

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 $\text{FeX}_3 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{NO}_3$) with tridentate ONX ($\text{X} = \text{O}, \text{S}, \text{N}$) pyridoxal semi-, thiosemi- and *S*-methylisothiosemicarbazones ($\text{H}_2\text{L}^1, \text{H}_2\text{L}^2, \text{H}_2\text{L}^3$, respectively) yielded high-spin octahedral mono- and bis(ligand) complexes of the formula $[\text{Fe}(\text{H}_2\text{L}^{1-3})\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$, $[\text{Fe}(\text{HL}^{1,2})_2]\text{Cl} \cdot n\text{H}_2\text{O}$ and $[\text{Fe}(\text{H}_2\text{L}^3)(\text{HL}^3)](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. 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 ($\text{H}_2\text{L}^1, \text{H}_2\text{L}^2$ and H_2L^3 , respec-

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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,⁷⁻⁹ complexes with pyridoxal semi- and isothiosemicarbazones appeared much later. Namely, in our previous works,¹⁰⁻¹² the syntheses and some physicochemical and structural characteristics of the complexes of Cu(II) and Pt(IV) with H_2L^1 , and Cu(II) complexes with H_2L^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 $H_2L^1 \cdot 2H_2O$, $H_2L^2 \cdot 3H_2O$, $H_2L^3 \cdot H_2O$ and complex $[Fe(HL^2)_2]Cl$, which were synthesized following previously described procedures.^{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 1×10^{-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 voltammograms. 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⁻¹ to 10 V s⁻¹.

Preparation of the protonated forms of the ligands and complexes

$H_2L^{1,2} \cdot HCl \cdot H_2O$. To a mixture of pyridoxal hydrochloride (10 mmol, Aldrich) and semicarbazide hydrochloride (10 mmol, Aldrich), *i.e.*, thiosemicarbazide hydrochloride (10 mmol, Merck), water (10 cm³) 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.

$[Fe(H_2L^{1-3})Cl_2(H_2O)]Cl$. To a warm suspension of the neutral forms of the ligands (1 mmol) in EtOH (10 cm³), $FeCl_3 \cdot 6H_2O$ (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.

$[Fe(HL^1)_2]Cl \cdot 4H_2O$. To 0.26 g (1 mmol) of $H_2L^1 \cdot 2H_2O$ in EtOH (10 cm³) was added 0.14 g (0.5 mmol) of $FeCl_3 \cdot 6H_2O$ 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 %).

$[Fe(HL^2)_2]Cl$. The complex was synthesized according to the previously described procedure.¹³

$[Fe(H_2L^3)(HL^3)](NO_3)_2 \cdot H_2O$. A mixture of 0.20 g (0.5 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$, 0.14 g (0.5 mmol) of $H_2L^3 \cdot H_2O$ and 0.05 g of LiOAc was dissolved with heating in EtOH (10 cm³). 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 $[Fe(HL^2)_2]Cl \cdot nH_2O$ ($n = 0, 2$)¹³ and $[Fe(HL^2)Cl_2]$.¹⁴ The data of elemental analysis and some physico-chemical characteristics of the newly-synthesized iron complexes with H_2L^1 and H_2L^3 in general, as well as of the novel mono(ligand) complex with H_2L^2 are given in Table I. Taking into account these results and those of the previously known complex $[Fe(HL^2)_2]Cl$, it can be concluded that all the three ligands form both mono- and bis(ligand) complexes with Fe(III). The mono(ligand) complexes considered in this work, whose composition can be described by the general formula $Fe(H_2L)Cl_3 \cdot H_2O$, were obtained in a good yield by the reaction of warm EtOH solutions of $FeCl_3 \cdot 6H_2O$ and the ligands in a mole ratio of 1:1. It should be pointed out that complexes of analogous composition were obtained with H_2L^1 and H_2L^2 , *i.e.*, with the neutral forms of the ligands, and in the case of the reaction of $FeCl_3 \cdot 6H_2O$ with their protonated forms H_3L^+ . Also, it is important to emphasize that the previously known $[Fe(HL^2)Cl_2]$ complex,¹⁴ involving the once-deprotonated form of the ligand, was synthesized starting from $FeCl_2$, and that, despite performing the reaction in a nitrogen atmosphere, the result was an iron(III) complex.

Bis(ligand) monocationic $[Fe(HL^1)_2]Cl \cdot 4H_2O$ and dicationic $[Fe(H_2L^3)(HL^3)](NO_3)_2 \cdot H_2O$ 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_2L^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 $[Fe(HL^2)_2]Cl$,¹³ whose voltammetric behaviour is also included here, was obtained by the reaction of anhydrous $FeCl_3$ and H_2L^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_2L^2 is the easiest and that of H_2L^3 the hardest. From the structures of these ligands (Fig. 1) it is evident that the phenolic

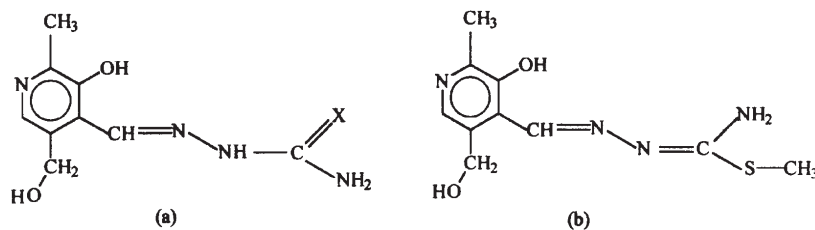


Fig. 1. Structural formulas of pyridoxal semi/thiosemicarbazones ($X = O \rightarrow H_2L^1$, $X = S \rightarrow H_2L^2$) (a) and *S*-methylisothiosemicarbazone (H_2L^3)(b).

hydroxyl and enol/thiol form of H_2L^1/H_2L^2 , *i.e.*, isothioamide group of H_2L^3 , can be deprotonated.

The results of X-ray structural analysis^{14,15} of the complex with the once-deprotonated form of H_2L^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 H_2L^2 ligand.⁷

The occurrence of one or more bands of different intensity at *ca.* 2800 cm^{-1} , belonging to the $\nu(NH^+)$ 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 H_2L^2 ligand,^{14–17} as well as of 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 N(1). The third donor atom in the case of H_2L^1 and H_2L^2 is the oxygen or sulphur of the amide or thioamide group, $-C(-NH_2) = X$ ($X = O, S$), respectively, whereas the third donor atom in the case of H_2L^3 is the nitrogen of the isothioamide group, $=C(-NH_2)-S-CH_3$. In all cases, one six-membered (pyridoxal) and one five-membered (semi/thiosemi/isothiosemicarbazide) metalocycles 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 analysis¹⁸ in the case of the complexes with H_2L^1 and H_2L^2 .

Simultaneously, these analyses showed that the mentioned two complexes have, apart from one molecule of the tridentate ONX ($X = O, S$) ligand, also an octahedral configuration formed by coordination of two chloride ions and one molecule of water. Probably, the $Fe(H_2L^3)Cl_3 \cdot H_2O$ complex also has such a structure, *i.e.*, in addition to the organic 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 $[\text{Fe}(\text{HL}^2)\text{Cl}_2]$ has a square-pyramidal structure.¹⁴

All three mono(ligand) complexes are well soluble in H_2O and DMF and somewhat less soluble in MeOH and EtOH. Their stability in H_2O and MeOH solutions are markedly different, which is also evident from the values of their molar conductivities λ_{M} (Table I). Namely, the λ_{M} values of their MeOH solutions are in the range of 124–150 $\text{S cm}^2 \text{mol}^{-1}$, *i.e.*, between the λ_{M} values for 1:1 and 1:2 types of electrolytes,¹⁹ whereas the λ_{M} values of the aqueous solutions correspond to those of a 1:3 type of electrolytes (for the H_2L^1 and H_2L^3 complexes) or to a 1:5 type of electrolyte (H_2L^2 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 λ_{M} of aqueous solutions of the H_2L^2 complex could also be explained by the formation of the very mobile H_3O^+ ion as a consequence of the deprotonation of the thiosemicarbazide fragment. In view of the fact that the λ_{M} value of the aqueous solutions of the other two complexes is at the upper limit of the λ_{M} 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 H_3O^+ ion. All these observations are in agreement with the previous supposition that deprotonation of H_2L^2 is the easiest and that of H_2L^3 the hardest, which corresponds to the trend of decreasing λ_{M} values of the corresponding complexes.

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

Ligands/Complex	Found (Calcd)/%			$\mu_{\text{eff}}^*/\mu_{\text{B}}$	$\lambda_{\text{M}}^{**}/\text{S cm}^2 \text{mol}^{-1}$ (solvent)
	C	H	N		
$\text{H}_2\text{L}^1 \cdot \text{HCl} \cdot \text{H}_2\text{O}$	39.80 (39.48)	5.80 (5.43)	19.86 (20.11)	–	126 (H_2O)
$\text{H}_2\text{L}^2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$	37.28 (36.67)	5.27 (5.13)	19.19 (19.01)	–	162 (H_2O)
$[\text{Fe}(\text{H}_2\text{L}^1)\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$	26.66 (26.73)	3.59 (3.49)	13.76 (13.86)	5.44	467 (H_2O) 124 (MeOH)
$[\text{Fe}(\text{H}_2\text{L}^2)\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$	25.32 (25.70)	3.41 (3.36)	13.52 (13.33)	5.34	580 (H_2O) 150 (MeOH)
$[\text{Fe}(\text{H}_2\text{L}^3)\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$	27.74 (27.64)	3.81 (3.71)	12.62 (12.90)	6.01	420 (H_2O) 136 (MeOH)
$[\text{Fe}(\text{HL}^1)_2]\text{Cl} \cdot 4\text{H}_2\text{O}$	35.46 (35.45)	4.81 (4.16)	18.25 (18.38)	5.29	78 (MeOH)
$[\text{Fe}(\text{H}_2\text{L}^3)(\text{HL}^3)](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	34.42 (34.64)	4.42 (4.15)	19.82 (19.86)	4.43	143 (MeOH)

* 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 ($\mu_{\text{eff}} = 5.75 \mu_{\text{B}}$), while its dihydrate is low-spin ($\mu_{\text{eff}} = 2.05 \mu_{\text{B}}$).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 II. Electronic spectral data for the ligands and complexes in DMF

Compound	$\lambda_{\text{max}}^{\text{a}}$ (ϵ^{b})
H ₂ L ¹ ·2H ₂ O	290(1.79); 329(0.77 <i>sh</i> ^c)
H ₂ L ¹ ·HCl·H ₂ O	306(1.40 <i>sh</i>); 321(1.47); 339(1.45)
H ₂ L ² ·3H ₂ O	284(1.04); 333(2.10)
H ₂ L ² ·HCl·H ₂ O	321(1.38); 349(1.43); 361(1.39 <i>sh</i>)
H ₂ L ³ ·H ₂ O	325(2.81 <i>bp</i> ^d); 352(2.69); 365 (2.39 <i>sh</i>)
[Fe(H ₂ L ¹)Cl ₂ (H ₂ O)]Cl	291(1.92); 355(1.20)
[Fe(H ₂ L ²)Cl ₂ (H ₂ O)]Cl	320(1.82); 356(1.97); 442(0.48 <i>sh</i>)
[Fe(H ₂ L ³)Cl ₂ (H ₂ O)]Cl	323(1.72); 353(1.72); 367(1.73); 404(1.17 <i>sh</i>)
[Fe(HL ¹) ₂]Cl·4H ₂ O	282(2.71); 348(1.40)
[Fe(HL ²) ₂]Cl	326(3.53); 351(3.66); 438(0.73 <i>sh</i>)
[Fe(H ₂ L ³)(HL ³)](NO ₃) ₂ ·H ₂ O	316(1.65 <i>sh</i>); 327(1.72); 351(1.72); 367(1.73)

^aIn nm. ^bIn M⁻¹ cm⁻¹ × 10⁻⁴. ^cShoulder. ^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 H_3L^+ and H_4L^{2+} species in the range of 315–400 nm.

The spectra of all the ligands of the type H_2L and $H_2L \cdot HCl$ protonated to the same extent by adding $HClO_4$ ($> 2H^+$ /ligand) have similar characteristics. The protonated H_2L^2 and H_2L^3 exhibit similar absorption, while the spectrum of the semicarbazone derivative is different, suggesting a different nature of the chromophore.

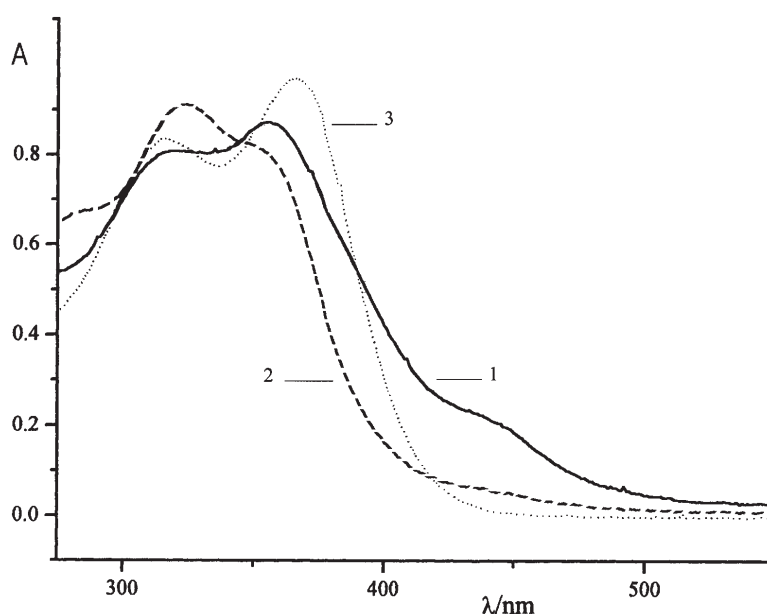


Fig. 2. Electronic spectra of $[Fe(H_2L^2)Cl_2(H_2O)]Cl$ in DMF: pure solvent (1) and after the addition of 0.1 M LiCl (2) and $HClO_4$ to the mole ratio 2 H^+ /Fe (3).

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 H_2L^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 $HClO_4$ to a mole ratio of (2–3) H^+ /Fe,

the resulting spectra have two characteristic bands at somewhat different wavelengths (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 conditions for a solution of the corresponding protonated ligand. Hence, the protonation product could be represented as H_4L^{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,^{22–24} 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(ligand) complexes of the cationic type is their pronounced dissociation in DMF, especially in the presence of chloride. In contrast to this, the previous series of complexes, being stable enough, was characterized by well-defined cyclic voltammograms. The reaction of the new complexes taking place in the presence of LiCl is accompanied by a visual change in their colour from brown to ruby-red and a spectrum 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 $[Fe(HL)_2][FeCl_4]$, dissociating in DMF into equimolar amounts of $[Fe(HL)]^{2+}$, $[FeCl_4]^-$ and (HL^-) .²² In contrast to them, the new ligands, coordinated as neutral molecules, give unstable $[Fe(H_2L)]^{3+}$ complexes, dissociating almost completely to Fe(III) and H_2L .

The appearance of the cyclic voltammogram for $[Fe(H_2L^3)Cl_2(H_2O)]Cl$ recorded in TBAP, as the least “aggressive” medium, is presented in Fig. 3. The reduction peaks, observed at three potential amplitudes (to -1.0 V), belong to one-electron processes, the first for $FeCl_4^-$, then that for $Fe(HL^3)^{2+}$ with perchlorate/chloride in the coordination sphere. The two most negative peaks represent the reduction of H_2L^3 , occurring on the pyridoxal and hydrazine fragment, respectively. The reduced complexes also exhibit instability: $[FeCl_4]^{2-}$ dissociates rapidly to $FeCl_2$ and $Fe(ClO_4)_2$, which are oxidized in two close peaks at about 0.0 V.²²

Oxidation of the complexes (in the amplitude range from $+0.6$ to $+1.6$ V) is represented by 2–3 multi-electron peaks involving processes on the ligand part, followed by decomposition of the molecule. The detailed electrochemistry of the ligand will be described in a subsequent paper.²⁵

LiClO₄. 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

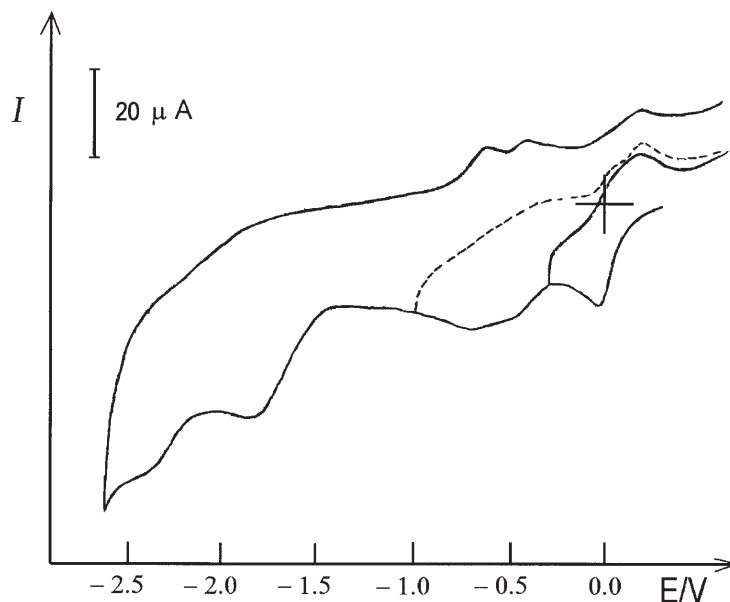


Fig. 3. Cyclic voltammograms for $[\text{Fe}(\text{H}_2\text{L}^3)\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$ in 0.1 M TBAP; 0.20 V s^{-1} .

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

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

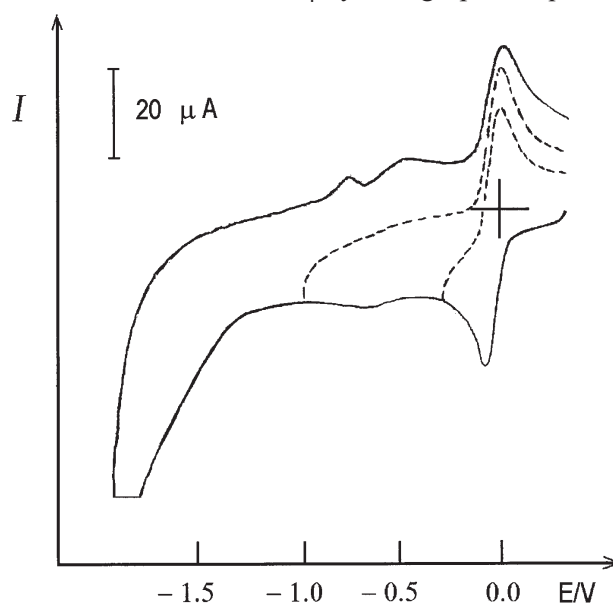


Fig. 4. Cyclic voltammograms for $[\text{Fe}(\text{H}_2\text{L}^3)\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$ in 0.1 M LiCl; 0.20 V s^{-1} .

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 $\text{Fe}(\text{HL}^3)^{2+}$ ($E_p^c = -0.68$ 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 $[\text{Fe}(\text{HL}^1)_2]\text{Cl}$ and $[\text{Fe}(\text{HL}^2)_2]\text{Cl}$, dissociate in DMF solution into several complex species. Another problem is the very poor solubility of the H_2L^2 complex – complete dissolution at a level of 1 mM required 3 h.

TBAP and LiClO₄. 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_2L^1 and about 50 % in the case of the H_2L^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

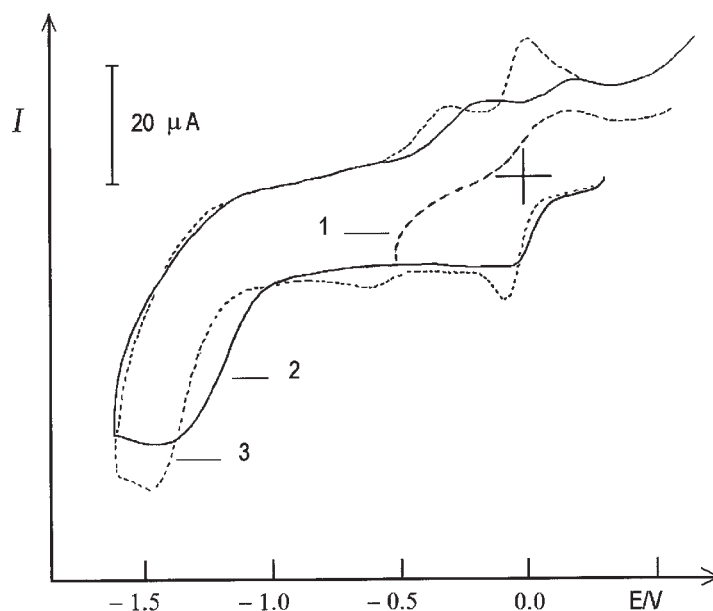


Fig. 5. Cyclic voltammograms for $[\text{Fe}(\text{HL}^2)_2]\text{Cl}$ in 0.1 M LiClO_4 – narrow (1) and broad (2) amplitude and after the addition of 0.1 M LiCl (3); 0.20 V s^{-1} .

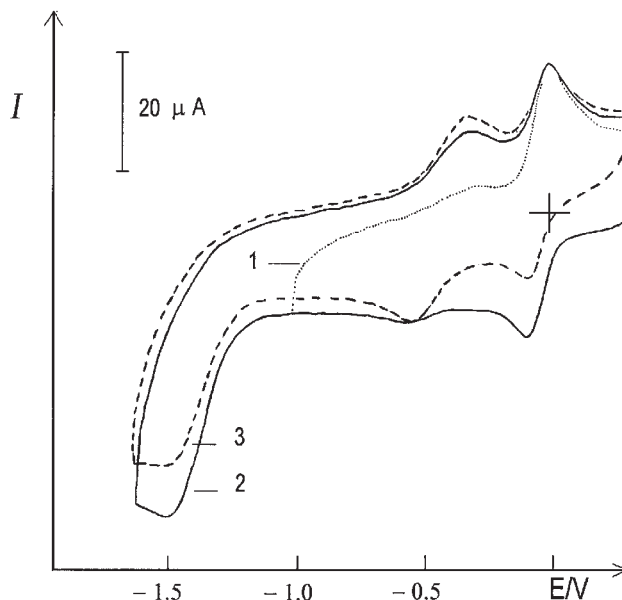


Fig. 6. Cyclic voltammograms for $[\text{Fe}(\text{HL}^2)_2]\text{Cl}$ in 0.1 M LiCl: 1st sweep, narrow (1) and broad (2) amplitude; 2nd sweep (3) at 0.20 V s^{-1} .

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.²⁶ However, the two processes merge in LiClO_4 , as described for the mono(ligand) complexes. Ligand oxidation, up to $+1.5 \text{ V}$, proceeds in three partially overlapped peaks, after which the complex decomposes into Fe(III) and the products of chemical reactions on the free ligand.

LiCl. 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^- , containing about 70 % of the total iron(III), there is a peak with $E_p^c = -0.56 \text{ V}$, corresponding to the reduction of $[\text{Fe}(\text{HL}^2)]^{2+}$. The irreversible one-electron peak at -1.47 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 ($< -2.0 \text{ V}$), Fe(II) is reduced to Fe(0).²⁶

A certain insight into the fine equilibria between the $(\text{HL}^2)^-$ 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 $\text{Fe}(\text{HL}^2)^+$ ($E_p^a \approx -0.30 \text{ V}$) on account of a decrease of the peak for FeCl_2 ($E_p^a = +0.02 \text{ V}$). 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 $(\text{HL}^2)^-$ 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 $\text{Fe}(\text{HL}^2)^+$ complex.

Dicationic complex. The complex $[\text{Fe}(\text{H}_2\text{L}^3)(\text{HL}^3)](\text{NO}_3)\cdot\text{H}_2\text{O}$, like the analogous semicarbazone compound, already dissociates to a large extent in the presence of an inert electrolyte, the dissociation into FeCl_4^- and H_2L^3 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 H_2L^3 , the $(\text{HL}^3)^-$ species exists also. It can be supposed that the ligand can be protonated to H_2L^3 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 HClO_4) served both to assess the stability of the complexes in acidic media and check the composition of particular species.²⁷ Protonation was carried out discontinuously and cyclic voltammograms were recorded after each increment of acid addition.

The cyclic voltammograms for $[\text{Fe}(\text{H}_2\text{L}^1)\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$ complex recorded before and after the addition of 2 H^+ /complex molecule are shown in Fig. 7. The peak for FeCl_4^- , obtained as the final product of protonation of all complex species in

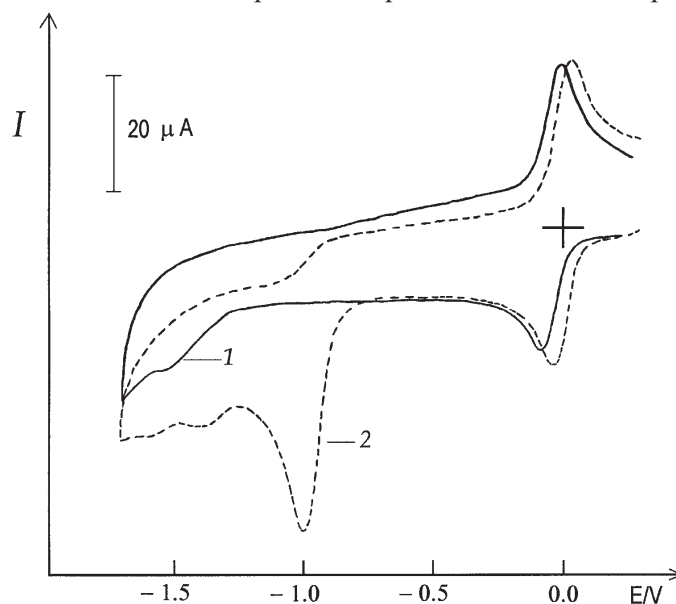


Fig. 7. Cyclic voltammograms for $[\text{Fe}(\text{H}_2\text{L}^1)\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$ in 0.1 M LiCl before (1) and after the addition of HClO_4 to the mole ratio 2 H^+ /Fe (2); 0.10 V s^{-1} .

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 $FeCl_4^-$ 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 $FeCl_4^-$ 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 H_2L was possible only with $[Fe(HL^1)_2]Cl$ and $[Fe(HL^2)_2]Cl$. 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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ИЗВОД

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

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Реакцијом топлих EtOH раствора $FeX_3 \cdot nH_2O$ ($X = Cl, NO_3$) са тридентатним семи-, тиосеми- и S-метилизотиосемикарбазоном пиридоксала (H_2L^1, H_2L^2 , односно H_2L^3) добијени су високоспински октаедарски моно- и bis(лиганд) комплекси формула $[Fe(H_2L^{1-3})Cl_2(H_2O)]Cl$, $[Fe(HL^{1,2})_2]Cl \cdot nH_2O$ и $[Fe(H_2L^3)(HL^3)](NO_3)_2 \cdot nH_2O$. Једињења су окарактерисана елементалном анализом, кондуктометријским и магнетохемијским мерењима, као и IR и UV-Vis спектрима. Извршено је детаљно волтаметријско испитивање добијених једињења у DMF у неколико помоћних електролита, истражене су природа електрохемијских процеса и равнотеже у раствору.

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REFERENCES

1. E. H. Abott, A. E. Martell, *J. Am. Chem. Soc.* **92** (1970) 5845
2. S. Capasso, F. Giordano, C. Mattia, L. Mazzarella, A. Ripamanti, *J. Chem. Soc. Dalton Trans* (1974) 2228
3. A. G. Sykes, R. D. Larsen, J. R. Fisher, E. H. Abott, *Inorg. Chem.* **30** (1991) 2911
4. P. Gili, M. G. Martin Reyes, M. G. Martin Zarza, M. F. C. Guedes da Silva, Y. -Y. Tong, A. J. L. Pombeiro, *Inorg. Chim. Acta* **225** (1997) 279

5. W. Henderson, L. L. Koh, J. D. Ranford, W. T. Robinson, J. O. Svensson, J. J. Vittal, Yu M. Wang, Y. Xu, *J. Chem. Soc. Dalton Trans* (1999) 3341
6. E. E. Snell, *Chemical and Biological Aspects of Pyridoxal Catalysis*, Pergamon, Oxford, 1963
7. M. Belicchi Ferrari, G. Gasparri Fava, C. Pelizzi, P. Tarasconi, G. Tosi, *J. Chem. Soc. Dalton Trans* (1986) 2455
8. J. S. Casas, E. E. Castellano, M. C. Rodriguez-Argüelles, A. Sanchez, J. Sordo, J. Zukerman-Schpector, *Inorg. Chim. Acta* **260** (1997) 183 and refs. therein
9. J. S. Casas, M. C. Rodriguez-Argüelles, U. Russo, A. Sanchez, J. Sordo, A. Vazques - Lopez, S. Pinelli, P. Lunghi, A. Bonati, R. Albertini, *J. Inorg. Biochem.* **69** (1998) 283
10. V. M. Leovac, V. S. Jevtović, G. A. Bogdanović, *Acta Cryst.* **C58** (2002) 514
11. D. Poleti, Lj. Karanović, V. M. Leovac, V. S. Jevtović, *Acta Cryst.* **C59** (2003) 73
12. N. Z. Knežević, V. M. Leovac, V. S. Jevtović, S. Grgurić-Šipka, T. J. Sabo, *Inorg. Chem. Commun.* **6** (2003) 561
13. M. Mohan, P. H. Modhuranath, A. Kumar, M. Kumar, N. K. Jha, *Inorg. Chem.* **28** (1989) 96
14. M. Belicchi Ferrari, G. Gasparri Fava, S. Pineli, C. Pelizzi, P. Tarasconi, *6th Yugoslav-Italian Crystallographic conference*, Pula, 1989, Abstracts p. 23
15. M. Belicchi Ferrari, G. Gasparri Fava, C. Pelizzi, P. Tarasconi, G. Tosi, *J. Chem. Soc. Dalton Trans* (1987) 227
16. M. Belicchi Ferrari, G. Gasparri Fava, M. Lanfranchi, C. Pelizzi, P. Tarasconi, *J. Chem. Soc. Dalton Trans* (1991) 1951
17. M. Belicchi Ferrari, G. Gasparri Fava, C. Pelizzi, G. Pelosi, P. Tarasconi, *Inorg. Chim. Acta* **269** (1998) 297
18. V. M. Leovac *et al.*, unpublished results
19. W. J. Geary, *Coord. Chem. Rev.* **7** (1971) 81
20. Yu. N. Kukushkin, *Khimiya koordinatsionnykh soedinenii*, Vysshaya shkola, Moskva, 1985
21. V. A. Kogan, V. V. Zelentsov, G. M. Larin, V. V. Lukov, *Kompleksy perekhodnykh metallov s gidrozonami*, Nauka, Moskva, 1990
22. L. Bjelica, Lj. Jovanović, *J. Electroanal. Chem.* **213** (1986) 85
23. L. J. Bjelica, Lj. S. Jovanović, V. M. Leovac, *Z. Phys. Chemie (Leipzig)* **269** (1988) 768
24. V. M. Leovac, Lj. S. Jovanović, L. J. Bjelica, V. I. Češljević, *Polyhedron* **8** (1989) 135
25. Lj. Jovanović *et al.*, in preparation
26. Lj. S. Jovanović, *Ph. D. Thesis*, Faculty of Science, University of Novi Sad, Novi Sad, 1986
27. Lj. Jovanović, L. Bjelica, F. F. Gaál, *Monatsh. Chem.* **116** (1985) 443
28. J. M. Sevilla, G. Cambron, T. Pineda, M. Blázquez, *J. Electroanal. Chem.* **381** (1995) 179
29. L. J. Bjelica, Lj. S. Jovanović, *Electrochim. Acta* **37** (1992) 371.