VOLTAMMETRIC STUDIES OF SOME NOVEL Fe(III) COMPLEXES WITH QUADRIDENTATE LIGANDS. THE AXIAL LIGAND-EXCHANGE REACTIONS IN DMF AND DMSO

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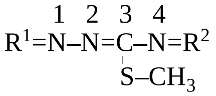
The electrochemistry of four novel Fe(III) complexes of the type [Fe(L)Cl], involving quadridentate ligands based on the condensation products of benzoylacetone-*S*-methylisothiosemicarbazone with salicylaldehyde, 5-chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde or 5-nitrosalicylaldehyde, was studied in DMF and DMSO at a GC electrode. All complexes undergo a two-step one-electron reductions, usually complicated by chemical reactions. In solutions containing Cl^-, the ligand-exchange reactions Cl^-–DMF and Cl^-–DMSO take place. Stability of the chloride-containing complexes was discussed in terms of the coordinated ligand effect, oxidation state of the central atom and, in particular, of the donor effect of the solvent. Some relevant kinetic data were calculated.

Among the numerous ligand-exchange reactions coupled to the processes of electrochemical oxidation and reduction of coordination compounds, those involving ligands in the axial positions are the most frequent. Such reactions have been studied in detail on the example of the Fe(III) and Fe(II) porphyrin complexes in nonaqueous media[1–5]. The Cl^-–DMF ligand exchange reaction served as the basis for a method of determination of the kinetic parameters and association constants of the complex ion and the axial ligand[1,4,5].

Our previous studies on voltammetric behaviour of different Fe(III) and Fe(IV) complexes with *S*-methylisothiosemicarbazide-based ligands in DMF showed that the electron transfer processes are accompanied by numerous chemical reactions of their decomposition[6–9]. Of special interest are the Cl^-–DMF ligand-exchange reactions observed with the quadridentate ligands[7–9].

The complexes studied in the present work, of the general formula [Fe(L)Cl], contain Fe(III) coordinated with the quadridentate ONNO ligands based on *N*(1)-benzoylisopropylidene-*N*(4)-salicylidene-*S*-methylisothiosemicarbazide.



$$\overset{}{R^1}{=}\overset{1}{N}{-}\overset{2}{N}{=}\overset{3}{\underset{\underset{\displaystyle S{-}CH_3}{|}}{C}}{-}\overset{4}{N}{=}R^2$$

R^1 = benzoylisopropylidene
R^2 = salicylidene (H_2L^1)
R^2 = 5-chlorosalicylidene (H_2L^2)
R^2 = 3,5-dichlorosalicylidene (H_2L^3)
R^2 = 5-nitrosalicylidene (H_2L^4)

In all the complexes these ligands are coordinated in their double-deprotonated forms L^1–L^4.

The above-mentioned complexes were studied by a voltammetric method in DMF and DMSO solvents, with a special reference to the ligand-exchange reactions. The rections of replacement of the axial Cl^- by a solvent molecule in an inert medium, and introduction of another Cl^- in the axial position in the presence of an excess of chloride were considered in a view of both the nature of the coordinated ligand L^{2-} and the donor properties of the solvent involved.

EXPERIMENTAL

Chemicals

The complexes were synthesized in our Institute and their purity was checked by elemental analysis[10]. The salts, LiCl and tetrabutylammonium perchlorate TBAP, were recrystallized before use. DMF and DMSO were dried over 4A molecular sieves for two days and distilled two times under the reduced pressure[11]. Only freshly distilled solvents were used. An aqueous solution of $6.2 \cdot 10^{-2}$ M $HClO_4$ was used for titration. Nitrogen for deaeration was purged by passing over copper scraps heated to 450 °C and through two columns filled with 4A molecular sieves.

Electrodes

A glassy carbon disc electrode (AMEL 493, Milan) was used as a working electrode. To ensure its proper functioning, it was polished with the fine alumina suspensions (Buehler Ltd., 0.5 and 0.05 μm). A glassy carbon plate (Sigri Elektrographit 2400, dimensions 1.6 × 2.0 × 0.2 cm) served as a working electrode in a controlled-potential electrolysis and a Pt ring of sufficiently large surface area as a counter electrode. An aqueous saturated calomel electrode SCE, with an asbestos tip (Ingold 303), connected to the solution via a double-junction salt bridge, served as a reference electrode.

Apparatus

An AMEL (Milan) voltammetric setup with the possibility of *iR* drop compensation was employed in all electrochemical experiments. The curves were recorded either on a Hewlett–Packard 7044A x–y recorder, or a Hewlett–Packard 1741A storage oscilloscope.

Electronic spectra were recorded on a Cary 219 spectrophotometer. An addition of $HClO_4$ solution was carried out by an automatic piston burette Radiometer ABU 12.

General Procedure

Solutions of 1 . 10^{-3} mol l^{-1} complexes in the presence of 0.1 mol l^{-1} supporting electrolytes were prepared by weighing the dried substances and dissolving them in a purified and freshly distilled solvent (DMF or DMSO). The purged and presaturated nitrogen was then bubbled through the solution (stirred with a magnetic stirrer) for 1 h, afterwards it was left to pass over the solution.

All experiments were performed at a room temperature, the solutions were thermostated at 25.0 ± 0.2 °C for kinetic measurements only. Peak potentials were determined with an accuracy of ±2 mV.

In all figures the voltammograms are presented with the negative potentials increasing to the left-hand side and with a cross marking the zero-values of the current and potential.

RESULTS AND DISCUSSION

The investigated Fe(III) complexes have in DMF and DMSO solutions an octahedral configuration, in which the organic ONNO ligand is in the meridial plane, and two axial positions are occupied either by solvent molecules or Cl^-. This assumption is based on voltammetric data, as well as on a close analogy of the voltammetric behaviour of the present complexes and the Fe(III) complexes of similar composition and structure[7,8]. A special aspect of the voltammetric behaviour of the present complexes is the Cl^-–DMF (DMSO) ligand-exchange reaction. To study these reactions, the experiments were carried out in the following media: “inert” (TBAP), “chloride-free” (TBAP plus stoichiometric amount of Ag^+, added to bind Cl^- from the complex), and “chloride” (LiCl) medium. What ligand will occupy the axial position depends on both the nature of the supporting electrolyte and donor properties of the solvent, and it will be discussed below.

Inert Medium

Figure 1 illustrates a general pattern of cyclic voltammograms for [Fe(L^1)Cl], for the complex reduction and oxidation in DMF solution containing TBAP.

In the potential range from 0 to –1.5 V, all the complexes are reduced in two one-electron processes corresponding to peaks I′ and III′. Both of them are accompanied by chemical reactions of the complex decomposition. In the potential range from –1.5 to –2.5 V, depending on the nature of the ligand, 2–3 additional peaks appear, that may be ascribed to the reduction processes taking prevailingly place on the ligand moiety. As a consequence of these, mostly irreversible processes, a partial decomposition of the complex takes place, which is evident from the curve in the subsequent anodic scan.

The oxidation of complexes takes place in 2–3 close peaks appearing in the potential range more positive than +1.0 V. They are characteristic for the oxidation of the ligand itself. The loss of 1–2 electrons is accompanied by irreversible chemical reactions. It is indicated by the absence of the reduction peaks and by the changes in the potential range of peaks I′ and III′ in the reverse scan.

Generally similar voltammetric pattern for reduction and oxidation processes of the complexes was recorded in DMSO. However, it should be mentioned that the peak currents are by about 30% lower than the corresponding values registered for DMF solutions. This can be explained in terms of higher viscosity of DMSO, which is directly reflected on the value of the diffusion coefficients and, consequently, on the peak currents.

A more detailed analysis of the reduction processes at peaks I′ and III′ indicates that both involve irreversible chemical reactions (Fig. 1). It is evident that the height (i_p) of peak IV′ is lower than that of peak III′; the ratio i_p(IV′)/i_p(III′) is below 1 for the scan rates $v < 20$ V s^{-1}. At higher scan rates, the baseline becomes very distorted. Besides, in the reverse anodic scan, 1–3 new peaks appear in the range from –0.5 to –1.0 V, whose total height increases up to 15% of i_p(III′) at scan rates $v > 5$ V s^{-1}. These peaks are more pronounced in DMSO, where two additional small peaks at a peak potentials (E_p) of +0.2 and +0.4 V appear. In the same potential range, the current ratios i_p(IV′)/i_p(III′) and i_p(II′)/i_p(I′) are below 1 even at $v = 20$ V s^{-1}. In addition, the slope $\Delta E_p/\Delta\log(v)$ for peak III′ at lower scan rates is about –60 mV per decade in both solvents. These data indicate the chemical reaction of the complex decomposition after the second reduction step.

In the narrower potential range in DMF (Fig. 2) the voltammogram is characterized by a single peak I′, which increases proportionally to $v^{1/2}$. In contrast to this, at lower sweep rates peak II′ is distorted (broadened), whereas at $v > 1$ V s^{-1} a new peak II″ appears. This new peak increases with v up to 15% of i_p(I′), while i_p(II′) decreases. It

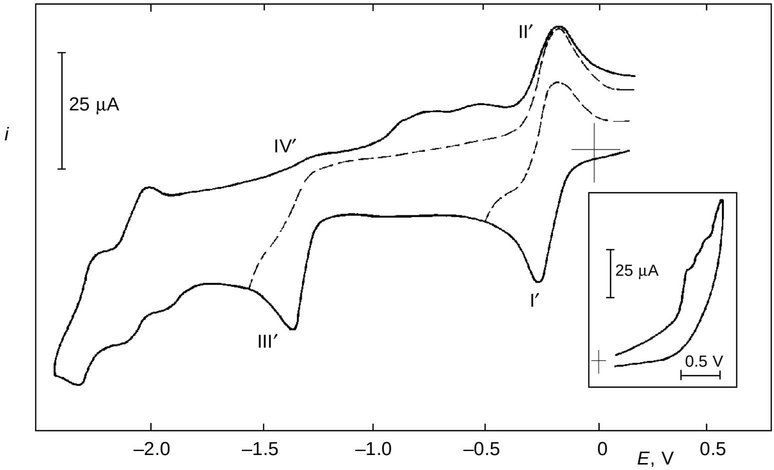


FIG. 1
Cyclic voltammograms, $v = 0.20$ V s^{-1}, for reduction and oxidation (inset) of [Fe(L^1)Cl] in 0.1 M TBAP (DMF)

suggests the occurrence of a kinetic equilibrium according to the equation (*C*) below. Such a behaviour is exhibited by all the investigated complexes, with a tendency of increasing the i_p(II″) value in the series $L^1 \rightarrow L^4$.

In contrast to DMF solutions, the complexes in DMSO in the same potential range behave reversibly, with no presence of peak II″. This suggests a greater stability of the complexes in this solvent.

Chloride-Free Medium

A consecutive addition of small volumes of $AgClO_4$ solution up to the $n(Ag^+)/n(Cl^-)$ ratio 1 : 1, to the dissolved complex in the presence of TBAP in DMF results in withdrawal of Cl^- from the octahedral [Fe(L)(DMF)Cl] molecule and its replacement by another DMF molecule. On the corresponding voltammogram, this results in a new couple of peaks I″/II″ at the potentials more positive by 100–200 mV, whose heights show an increase on the account of a decrease of the existing I′/II′ couple. In the final solution, the newly-formed "chloride-free" complex is stable and the peaks I″/II″ behave reversibly (Fig. 3*a*, curve *2*). The changes in i_p values for peaks I′ and I″ with the increase in $n(Ag^+)/n(Cl^-)$ are not linear (Fig. 3*b*), which is probably a consequence of a kinetic equilibrium involving two complex species.

Peak III′ does not change with the addition of Ag^+, which indicates that the complex species reduced at this potential remains unchanged.

In contrast to the above, a successive addition of small portions of $AgClO_4$ to the complex solution in DMSO (TBAP) to an amount equimolar to the Cl^- content in the complex caused no change in the appearance of the cyclic voltammograms. The main features of both reduction processes remained the same as in TBAP, which indicates

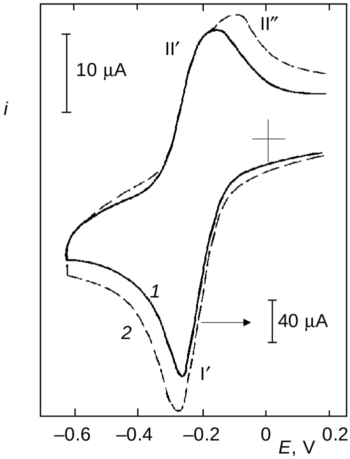


FIG. 2
Cyclic voltammograms for the first reduction of $[Fe(L^1)Cl]$ in 0.1 M TBAP (DMF) at the scan rate of 0.20 V s^{-1} (*1*), 5 V s^{-1} (*2*)

that the chloride in the complex was already replaced by one DMSO molecule. Therefore, the Fe(III) species is present in the form of the $[Fe^{III}(L)(DMSO)_2]^+$ complex, and only its weak ion-pairing with Cl^- can be postulated.

Effect of Cl^-

The addition of Cl^- (LiCl) causes an effect opposite to that mentioned above, as it is shown for $[Fe(L^2)Cl]$ in Fig. 3*a*.

At low Cl^- concentrations (≤ 10 mmol l^{-1}), the potentials of the I′/II′ couple for all the complexes shift to negative direction with the $\Delta E_p/\Delta \log [Cl^-]$ slope of about –40 mV (Fig. 3*c*, curve *1*), whereas at higher Cl^- concentrations E_p potential becomes independent on chloride concentration for all L^1–L^4 ligands. In all cases, the addition of Cl^- results in a decrease of potential difference ΔE_p for couple I′/II′ and of the width of peak II′ (peak II″ disappears) to the values corresponding to a one-electron quasireversible process (peaks I/II). This clearly indicates that these processes in a chloride medium involve the complex species exclusively in their chloride form.

On the other hand, an excess of Cl^- causes a shift of the peak III′ potential to negative direction with a slope ranging from –40 to –60 mV per decade of $[Cl^-]$ for $L^1 \rightarrow L^4$. For

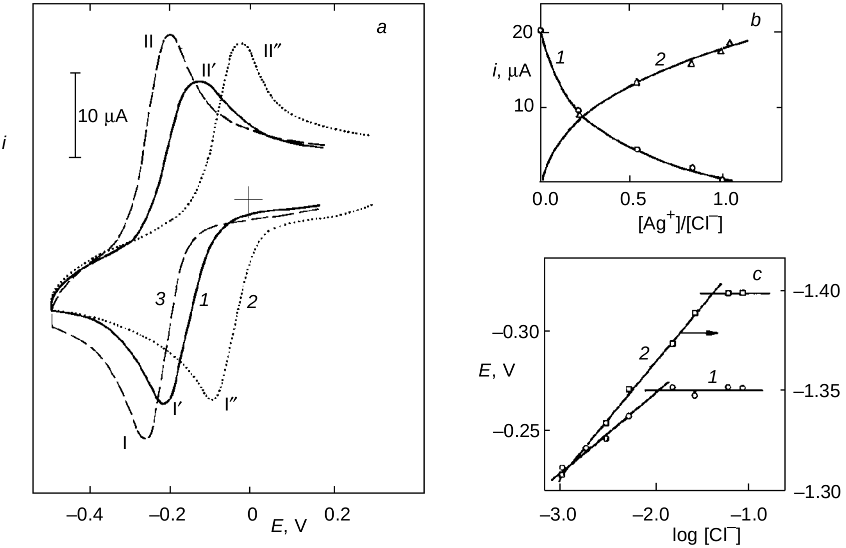


FIG. 3
Effects of Ag^+ and Cl^- on cyclic voltammograms (0.20 V s^{-1}) for 1 mM $[Fe(L^2)Cl]$ in DMF, *a* in 0.1 M TBAP (*1*), after adding 1 mM Ag^+ (*2*), or 84 mM Cl^- (*3*); *b* variation of peak currents with $[Ag^+]$ peak I′ (*1*), peak I″ (*2*); *c* variation of peak potentials with $[Cl^-]$ peak I′ (*1*), peak III′ (*2*), concentration of Cl^- in mol l^{-1}

the complexes with L^3 and L^4 the slope is monotonous in the whole concentration range, whereas for the complexes involving L^1 and L^2 at higher concentrations of Cl^- (>60 mmol l^{-1}) it becomes independent on $[Cl^-]$ as folows from Fig. 3*c*, curve *2*.

An analysis of the slope for E_p(I′) indicates that the reduction of the complex is accompanied by a release of one Cl^- ion from the reacting species. In contrast to this, a decrease in the $\Delta E_p/\Delta\log [Cl^-]$ at $[Cl^-]$ > 10 mmol l^{-1} indicates an increased stability of the reduced dichloride complex involving L^1 and L^2.

As the reduction processes in the presence of an excess of Cl^- are accompanied by a release of one Cl^- ion per reacting entity both at peak I′ and III′, it can be supposed that the dichloride species $[Fe(L)Cl_2]^-$ is formed by the replacement of one DMF molecule with another Cl^- ion. This is also evidenced as a change in the corresponding electronic spectra – the band at 450–465 nm shifts by about 10 nm to higher wavelengths, and the newly-formed band has a molar absorptivity of (1–1.5) . 10^4 l mol^{-1} cm^{-1}, corresponding undoubtedly to d–π^* interactions in the complex.

The situation with DMSO complexes is somewhat different. At a 100-fold excess of chloride (0.1 M LiCl) the shift of potentials of I′/II′ is about 60–80 mV, which suggests formation of a monochloride complex $[Fe^{III}(L)(DMSO)Cl]^0$. On the other hand, peak III′ remains at the same potential as in the above two media, indicating that the same species, i.e. $[Fe^{II}(L)(DMSO)_2]^0$, is involved in all three cases.

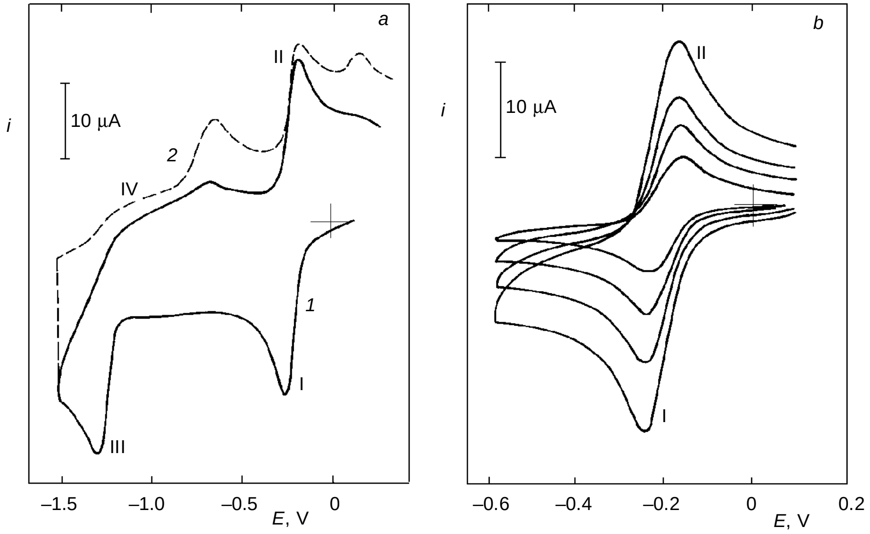


FIG. 4

Cyclic voltammograms for $[Fe(L^3)Cl]$ in 0.1 M LiCl (DMF). *a* At sweep rate 0.20 V s^{-1} (*1*), after holding the electrode at –1.50 V for 25 s (*2*); *b* peaks I/II at sweep rates 0.20, 0.10, 0.05 and 0.02 V s^{-1}

Chloride Medium

In the presence of 0.1 M LiCl (Fig. 4) the cyclic voltammogram is generally similar to that obtained in the presence of TBAP (Fig. 1). The complex anion $[Fe(L)Cl_2]^-$ is reduced in two one-electron processes corresponding to peak couples I/II and III/IV. The first process is apparently uncomplicated (Fig. 4*b*), but chemical complications are obvious after the second reduction, even at high sweep rates.

On the whole, the behaviour of the investigated complexes in this medium is quite similar to that described for Fe(III) complexes with similar quadridentate ligands[7,8]. As a rule, of the four investigated complexes those involving L^1 and L^2 on the one hand, and L^3 and L^4 on the other, have similar voltammetric characteristics. The I/II peaks for L^1 and L^2 have the characteristics of a quasireversible electron transfer followed by the first-order irreversible chemical reaction and the slope $\Delta E_p/\Delta \log(v)$ has three distinct segments: –20 mV ($v < 0.2$ V s^{-1}), 0 mV ($0.2 < v < 2$ V s^{-1}), and –30 mV ($v > 2$ V s^{-1}). With the L^3 and L^4 complexes at $v > 5$ V s^{-1} the baseline beyond peak I is deformed and the peak looks more like a polarographic wave. At the same time, the potential of this peak is markedly shifted, so that the $\Delta E_p/\Delta \log(v)$ for $v \leq 0.2$ V s^{-1} is about –20 mV, and at higher scan rates increases up to –60 mV. However, even at higher sweep rates, the anodic peak retains its shape, and the $\Delta E_p/\Delta \log(v)$ for $v < 2$ V s^{-1} is about 10 mV. As this is observed only in a medium containing an excess of chloride, it is probable that such a behaviour is a consequence of introducing another Cl^- ion in the axial position of the complex. With the complexes containing electrophilic substituents in the meridial plane (L^2–L^4), the electronation process induces certain electrostatic interactions with the chloride in axial position, which hinders stabilization of the reduced species.

The cyclic voltammograms of complexes recorded for DMSO solutions in the presence of 0.1 M LiCl are generally similar to those presented in Fig. 4. The first peak couple I/II is characteristic of a quasireversible electron transfer followed by a chemical reaction. Depending of the scan rate, the slope $\Delta E_p/\Delta \log(v)$ has three distinct segments: –20 mV ($v \leq 0.2$ V s^{-1}), –10 mV ($0.20 < v < 2.0$ V s^{-1}) and –30 mV ($v > 5$ V s^{-1}). Therefore, it can be supposed that the chemical reaction following the electron transfer at peak I is most probably the release of Cl^-. As the process at peak III takes place at the same potential as in the presence of TBAP, the mechanism of this process should also be identical.

To illustrate the correlation between the reduction processes and the nature of the ligand, the potentials of peaks I and III for all three investigated media in both solvents are schematically presented in Fig. 5. As can be seen, the potentials for peak I are within a range of 80 mV (LiCl) to 120 mV (TBAP + Ag^+), while potentials for peak III are within 200 mV in all three media. Having in mind the sequence of the potentials within the series of complexes $L^1 \rightarrow L^4$, it is obvious that the introduction of an electrophilic substituent into the benzene ring makes reduction of the complex easier, especially as the addition of the second electron is concerned.

In Tables I and II are presented the voltammetric characteristics of four investigated complexes in LiCl in the two solvents. All the parameters are similar for the corresponding complexes in both solvents, except for the peak current functions, which are by 30% lower for the DMSO solutions, as explained before. It should be noted that, due to the ion-pairing with Li^+, the multielectron reduction of the L^4 complex is much

TABLE I
Cyclic voltammetric data for Fe(III) complexes obtained in the presence of 0.1 M LiCl in DMF

Complex	v, V s^{-1}	E_p, V			$i_p/c\ v^{1/2,a}$		i_p(II)/i_p(I)
		I	II	III	I	III	
$[Fe(L^1)Cl]$	0.02	–0.288	–0.227	–1.425	56.8	59.1	0.92
	0.20	–0.308	–0.218	–1.490	54.6	56.1	0.96
$[Fe(L^2)Cl]$	0.02	–0.262	–0.193	–1.352	54.0	54.0	1.00
	0.20	–0.275	–0.187	–1.419	53.9	52.6	0.97
$[Fe(L^3)Cl]$	0.02	–0.220	–0.158	–1.270	49.6	49.6	1.00
	0.20	–0.236	–0.152	–1.330	49.8	48.4	1.00
$[Fe(L^4)Cl]$	0.02	–0.217	–0.149	i.d.[b]	48.4	i.d.[b]	0.98
	0.20	–0.234	–0.143	~–1.28	48.4	159.8	1.00

[a] In μA $mmol^{-1}$ l $V^{-1/2}$ $s^{1/2}$; [b] ill-defined peak.

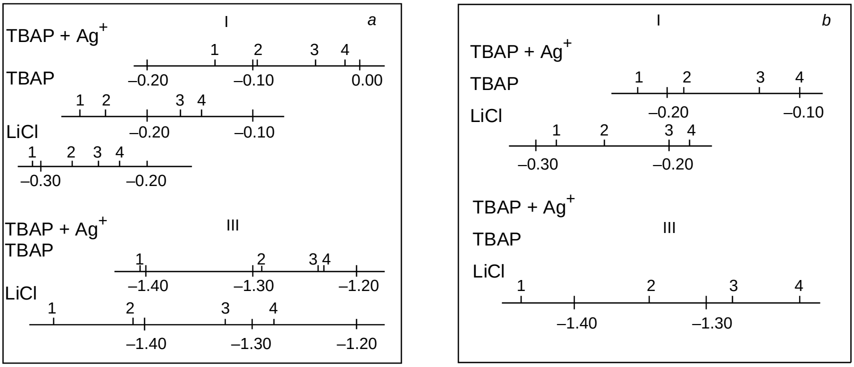


FIG. 5
Peak potentials in V, at scan rate of 0.20 V s^{-1}, for the first (I) and second (III) reduction of L^1–L^4 complexes (numbers 1–4) in three electrolytes in DMF (*a*) and DMSO (*b*)

easier, so that the corresponding peak almost overlaps with peak III. Hence, the determination of peak III potential for this complex, especially in DMF, is rather uncertain. The reduction at peak III is followed by a fast irreversible chemical reaction of the complex decomposition. It is evident from the $\Delta E_p/\Delta \log (v)$ slope of about –60 mV at lower *v*, from a decrease or even absence of the corresponding oxidation peak IV, and from the appearance of the new oxidation peaks (Fig. 4*a*). These new peaks (at about –0.6 and +0.2 V) are especially pronounced after holding the electrode potential beyond peak III (Fig. 4*a*, curve *2*), which is accompanied by a decrease in peak II. These data indicate the complexity of the degradation processes of $[Fe(L)(DMF)Cl]^{2-}$, which most probably involves decomposition of the ligand itself. This is also confirmed by the unsuccessful electrochemical regeneration of the starting complex after the reduction at potential of peak III. An additional problem represents the blocking of the electrode surface at the potential of about –0.6 V by adsorption of some ligand decomposition products. On the other hand, the appearance of new peaks at +0.4 V and at about –0.8 V, characteristic for oxidation of the reduced Fe(III) complexes with the terdentate benzoylacetone *S*-methylisothiosemicarbazone[10], suggests that partial decomposition of the complex proceeds via elimination of the salicylaldehyde fragment from the condensated ligand molecule.

TABLE II
Cyclic voltammetric data for Fe(III) complexes obtained in the presence of 0.1 M LiCl in DMSO

Complex	v, V s^{-1}	E_p, V			$i_p/c\ v^{1/2,a}$		i_p(II)/i_p(I)
		I	II	III	I	III	
$[Fe(L^1)Cl]$	0.02	–0.269	–0.211	–1.392	35.1	41.2	1.00
	0.20	–0.285	–0.208	–1.447	34.3	40.6	0.96
$[Fe(L^2)Cl]$	0.02	–0.226	–0.171	–1.288	31.8	34.6	0.96
	0.20	–0.248	–0.166	–1.344	32.4	33.8	0.96
$[Fe(L^3)Cl]$	0.02	–0.184	–0.124	–1.222	35.8	36.7	1.00
	0.20	–0.200	–0.119	–1.282	36.5	38.1	0.95
$[Fe(L^4)Cl]$	0.02	–0.169	–0.106	–1.166	35.5	46.0	0.97
	0.20	–0.185	–0.101	–1.220	34.6	45.5	0.96

[a] In μA mmol^{-1} l V$^{-1/2}$ s$^{1/2}$.

MECHANISM OF ELECTRODE REACTIONS IN DMF

As it was already mentioned, the processes corresponding to peak couples I/II are followed by the Cl^-–DMF ligand-exchange reaction, which is the more pronounced the lower is the Cl^- concentration. In the presence of TBAP, the first-order reaction rate constant k_1 for the release of the first Cl^- is about 10 s^{-1}. This was determined at $v_i = 0.5$ V s^{-1}, i.e. the scan rate corresponding to the intersection of linear segments of the E_p/log (v) curve[12], for the majority of complexes. In the presence of 0.1 M LiCl this constant is about 4 s^{-1} ($v_i \approx 0.10$–0.20 V s^{-1}).

With no Cl^- added to the solution, the first reduction processes are described by Eqs (*A*)–(*C*). Equation (*A*) is in presence of TBAP + Ag^+ (peaks I″/II″),

$$[Fe^{III}(L)(DMF)_2]^+ + e \rightleftharpoons [Fe^{II}(L)(DMF)_2]^0 \qquad (A)$$

while Eq. (*B*) in presence of TBAP (peaks I′/II′)

$$[Fe^{III}(L)(DMF)Cl]^0 + e \rightleftharpoons [Fe^{II}(L)(DMF)Cl]^- \qquad (B)$$

$$[Fe^{II}(L)(DMF)Cl]^- + DMF \underset{k_a}{\overset{k_d}{\rightleftharpoons}} [Fe^{II}(L)(DMF)_2]^0 + Cl^- . \qquad (C)$$

Reaction (*C*) represents the kinetic equilibrium (characterized by $K_1^{II} = k_a/k_d$) involving two Fe(II) complex species. Hence, when lower scan rates are applied, the complex is oxidized prevailingly in its chloride form (peak II′). At moderate scan rates ($0.20 < v < 5$ V s^{-1}), the i_p of the oxidation peak II″, involving $[Fe^{II}(L)(DMF)_2]^0$, increases up to 15% of that corresponding to the total concentration of the complex. Finally, at $v > 10$ V s^{-1}, the effect of reaction (*C*) disappears, and the complex is again oxidized entirely at peak II′.

After oxidation, the chloride-free species is transformed into the starting reactant by the following ligand-exchange reaction.

$$[Fe^{III}(L)(DMF)_2]^+ + Cl^- \overset{K_1^{III}}{\rightleftharpoons} [Fe^{III}(L)(DMF)Cl]^0 + DMF \qquad (D)$$

For the sake of simplicity, we shall omit partial constants k_a and k_d and use only the corresponding equilibrium constants K, representing the ratio k_a/k_d.

On the basis of the above reactions we can postulate Scheme 1.

To calculate K_1^{II} and K_1^{III} in reactions (*C*) and (*D*) it is necessary to know the E^0 values for the complexes in the chloride and chloride-free media. In the chloride-free medium, the complex exhibits a reversible behaviour in a wide range of scan rates, and the mean value of the potential $(E_p^a + E_p^c)/2 = E^{0\prime}$ can be taken instead of E^0. With the monochloride species, however, several difficulties arise, so that the corresponding calculations are only approximate. First of all, although the complexes in TBAP are originally present in their monochloride form, the existence of a chloride-free species in the solution (though indiscernible on the reduction peaks) cannot be neglected. In addition, because of fast dissociation (*C*), a reversible behaviour of the monochloride species at moderate scan rates cannot be registered. Finally, at higher scan rates the electron transfer process is apparently irreversible, so that the calculations are not possible. Although at the complex/chloride ratio of 1 : 2 (chloride concentration of 2 mmol l^{-1}) peak II″ disappears, and the first two difficulties are apparently eliminated, the possibility of the existence of dichloride species causes the $E^{0\prime}$ values to be considered only as the conditional ones.

By substituting the corresponding $E^{0\prime}$ values into Eq. (*1*)

$$\frac{E^{0\prime}_{\mathrm{Cl}} - E^{0\prime}_{\mathrm{DMF}}}{0.059} = \log \frac{K_1^{\mathrm{II}}}{K_1^{\mathrm{III}}} \qquad (1)$$

we obtain the $K_1^{\mathrm{III}}/K_1^{\mathrm{II}}$ values presented in Table III.

The ratio $K_1^{\mathrm{III}}/K_1^{\mathrm{II}}$ for particular complexes reflects the relative affinities of Fe(III) and Fe(II) species toward Cl^- in the axial position. The obtained values increase in the series $L^1 \rightarrow L^4$, which indicates a decreasing stability of the Fe(II) monochloride species in comparison to the Fe(III) complexes containing ligands with electrophilic substituents. On the other hand, the obtained values of $K_1^{\mathrm{III}}/K_1^{\mathrm{II}}$ for the L^4 complex indicate a pronounced instability of the monochloride complex after its reduction at peak I′, caused by the presence of the strong electrophilic NO_2 group on the benzene ring.

Unfortunately, the determination of individual values of the above equilibrium constants was not possible because of the lack of a suitable independent method. Spectrophotometric method[1] was not applicable because the charge-transfer band at 450 nm, characteristic for Fe(III) complex, is partly overlapped with the main band. Thus, the shift of the monochloride complex band in the presence of TBAP to higher wavelengths, amounting to about 5–10 nm, could be determined with a great uncertainty.

$$\begin{tikzcd}
E^{0\prime}_{\mathrm{DMF}} & {[\mathrm{Fe^{III}(L)(DMF)_2}]^+ + \mathrm{Cl}^-} \arrow[r, rightleftharpoons, "K_1^{\mathrm{III}}"] \arrow[d, rightleftharpoons, "+\mathrm{e}"', "-\mathrm{e}"] & {[\mathrm{Fe^{III}(L)(DMF)Cl}]^0 + \mathrm{DMF}} \arrow[d, rightleftharpoons, "+\mathrm{e}"', "-\mathrm{e}"] & E^{0\prime}_{\mathrm{Cl}} \\
 & {[\mathrm{Fe^{II}(L)(DMF)_2}]^0 + \mathrm{Cl}^-} \arrow[r, rightleftharpoons, "K_1^{\mathrm{II}}"] & {[\mathrm{Fe^{II}(L)(DMF)Cl}]^- + \mathrm{DMF}} &
\end{tikzcd}$$

SCHEME 1

The presence of an excess of Cl^- ions (LiCl) yields the dichloride species

$$[Fe^{III}(L)(DMF)(Cl)]^0 + Cl^- \overset{K_2^{III}}{\rightleftharpoons} [Fe^{III}(L)Cl_2]^- + DMF \qquad (E)$$

which is reduced at peak I

$$[Fe^{III}(L)Cl_2]^- + e \rightleftharpoons [Fe^{II}(L)Cl_2]^{2-} . \qquad (F)$$

The stability of the obtained dianion is dependent on the chloride concentration in the solution.

$$[Fe^{II}(L)Cl_2]^{2-} + DMF \overset{K_2^{II}}{\rightleftharpoons} [Fe^{II}(L)(DMF)Cl]^- + Cl^- \qquad (G)$$

In the case of the L^4 complex, it can be postulated that a further slow dissociation (*C*) may occur due to a lower affinity toward Cl^- ions.

For the complexes in chloride medium we can write Scheme 2 which, via an equation analogous to Eq. (*1*), enables the determination of the K_2^{III}/K_2^{II} ratio.

To determine the potential $E^{0'}_{2Cl}$ we used the potentials of peaks I/II at the scan rates 0.05–0.50 V s^{-1} in a medium containing 20 mM Cl^-. An increase of the scan rate at higher Cl^- concentrations resulted in a certain decrease of reversibility, especially with the L^3 and L^4 complexes. As it was already mentioned, the explanation may be due to the electrostatic interaction of two axial Cl^- ions and the coordinated ligand containing a strong electrophilic substituent.

TABLE III
Values for reversible potentials and ratios of equilibrium constants for the first reduction process of Fe(III) complexes in DMF and DMSO. Reversible potentials are expressed as $E^{0'} = (E_p^a + E_p^c)/2$ for the complexes in DMF: TBAP + Ag^+ ($E^{0'}_{DMF}$), TBAP + 2 mM Cl^- ($E^{0'}_{Cl}$) and TBAP + 20 mM Cl^- ($E^{0'}_{2Cl}$); in DMSO: TBAP ($E^{0'}_{DMSO}$), and 0.1 M LiCl ($E^{0'}_{Cl}$). The equilibrium constants for the processes defined by Eqs (*C*), (*D*), (*E*) and (*G*)

Complex	Solvent	$E^{0'}_S$, V	$E^{0'}_{Cl}$, V	$E^{0'}_{2Cl}$, V	K_1^{III}/K_1^{II}	K_2^{III}/K_2^{II}
$[Fe(L^1)Cl]$	DMF	–0.103	–0.230	–0.267	142.1	4.2
	DMSO	–0.180	–0.246	–	13.1	–
$[Fe(L^2)Cl]$	DMF	–0.061	–0.194	–0.230	179.6	4.1
	DMSO	–0.144	–0.207	–	11.7	–
$[Fe(L^3)Cl]$	DMF	–0.005	–0.139	–0.188	186.8	6.8
	DMSO	–0.081	–0.160	–	21.8	–
$[Fe(L^4)Cl]$	DMF	+0.037	–0.123	–0.184	515.1	10.8
	DMSO	–0.058	–0.142	–	26.5	–

As in the case of similar Fe(III) complexes[7], the obtained ratios K_2^{III}/K_2^{II} are much lower than the corresponding K_1^{III}/K_1^{II} values obtained for the monochloride complexes. This means that the stability of dichloride complexes in chloride medium does not depend significantly on the oxidation state of the central atom.

$$\begin{tikzcd}
E^{0'}_{\mathrm{Cl}} & {[\mathrm{Fe^{III}(L)(DMF)Cl}]^0 + \mathrm{Cl}^-} \arrow[r, shift left, "K_2^{III}"] \arrow[d, shift right, "+\mathrm{e}"'] & {[\mathrm{Fe^{III}(L)Cl_2}]^- + \mathrm{DMF}} \arrow[l, shift left] \arrow[d, shift right, "+\mathrm{e}"'] & E^{0'}_{2\mathrm{Cl}} \\
 & {[\mathrm{Fe^{II}(L)(DMF)Cl}]^- + \mathrm{Cl}^-} \arrow[u, shift right, "-\mathrm{e}"'] \arrow[r, shift left, "K_2^{II}"] & {[\mathrm{Fe^{II}(L)Cl_2}]^{2-} + \mathrm{DMF}} \arrow[l, shift left] \arrow[u, shift right, "-\mathrm{e}"'] &
\end{tikzcd}$$

SCHEME 2

Second-Reduction Processes

The reduction at the potentials of peaks III/IV, III′/IV′ is followed by fast decomposition of the reduced complex, in a consequence of the electron transfer taking place prevailingly on the ligand.

An identical position of the second reduction peak for all the complexes in TBAP and chloride-free (TBAP + Ag^+) medium indicates that in both cases the process involves the same species, containing no Cl^-. Therefore, the complex reduced at peak III′ is formed either by reaction (*A*) or by reactions (*B*) and (*C*). The reduction can be presented as follows.

$$[\mathrm{Fe^{II}(L)(DMF)_2}]^0 + \mathrm{e} \rightleftharpoons [\mathrm{Fe^{I}(L)(DMF)_2}]^- \qquad (H)$$

$$[\mathrm{Fe^{I}(L)(DMF)_2}]^- \longrightarrow \text{products} \qquad (I)$$

The rate constant k_2 cannot be calculated from the voltammetric data because the complexes did not show reversible behaviour at the scan rates employed.

In a chloride medium at the potential of peak III the monochloride species formed by reaction (*G*) is reduced (*J*).

$$[\mathrm{Fe^{II}(L)(DMF)Cl}]^- + \mathrm{e} \rightleftharpoons [\mathrm{Fe^{I}(L)(DMF)Cl}]^{2-} \qquad (J)$$

The resulting dianion exhibits significantly higher stability in comparison to the corresponding chloride-free analogue, especially in the case of the L^1 and L^2 complexes. This is probably due to the dianion stabilization by forming short-living ion pair with Li^+ of the supporting electrolyte.

The corresponding stability constants of the Fe(I) and Fe(II) chloride species could not be calculated because no reversible voltammetric behaviour could be observed at the available scan rates.

Mechanism of Electrode Reactions in DMSO

The main difference between the reactions of the complexes in DMF and DMSO comes from the different composition of the complex species in the particular electrolytes. Namely, as DMSO is a stronger donor than Cl^- the ligand-exchange reaction Cl^-–DMSO does not readily occur. Moreover, the formation of the anionic chloride-containing complexes of Fe(III) in DMSO is not known in the literature[13].

In the inert and chloride-free media, the $[Fe^{III}(L)(DMSO)_2]^+$ species present in the solution undergoes reduction in two processes analogous to reactions (*A*) and (*H*).

In chloride medium, the ligand-exchange reaction DMSO–Cl^- analogous to Eq. (*D*) takes place, resulting in formation of a monochloride complex. This complex is reduced in two steps, the first being analogous to Eqs (*B*) and (*C*) and the second one to Eqs (*H*) and (*I*).

The processes taking place at the potentials of peaks I/II are linked by a square-scheme analogous to that for the complexes in DMF solutions containing the inert medium (TBAP).

The ratios of the corresponding constants K_1^{III} and K_1^{II} (Table III) are about one order of magnitude lower in DMSO than those observed in DMF solutions, which is a consequence of smaller differences in the affinities of Fe(III) and Fe(II) complexes towards chloride.

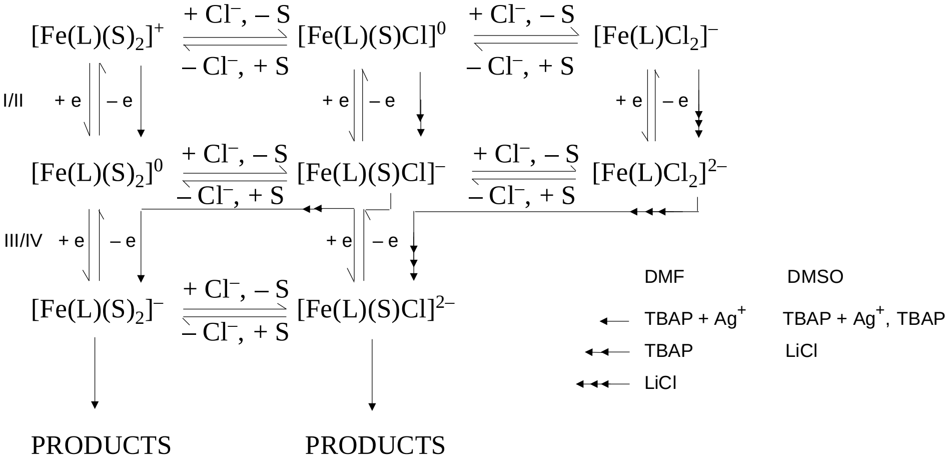


FIG. 6
General reaction scheme. Here S represents a solvent

A general reaction scheme for the processes in both two solvents and in all three electrolytes is presented in Fig. 6. Generally, it is evident that all the homogeneous and heterogeneous equilibria are governed by the ligand-exchange reaction Cl^-–solvent.

OTHER EFFECTS

Effect of H^+

The acid–base properties of the complexes in both solvents were studied in the presence of an excess of LiCl. Being relatively weak bases, the complexes of either Fe(III) or Fe(II) do not react with phenol. However, after adding H^+ in the form of $HClO_4$, the ligand is protonated, and the cyclic voltammograms recorded for a DMSO solution of $[Fe(L^3)Cl]$ are presented in Fig. 7. The decrease of the current in peak I is accompanied by a proportional increase in the current of the peak at about +0.03 V. A complete protonation yields the free ligand H_2L and $[FeCl_4]^-$ and $[Fe^{III}Cl(DMSO)_5]^{2+}$ in DMF and DMSO, respectively. In contrast to the Fe(III) complexes with the terdentate ligands based on salicylaldehyde *S*-methylisothiosemicarbazone, whose protonation in DMF is fast and stoichiometric[14,15], the corresponding complexes with the quadridentate ligands are not readily decomposed[7]. In DMF solutions, the presently investigated complexes react with H^+ in an approximate ratio 1 : 2, whereas in DMSO this ratio amounts even to 1 : 3. Although the protonation reaction in the two solvents is the same, in view of a lower stability of the Fe(III) chloride complex in DMSO, a complete complex decomposition in this solvent can be achieved only in the presence of an excess of H^+.

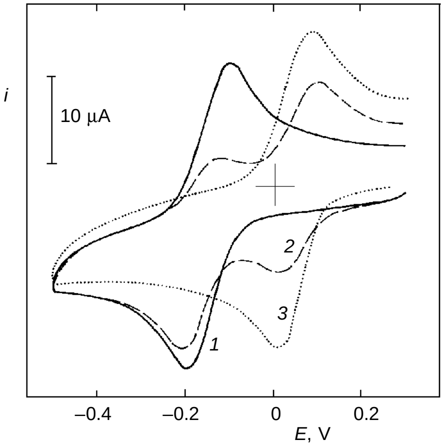


FIG. 7
Effect of H^+ on cyclic voltammograms (0.20 V s^{-1}) for $[Fe(L^3)Cl]$ in DMSO, 0.1 M LiCl. Mole ratio $[H^+]/[Fe(L^3)Cl]$: *1* 0, *2* 1.2, *3* 2.8

Taft's Correlation

To examine the effect the nature of the ligand exerts on particular electrochemical processes, an attempt was made to correlate the voltammetric data with the Hammett substituent constants σ_x for different ligands. The mid-point potentials, $(E_p^a + E_p^c)/2$, serving instead of the E^0 values, were determined under the conditions of a reversible behaviour of the complexes, and are related to all three media in DMF and to inert and chloride media in DMSO. The obtained linear relationships are presented in Fig. 8.

A linear dependence of $E^{0\prime}$ on $\Sigma\sigma_x$ indicates the central atom experiences a significant electric charge effect of the halogen atoms introduced in the *ortho* and *para* position (counting from the phenolic oxygen). A positive shift of the potentials with $\Sigma\sigma_x$ suggests that, as a consequence of the induction effect of the substituent, the charge on the central atom is lowered, which makes reduction of the complexes easier. However, the deviation of the $E^{0\prime}$ value for the L^4 complex from the linearity can be explained by the existence of additional electrostatic effects, which have not been taken into account.

By taking into account the $\Sigma\sigma_x$ values[16] of 0, +0.23 and +0.43 for the L^1, L^2 and L^3 complexes respectively, and using the general equation

$$E^{0\prime} = \rho \sum \sigma_x + d \tag{2}$$

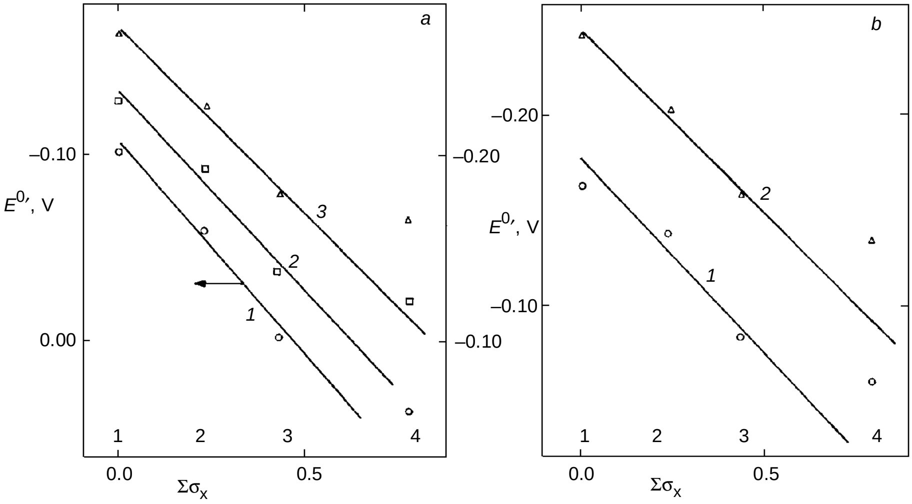


FIG. 8

Plot of $E^{0\prime}$ for the first reduction processes in DMF (*a*) and DMSO (*b*) for L^1–L^4 complexes vs $\Sigma\sigma_x$ values in the presence of *a* TBAP + Ag^+ (*1*), TBAP + 2 mM Cl^- (*2*) and TBAP + 20 mM Cl^- (*3*); *b* TBAP (*1*) and LiCl (*2*) the following straight line parameters ρ (reaction constant) and *d* (potential corresponding to the parent L^1 compound) were calculated. In DMF (TBAP + Ag^+), ρ = +0.23, *d* = –0.106, *r* = 0.9925; (TBAP + 2 mM Cl^-), ρ = +0.21, *d* = –0.234, *r* = 0.9598; (TBAP + 20 mM Cl^-, ρ = +0.18, *d* = –0.269, *r* = 0.9969.

In DMSO (TBAP), ρ = +0.23, *d* = –0.185, *r* = 0.9805; (LiCl), ρ = +0.20, *d* = –0.248, *r* = 0.9956.

As it can be seen from the above, the values of reaction constants are close each to other for all the investigated media. This certainly means that the presence of chloride in the axial position of the complex does not compensate for the induction effect of the ligand substituent exerts on the charge of the central atom.

As far as the data for peak III are concerned, a linear correlation of E_p values (instead of $E^{0\prime}$) with the $\Sigma\sigma_x$ values for the L^1–L^3 complexes, although not quantitative in nature, still reflects a great influence of the ligand on the second reduction process. This is evidenced by the reaction constant value of +0.38 and the differences in peak potentials of about 200 mV observed in all media.

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