Transition metal complexes with thiosemicarbazide-based ligands. Part 47. Synthesis, physicochemical and voltammetric characterization of iron(III) complexes with pyridoxal semi-, thiosemi- and S-methylisothiosemicarbazones

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Abstract: The reaction of warm EtOH solutions of FeX₃·nH₂O (X = Cl, NO₃) with tridentate ONX (X = O, S, N) pyridoxal semi-, thiosemi- and S-methylisothiosemi-cabazones (H₂L₁, H₂L₂, H₂L₃, respectively) yielded high-spin octahedral mono- and bis(ligand) complexes of the formula [Fe(H₂L₁)Cl₂(H₂O)]Cl, [Fe(HL₁₂)₂Cl·nH₂O and [Fe(H₂L₃)(HL₃)](NO₃)₂H₂O. The compounds were characterized by elemental analysis, conductometric and magnetochemical measurements, IR and UV-Vis spectra. Besides, a detailed voltammetric study of the complexes was carried out in DMF solution in the presence of several supporting electrolytes, to characterize the nature of the electrode processes and solution equilibria.

Keywords: iron(III) complexes, pyridoxal semi-, thiosemi- and isothiosemicarbazones, physicochemical and voltammetric studies.

INTRODUCTION

Transition metal complexes with Schiff bases derivatives of pyridoxal, e.g., 3-hydroxymethyl-2-methylpyridine-4-carboxaldehyde (one of the forms of vitamin B₆), amines and amino acids, are the subject of strong interest for many researchers.¹⁻⁵ The reason for this lies in the fact that these compounds can serve as models for studying a wide range of biological reactions catalyzed by enzymes in which pyridoxal phosphate appears as an essential component.¹⁻³ It has been shown that, in the presence of metal ions, free pyridoxal can catalyze most of the known enzymatic reactions in which pyridoxal phosphate acts as a co-enzyme.¹,⁶

A special group of Schiff bases pyridoxal derivatives as ligands are the tridentate semi-, thiosemi- and isothiosemicarbazones (H₂L₁, H₂L₂ and H₂L₃, respec-
tively) (Fig. 1). In contrast to the metal complexes with pyridoxal thiosemicarbazones, the study of which began in 1986, so that a substantial number of complexes not only with transition but also with non-transition metals have been synthesized,\textsuperscript{7–9} complexes with pyridoxal semi- and isothiosemicarbazones appeared much later. Namely, in our previous works,\textsuperscript{10–12} the syntheses and some physicochemical and structural characteristics of the complexes of Cu(II) and Pt(IV) with $\text{H}_2\text{L}^1$, and Cu(II) complexes with $\text{H}_2\text{L}^3$ were described.

In continuation of our studies on the complexing properties of these ligands, the syntheses and some physicochemical and voltammetric characteristics of their iron(III) complexes are described in this paper.

**EXPERIMENTAL**

**Chemicals and methods**

All chemicals used were commercially available products of analytical reagent grade. The exceptions were the ligands $\text{H}_2\text{L}^1\cdot \text{H}_2\text{O}$, $\text{H}_2\text{L}^2\cdot 3\text{H}_2\text{O}$, $\text{H}_2\text{L}^3\cdot \text{H}_2\text{O}$ and complex $[\text{Fe}(\text{HL})_2]\text{Cl}$, which were synthesized following previously described procedures.\textsuperscript{7,10–13}

Elemental (C, H, N) analysis of air-dried samples was carried out by standard micromethods in the Centre for Instrumental Analysis, Faculty of Chemistry, Belgrade.

Magnetic susceptibility measurements were made at room temperature using a magnetic susceptibility balance MSB-MKL (Sherwood Scientific Ltd., Cambridge, England). The data were corrected for diamagnetic susceptibilities.

Molar conductivities of freshly-prepared $1\times 10^{-3}$ M solution were measured on a Jenway 4010 conductivity meter.

IR-spectra (KBr disc) were recorded using a Perkin-Elmer FTIR 31725X.

Electronic spectra were recorded in DMF solutions (Merck, spectroscopic grade) on the Secomam instrument (Anthelie 2, advanced).

Voltammetric experiments were performed in freshly distilled DMF solutions. The salts serving as supporting electrolytes (tetrabutylammonium perchlorate, TBAP, and lithium perchlorate and chloride) were used after recrystallization, usually at a concentration of 0.1 M. The ligands and complexes were dried at 120–140°C and 1 mM solutions were thoroughly purged with nitrogen. An AMEL three-electrode voltammetric set-up was used together with a Hewlett Packard X-Y recorder and a storage oscilloscope for recording the voltamograms. A glassy carbon (3 mm diameter) disc (the working electrode) was coupled to a Pt wire (counter electrode) and an aqueous calomel electrode (SCE, reference electrode) connected to the working solution via a salt bridge. The potentials, referred to SCE, were frequently checked with ferrocene as an internal standard.

Since most of the complexes and ligands, and especially the products of electrochemical reactions exhibited strong adsorption, the GC electrode surface had to be frequently polished with a fine alumina suspension, in some cases before each scan. The experiments were performed in the range of scan rates from 10 mV s\textsuperscript{-1} to 10 V s\textsuperscript{-1}.

**Preparation of the protonated forms of the ligands and complexes**

$\text{H}_2\text{L}^1\cdot \text{HCH}_2\text{O}$. To a mixture of pyridoxal hydrochloride (10 mmol, Aldrich) and semicarbazide hydrochloride (10 mmol, Aldrich), i.e., thiosemicarbazide hydrochloride (10 mmol, Merck), water (10 cm\textsuperscript{3}) was added and the mixture heated to complete dissolution of the reactants. After 10 h, the precipitated yellowish needle-like crystals were separated by filtration and washed with EtOH. Yield: 86 and 68 %, respectively.

$[\text{Fe}(\text{HL})_2\cdot \text{Cl}_2\cdot \text{H}_2\text{O}]\text{Cl}$. To a warm suspension of the neutral forms of the ligands (1 mmol) in EtOH (10 cm\textsuperscript{3}), FeCl\textsubscript{3}·6H\textsubscript{2}O (1 mmol) was added and the mixture heated to complete dissolution of the ligand. The brown solution was left for 20 h at room temperature. The brown crystals which formed were filtered and washed with EtOH. Yield: 62, 87 and 69 %, respectively.
{Fe(HL\textsubscript{1})\textsubscript{2}}\textsubscript{2}Cl\textsubscript{4}H\textsubscript{2}O. To 0.26 g (1 mmol) of H\textsubscript{2}L\textsubscript{1}2H\textsubscript{2}O in EtOH (10 cm\textsuperscript{3}) was added 0.14 g (0.5 mmol) of FeCl\textsubscript{3}6H\textsubscript{2}O and the mixture heated to complete dissolution of the ligand. Then, 0.06 g (1 mmol) of LiOAc was added to the brown solution and dissolved by heating. The brown-black glittering crystals which formed in the course of 50 h were filtered and washed with EtOH. Yield: 0.14 g (46 %).

{Fe(HL\textsubscript{2})\textsubscript{2}}\textsubscript{2}Cl. The complex was synthesized according to the previously described procedure\textsuperscript{13}.

{Fe(HL\textsubscript{3})\textsubscript{2}(HL\textsubscript{3})\textsubscript{2}}(NO\textsubscript{3})\textsubscript{2}H\textsubscript{2}O. A mixture of 0.20 g (0.5 mmol) of Fe(NO\textsubscript{3})\textsubscript{3}9H\textsubscript{2}O, 0.14 g (0.5 mmol) of H\textsubscript{2}L\textsubscript{3}2H\textsubscript{2}O and 0.05 g of LiOAc was dissolved in EtOH (10 cm\textsuperscript{3}). The warm brown solution was filtered and left at room temperature for 50 h. The black crystals were filtered and washed with EtOH. Yield: 0.14 g (79 %).

RESULTS AND DISCUSSION

Synthesis, general physicochemical characteristics and geometrical configuration of the complexes

Until now, the only known complexes of iron with the mentioned ligands were the complexes {Fe(HL\textsubscript{1})\textsubscript{2}}\textsubscript{2}Cl\textsubscript{n}H\textsubscript{2}O (n = 0, 2)\textsuperscript{13} and {Fe(HL\textsubscript{2})Cl\textsubscript{2}}\textsuperscript{14}. The data of elemental analysis and some physico-chemical characteristics of the newly-synthesized iron complexes with H\textsubscript{2}L\textsubscript{1} and H\textsubscript{2}L\textsubscript{3} in general, as well as of the novel mono(ligand) complex with Fe(III). The mono(ligand) complexes considered in this work, whose composition can be described by the general formula Fe(HL\textsubscript{1})Cl\textsubscript{3}H\textsubscript{2}O, were obtained in a good yield by the reaction of warm EtOH solutions of FeCl\textsubscript{3}6H\textsubscript{2}O and the ligands in a mole ratio of 1:1. It should be pointed out that complexes of analogous composition were obtained with H\textsubscript{2}L\textsubscript{1} and H\textsubscript{2}L\textsubscript{3} in general, as well as of the novel mono(ligand) complex with Fe(III). The mono(ligand) complexes considered in this work, whose composition can be described by the general formula Fe(HL\textsubscript{1})Cl\textsubscript{3}H\textsubscript{2}O, were obtained in a good yield by the reaction of warm EtOH solutions of FeCl\textsubscript{3}6H\textsubscript{2}O and the ligands in a mole ratio of 1:1.

Bis(ligand) monocationic {Fe(HL\textsubscript{1})\textsubscript{2}}\textsubscript{2}Cl\textsubscript{4}H\textsubscript{2}O and dicationic {Fe(HL\textsubscript{3})\textsubscript{2}(HL\textsubscript{3})\textsubscript{2}}(NO\textsubscript{3})\textsubscript{2}H\textsubscript{2}O complexes, were also obtained in the reaction of EtOH solutions of the ligands with the corresponding iron(III) salt in the respective mole ratios 2:1 and 1:1 after partial neutralization (LiOAc) of the reaction solution. To our knowledge, the obtained cationic complex with H\textsubscript{2}L\textsubscript{3}, containing both the neutral and once-deprotonated forms of the ligand, represents the first Fe(III) complex with this charge with a diprotic tridentate Schiff base. The previously known {Fe(HL\textsubscript{1})\textsubscript{2}}\textsubscript{2}Cl,\textsuperscript{13} whose voltammetric behaviour is also included here, was obtained by the reaction of anhydrous FeCl\textsubscript{3} and H\textsubscript{2}L\textsubscript{2} in absolute EtOH.

On the basis of the conditions of synthesis of all three bis(ligand) complexes, it can be concluded that the deprotonation of H\textsubscript{2}L\textsubscript{2} is the easiest and that of H\textsubscript{2}L\textsubscript{3} the hardest. From the structures of these ligands (Fig. 1) it is evident that the phenolic
hydroxyl and enol/thiol form of \( \text{H}_2\text{L}^1/\text{H}_2\text{L}^2 \), i.e., isothioamide group of \( \text{H}_2\text{L}^3 \), can be deprotonated.

The results of X-ray structural analysis\(^{14,15} \) of the complex with the once-deprotonated form of \( \text{H}_2\text{L}^2 \) show that this form of the ligand results from deprotonation of the thiol form of the thiosemicarbazide moiety, whereby the pyridoxal fragment is in the form of a zwitter ion, i.e., the pyridine nitrogen is protonated on account of the deprotonation of the phenolic hydroxyl. Further deprotonation (the pyridine nitrogen) yields the dianionic form of the ligand.\(^{16} \) There is no doubt that an analogous deprotonation sequence also holds for the other two ligands. Such a deprotonation sequence is the consequence of the strong basicity of the pyridine nitrogen, which explains the zwitter-ionic nature of not only the coordinated but also the uncoordinated \( \text{H}_2\text{L}^2 \) ligand.\(^{7} \)

The occurrence of one or more bands of different intensity at ca. 2800 cm\(^{-1} \), belonging to the \( \nu(\text{NH}^+) \) vibrations of the protonated pyridine nitrogen,\(^{7} \) in the IR spectra of both the coordinated and uncoordinated ligand in the complexes is proof of the zwitter-ionic form of both.

X-Ray structural analyses of a number of complexes of various metals with the \( \text{H}_2\text{L}^2 \) ligand,\(^{14-17} \) as well as of \( \text{Cu(II)} \) complexes with the other two ligands,\(^{10,11} \) showed that all three ligands are coordinated as a tridentate entity. Thus, two donor atoms are the same – the phenolic oxygen and the hydrazinic nitrogen \( \text{N}(1) \). The third donor atom in the case of \( \text{H}_2\text{L}^1 \) and \( \text{H}_2\text{L}^2 \) is the oxygen or sulphur of the amide or thioamide group, \(-\text{C}(\text{--NH}_2) = X (X = \text{O, S}), \) respectively, whereas the third donor atom in the case of \( \text{H}_2\text{L}^3 \) is the nitrogen of the isothioamide group, \(-\text{C}(\text{--NH}_2)\text{--SCH}_3, \) In all cases, one six-membered (pyridoxal) and one five-membered (semi/thiosemi/isothiosemicarbazide) metallocycles are formed. Most probably, such a mode of coordination of these ligands is also realized in all the obtained complexes with iron(III), which has been confirmed by X-ray structural analysis\(^{18} \) in the case of the complexes with \( \text{H}_2\text{L}^1 \) and \( \text{H}_2\text{L}^2 \).

Simultaneously, these analyses showed that the mentioned two complexes have, apart from one molecule of the tridentate \( \text{ONX} (X = \text{O, S}) \) ligand, also an octahedral configuration formed by coordination of two chloride ions and one molecule of water. Probably, the \( \text{Fe(H}_2\text{L}^3)\text{Cl}_2\text{H}_2\text{O} \) complex also has such a structure, i.e., in addition to the organic \( \text{ONN} \) ligand there are two chloro- and one aqua-ligand. That one water
molecule is coordinated is also indicated by its relatively high temperature of evolution (≈150 °C), at which temperature the other two complexes are also dehydrated. It should be noticed that the previously synthesized [Fe(HL₂Cl₂] has a square-pyramidal structure.¹⁴

All three mono(ligand) complexes are well soluble in H₂O and DMF and somewhat less soluble in MeOH and EtOH. Their stability in H₂O and MeOH solutions are markedly different, which is also evident from the values of their molar conductivities λM (Table I). Namely, the λM values of their MeOH solutions are in the range of 124–150 S cm² mol⁻¹, i.e., between the λM values for 1:1 and 1:2 types of electrolytes,¹⁹ whereas the λM values of the aqueous solutions correspond to those of a 1:3 type of electrolytes (for the H₂L₁ and H₂L₃ complexes) or to a 1:5 type of electrolyte (H₂L² complex).²⁰ This means that in methanolic solution, partial replacement of the coordinated chloride ions by solvent molecules occurs, the replacement in aqueous solution being complete. The extremely high value of λM of aqueous solutions of the H₂L² complex could also be explained by the formation of the very mobile H₃O⁺ ion as a consequence of the deprotonation of the thiosemicarbazide fragment. In view of the fact that the λM value of the aqueous solutions of the other two complexes is at the upper limit of the λM range of values for a 1:3 type of electrolyte, it is possible that the same phenomenon is also involved, but at a lower concentration of H₃O⁺ ion. All these observations are in agreement with the previous supposition that deprotonation of H₂L² is the easiest and that of H₂L³ the hardest, which corresponds to the trend of decreasing λM values of the corresponding complexes.

### Table I. Some physical characteristics and analytical data of the newly synthesized compounds

<table>
<thead>
<tr>
<th>Ligands/Complex</th>
<th>Found (Calcd)%</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>μeff*/μB</th>
<th>λM*/S cm² mol⁻¹ (solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂L₁·HCl·H₂O</td>
<td>39.80 (39.48)</td>
<td>5.80</td>
<td>19.86</td>
<td>–</td>
<td>–</td>
<td>126 (H₂O)</td>
</tr>
<tr>
<td>H₂L₂·HCl·H₂O</td>
<td>37.28 (36.67)</td>
<td>5.27</td>
<td>19.19</td>
<td>–</td>
<td>–</td>
<td>162 (H₂O)</td>
</tr>
<tr>
<td>[Fe(H₂L₁)Cl₂(H₂O)]Cl</td>
<td>26.66 (26.73)</td>
<td>3.59</td>
<td>13.76</td>
<td>5.44</td>
<td>467 (H₂O)</td>
<td>124 (MeOH)</td>
</tr>
<tr>
<td>[Fe(H₂L₂)Cl₂(H₂O)]Cl</td>
<td>25.32 (25.70)</td>
<td>3.41</td>
<td>13.52</td>
<td>5.34</td>
<td>580 (H₂O)</td>
<td>150 (MeOH)</td>
</tr>
<tr>
<td>[Fe(H₂L₃)Cl₂(H₂O)]Cl</td>
<td>27.74 (27.64)</td>
<td>3.81</td>
<td>12.62</td>
<td>6.01</td>
<td>420 (H₂O)</td>
<td>136 (MeOH)</td>
</tr>
<tr>
<td>[Fe(HL₁)₂]Cl₄·H₂O</td>
<td>35.46 (35.45)</td>
<td>4.81</td>
<td>18.25</td>
<td>5.29</td>
<td>78 (MeOH)</td>
<td></td>
</tr>
<tr>
<td><a href="NO%E2%82%83">Fe(H₂L₃)(HL₃)</a>₂·H₂O</td>
<td>34.42 (34.64)</td>
<td>4.42</td>
<td>19.82</td>
<td>4.43</td>
<td>143 (MeOH)</td>
<td></td>
</tr>
</tbody>
</table>

* At 23 °C; ** c = 1 mM
As far as the bis(ligand) complexes are concerned, there is no doubt that they have an octahedral configuration in which, because of its planarity, the ligands assume mer- positions. As with mono(ligand) complexes, they are also well soluble in H₂O and DMF (with exception of the H₂L² complex) and less soluble in MeOH and EtOH. The molar conductivities of their MeOH solutions are in full agreement with the proposed coordination formulas.

With the exception of [Fe(H₂L₃)Cl₂(H₂O)]Cl (Table I) and [Fe(HL₂)₂]Cl,¹³ which have µ_eff values characteristic of pure high-spin Fe(III) complexes, the other complexes have somewhat lower µ_eff values, which could be explained in terms of the “admixture” of low-spin complexes. In relation to this, it is important to mention that there are literature data²¹ about Fe(III) complexes, mainly with the tridentate thiosemicarbazones, the spin state of which depends even on the outer-sphere ion, as well as on the number of molecules of crystalline water. An example of this is just the [Fe(HL₂)₂]Cl complex, which at room temperature is high-spin (µ_eff = 5.75 µ_B), while its dihydrate is low–spin (µ_eff = 2.05 µ_B).¹³

Electronic spectra

The spectra of the neutral and protonated forms of the ligands were recorded over the available region in DMF, from 270 to 800 nm, as well in the presence of LiCl (serving as supporting electrolyte in the voltammetric measurements). The spectra of the complexes were also recorded under similar conditions, and the characteristic parameters are given in Table II.

<table>
<thead>
<tr>
<th>TABLE II. Electronic spectral data for the ligands and complexes in DMF</th>
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<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>H₂L₁·2H₂O</td>
</tr>
<tr>
<td>H₂L₁·HCl·H₂O</td>
</tr>
<tr>
<td>H₂L²·3H₂O</td>
</tr>
<tr>
<td>H₂L²·HCl·H₂O</td>
</tr>
<tr>
<td>H₂L³·H₂O</td>
</tr>
<tr>
<td>[Fe(HL₁)₂]Cl₂·(H₂O)Cl</td>
</tr>
<tr>
<td>[Fe(HL₂)₂]Cl₂·(H₂O)Cl</td>
</tr>
<tr>
<td>[Fe(HL₂)₃]Cl₂(H₂O)Cl</td>
</tr>
<tr>
<td>[Fe(HL₁)₃]Cl·4H₂O</td>
</tr>
<tr>
<td>[Fe(HL₂)₃]²Cl</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">Fe(HL₃)₃</a>₂·H₂O</td>
</tr>
</tbody>
</table>

*a*In nm. **b**In M⁻¹ cm⁻¹ × 10⁻⁴. *Shoulder. dBroad peak.*

The spectra of all three ligands are characterized by 2–3 bands in the range of 270–450 nm. The difference in the spectral patterns is due to the structural differ-
ences of the compounds. As could be expected, the addition of LiCl to the ligand solutions caused no significant changes in their spectra. Ligand protonation, however, resulted in a decrease of the absorption at $\lambda < 360$ nm, with the simultaneous appearance of new bands characteristic of the absorption of $\text{H}_2\text{L}^+$ and $\text{H}_4\text{L}^2+$ species in the range of 315–400 nm.

The spectra of all the ligands of the type $\text{H}_2\text{L}$ and $\text{H}_2\text{L} \cdot \text{HCl}$ protonated to the same extent by adding $\text{HClO}_4 (> 2\text{H}^+/\text{ligand})$ have similar characteristics. The protonated $\text{H}_2\text{L}^2$ and $\text{H}_3\text{L}^3$ exhibit similar absorption, while the spectrum of the semicarbazone derivative is different, suggesting a different nature of the chromophore.

The complexes absorb in the range of 270–600 nm, the appearance of a particular spectrum depending mainly on the coordinated ligand. A common characteristic of all these spectra is the absence of bands that could be ascribed to $d-d$ transitions (Fig. 2). The band at $\lambda < 400$ nm corresponds to the absorption of the ligand part of the molecule ($\pi \rightarrow \pi^*$), which is evident from the absorption of the ligand itself, especially with the $\text{H}_2\text{L}^1$ complexes. This means that the bonds in the Fe(III) complex with this ligand are weakest, which was also confirmed by voltammetric experiments.

The addition of LiCl to a solution of a complex changes the appearance of the absorption curve, which becomes more similar to the spectrum of the ligand itself, suggesting a partial dissociation of the molecule (Fig. 2, curve 2). This was also confirmed by the disappearance of the charge-transfer bands ($\lambda > 400$ nm) in the spectra of all the complexes. On addition of $\text{HClO}_4$ to a mole ratio of (2–3) $\text{H}^+/\text{Fe}$,

![Fig. 2. Electronic spectra of $[\text{Fe}(\text{H}_2\text{L})_2\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$ in DMF: pure solvent (1) and after the addition of 0.1 M LiCl (2) and $\text{HClO}_4$ to the mole ratio 2 $\text{H}^+/\text{Fe}$ (3).](image)
the resulting spectra have two characteristic bands at somewhat different wave-
lengths (in the region of 305–332 and 340–390 nm), depending on the nature of the
complex. Moreover, the bands correspond to those obtained under the same condi-
tions for a solution of the corresponding protonated ligand. Hence, the protonation
product could be represented as \( \text{H}_4\text{L}^2+ \), whereby the protonation sites may be the
phenolic oxygen and one of the nitrogen atoms of the hydrazine moiety.

**Voltammetric studies**

In view of the experience gained in studying Fe(III) complexes with similar ligands – salicylaldehyde semi-, thiosemi and \( S \)-methylisothiosemicarbazone in DMF, it was interesting to study the behaviour of the new complexes under the same conditions.

A marked characteristic of the newly synthesized mono(ligand) and bis(li-
gand) complexes of the cationic type is their pronounced dissociation in DMF, es-
specially in the presence of chloride. In contrast to this, the previous series of com-
plexes, being stable enough, was characterized by well-defined cyclic voltammo-
grams. The reaction of the new complexes taking place in the presence of LiCl is accompa-
nied by a visual change in their colour from brown to ruby-red and a spec-
trum characterizing the absorption of the displaced ligand.

For the sake of legibility the results will be presented according to the complex
type with reference to specific features of a particular coordinated ligand.

**Mono(ligand) complexes**

The previously studied complexes of this type with salicylaldehyde derivatives as ligands behaved as coordination dimers [\( \text{Fe(HL)}_2][\text{FeCl}_4] \], dissociating in DMF into equimolar amounts of [\( \text{Fe(HL)}^2+ \), [\( \text{FeCl}_4^- \) and (HL–)]. In contrast to them, the new ligands, coordinated as neutral molecules, give unstable [\( \text{Fe(H}_2\text{L})^3+ \) complexes, dis-
sociating almost completely to Fe(III) and \( \text{H}_2\text{L} \).

The appearance of the cyclic voltammogram for [\( \text{Fe(H}_2\text{L}_3\text{Cl}_2(\text{H}_2\text{O})\text{Cl} \) recorded in TBAP, as the least “aggressive” medium, is presented in Fig. 3. The reduc-
tion peaks, observed at three potential amplitudes (to –1.0 V), belong to one-electron processes, the first for \( \text{FeCl}_4^- \), then that for [\( \text{Fe(HL)}^2+ \) with perchlorate/chloride in the coordination sphere. The two most negative peaks represent the reduction of \( \text{H}_2\text{L}_3 \), occurring on the pyridoxal and hydrazine fragment, respectively. The reduced complexes also exhibit instability: [\( \text{FeCl}_4^2- \) dissociates rapidly to \( \text{FeCl}_2 \) and \( \text{Fe(ClO}_4)_2 \), which are oxidized in two close peaks at about 0.0 V.

Oxidation of the complexes (in the amplitude range from +0.6 to +1.6 V) is repre-
sented by 2–3 multi-electron peaks involving processes on the ligand part, fol-
lowed by decomposition of the molecule. The detailed electrochemistry of the
ligand will be described in a subsequent paper.

**LiClO\(_4\)**. The addition of LiClO\(_4\) to the solution of these complexes results in changes of the voltammogram in the part corresponding to ligand reduction, the
cathodic peaks being shifted to more positive potentials, overlapping thus with the first peak. This effect is probably a consequence of ion-pairing of Li$^+$ and the product of the multielectron reduction of the ligand.$^{22}$

$\textit{LiCl}$. The voltammogram of the mono(ligand) complex (Fig. 4) shows that excess of Cl$^-$ stabilizes the reaction of FeCl$_4$$^-$, yielding a pair of quasi-reversible peaks
at $E_p^c = -0.08$ V. The current corresponding to this peak is approximately equivalent to the total Fe(III) content, which is also evident from the voltammogram, in which the peak current for Fe(HL)$^2$+ ($E_p^c = -0.68$ V) does not exceed 10–20 %. At potentials more negative than −1.5 V, partial overlap of several reduction processes at the ligand is observed. The electron transfer processes are followed by irreversible chemical reactions whereby the complex decomposes into several species with marked tendency of adsorption (e.g., the oxidative peak at −0.8 V).

**Bis(ligand) complexes**

*Monocationic complexes.* Complexes of this type, represented in the crystalline state by the formulas [Fe(HL)$^1_2$]Cl and [Fe(HL)$^2_2$]Cl, dissociate in DMF solution into several complex species. Another problem is the very poor solubility of the H$_2$L$^2$ complex – complete dissolution at a level of 1 mM required 3 h.

**TBAP and LiClO$_4$**. Both the investigated complexes in these two electrolytes (Fig. 5, curve 1) behave in basically the same way to a potential of −1.60 V: 2–3 reduction peaks with $E_p^c > -0.7$ V are characteristic of the different Fe(III)-containing species. The dominant peak at −0.05 V belongs to FeCl$_4^-$ and contains about 30 % of the total iron(III) in the case of the H$_2$L$^1$ and about 50 % in the case of the H$_2$L$^2$ complexes (determined after protonation, *vide infra*). In the potential region more negative than −1.4 V, the free ligand is reduced in an irreversible one-electron process. However, the peak is actually composed of two peaks of similar potentials ($\Delta E_p^c < 150$ mV), the more positive of which is supposed to belong to the residual

![Cyclic voltammograms for Fe(HL)$^2_2$Cl in 0.1 M LiClO$_4$ – narrow (1) and broad (2) amplitude and after the addition of 0.1 M LiCl (3); 0.20 V s$^{-1}$.](image-url)
undissociated bis(ligand) complex and the more negative one represents the irreversible one-electron reduction of the free ligand.

In TBAP, a further ligand reduction is represented by two peaks at –1.9 and –2.2 V, corresponding to a process on the thiosemicarbazide moiety. However, the two processes merge in LiClO₄, as described for the mono(ligand) complexes. Ligand oxidation, up to +1.5 V, proceeds in three partially overlapped peaks, after which the complex decomposes into Fe(III) and the products of chemical reactions on the free ligand.

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\text{LiClO}_4. \text{ The voltammetric behaviour of the complexes in this electrolyte is better defined (Fig. 5, curve 3). In addition to the dominant reduction peak of FeCl}_4^-\text{, containing about 70\% of the total iron(III), there is a peak with } E^{\text{pc}} = -0.56 \text{ V, corresponding to the reduction of } [\text{Fe(HL}_2^-}]^{2+}. \text{ The irreversible one-electron peak at } -1.47 \text{ V represents the reduction of free ligand. Further reduction in this electrolyte occurs in one multielectron peak formed by the overlapping of the two previous peaks, the processes taking place on the thiosemicarbazide fragment. Besides, in the same potential range (< –2.0 V), Fe(II) is reduced to Fe(0).} \]

A certain insight into the fine equilibria between the (HL₂)⁻ and Cl⁻ complexes of Fe(III) and Fe(II) can be gained by considering the voltammograms obtained after repetitive cycling in the working potential amplitude (Fig. 6). It is evident that a potential excursion to include the reduction of the ligand results in an increase of the oxidation peak for Fe(HL₂)⁺ (\(E^{\text{pa}} \approx -0.30 \text{ V}\)) on account of a decrease of the peak for FeCl₂ (\(E^{\text{pa}} = +0.02 \text{ V}\)). This ratio of concentrations of the complex
species, altered in comparison with the initial one, is evident from the second sweep (curve 3), amounting almost to 1:1 for the chloride and (HL²⁻)⁻ complexes. Such behaviour provokes the conclusion that in contrast to Fe(III), which exhibits high affinity toward Cl⁻, Fe(II) shows a greater stability in the Fe(HL²⁺)⁺ complex.

**Dicationic complex.** The complex [Fe(H₂L³⁻)(HL³⁻)](NO₃)·H₂O, like the analogous semicarbazone compound, already dissociates to a large extent in the presence of an inert electrolyte, the dissociation into FeCl₄⁻ and H₂L³⁻ being practically complete in the presence of excess Cl⁻. The poorly defined peaks at potentials more negative than –1.35 V do not allow the establishment whether, in addition to H₂L³⁻, the (HL³⁻)⁻ species exists also. It can be supposed that the ligand can be protonated to H₂L³⁻ by a proton from the traces of water or acidic impurities, which is confirmed by the electronic spectrum which in the presence of LiCl looks more like that of the ligand itself.

**Complexes in the presence of H⁺**

The addition of H⁺ (aqueous solution of HClO₄) served both to assess the stability of the complexes in acidic media and check the composition of particular species. Protonation was carried out discontinuously and cyclic voltammograms were recorded after each increment of acid addition.

The cyclic voltammograms for [Fe(H₂L¹⁻)Cl₂(H₂O)]Cl complex recorded before and after the addition of 2 H⁺/complex molecule are shown in Fig. 7. The peak for FeCl₄⁻, obtained as the final product of protonation of all complex species in

![Fig. 7. Cyclic voltammograms for [Fe(H₂L¹⁻)Cl₂(H₂O)]Cl in 0.1 M LiCl before (1) and after the addition of HClO₄ to the mole ratio 2 H⁺/Fe (2); 0.10 V s⁻¹.](image)
the presence of LiCl, does not change essentially with respect to the initial peak. A small increase in the peak current after the addition of H⁺ is a consequence of the somewhat enhanced reversibility of the process and a shift of the potential to more positive values has been observed in mixed DMF-water solutions.28

The fact that there is no increase in the current of the FeCl⁴⁻ peak which could be ascribed to ligand displacement, suggests that none of the ligand forms are bound into the complex. The height of the new peak, that for all three ligands appears at about –0.95 to –1.0 V, increases two fold for the mono(ligand) and four fold for the bis(ligand) complexes compared to that of FeCl⁴⁻ and attains its maximum at (2–3) H⁺/Fe. The process has the characteristics of a successive transfer of two electrons, coupled most probably with protonation,29 which will be dealt with in more detail in another paper.25

Of all the investigated iron complexes, protonation of HL⁻ to H₂L was possible only with [Fe(HL₁)₂]Cl and [Fe(HL₂)₂]Cl. However, in both cases the H⁺ consumption was significantly lower than the theoretical one, which may be a consequence of the partial extraction of protons from the medium itself.

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КОМПЛЕКСИ ПРЕЛАЗНИХ МЕТАЛА НА БАЗИ ТИОСЕМИКАРБАЗИДА. ДЕО 47.
СИНТЕЗА, ФИЗИЧКО-ХЕМИЈСКА И ВОЛТАМЕТРИЈСКА КАРАКАТЕРИЗАЦИЈА
КОМПЛЕКСА Fe(III) СА СЕМИ-, ТИОСЕМИ- И S-МЕТИЛИЗОТИОСЕМИКАРБАЗОНОМ ПИРИДОКСАЛА

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Реакцијом топлих EtOH раствора FeX₃•nH₂O (X = Cl, NO₃) са тридентатним семи-, тиосеми- и S-метилизотиосемикарбазоном пиридоксала (H₂L₁, H₂L₂, односно H₂L₃) добијени су високоспецифски октаедарски моно- и бис(лиган) комплекси формула [Fe(H₂L₁)₂Cl₂(H₂O)]Cl, [Fe(HL₁)(Cl)•nH₂O и [Fe(H₂L₂)(HL₂)(NO₃)]•2H₂O. Једињења су окрашена елементалном анализом, кондуктометријским и магнетохемијским мережама, као и IR и UV-Vis спектрима. Извршено је детаљно волтаметријско испитивање добијених једињења у DMF у неколико помоћних електролита, истражене су природе електрохемијских процеса и равнотеже у раствору.

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