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ELECTROCHEMICAL STUDIES ON MIXED-LIGAND IRON(II) COMPLEXES CONTAINING ISOCYANIDES AND PHOSPHINES

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Summary

Voltammetry at a stationary platinum electrode and polarography were carried out in dichloromethane (0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte) for complexes of the type $[FeX(CNR)_2L_3][ClO_4]$ [X = Cl, Br or I; L = $PPh(OEt)_2$; R = phenyl, 4-methylphenyl, 4-methoxyphenyl, 2-methylphenyl or 2,6-dimethylphenyl] and for $[Fe(CNR)_3L_3][ClO_4]_2$ [L = $PPh(OEt)_2$; R = cyclohexyl]. A mechanism of the redox process for both oxidation and reduction is postulated. A simple redox change without any complication from chemical reaction occurs in the case of oxidation at a platinum electrode, whereas the reduction is complicated by a subsequent chemical reaction.

Introduction

In previous papers we reported [1,2] the synthesis of a new series of mixed-ligand hexacoordinate complexes of iron(II) with isocyanides and phosphines ligands and suggested structures for them in solution on the basis of IR and ^{1}H NMR data. In an extension of our studies on the chemistry of isocyanide complexes we have undertaken a study of the redox behaviour in an aprotic medium of the mixed-ligand complexes $[FeX(CNR)_2L_3][ClO_4]$ (X = Cl, Br or I; R = C_6H_4, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 2-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$; L = $PPh(OEt)_2$) and $[Fe(CNR)_3L_3][ClO_4]_2$ (R = C_6H_{11}; L = $PPh(OEt)_2$), with the aim of throwing light on the oxidation and reduction mechanism and of determining the influence of halogen and isocyanide substituents on heterogeneous redox

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processes. Results obtained during a study of mixed-ligand pentacoordinate complexes of cobalt(I) with isocyanides and phosphines [3] suggested to us that electrochemistry in non-aqueous solvents might provide useful information about the redox properties of the iron(II) complexes. Earlier polarographic results obtained in aqueous solution failed to give the desired information [4,5].

Experimental section

Materials

Complexes of the type $[FeX(CNR)_2L_3][ClO_4]$ (R = phenyl, 4-methylphenyl, 4-methoxyphenyl, 2-methylphenyl, or 2,6-dimethylphenyl; L = diethylphenylphosphonite; X = Cl, Br, or I) and $[Fe(CNR)_3L_3][ClO_4]_2$ (R = cyclohexyl) were prepared by procedures already described [1,2]. Dichloromethane (DCM, grade for spectroscopy, Uvasol from Merck, Darmstadt, Germany) was used as a solvent because it is effectively inert toward the compounds studied under the conditions of the experiments. DCM was stored over calcium carbonate and distilled from phosphorus pentoxide before use.

The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was prepared by the methathetical reaction between tetrabutylammonium hydroxide (10% aqueous solution, from Lachema, Czechoslovakia) and perchloric acid (from Carlo Erba, Italy). The salt was recrystallized three times from water, dried under vacuum for five days at 60°C, and stored over phosphorus pentoxide. Other chemicals used were of reagent grade (Lachema, Czechoslovakia).

Apparatus

All voltammetric measurements were carried out with a multipurpose electrochemical apparatus [6]. An XY recorder (BAK 4T, Aritma Prague, Czechoslovakia) and Tectronic 5103 osciloscope were used as recording devices. Compensation for ohmic drop between the tip of the reference electrode and working electrode was made by means of a positive feedback technique [7], including a stabilization circuit [8]. Bis(diphenyl)chromium iodide was used as a reference compound in order to test all the devices [9] and as a standard for the electrode behaviour of iodide in DCM.

Polarographic and commutated polarographic experiments were performed with a Radelkis OH-102 polarograph. The Kalousek commutator was made at the J. Heyrovsky Institute and the *iR* drop in the electrolysis cell was compensated by use of a Metroohm electronic compensator.

Large scale electrolysis at platinum and mercury electrodes was carried out using a high voltage D.C. power supply BM 208 (Tesla Brno, Czechoslovakia). The potential of the working electrode was controlled manually. An analog integrator, Amel model 558, was used for measuring the cell current.

All measurements were made in a universal modular electrolysis vessel [10] employing a three-electrode system. A stationary platinum electrode (platinum wire, 0.05 cm in diameter) and a rotating platinum electrode (platinum rod of a diameter of 2 mm in a Teflon rod) were used as working electrodes. A hammer kept the drop time of the dropping mercury electrode (DME) constant at 3.17 s. The flow rate was $m = 0.275\ \mathrm{mg\ s^{-1}}$ with a mercury column height of 30 cm.

A platinum plate (2 cm X 2 cm) was used as the auxiliary electrode. All potential values were referred to a calomel reference electrode (CE) filled with 1 mol dm^{-3} aqueous lithium chloride and joined to the study solution by means of a salt bridge having a sharp porous ceramic tip. The bridge was filled with an aqueous solution of 0.1 mol dm^{-3} sodium perchlorate in order to eliminate chlorides. In the case of low-temperature experiments, a 0.1 mol dm^{-3} TBAP solution in DCM was used instead of an aqueous bridge.

ESR spectra were measured using a Varian E4 spectrometer and active species were generated in the ESR cell by electrolysis at a platinum electrode at a constant potential as indicated by the voltammetric measurements.

Low temperature experiments were carried out at —75°C using a mixture of acetone and solid carbon dioxide.

All operations and voltammetric measurements were carried out under argon in Schlenk type glassware [11].

Results

Voltammetry at rotating platinum disc electrode

The complexes $[FeX(CNR)_2L_3][ClO_4]$ and $[Fe(CNR)_3L_3][ClO_4]_2$ were investigated in DCM solutions of 0.1 mol dm^{-3} TBAP at a platinum rotating disc electrode (RDE). The voltammograms show two waves, one oxidation and one reduction process. The available voltammetric data (half-wave potential, slope of the voltammetric curves, and relative values of limiting currents) are shown in Table 1.

Logarithmic analyses of both voltammetric curves indicate a slow electron transfer step in the electrode process. In order to obtain reliable data a careful compensation of R_u ("uncompensated resistance") was made. The degree of compensation was determined by means of positive feedback using the slope of the voltammetric curve of the reference compound, 60 mV under the given conditions.

TABLE 1

VOLTAMMERIC DATA OBTAINED AT PLATINUM ROTATING DISC ELECTRODE

Compounds [a]	$E_{1/2}$ [b]	Slope [c]	R [d]	$E_{1/2}$ [e]	Slope [c]	R [d]
$[FeCl\{2,6\text{-}(CH_3)_2C_6H_3NC\}_2L_3]^+$	+1.194	66.2	0.99	—1.5 —1.935	irr.	2.2
$[FeCl(4\text{-}CH_3C_6H_4NC)_2L_3]^+$	+1.205	120.9	1.15	—1.745 —1.930	irr.	1.9
$[FeCl(4\text{-}CH_3OC_6H_4NC)_2L_3]^+$	+1.149	107.5	1.10	—1.701	140.4	2.25
$[FeCl(2\text{-}CH_3C_6H_4NC)_2L_3]^+$	+1.242	99.9	0.98	—1.900	207.9	2.2
$[FeCl(C_6H_5NC)_2L_3]^+$	+1.223	92.0	0.95	—1.828	148.1	1.80
$[FeBr(4\text{-}CH_3C_6H_4NC)_2L_3]^+$	+1.190	94.9	1.01	—1.826	207.3	2.3
$[FeI(4\text{-}CH_3C_6H_4NC)_2L_3]^+$	+1.075	66.5	0.90	—1.733	213.1	2.2
$[Fe(C_6H_{11}NC)_3L_3]^{2+}$	+1.904	62.4	0.97	—1.766	95.4	1.8

[a] $L = PhP(OEt)_2$. [b] Anodic wave; $E_{1/2}$ in volts measured vs. reference electrode in DCM at 293 K, 0.1 mol dm^{-3} TBAP. [c] Slope in millivolts. [d] $R = i_L/i_R$ in relative height of peak current vs. reference compounds, working electrode has diameter 1 mm, scan rate $v = 0.0058$ V s^{-1}, $\omega = 14$ rad s^{-1}. [e] Cathodic wave.

From Table 1 it is evident that while in the case of reduction waves the process is totally irreversible, in the case of oxidation of compounds with R = 2,6-dimethylphenyl, cyclohexyl and iodo-derivative the electrode process is quasi reversible. Comparison of the limiting currents of the complexes with the reference compound indicates that the oxidation process corresponds to a one-electron exchange, while two electrons are exchanged upon reduction in the voltammetric time scale.

Cyclic voltammetry

Using a platinum wire electrode as the working microelectrode enable us to examine the redox behaviour of the compounds under study within the range +1.8 to −2.5 V. Cyclic voltammograms (Fig. 1) show one redox couple in the range of the half-wave potential of the RDE oxidation voltammetric curves (Fig. 1; curve a). In the range of the RDE reduction voltammetric curves a reduction peak was observed, the height of which was twice the height of the corresponding oxidation peak (Fig. 1, peak b). In addition to this reduction peak, the cyclic voltammogram shows two oxidation peaks (Fig. 1, peaks c and d). Values of E_p and ΔE_p taken from cyclic voltammograms are given in Table 2. In the case of the redox couple at more positive potentials, i.e. peak a, the ratio of anodic to cathodic currents is equal to one and shows no change with increased scan rate. Values of ΔE_p indicate a quasi-reversible electron transfer process. ΔE_p increases with increasing scan rate in accord with theory [12]. In the range of negative potentials at scan rate of 100 V s^{-1} the height of peak b was lower than that of the original peak; at the same time the peaks c and d increase.

Overall, the voltammograms obtained using the multi mode were analogous

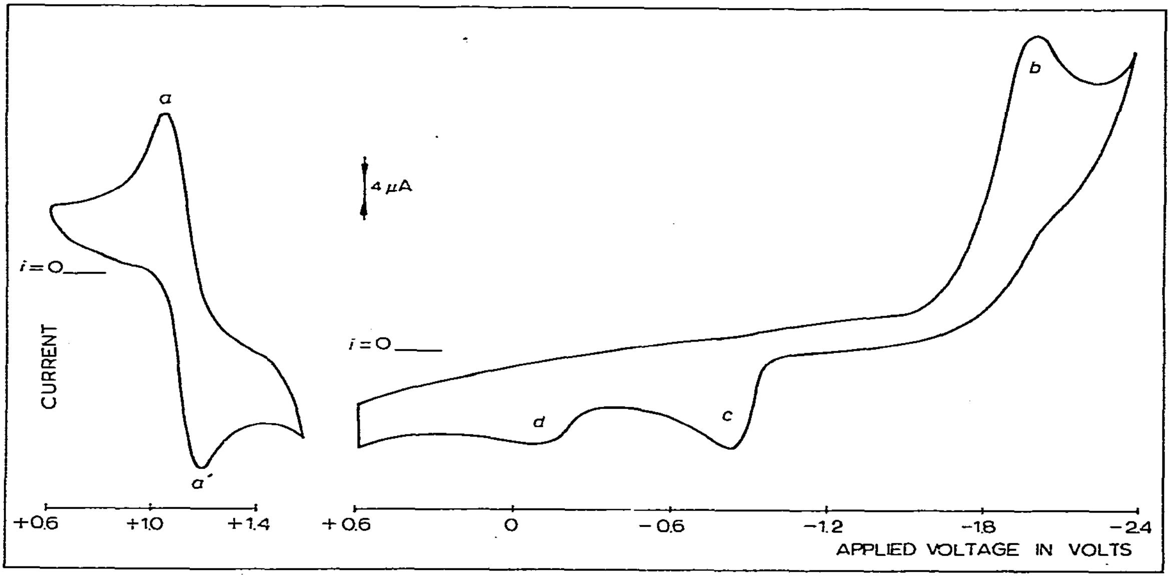


Fig. 1. Cyclic voltammogram (mode single) of $[FeCl(CNR)_2L_3]^+$ (R = 4-$CH_3OC_6H_4$) in DCM (0.1 mol dm^{-3} TBAP) at a stationary platinum electrode. Scan rate v = 0.1957 V s^{-1}. Temperature 293 K.

TABLE 2

CYCLIC VOLTAMMETRY DATA AT A PLATINUM STATIONARY ELECTRODE

Compounds [a]	$(E_p)_a$ [b]	$(E_p)_c$	ΔE_p	$(E_p)_a$	$(E_p)_c$	ΔE_p	$(E_p)_c$
$[FeCl\{2,6\text{-}(CH_3)_2C_6H_3NC\}_2L_3]^+$	1.190	+1.085	0.105	—0.830	—0.960	0.130	—1.700 —1.950
$[FeCl(4\text{-}CH_3C_6H_4NC)_2L_3]^+$	1.070	+1.240	0.170	—0.770	—0.970	0.200	—1.670 —1.900
$[FeCl(4\text{-}CH_3OC_6H_4NC)_2L_3]^+$	1.030	+1.190	0.160	—0.80	—0.970	0.170	—2.00
$[FeCl(2\text{-}CH_3C_6H_4NC)_2L_3]^+$	1.210	+1.085	0.125	—0.750	—0.970	0.220	—1.900
$[FeCl(C_6H_5NC)_2L_3]^+$	1.230	+1.120	0.110	—0.750	—0.880	0.130	—1.850
$[FeBr(4\text{-}CH_3C_6H_4)_2L_3]^+$	1.215	+1.105	0.110	—0.760	—1.000	0.240	—1.870
$[FeI(4\text{-}CH_3C_6H_4)_2L_3]^+$	1.050	+0.930	0.120	—0.780	—0.950	0.170	—1.850
$[Fe(C_6H_{11}NC)_3L_3]^{2+}$	1.903	+1.798	0.105	—0.950	—1.170	0.220	—1.810

[a] $L = PhP(OEt)_2$. [b] E_p measured in volts vs. reference electrode in DCM 0.1 mol dm^{-3} TBAP; scan rate v = 0.098 V s^{-1}; temperature 293 K.

to the cyclic voltammograms obtained during large scale electrolysis and stepwise recording of the voltammograms in the single mode (see Fig. 2). Oxidation peaks c and d (Fig. 1) refer to the products of electrode reduction of the species at peak b. When the potential is reversed before reduction peak b, no oxidation peaks are observed. When reversing the potential in a range where the reduction proceeds (peak b), peak b′ and the corresponding reduction peak b″ (Fig. 2) appear.

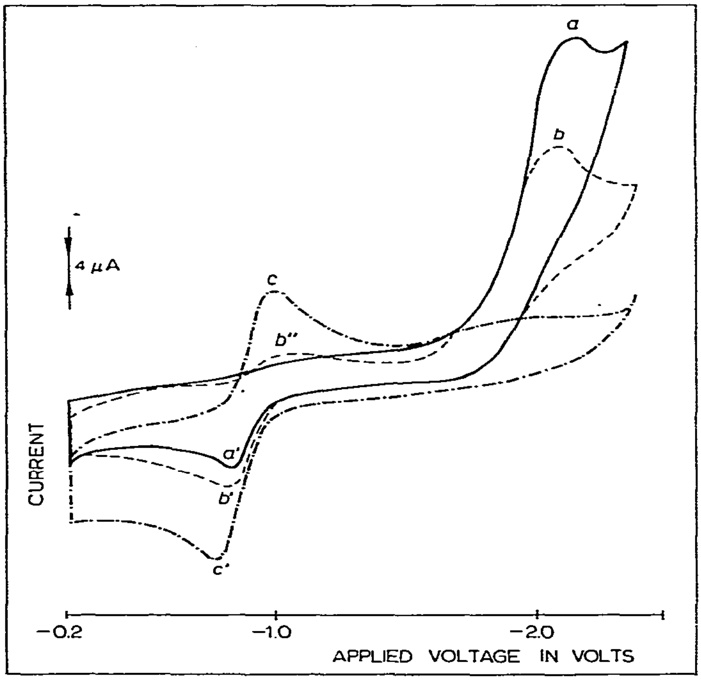


Fig. 2. Cyclic voltammogram (mode single) of $[FeCl(CNR)_2L_3]^+$ (R = $4\text{-}CH_3OC_6H_4$) in DCM (0.1 mol dm^{-3} TBAP) at stationary platinum electrode obtained during the electrolysis at constant potential —2.0 V. Curve a = before electrolysis; Curve b = in the course of electrolysis; Curve c = after electrolysis.

Polarography

The compounds under study were reduced at a dropping mercury electrode in DCM (0.1 mol dm^{-3} TBAP) in one step. The limiting current of this reduction step is diffusion controlled and depends linearly on the concentration in the range $1 \times 10^{-4} : 1 \times 10^{-2}$ mol dm^{-3}. Polarographic data are summarized in Table 3. Values of the half-wave potential are slightly more positive than those at the platinum RDE, and in the case of bromo and cyclohexyl derivatives (polarographic waves) they exhibit current maxima.

Comparison of diffusion current constants for the complexes with those of the reference compound again indicate the transfer of two electrons in the reduction step. Values of slopes of polarographic waves confirm the polarographic irreversibility of the reduction process.

Kalousek commutator technique

The Kalousek commutator technique was used to study the products of the electrode processes. Three oxidation waves were observed on the commutated polarographic wave.

The polarogram gives information analogous to that from the cyclic voltammogram; all the products of the electrode processes are oxidized at the DME in irreversible steps. The half-wave potential of the first oxidation wave corresponds to peak c (Fig. 1) in the cyclic voltammograms and varies slightly with change in R in the ligand CNR. The second oxidation wave, with a constant half-wave potential (next OV) for the series of complexes, corresponds to peak d (Fig. 1). All the complexes, including the cyclohexyl derivative, gave similar commutated polarographic waves.

Thus, the possibility of cleavage of halogen (ligand X) from the coordination sphere of the complex could be excluded. This result was confirmed when the anodic waves of the iodo-derivative were compared with that of a reference compound [13]. Two polarographic oxidation waves of the reference compound with $E_{1/2} = -0.45$ and +0.05 V belong to the oxidation of iodide and

TABLE 3

POLAROGRAPHIC DATA

Compounds [a]	$E_{1/2}$ [b]	Slope [c]	i_d/c [d]
$[FeCl\{2,6\text{-}(CH_3)_2C_6H_3NC\}_2L_3]^+$	−1.785	90	1.84
	−1.520	—	—
$[FeCl(4\text{-}CH_3C_6H_4NC)_2L_3]^+$	−1.790	99	1.60
	−1.540	—	—
$[FeCl(4\text{-}CH_3OC_6H_4NC)_2L_3]^+$	−1.770	133	1.88
$[FeCl(2\text{-}CH_3C_6H_4NC)_2L_3]^+$	−1.693	182	1.72
$[FeCl(C_6H_5NC)_2L_3]^+$	−1.660	123	1.68
$[FeBr(4\text{-}CH_3C_6H_4NC)_2L_3]^+$	(−1.630)	max.	2.00
$[FeI(4\text{-}CH_3C_6H_4NC)_2L_3]^+$	−1.477	193	1.60
$[Fe(C_6H_{11}NC)_3L_3]^{2+}$	(−1.605)	max.	1.60
$[Cr(C_6H_5)_2]^+$	−0.860	60	0.82

[a] L = $PhP(OEt)_2$. [b] $E_{1/2}$ in volts measured vs. reference electrode in DCM at 293 K, 0.1 mol dm^{-3} TBAP for cathodic wave. [c] Slope of polarographic wave in millivolts. [d] Diffusion current constant in A $mmol^{-1}$. (max = current maximum, $E_{1/2}$ in brackets are apparent).

tri-iodide, respectively, under our conditions. No such waves were found in the commutated polarograms in the case of the iodo-derivative.

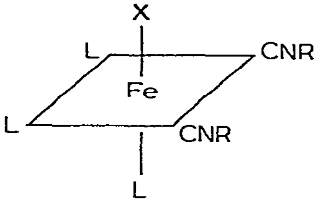
Large scale electrolysis

Electrolysis was carried out at platinum plate and at mercury pool electrodes in order to determine the end products of the electrode processes. Figure 2 shows the course of the electrolysis on platinum at a constant potential corresponding to peak b (Fig. 1). During electrolysis peak b decreases and a new redox couple appears, with the ratio i_a/i_c equal to one. The height of the new reduction peak corresponds to half that of the original reduction peak b (see Fig. 2, curve c).

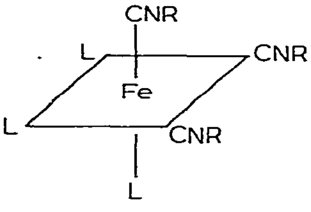
The course of the electrolysis at a mercury pool electrode is analogous to that at platinum. Polarograms taken during electrolysis at a constant potential are identical with commutated polarograms under the same conditions. The main product of the electrolysis decomposed after being kept under argon for several hours.

Discussion

It is well known that hexacoordinate complexes of the type $[FeX(CNR)_2L_3]^+$ can exist in several isomeric configurations, which are present in equilibrium. The energetic differences between stereoisomers determines which is the most stable under a given set of conditions. On the basis of experimental data reported in previous papers [1,2] it was deduced that the starting material with composition $[FeX(CNR)_2L_3]^+$ exists in CH_2Cl_2 solution mainly as a monomer with the isomeric configuration denoted as *fac(cis), X-axial* (see a). This means that the ligands L are in a facial (*fac*) configuration, the ligands CNR are in a *cis* disposition and ligand X is on the *Z*-axis of the octahedron. In the case of R = cyclohexyl, we obtained the complex $[Fe(CNR)_3L_3]^{2+}$ in which the most stable configuration is facial (see b). These two isomers are the most stable in respect of the electronic configuration of the complexes, which are diamagnetic with the central atom in a formal oxidation state II. Reduction of the starting material proceeds via a two-electron step. It can be assumed that the initial reduction product has the same configuration as the starting material, i.e. *fac(cis), X-axial*, while the voltammetric irreversibility of the reduction process at a platinum electrode and the total polarographic irreversibility at the DME may indicate an instability in the primary product of the electrode reaction. A subsequent chemical reaction must be very rapid under the given conditions relative to the voltammetric time scale, because of the very low stability of hexacoordi-



a



b

nate species with iron in a formal oxidation state of 0. Increased electron density at the metal center appears to facilitate loss of ligands as a mechanism for decreasing electron density at the metal [15]. The stable product resulting from this structural change can be oxidized in a one-electron step (peak c, Fig. 1), giving rise to a species with electronic configuration $3d^7$. The observation of an additional oxidation process in both the commutated polarograms and cyclic voltammograms (peak d, Fig. 1) indicates a further oxidation of the species produced in peak c, Fig. 1.

The proposed mechanism of the reduction electrode process can be summarized in the following scheme:

$$\mathrm{Fe^{II}} \xrightarrow{+2e} \mathrm{Fe^{0}} \xrightarrow{k} \mathrm{Fe^{0}} + \mathrm{L} \text{ (peak b)} \tag{1}$$

fac(cis) *fac(cis)*

$$\mathrm{Fe^{0}} \xrightarrow{-1e} \mathrm{Fe^{I}} \text{ (peak c)} \tag{2}$$

($\mathrm{L} = \mathrm{PPh(OEt)_2}$ or CNR)

To confirm the suggested mechanism we carried out experiments at low temperature. Figure 3 is a cyclic voltammogram taken at 198 K at a rapid scan rate. In comparison with Fig. 1, it can be seen that instead of the original irreversible peak b (Fig. 1), an associated redox couple appears (Fig. 3, peaks a and b). The decrease in temperature significantly influences the subsequent chemical reaction involving loss of a ligand (L); however, even under these conditions the chemical reaction is so fast that only a partial reoxidation of the primary product is seen.

The experimental data indicate that oxidation of the species $[\mathrm{FeX(CNR)_2L_3}]^+$ at a platinum electrode in DCM is a simple reversible process (eq. 3) without complications from chemical reactions on the voltammetric time scale. Oxidation proceeds in one step by exchange of one electron and is characterized by a rapid electron transfer reaction. On the voltammetric time scale no change in composition or isomeric configuration were observed. With

$$\mathrm{Fe^{II}} \underset{+1e}{\overset{-1e}{\rightleftharpoons}} \mathrm{Fe^{III}} \tag{3}$$

fac(cis) *fac(cis)*

regard to the simple electron transfer mechanism the experimental data may be convenient for correlation purposes. The data given in Tables 1 and 2 indicate that $E_{1/2}$ and E_p depend on the composition of the iron complex. Only variations in α (transfer coefficient) can have a significant influence on the correlations because of variations of the steric environment in the transition states during charge transfer reaction caused by the changes in structure near the reaction center. Our experimental data indicate that the half-wave potential depends to some extent on the substituent R in the CNR ligand for given X and L. Oxidation seems to be facilitated when electron-donating groups are present and this is in agreement with results in the case of analogous cobalt compounds [3]. Dependence of the oxidation half-wave potential on X at constant L and

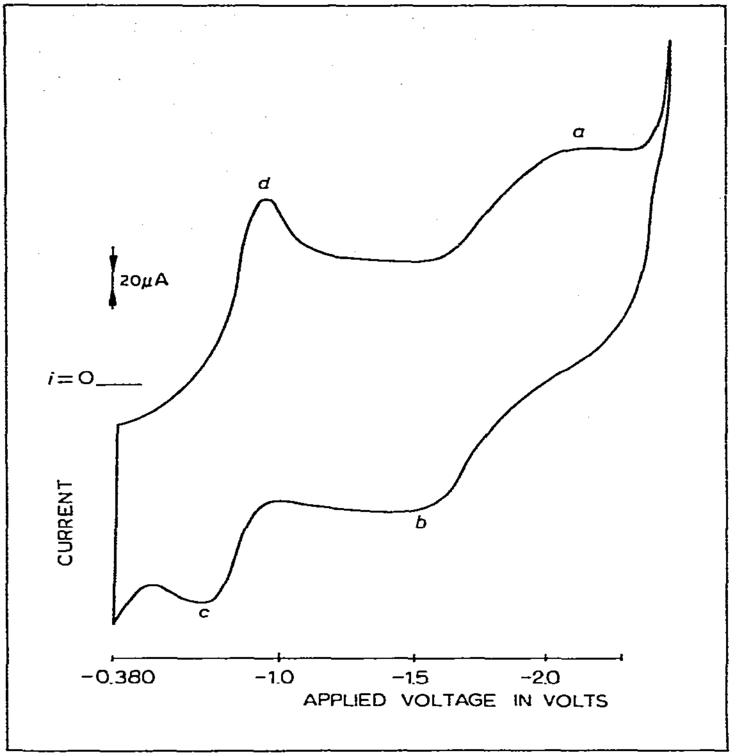


Fig. 3. Cyclic voltammogram (mode multi) of $[FeCl(CNR)_2L_3]^+$ (R = $4\text{-}CH_3OC_6H_4$) in DCM (0.1 mol dm^{-3} TBAP) at a stationary platinum electrode at low temperature (198 K). The reference electrode salt bridge was filled with supporting electrolyte. Scan rate 94.78 V s^{-1}. The voltammogram was recorded by means of sample- and -hold circuit on X-Y recorder.

CNR also seems to be significant. On going from Cl to I, the half-wave potentials move toward more negative potentials, thus facilitating oxidation.

The variations in half-wave potentials can be explained by direct interaction of the substituent (ligand X) with the central metal. In the case of the group CNR the influence of R proceeds through the -NC- functionality, and in our case through the benzene ring. These results indicate that the redox orbital is mainly localized on the metal.

The *fac*-$[Fe(CNR)_3L_3]^{2+}$ derivative is the most stable with respect to oxidation. The half-wave potential for oxidation of this derivative in comparison with that for the other derivatives is about 0.9 V more positive.

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