}E_{pa}$ (mV vs E.C.S)	$1^{\circ}E_{pc}$ (mV vs E.C.S)	$2^{\circ}E_{pc}$ (mV vs E.C.S)
$[\text{Fe}(\text{CN})_5\text{MN}]^{3-/2-}$	100 ^a	315	150 ^a	350
$[\text{Fe}(\text{CN})_5\text{SN}]^{3-/2-}$	118 ^a	323	159 ^a	369
$[\text{Fe}(\text{CN})_5\text{SN}]^{3-/2-}$	97 ^b	318	144 ^b	364
$[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-/2-}$	95 ^a		146	

^aAqueous media, K_2SO_4 , $\mu = 1.25$, $\text{pH} = 9.3$; $26.0 \pm 0.1^\circ\text{C}$; ^bAqueous media, K_2SO_4 , $\mu = 1.25$; $\text{pH} = 9.3$; $26.0 \pm 0.1^\circ\text{C}$ (in this measurement, the complex was dissolved, and then, the strong electrolyte was added).

That is, the nitrile complex is replaced by a water molecule and a chemical equilibrium is established.

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