Polyhedron Vol. 4, No. 2, pp. 233–242, 1985
Printed in Great Britain.

0277-5387/85 \$3.00 + .00

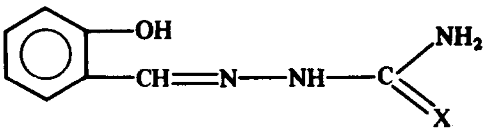
SYNTHESIS, PHYSICOCHEMICAL PROPERTIES AND VOLTAMMETRIC CHARACTERIZATION OF SOME NEW Fe(III) COMPLEXES WITH SEMICARBAZONE-BASED LIGANDS

VUKADIN M. LEOVAC,* LUKA BJELICA and LJILJANA JOVANOVIĆ
Institute of Chemistry, Faculty of Sciences, V. Vlahovića 2, 21000 Novi Sad, Yugoslavia

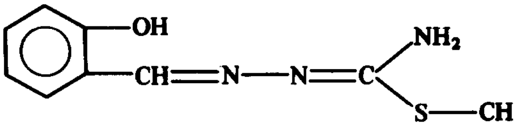
(*Received* 10 *February* 1984; *accepted* 16 *April* 1984)

Abstract—Several bis(ligand) octahedral complexes of iron(III) with salicylaldehyde semi-, thiosemi-, and S-methylthiosemi- carbazones have been synthesized and characterized by elemental analysis, conductivity and magnetic measurements, electronic and IR spectra, as well as by linear sweep and cyclic voltammetry. General procedures for the syntheses of all types of complexes have been established, giving better defined reaction conditions. Physicochemical properties of the novel complexes have been related to those of the already known compounds of the same type.

It has been established[1–4] that salicylaldehyde semicarbazone (H_2L^1), thiosemicarbazone (H_2L^2), and S-methylthiosemicarbazone (H_2L^3):



($X{=}O \sim H_2L^1$; $X{=}S \sim H_2L^2$)



(H_2L^3)

use in coordination with Fe(III) the following sets of donor atoms: ONO, ONS and ONN, respectively. Depending on pH of the reacting medium, these ligands can take part in coordination either as mono- (HL^-) or di-anion (L^{2-}). The syntheses of the following types of octahedral bis(ligand) chelate complexes of Fe(III): $[Fe(HL)_2]X$ ($X = Cl$, etc., $HL = HL^1$, HL^3)[1,4]; $Fe(HL)L$ ($HL = HL^3$, $L = L^3$)[4]; and $M[FeL_2]$ (M = Li, NH_4, etc. L = L^1, L^2)[1,3] have been reported in addition to the mono(ligand) complexes $Fe(HL)Cl_2$ (HL = HL^1, HL^2, HL^3).[1,2,4]

Not all types of Fe(III) bis(ligand) complexes have been prepared with each of the above ligands so, we have investigated the preparation of the missing complexes (i.e. $Fe(HL^1)L^1$, $Li[FeL_2^1]$, $[Fe(HL^2)_2]Cl$, $Fe(HL^2)L^2$, and $Li[FeL_2^3]$). The novel complexes have been characterized both crystalline and in solution, and their physicochemical properties have been related to those of the already known compounds.

EXPERIMENTAL

Chemicals and methods

The ligands employed in syntheses were prepared according to procedures described earlier.[5,6] For all syntheses only the Merck $FeCl_3{\cdot}6H_2O$ reagent grade was used. Other chemicals for syntheses were also of p.a. quality of different make.

The voltammetric, conductometric and spectrophotometric measurements were carried out in spectroscopic and freshly distilled p.a. solvents, respectively. The salts serving as supporting electrolytes (tetrabutylammonium perchlorate, TBAP, lithium perchlorate and lithium chloride) were used after recrystallization.

The C,H,N analysis procedure and magnetic susceptibility measurements have been described earlier.[7]

Chlorine was determined by combustion after Schöniger followed by titration with silver nitrate.

For all measurements the air-dry complexes were used except for voltammetric investigations, where drying at 110°C was applied.

Conductivity measurements were carried out using a conductivity meter Radiometer CDM3.

---

*Author to whom correspondence should be addressed.

IR spectra were recorded in KBr, employing a Perkin–Elmer 457 instrument.

Electronic spectra within the range of 37,000–12,500 cm^{-1} were recorded for the solutions of complexes in N,N-dimethylformamide (DMF) on a Cary 219 spectrophotometer.

Voltammetric experiments were carried out in the thoroughly deaerated (with purged nitrogen) 1 mM solutions of complexes in DMF, containing 0.1 M supporting electrolyte. An AMEL three-electrode set-up was used together with a Hewlett Packard 7044A *x–y* recorder, or a Hewlett Packard 1741A storage oscilloscope for recording the voltammograms. As the working electrode a glassy carbon disc (geometric surface area: 7 mm^2) was used with a Pt ring counter electrode. An aqueous saturated calomel electrode (Ingold) served as reference and all potentials are reported with respect to this electrode. The experiments were carried out at room temperature, and IR drop corrections were made, when necessary.

Preparation of complexes

For a comparative study of the novel and the already synthesized complexes we prepared all of them according to our own procedures. Since some significant alterations were made in the already known procedures, we have included them here, along with the original ones.

$[Fe(HL^1)_2]Cl\cdot H_2O$. The mixture of 1.0 g of $FeCl_3\cdot 6H_2O$ and 1.2 g of H_2L^1 was dissolved by heating in 15 cm^3 of EtOH (pH 0.4). By adding aqueous ammonia the pH was adjusted to 1.0. This was accompanied by a change of colour of the solution from yellow–brown to deep-purple. The solution was left at room temperature for 24 hr. The black crystals obtained were filtered off and washed with EtOH and Et_2O. Yield: 0.8 g.

$[Fe(HL^2)_2]Cl$. 0.6 g of $FeCl_3\cdot 6H_2O$ was dissolved by heating in 15 cm^3 of EtOH and mixed with 0.5 g of $NaOAc\cdot 3H_2O$. After addition of the acetate pH changed from the initial 1.5 to 2.0. The precipitated NaCl was, after solution cooling to room temperature, filtered off and 0.95 g of H_2L^2 was added to the solution. The mixture was heated gently for 5 min with constant stirring. The ligand dissolution was accompanied by precipitation of black crystals, which, after keeping the reacting mixture at room temperature for 1 hr, were filtered off and washed with EtOH and Et_2O. Yield: 0.9 g.

$Fe(HL^1)L^1\cdot H_2O$. 0.50 g of $[Fe(HL^1)_2]Cl\cdot H_2O$ was dissolved by heating in 30 cm^3 of MeOH. The warm mixture was filtered, then 0.1 g of $LiOAc\cdot 2H_2O$ added to the solution and the reacting mixture heated for about 10 min. A colour change from deep-purple to brown was noticeable. The reacting mixture was left at room temperature for 5 hr. The black crystals were washed with MeOH and Et_2O. Yield: 0.35 g.

$Fe(HL^2)L^2$ was prepared in a way analogous to the preceeding one. In contrast to the former one, this complex was also obtained by a direct synthesis, as follows:

The mixture of 0.6 g of $FeCl_3\cdot 6H_2O$ and 1.0 g of $NaOAc\cdot 3H_2O$ was dissolved by heating in 15 cm^3 of EtOH. The NaCl was filtered off, and to the solution (pH 6) a portion of 0.8 g of H_2L^2 was added. The mixture was heated gently to the complete ligand dissolution (about 10 min). The obtained microcrystalline black precipitate was filtered off and washed with EtOH and Et_2O. Yield: 0.70 g.

$Li[FeL^1_2]\cdot 3H_2O$. The mixture containing 0.70 g of $[Fe(HL^1)_2]Cl\cdot H_2O$ and 0.080 g of $LiOH\cdot H_2O$ in 10 cm^3 of EtOH was heated gently† for 5 min and the solution after filtration left at room temperature for 24 hr. The microcrystalline black crystals were washed with the EtOH–Et_2O (1:1) mixture, and finally with Et_2O. Yield: 0.35 g.

$Li[FeL^2_2]\cdot H_2O$. The mixture of 0.45 g of $Fe(HL^2)L^2$ and 0.080 g of $LiOH\cdot H_2O$ in 7 cm^3 of MeOH was heated for 5 min. Dissolution of the starting complex was accompanied by formation of the needle-like black–green crystals, which, after solution cooling to room temperature, were filtered off and washed with MeOH and Et_2O. Yield: 0.35 g.

$Li[FeL^3_2]\cdot H_2O$. 0.94 g of $Fe(HL^3)L^3$ was added into 20 cm^3 of MeOH and all heated gently. Afterwards, to it was added 0.125 g of $LiOH\cdot H_2O$ dissolved in 5 cm^3 of MeOH, and the reacting mixture heated gently to complete dissolution of the complex. After warm filtration, 10 cm^3 of Et_2O were added and the solution left in a closed vessel at room temperature for 15 hr. The black cubic crystals obtained (which if powdered are of dark-green colour) were filtered off and washed with MeOH and Et_2O. Yield: 0.60 g.

If the solution after filtration was transferred to an evaporating dish and left to concentrate at room temperature to one third of the starting volume, greenish flaky crystals were formed. The crystals were washed with 10 cm^3 of MeOH–Et_2O (1:1) mixture, and finally with Et_2O. Yield: 0.60 g. (This, easier soluble, modification was chemically identical to the former one.)

---

†Overheating of the mixture resulted in complex degradation and precipitation of the ligand.

$Fe(HL^1)Cl_2{\cdot}2H_2O$. The mixture of 0.45 g of H_2L^1 and 1.5 g of $FeCl_3{\cdot}6H_2O$ was dissolved by heating in 5 cm^3 of acetone. The green solution after filtration was left in an open Erlenmeyer flask for about 3 days. The black crystals were filtered off and washed with EtOH and Et_2O. Yield: 0.20 g.

$Fe(HL^2)Cl_2{\cdot}H_2O$. 0.80 g of $FeCl_3{\cdot}6H_2O$ and 0.50 g of H_2L^2 were dissolved by heating in 7 cm^3 of EtOH and left at room temperature for 24 h. The black crystals were filtered off and washed with EtOH, then with 20 cm^3 of the EtOH–Et_2O (1 : 1) mixture and finally wiht Et_2O. Yield: 0.35 g.

Complexes $[Fe(HL^3)_2]Cl$, $Fe(HL^3)L^3$ and $Fe(HL^3)Cl_2$ were prepared following strictly the procedures described earlier.[4]

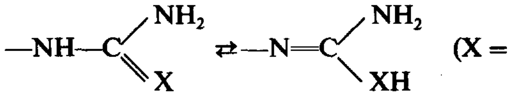
RESULTS AND DISCUSSION

Syntheses and general characteristics of complexes

The results of elemental analysis of the complexes obtained by the above procedures have been presented in Table 1.

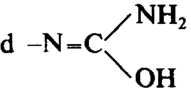
Formation of different types of complexes is made possible by coordination of the ligand either as a mono- or di-anion. The mono-anion, HL^-, results from deprotonation of the phenolic OH group, leading to formation of the cationic complex, $[Fe(HL)_2]^+$†. For an efficient crystallization of this complex, the ethanolic solution of the Fe(III) salt ought to have pH 1–2. This can be adjusted by adding the necessary amount of either aqueous ammonia, or ethanolic solution of $NaOAc{\cdot}3H_2O$.

Complexes of the non-electrolyte type, Fe(HL)L, to which in a DMF solution (as it will be discussed later on) corresponds, most probably, a dimeric formula $[Fe(HL)_2][FeL_2]$, are formed as the result of a further deprotonation of the ligand, leading to its di-anionic form, L^{2-}. This deprotonation is made possible in the case of semi- and thiosemi- carbazones by a tautomeric equilibrium:



$$-NH-C(=X)NH_2 \rightleftarrows -N=C(XH)NH_2 \quad (X = O, S)$$

taking place at the chalcogen atom. In contrast to this, the di-anion form in the case of S-methylthiosemicarbazone is formed by deprotonation (apart from phenolic group) of the coordinated NH_2 group.[4]

Syntheses of the crystalline complexes of the non-electrolyte type with all three ligands were accomplished in two different ways, i.e. by direct and indirect synthesis. The first method involved reacting the ethanolic solution of Fe(III) hydroxoacetate (obtained in the reaction of $FeCl_3{\cdot}6H_2O$ and $NaOAc{\cdot}3H_2O$, after removal of NaCl) and a stoichiometric amount of the ligand. The indirect synthesis can be realized either by reacting the methanolic solution of the cationic complex and an excess of $LiOAc{\cdot}2H_2O$, or, by mixing the methanolic solutions of the corresponding cationic and anionic complex in a stoichiometric ratio. In all three cases the complexes of a satisfactory purity are formed. This holds for H_2L^2 and H_2L^3 complexes, while the direct synthesis in the case of H_2L^1 resulted in $[Fe(HL^1)_2]OAc{\cdot}H_2O$. This indicates a hindered deprotonation of the OH group from the enolized  $-N=C(NH_2)OH$ fragment.

The anionic type of complexes, i.e. the corresponding lithium salts, $Li[FeL_2]{\cdot}xH_2O$, were obtained in the reaction of alcoholic solutions of either cationic, or, non-electrolyte complexes and a smaller excess of $LiOH{\cdot}H_2O$.

In contrast to the above group, the mono-(ligand) complexes can be obtained from concentrated solutions of $FeCl_3{\cdot}6H_2O$ and the corresponding ligand in EtOH and Me_2CO, respectively, in the presence of an excess of the Fe(III) salt.

All described complexes are black crystals, while in powdered state they are brown. The exception is $Li[FeL^3_2]{\cdot}H_2O$ which is green. The complexes are mostly soluble in MeOH, EtOH and DMF; the solubility of the anionic and mono(ligand) complexes being generally the highest and that of the non-electrolyte type the lowest. The former two types of complexes are moderately soluble in water, the others being practically insoluble. Dissolution in water is often accompanied by the complex decomposition. All the complexes are insoluble in Et_2O.

On the basis of the data presented in Table 2, it can be concluded that mono(ligand) and cationic complexes are thermally less stable than other types of complexes. The common characteristic of the non-electrolyte complexes is that they are susceptible to certain changes at higher temperatures, which are not easily observable due to

---

†Isolation of the crystalline $[Fe(HL^1)_2]Cl.H_2O$, described earlier,[1] was not possible with the $FeCl_3.6H_2O$ at our disposal without a pH adjustment; the later fact was not mentioned in the original work.

Table 1. Analytical data for Fe(III) complexes

Complex	C(%)		H(%)		N(%)		Cl(%)		H_2O(%)	
	a	b	a	b	a	b	a	b	a	b
$Fe(HL^1)Cl_2\cdot 2H_2O$	28.99	28.18	4.26	3.55	12.94	12.32	20.24	20.79	10.91	10.57
$[Fe(HL^1)_2]Cl\cdot H_2O$	41.43	41.27	4.08	3.90	18.48	18.04	7.54	7.61	3.33	3.87
$Fe(HL^1)L^1\cdot H_2O$	45.41	44.78	4.43	3.99	19.61	19.57				
$Li[FeL^1_2]\cdot 3H_2O$	40.08	40.79	4.32	4.28	17.25	17.83			10.53	11.47
$Fe(HL^2)Cl_2\cdot H_2O^c$	29.16	28.35	3.03	2.97	12.45	12.39	20.80	20.92	4.70	5.31
$[Fe(HL^2)_2]Cl$	40.22	40.06	3.56	3.36	17.38	17.55	7.24	7.38		
$Fe(HL^2)L^2$	43.54	43.35	3.50	3.41	19.21	18.95				
$Li[FeL^2_2]\cdot H_2O^d$	40.78	41.13	3.59	3.45	18.13	17.98				
$Li[FeL^3_2]\cdot 2H_2O$	42.19	42.12	4.37	4.32	16.28	16.36			7.50	7.02

[a] Found. [b] Calculated. [c] $Fe(HL^2)Cl_2\cdot 2.5\ H_2O$ reported in ref. 2. [d] $Li[FeL^2_2]\cdot 2H_2O$ reported in ref. 3.

their dark colour. After these changes, on elevation of temperature, the substance decomposes with evolution of gaseous products. Thus, no melting occurs. Some other complexes behave similarly.

Molar conductivity

The results of molar conductivity measurements have been presented in Table 2. Although the selected solvents, MeOH and DMF, are not the best for conductivity measurements, due to their possible interactions with the dissolved complexes,[8] they were chosen to support the suggested formulae, for the reason of a relatively good solubility of the studied complexes. In general, the conductivities of all types of complexes are lower in DMF than usually expected for 1:1 electrolytes (65–90) while the values measured in MeOH fall mostly within the range for 1:1 electrolytes (80–115).[8]

The lower conductivity of cationic complexes in DMF can be explained by possible interaction of the complexed Fe(III) species with almost unsolvated Cl^- (the donor/acceptor properties of

Table 2. Physical properties of investigated Fe(III) complexes

Complex	Conductivity, Λ_M[a]		M_p,	μ_{eff}(solid)[b],
	MeOH	DMF	°C	BM
$Fe(HL^1)Cl_2\cdot 2H_2O$	110.4	54.9[c]	260[d]	5.22
$[Fe(HL^1)_2]Cl\cdot H_2O$	78.7	36.1	238	5.86
$Fe(HL^1)L^1\cdot H_2O$	e	7.8[c]	>400[d]	5.84
$Li[FeL^1_2]\cdot 3H_2O$	43.2	51.5	295	6.03
$Fe(HL^2)Cl_2\cdot H_2O$	81.8	49.9[c]	200	5.99
$[Fe(HL^2)_2]Cl$	84.3	19.1	228	5.87
$Fe(HL^2)L^2$	e	91.2[c]	258[d]	5.85
$Li[FeL^2_2]\cdot H_2O$	77.2	48.6	>340[d]	2.73
$Fe(HL^3)Cl_2$	82.1	45.6[c]	235	5.75
$[Fe(HL^3)_2]Cl$	87.4	27.1	219	5.86
$Fe(HL^3)L^3$	14.2[c]	6.4[c]	>380[d]	5.89
$Li[FeL^3_2]\cdot 2H_2O$	76.5	29.7	260	5.95

[a] In $S\ mol^{-1}\ cm^2$; 1 mM at 23°C. [b] Measured at 298 K. [c] Calculated for dimer. [d] Temperature at which change occurs, decomposition without melting. [e] Sparingly soluble.

DMF and Cl^- are about the same),[9] resulting thus in the ion-pair formation. The same holds for anionic complexes where Li^+ solvation by DMF must be taken into account. In addition, although it is not obvious from the first sight, the non-electrolyte complexes in DMF may be still present in the dimeric form, i.e. $[Fe(HL)_2][FeL_2]$, as it was confirmed by voltammetric study (see later). The extremely low conductivity of these complexes (with the exception of the thiosemicarbazone one) can be explained also by interactions of the weakly solvated constituent cation and anion. In contrast to this, the suggested dimeric structure for non-electrolyte complexes could not be confirmed in MeOH, because of low solubility of the two complexes and the inconvenience of MeOH as solvent in voltammetric measurements. Finally, the supposed dimeric formula of the mono(ligand) complexes in DMF, i.e. $[Fe(HL)_2][FeCl_4]$, is suggested (apart from the voltammetric experiments) by the data characteristic for 1:1 electrolytes.

Magnetic susceptibilities

As can be seen from Table 2, all of the complexes, with the exception of $Li[FeL^2_2]\cdot H_2O$, have at room temperature the values for effective magnetic moments characteristic for the high-spin octahedral Fe(III) complexes (term $^6A_1$). This means that neither a change in charge of the complex/ligand, nor even a change of the set of coordinated atoms from N_2O_4 (in H_2L^1) via $N_2O_2S_2$ (in H_2L^2) to N_4O_2 (in H_2L^3), have enough influence on the strength of the ligand field sufficient to change the spin state of the central Fe(III) ion. The only exception is, as stated above, $Li[FeL^2_2]\cdot H_2O$, which as well as the earlier described di-hydrate $Li[FeL^2_2]\cdot 2H_2O$ (μ_{eff} (300) = 2.19 B.M.),[3] has the effective magnetic moment characteristic for a low-spin Fe(III) state (term $^2T_2$).

Such low μ_{eff} values for the obtained complex, as well as for the already reported di-hydrate, is not, undoubtedly, a consequence of the change of charge on the ligand, but is due to the strong polarizing effect of the Li^+ ion.[3]

IR spectra

As has been already mentioned,[1-3] each of the ligands under consideration use three donor atoms† in coordination. Two donor atoms are common for all three ligands, namely: oxygen from the phenolic hydroxyl and nitrogen from the azomethine group. The third donor atom in H_2L^1 is oxygen of the C=O group,[1] the sulphur of the analogous C=S group[2] in H_2L^2 and the nitrogen from the NH_2 group[3] in H_2L^3.

The IR spectra of the ligands and complexes described here, indicate that the above donor atoms are engaged in coordination. The strong band appearing at 1270 cm^{-1} in the IR spectra of all three ligands, assigned to valence vibration of the phenolic C–O group,[12] is shifted in the complexes toward higher energies ($1290 \pm 10\ cm^{-1}$), indicating that the oxygen takes part in coordination.

The very strong and sharp band for the azomethine group, $\nu(C=N)$, which in the spectra for free ligands H_2L^2 and H_2L^3 is at $1600 \pm 10\ cm^{-1}$, is shifted for complexes by about 10 cm^{-1} to lower energies,[13,14] while in the case of H_2L^1 complexes it is shifted by the same amount in the opposite direction.[10]

The very strong band $\nu(C=O)(H_2L^1)$, appearing at 1690 cm^{-1} in the ligand spectrum is also shifted due to coordination towards lower frequencies ($\Delta\nu = 45\ cm^{-1}$).

An indication that the sulphur atom in H_2L^2 (as the third donor atom) is coordinated, is the absence of the bands at 1070 and 1370 cm^{-1}, corresponding to ν_s and $\nu_{as}(C=S)$ in the free ligand spectrum.[15]

Coordination of nitrogen from the NH_2 group of H_2L^3 can be substantiated by its deprotonation leading to a di-anionic form of the ligand, and by a shift of the strong and sharp $\delta(NH_2)$ band from 1635 to 1600 cm^{-1}. It should be mentioned that this band in the spectra for other two ligands is not well separated from the main $\nu(C=N)$ band. Therefore, it appears as a shoulder at 1615 cm^{-1}, remaining in complexes, practically, at the same position.

Electronic spectra

The corresponding electronic spectral data for all types of complexes in DMF are given in Table 3. It is common for all complexes that only a few well developed absorption maxima ($\epsilon < 7{,}000$) are formed in the visible region, the other appearing as broad absorption bands or shoulders. Thus, the main spectral characteristics of a particular type of complexes arise in UV region, where they are influenced by the structure of the ligand involved in coordination. Generally, the UV spectra of cationic and mono(ligand) species resemble the

---

†In Refs. 10 and 11 the examples have been reported for a bidentate coordination of salicylaldehyde semicarbazone.

Table 3. Electronic spectral data for Fe(III) complexes in DMF

Complex	$\lambda^{a}_{max}(\varepsilon^{b})$
$Fe(HL^1)Cl_2 \cdot 2H_2O^c$	18,250(0.31), 31,450(2.56), 36,230(4.53)
$[Fe(HL^1)_2]Cl \cdot H_2O$	18,800(0.30), 22,320(sh)^d, 31,250(sh), 32,680(sh), 36,100(3.80)
$Fe(HL^1)L^1 \cdot H_2O^c$	22,830(0.86), 28,730(3.54), 33,110(sh), 35,710(6.24)
$Li[FeL^1_2] \cdot 3H_2O$	~17,600(b.p.)^e, 20,490(sh), 23,360(0.42), 28,410(2.98), 34,960(2.17)
$Fe(HL^2)Cl_2 \cdot H_2O^c$	~19,000(sh), 28,650(sh), 29,940(4.85), 30,960(4.63 sh), 32,570(4.56), 33.670(4.48 sh)
$[Fe(HL^2)_2]Cl$	~19,100(sh), ~23,200(sh), 28,650(sh), 30,030(4.10), 31,150(sh), 32,470(3.50), 33.560(sh)
$Fe(HL^2)L^{2c}$	20,160(sh), 30,030(sh), 31,050(5.56 sh) 34,500(6.0 b.p.)
$Li[FeL^2_2] \cdot H_2O$	16,500(0.19), 27,100(1.88 sh), 31,250(2.10), 36,360(2.60)
$Fe(HL^3)Cl_2{}^c$	22,520(0.43), 28,570(sh), 30,030(3.64), 31,150(sh), 32,900(sh), 34,130(4.25)
$[Fe(HL^3)_2]Cl$	22,520(0.31), 28,570(sh), 29,850(3.16), 32,890(3.0 sh), 34,250(3.34)
$Fe(HL^3)L^{3c}$	21,270(1.22), 28,820(4.92), 31,350(4.84), 35,090(6.26)
$Li[FeL^3_2] \cdot 2H_2O$	~16,700(0.15), 21,190(0.74), 31,250(2.72), 36,360(2.09)

^{a}In cm^{-1}. ^{b}In $dm^3\ mol^{-1}\ cm^{-1} \times 10^{-4}$. ^{c}Taken as dimer. ^{d}Shoulder. ^{e}Broad peak.

spectra of ligand alone, with usually two well separated absorption bands. For thiosemi- and S-methylthiosemi- carbazone complexes the main absorption occurs at $\sim 30{,}000\ cm^{-1}$ ($\epsilon > 30{,}000$) and in the range of $32{,}000$–$34{,}000\ cm^{-1}$ ($\epsilon 30{,}000$–$40{,}000$) where two insufficiently separated absorption maxima are observed. The exceptions are the semicarbazone complexes of the same type, where one of two main peaks appearing in the spectrum of the ligand alone at $31{,}000\ cm^{-1}$ in the complexes disappears. The other significant maximum in these spectra at $\sim 36{,}000\ cm^{-1}$ ($\epsilon > 30{,}000$) is also present in the spectrum of the ligand itself.

The spectra for all three anionic complexes differ from each other and from those for corresponding ligands. The common characteristic of $Li[FeL^2_2]$ and $Li[FeL^3_2]$ is the appearance of a band at $\sim 36{,}000\ cm^{-1}$ ($\epsilon > 20{,}000$) which does not exist in the corresponding ligand spectrum. This reflects the structural/electronic differences of the ligand in H_2L and L^{2-} form.

Electronic spectra of non-electrolyte type of complexes resemble the superimposed spectra of the corresponding cationic and anionic species. It also may be a confirmation of the supposed dimeric structure of the non-electrolyte complexes in DMF solutions.

Finally, it is well known that the electronic spectra of iron(III) complexes contain only exceptionally *d–d* transitions; the bands being sometimes overlapped by the strong charge transfer absorptions.[16] Hence, it might be expected that all absorptions in the studied complexes occuring below $29{,}000\ cm^{-1}$ belong to $d-\pi^*$ interactions. The absorptions at $>29{,}000\ cm^{-1}$, since they are in

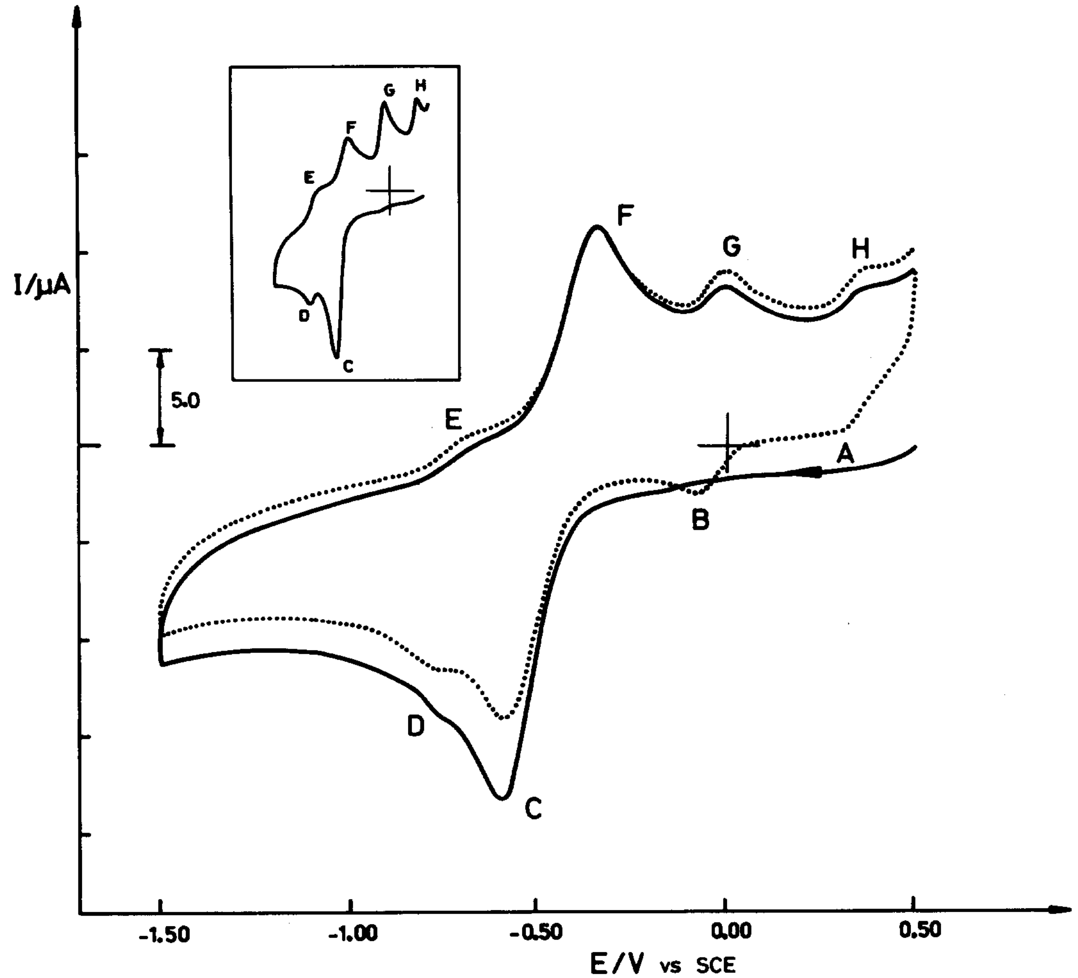


Fig. 1. Cyclic voltammograms for $[Fe(HL^2)_2]Cl$ and $[Fe(HL^3)_2]Cl$ (inset); 1 mM DMF solutions, 0.1 M LiCl. ———, 1st cycle; . . . . . , 2nd cycle. Sweep rate: 0.200 V s^{-1}.

some way present in the ligand spectrum, may be attributed to the ligand π–π^* transitions.

Voltammetric studies

It has been found that shapes of cyclic voltammograms for some complexes are greatly affected by the nature of the supporting electrolyte present in the solution. In the presence of an "inert" electrolyte, such as TBAP, the voltammetric curves, with exception of those for the anionic complexes, are ill-defined and difficult to interpret. The addition of LiCl to the solutions of H_2L^2 and H_2L^3 complexes resulted in much better defined voltammograms. This favourable effect can be ascribed both to the ability of Fe(III) to form relatively stable complexes with chloride, and to the ion-pairing effect of the lithium ion. Hence, all the voltammograms presented were recorded for the complex solutions containing 0.1 M lithium chloride. On the other hand, it appeared that the electrode reactions in the presence of this electrolyte are coupled to a number of chemical reactions†.

We have presented here the voltammetric characteristics for the novel complexes in comparison to those of the already known compounds. To facilitate discussion, all the reduction-oxidation peaks have been identified and denoted by capital letters.

Cyclic voltammogram for the newly synthesized cationic complex $[Fe(HL^2)_2]Cl$ (Fig. 1) is quite similar to that (shown in the inset) for the analogous compound in the H_2L^3 series.[18] Thus, similarity of the cyclic voltammograms is another confirmation of the supposed complex type. From the difference between the first and the second scan it can be concluded that only the main reduction

---

†A detailed electrochemical study of the full range of Fe(III) complexes with all three ligands, including the possible reaction schemes, will be described elsewhere.[17]

peak (denoted as C) and its oxidation counterpart (F) are directly related to the species present in the bulk; the other peaks being the consequences of coupled chemical reactions. The detailed studies showed that the species corresponding to peak C is not a bis(ligand) complex cation $[Fe(HL^2)_2]^+$, but a mono(ligand) one, $[Fe(HL^2)Cl_x]^{2-x}$, where x is most likely equal to 3. The C–F separation is, within the range of scan rates employed, characteristic for an apparent quasi-reversible one-electron process, involving chemical complications. The reduction peak D (oxidation counterpart: E), which in this case is much less separated from peak C if compared to the picture shown in the inset, obtained at the same sweep rate, can be assigned to the reduction of the anionic species $[FeL^2_2]^-$, formed by a chemical reaction following the electronation at C. After an oxidation at potential E, this species undergoes a further oxidation at peak H (reduction counterpart: A), after which follows another chemical reaction. Peak G (counterpart: B) represents the oxidation of $FeCl_2$, resulting from another chemical reaction i.e. the ligand releasing process occuring after the reduction at peak C.

The cyclic voltammograms presented for Li$[FeL^3_2]$ (Fig. 2) were recorded within two complementary potential amplitudes. The reason was the inability of the voltammetric equipment employed to complete a full cycle when an asymmetric potential signal was applied. It is evident that voltammetric behaviour of complexes of this type is much simpler than of the former ones. The

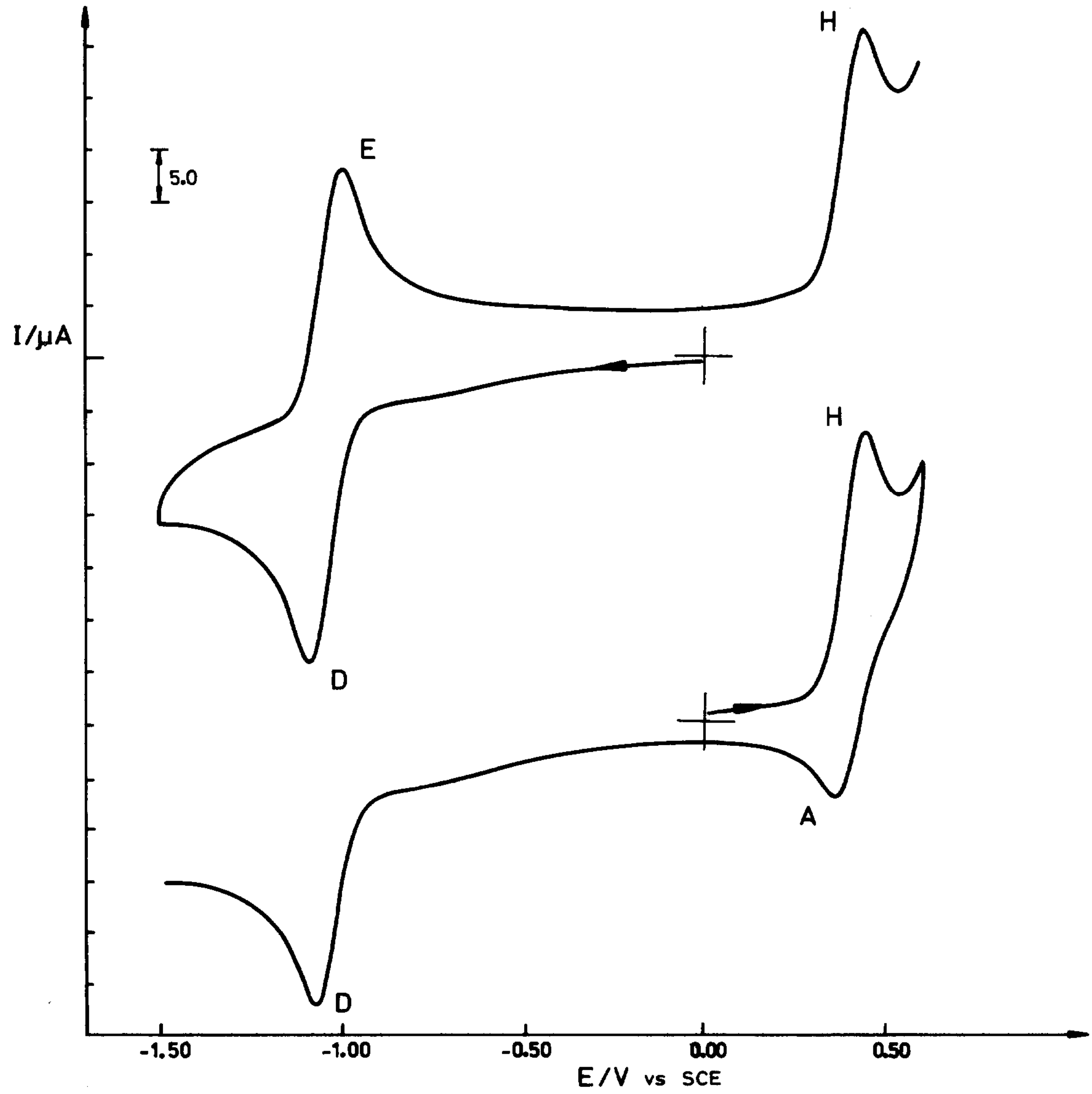


Fig. 2. Cyclic voltammograms for Li$[FeL^3_2]$; 1 mM DMF solution, 0.1 M LiCl. Sweep rate: 0.200 V s^{-1}.

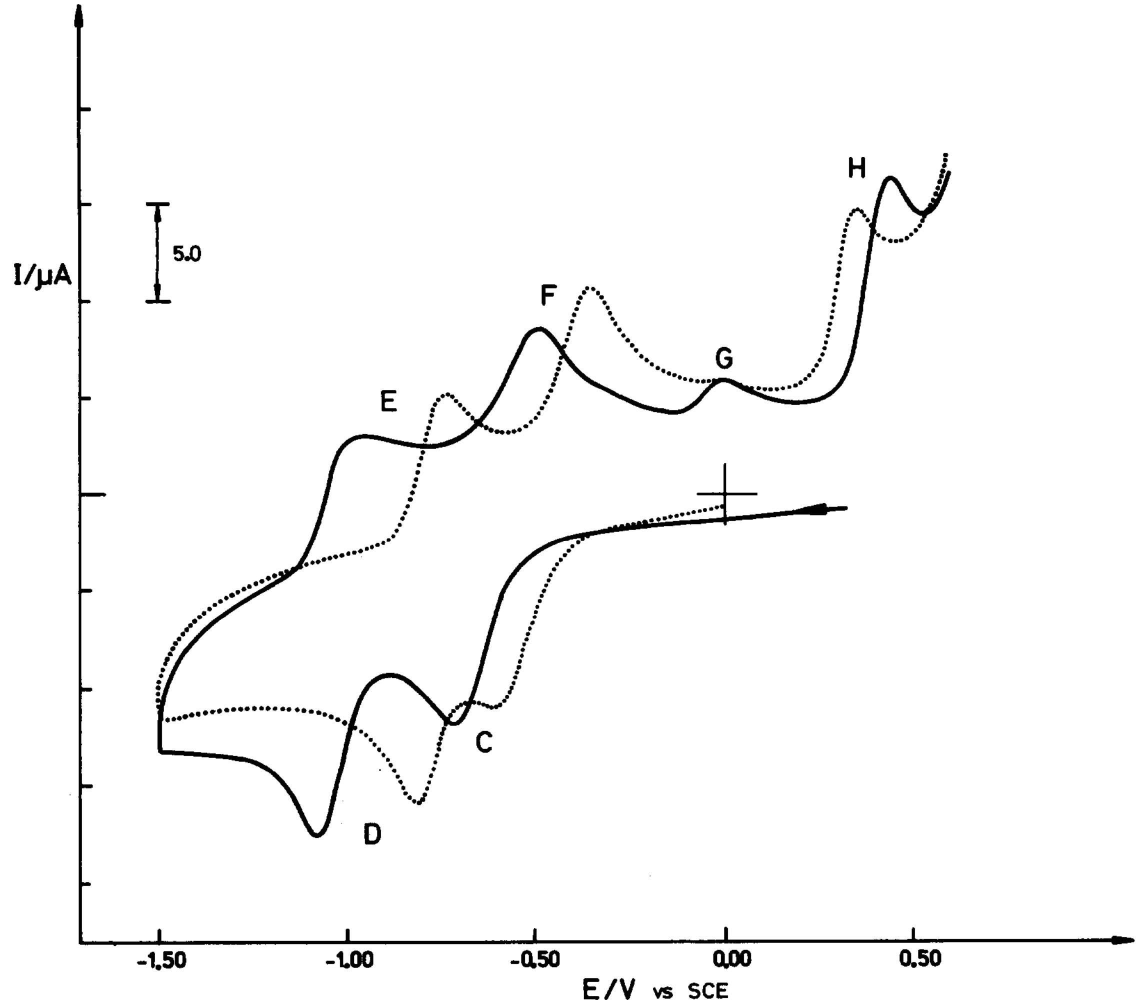


Fig. 3. Cyclic voltammograms for 0.5 mM DMF solutions of non-electrolyte complexes, 0.1 M LiCl. ....., $Fe(HL^2)L^2$; ———, $Fe(HL^3)L^3$. Sweep rate: 0.200 V s^{-1}.

complex is reduced in a one-electron quasi-reversible process (peak D; counterpart: E) and oxidized in a similar process (peak H; counterpart: A). The peak assignation was accomplished on the basis of the voltammograms for $[Fe(HL^3)_2]Cl$ and $Fe(HL^3)L^3$, as well as for $Li[FeL^3_2]$.[19]

Since for the anionic complex solutions containing TBAP or $LiClO_4$ the cyclic voltammograms obtained were generally of the same shape as the above ones, it can be concluded that Cl^- ion has no effect on the primary reactants, nor on the electrode reaction products. The difference in D/E peak potentials for the voltammograms recorded in the presence of TBAP and Li salts, respectively, consists in their anodic shifting with increasing Li^+ concentration, due to the ion-pair formation of Li^+ with both the reduced dianionic $[FeL_2]^{2-}$ and (to some extent) the original $[FeL_2]^-$ species.

Cyclic voltammograms for the non-electrolyte type of complexes, $Fe(HL^2)L^2$ and $Fe(HL^3)L^3$ (Fig. 3) do not reflect properties of the one unique species, but, as it can be concluded from the voltammograms shown in Figs. 1 and 2, they are composed of the parts characteristic for the corresponding cationic and anionic complex. This gives strong support to the idea that a more appropriate coordination formula for these complexes in DMF solutions should be $[Fe(HL)_2][FeL_2]$‡. As it has been already mentioned, this was also confirmed in the complex synthesis by mixing solutions of the corresponding constituent complexes. It should be mentioned that a similar conclusion on a dimeric nature is also valid for $Fe(HL)Cl_2$ complexes, whose more correct coordination formula, as stated above, should be $[Fe(HL)_2][FeCl_4]$.

Some cyclic voltammetry data on the non-electrolyte complexes obtained at glassy carbon

---

‡Another piece of evidence suggesting the same could be gained from the rotating disc experiments, resulting in two well defined waves, characteristic for pure cationic and anionic complexes, respectively.

Table 4. Cyclic voltammetry data for non-electrolyte type complexes on glassy carbon electrode[a]

Complex	v^b	$E^c_{p(C)}$	$E_{p(F)}$	$E_{p(D)}$	$E_{p(E)}$	$E_{p(H)}$	$E_{p(A)}$	$\frac{I^d_{p(C)}}{c\ v^{1/2}}$	$\frac{I_{p(D)}}{c\ v^{1/2}}$	$\frac{I_{p(H)}}{c\ v^{1/2}}$
$Fe(HL^1)L^1\cdot H_2O$	0.02	i.d.[e]	i.d.	-1.01	i.d.	+0.69	f	i.d.	41.4	i.d.
	0.20	-0.74	-0.43	-1.03	i.d.	+0.72	f	i.d.	43.1	i.d.
	2.00	-0.79	-0.37	-1.09	i.d.	i.d.	f	i.d.	42.1	i.d.
$Fe(HL^2)L^2$	0.02	-0.53	-0.40	-0.81	-0.74	+0.34	g	52.2	52.2	58.8
	0.20	-0.60	-0.35	-0.81	-0.73	+0.36	+0.28	49.1	49.1	55.7
	2.00	-0.66	-0.32	-0.83	-0.73	+0.37	+0.27	i.d.	i.d.	55.8
$Fe(HL^3)L^3$	0.02	-0.64	i.d.	-1.05	i.d.	+0.42	g	48.9	62.7	55.8
	0.20	-0.70	-0.51	-1.07	-0.97	+0.44	+0.37	55.2	59.5	53.3
	2.00	-0.76	-0.46	-1.10	-0.97	+0.45	+0.36	53.7	59.0	53.9

[a] In DMF solution, complex 0.5 mM(taken as dimer), 0.1 M LiCl supporting electrolyte. [b] Sweep rate, in V s^{-1}. [c] Electrode potentials in V vs. SCE. Letters in parentheses denote the corresponding peak. [d] In μA mM^{-1} $V^{-1/2}$ $s^{1/2}$. [e] Ill-defined peak. [f] Irreversible oxidation at H, no reduction peak A at the subsequent scan. [g] Due to the coupled chemical reaction, no peak A appear at this sweep rate.

electrode have been given in Table 4. Comparing the peak potentials for C/F, D/E and A/H couples for these complexes, it can be concluded that the thiosemicarbazone complexes are more easily reduced/oxidized than those of the other two classes of complexes. The effect is most pronounced in the case of D/E couple corresponding to bis(ligand) anionic species, where two sulphur atoms involved in coordination can facilitate stabilization of the product formed by the electron transfer.

The $\Delta E_p/\Delta \log v$ analysis gave a slope of about 60 mV per tenfold increase in sweep rate for peaks C/F, but less than 30 mV for all other peak couples. This indicates the possible kinetic complications, described above.

The voltammograms for the H_2L^1 complexes were not well defined (especially at higher sweep rates) in all supporting electrolytes used. Hence, they were less suitable for analysis. The exception was the anionic complex which behaves similarly to the analogous compounds described above.

Acknowledgement—The authors thank the Scientific Fund of SAP Vojvodina for financial support of the present work.

REFERENCES

1. N. M. Samus and V. G. Chebanu, *Zhur. Neorg. Khim.* 1969, **14**, 2089.
2. A. V. Ablov and N. V. Gerbeleu, *Zhur. Neorg. Khim.* 1965, **10**, 61.
3. V. V. Zelentsov, A. V. Ablov, K. I. Turte, R. A. Stukan, N. V. Gerbeleu, E. V. Ivanov, A. P. Bogdanov, N. A. Barba and V. G. Bodyu, *Zhur. Neorg. Khim.* 1972, **17**, 1929.
4. N. V. Gerbeleu, K. I. Turte, V. D. Canić, V. M. Leovac and V. B. Arion, *Koordinatsionnaya Khimiya* 1980, **6**, 446.
5. A. I. Vogel, *A Text-book of Practical Organic Chemistry, p.* 344. Longman, London (1972).
6. Gy. Argay, A. Kálmán, B. Ribár, V. M. Leovac and A. F. Petrović, *Monatsh. Chem.* 1983, **114**, 1205.
7. V. M. Leovac, V. Divjaković, D. Petrović, Gy. Argay and A. Kálmán, *Polyhedron* 1983, **2**, 1307.
8. W. J. Geary, *Coord. Chem. Rev.* 1971, **7**, 81.
9. V. Gutman, *Khimiya koordinatsionnykh soedinenii v nevodnykh rastvorakh*, trans. from English, p. 217. Mir, Moscow (1971).
10. R. N. Ray and B. K. Mohapatra, *Indian J. Chem.* 1980, **19A**, 590.
11. P. L. Maurya, B. V. Agarwala and A. K. Deu, *Indian J. Chem.* 1980, **19A**, 807.
12. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, p. 108 Methuen, London (1959).
13. D. M. Wiles and T. Supruchuk, *Canad. J. Chem.* 1969, **47**, 1097.
14. M. S. Patil and J. R. Shah, *J. Indian Chem. Soc.* 1981, **58**, 944.
15. N. V. Gerbeleu, *Zhur. Neorg. Khim.* 1968, **13**, 2467.
16. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, p. 761. Wiley-Interscience, New York (1980).
17. L. Bjelica, Lj. Jovanović and V. M. Leovac, to be published.
18. L. Bjelica, Lj. Jovanović, V. Leovac and F. Gaál, *7th Yugoslav Symposium on Electrochemistry*, pp. 163–167. Ohrid (1981).
19. Lj. Jovanović, L. Bjelica and V. Leovac, *8th Yugoslav Symposium on Electrochemistry*, pp. 30–34, Dubrovnik (1983).