

New Coordination Compounds of Fe(III) with Ligand from N-hydroxysuccinimide, with Applications in Ecologic Leather Tanning Technologies

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This paper presents the synthesis and study of three new complexes of iron (III) resulting from the interaction of FeCl₃ with N-hydroxysuccinimide in central atom: ligand ratio of 1:1, 1:2 and 1:3. For the study of the new compounds, specific methods for characterisation of complex combinations in solid state were used (derivatography, IR spectroscopy, Mossbauer spectroscopy, X-ray diffraction). The compounds thus obtained (central atom in octahedral arrangement, with high spin and triclinic crystal system) were tested, yielding good results in leather processing technologies, with the aim of totally or partially replacing chromium salts in the tanning operation.

Keywords: Fe(III) complexes, n-hydroxysuccinimide ligand, ecologic tanning, IR and Mossbauer spectroscopy, X-ray diffraction

The desire to totally or partially replace chromium compounds in leather tanning technologies and considerations regarding pollution and toxicity, which have induced international regulations, have led to the synthesisation and study of new tanning compounds from iron, complex combinations from the reaction of Fe³⁺ with N-hydroxysuccinimide in central atom: ligand ratio of 1:1, 1:2 and 1:3, with the following formulas: FeC₄H₄NO₃(OH)₂(H₂O)₂, Fe(C₄H₄NO₃)₂(OH)H₂O, Fe(C₄H₄NO₃)₃ [1-3].

The novelty of the paper consists in the use of N-hydroxysuccinimide ligand for the first time to obtain complex tanning combinations [2].

The study of compounds in solid state to establish their chemical composition was performed using methods such as derivatography, infrared spectroscopy, Mossbauer spectroscopy and X-ray diffraction [2-11].

Experimental part

Materials and methods

Experiments were conducted using solutions of 10⁻²M concentrations of FeCl₃ · 6H₂O – Merk and the N-hydroxysuccinimide ligand – Fluka.

Compounds in solid state were obtained by recrystallizing concentrated solutions.

For tanning experiments the following were used: pickled bovine leather weighing 25/30kg –Pielorex SA (prepared for tanning).

The equipment used in experiments is listed below:

- infrared absorption spectra of coordination compounds studied were recorded on solid samples in the 200-400 cm⁻¹ range employing the KBr pelleting method using an FTIR 660 Plus photometer;

- studied compounds were characterized by X-ray diffraction using a Bruker D8 Advan CE diffractometer with a nickel filter, copper anode;

- thermal stability of studied compounds was studied using the pelleting method with KBr 660 Plus using a Diamond TG/DTA derivatograph produced by Perkin Elmer – USA.

- Mossbauer spectra of compounds presented in this paper were recorded using an electronic device with uniformly accelerated motion using isotope ⁵⁷Cr as radiation source at temperatures of 80K and 300K;

- shrinkage temperatures of leather samples (pre)tanned with the new tanning compounds were determined using the classical method of immersion in warm water using a Giuliani device–Italy, as well as by differential scanning calorimetry using a DSC 204 F1 device Phoenix-Netsch Germany;

- leather tanning experiments with the new tanning compounds were performed using a Fane-Faloppi Italy tanning drum for laboratory experiments.

Thermal stability of complexes formed by dynamic thermogravimetry was studied to determine reaction rates and implicitly, obtain information on the reaction mechanism and values of kinetic parameters.

Infrared absorption spectra of coordination compounds studied were recorded to determine changes in frequencies of chemical bonds occurring by formation of coordination compounds.

Mossbauer spectra were recorded on an electrodynamic device with uniformly accelerated motion. Determinations were performed at temperatures of 80°K and 300°K using isotope ⁵⁷Cr as radiation source in chromium matrix. Values of isomer displacement were compared with standard Na₂[Fe(CN)₅NO] (sodium nitroprusside) with a doublet with ΔE₀ and δ values of 1.76 and 0.165 mm/s, respectively.

In order to characterize compounds of Fe³⁺ with N-hydroxysuccinimide by X-ray diffraction, diffractograms were recorded in the 2 - 60°C range, at room temperature

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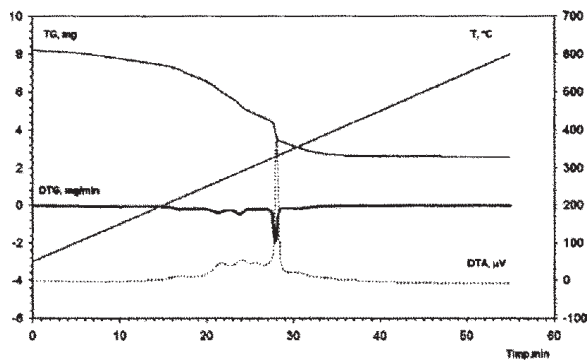


Fig. 1 Thermogram of the complex $[\text{Fe}(\text{C}_4\text{H}_4\text{NO}_3)(\text{OH})_2(\text{H}_2\text{O})_2]$

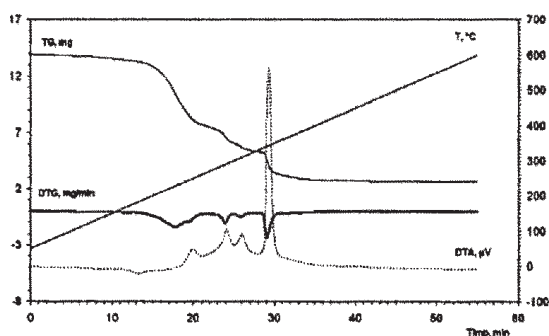
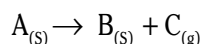


Fig. 2 Thermogram of the complex $[\text{Fe}(\text{C}_4\text{H}_4\text{NO}_3)_3]$

Results and discussions

Thermogravimetric Analysis

Thermal decompositions of the three complexes of iron (III) with N-hydroxysuccinimide (in ratios of 1:1, 1:2 and 1:3) occur in stages with the initial (T_i) and final (T_f) temperatures presented in table 1, by the following type of reaction:



Although at a first glance, the equation seems simple, the process of decomposition of inorganic solids is a very complex one, occurring in several stages, with the reaction rate determined by one of these stages [12].

For all studied complexes, the final solid product was Fe_2O_3 to which volatile products are added, whose composition was not determined.

Thermograms recorded are presented in figures 1, 2 and 3.

Tables 1, 2 and 3 present temperature ranges for thermal decompositions, practical and theoretical mass losses for complexes Fe-I (Fe^{3+} :N-hydroxysuccinimide 1:1), Fe-

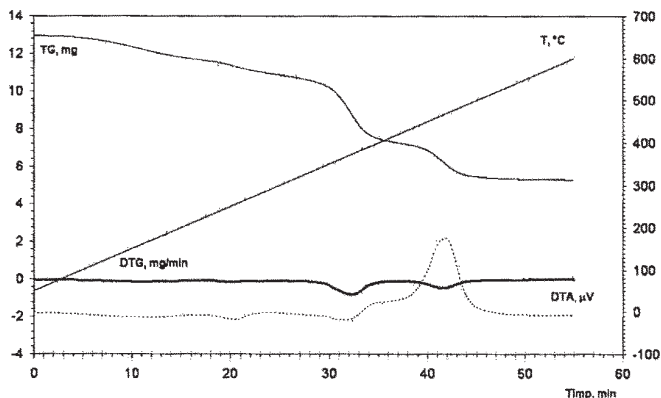
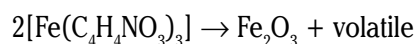


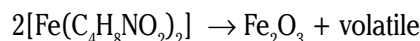
Fig. 3 Thermogram of the complex $[\text{Fe}(\text{C}_4\text{H}_8\text{NO}_2)_2]$

II(Fe^{3+} :N-hydroxysuccinimide 1:2) and Fe-III(Fe^{3+} : N-hydroxysuccinimide 1:3).

For the second complex, $[\text{Fe}(\text{C}_4\text{H}_4\text{NO}_3)_2]$, the global reaction of thermal decomposition for which the theoretical percentage of volatile loss was calculated is the following:



For the third studied complex, $[\text{Fe}(\text{C}_4\text{H}_8\text{NO}_2)_2]$, the global reaction of thermal decomposition for which the theoretical percentage of volatile loss was calculated is the following:



As seen from the correlation of experimental and theoretical data, decomposition of the three iron complexes occurs down to iron oxide, Fe_2O_3 .

Kinetic parameters calculated from experimental data using the Freeman-Carroll method, for each complex and for each stage are presented in tables 4, 5 and 6.

Values of parameters of thermal decomposition reactions were determined using the Freeman-Carroll method [14-15], also in accordance with interpretation of experimental data of other authors [15-16].

Thermal decomposition processes in the gas-solid-gas system are characterised by reaction orders with values between 0 and 1 [14-16]. Fractional values of the order of reaction for the studied complexes are due to the fact that the actual chemical reaction is favoured by phenomena of transport of volatile complexes through the solid and by phenomena of interface or free surface vaporisation of the solid compound.

$[\text{Fe}(\text{C}_4\text{H}_4\text{NO}_3)(\text{OH})_2(\text{H}_2\text{O})_2]$ complex, $w_0=8.575$ mg						
Stage	$T_i, ^\circ\text{C}$	$T_f, ^\circ\text{C}$	w_r (mg)	% $w_{\text{volatile,p}}$	% $w_{\text{volatile,t}}$	$\epsilon_r, \%$
1	119.83	208.17	7.335	68.8	66.72	3.1
2	208.17	284.17	5.528			
3	284.17	305	4.872			
4	305	403.33	2.675			

$[\text{Fe}(\text{C}_4\text{H}_4\text{NO}_3)_3]$ complex, $w_0=14.187$ mg						
Stage	$T_i, ^\circ\text{C}$	$T_f, ^\circ\text{C}$	w_r (mg)	% $w_{\text{volatile,p}}$	% $w_{\text{volatile,t}}$	$\epsilon_r, \%$
1	169.33	269.17	7.519	79.7	79.94	0.3
2	269.17	302.8	6.005			
3	302.8	328.67	5.318			
4	328.67	387.67	2.88			

$[\text{Fe}(\text{C}_4\text{H}_8\text{NO}_2)_2]$ complex, $w_0=13.163$ mg						
Stage	$T_i, ^\circ\text{C}$	$T_f, ^\circ\text{C}$	w_r (mg)	% $w_{\text{volatile,p}}$	% $w_{\text{volatile,t}}$	$\epsilon_r, \%$
1	112	323	10.65	60.87	64.92	6.2
2	323	419	7.257			
3	419	507.5	5.148			

Table 1
RANGES OF DECOMPOSITION TEMPERATURES AND PRACTICAL AND THEORETICAL LOSSES FOR THE COMPLEX $[\text{Fe}(\text{C}_4\text{H}_4\text{NO}_3)(\text{OH})_2(\text{H}_2\text{O})_2]$

Table 2
RANGES OF DECOMPOSITION TEMPERATURES AND PRACTICAL AND THEORETICAL LOSSES FOR THE COMPLEX $[\text{Fe}(\text{C}_4\text{H}_4\text{NO}_3)_3]$

Table 3
RANGES OF DECOMPOSITION TEMPERATURES AND PRACTICAL AND THEORETICAL LOSSES FOR THE COMPLEX $[\text{Fe}(\text{C}_4\text{H}_8\text{NO}_2)_2]$

<i>[Fe(C₄H₄NO₃)(OH)₂(H₂O)₂]complex</i>						
Stage	E, kJ/mol	n	r ²	T _{max} , °C	ln A	A, min ⁻¹
1	19.5	0.3	0.9705	155	1.7	5.48
2	40.63	0.7	0.9810	263.5	9	8149.32
3	62.5	0.81	0.9627	290	13.35	6.27·10 ⁵
4	146	0.9	0.958	327	29.26	5.1·10 ¹²

Table 4
KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION REACTION OF THE COMPLEX [Fe(C₄H₄NO₃)(OH)₂(H₂O)₂].

<i>[Fe(C₄H₄NO₃)₃]complex</i>						
Stage	E, kJ/mol	n	r ²	T _{max} , °C	ln A	A, min ⁻¹
1	23.8	0.4	0.9345	228	5.71	302.52
2	45	0.7	0.9545	291.5	9.585	1.455·10 ⁴
3	78	0.85	0.97	309.3	15.11	3.64·10 ⁶
4	306	1.12	0.968	344.5	47.6	47.6·10 ²⁰

Table 5
KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION REACTION OF THE COMPLEX [Fe(C₄H₄NO₃)₃].

<i>[Fe(C₄H₈NO₂)₂] complex</i>						
Stage	E, kJ/mol	n	r ²	T _{max} , °C	ln A	A, min ⁻¹
1	21.8	0.35	0.9280	257	4.95	140.6
2	51	0.55	0.9670	370.3	9.53	1.38·10 ⁴
3	132.5	0.9	0.9755	466.5	21.55	2.28·10 ⁹

Table 6
KINETIC PARAMETERS OF THE THERMAL DECOMPOSITION REACTION OF THE COMPLEX [Fe(C₄H₈NO₂)₂].

The order of reaction increases from stage to stage, as noticed in this work, as well as in other bibliographical studies [14-16].

Infrared Absorption Spectra

The IR spectra of the studied compounds have led to the following findings:

-an internal characteristic band where the peak is situated in the 1850-1650 cm⁻¹ range corresponds to stretching vibrations (valence) of carbon. The carbonyl band is located in the 1750-1700 cm⁻¹ range. Coordination of this group through the oxygen atom with Fe(III) shifts this band towards lower frequencies in accordance with literature data but also with spectra recorded experimentally for the new synthesised compounds. The carbonyl of the free N-hydroxysuccinimide ligand has the vibration band at 1695-1645 cm⁻¹. These shifts of vibration bands indicate coordination of central atoms of Fe(III) with oxygen atoms in the carbonyl group (Fe ← O=C).

-for the OH group, the most important band is located in the 1140-1230 cm⁻¹ range to which others are added, particularly the band at 3200-3600 cm⁻¹ which is noticed in the case of the free ligand;

-in the case of intermolecular hydrogen bonds, the band at 3200-3400 cm⁻¹ is noticed, and in the case of intermolecular bonds, particularly with C=O specific to N-hydroxysuccinimide, this band occurs in the 3000-3200 cm⁻¹ range.

-the OH group in the ligand (from N-OH) interacts by substituting H⁺ with Fe³⁺ and forms the N-O-Fe bond. The new O-Fe bond is highlighted in the absorption spectrum at 550 cm⁻¹.

Figure 4 presents infrared absorption spectra for the Fe-I complex

Mossbauer Absorption Spectra

Parameters of Mossbauer spectra were processed according to data in the literature [18, 19] and are presented in table 7.

For all studied compounds, the electronic configuration of the central ion corresponds to the high spin configuration and the Fe-ligand bond is relatively ionic. The value of isomeric displacement is found to be the same in complexes where the central atom is Fe(III) and ligands come from the same type of donor atoms, which in our case is oxygen.

We also found a higher temperature dependency of the isomer displacement compared to the one obtained, which in most cases is 0.05 mm/s -100°C. This increase of the isomer displacement is in accordance with the second degree Doppler effect.

The values of E₀ parameters (table 2) lead to the conclusion that the Fe(III) central atom has an octahedral configuration in all studied compounds, with electrons arranged in accordance with the theory of the crystalline field theory.

Compound	T(K)	δ(mm/s)	Δ E ₂ (mm/s)	Γ (mm/s)
Fe-I	300	0.50	0.80	0.30; 0.70
	80	0.71	0.57	0.67
Fe-II	300	0.50	0.05	0.75
	80	0.65	0.20	0.50
Fe-III	300	0.45	0.75	0.55
	80	0.61	0.83	0.43

Table 7
VALUES OF MOSSBAUER PARAMETERS FOR THE STUDIED COMPOUNDS

	a(A)	b(A)	c(A)	α	β	γ
Fe-I	18.682	25.121	26.769	81°50'	72°50'	134°
Fe-II	23.898	32.284	31.984	85°10'	76°50'	135°

Table 8
VALUES OF PARAMETERS OF CRYSTALLINE NETWORKS FOR FE-I AND FE-II COMPLEXES

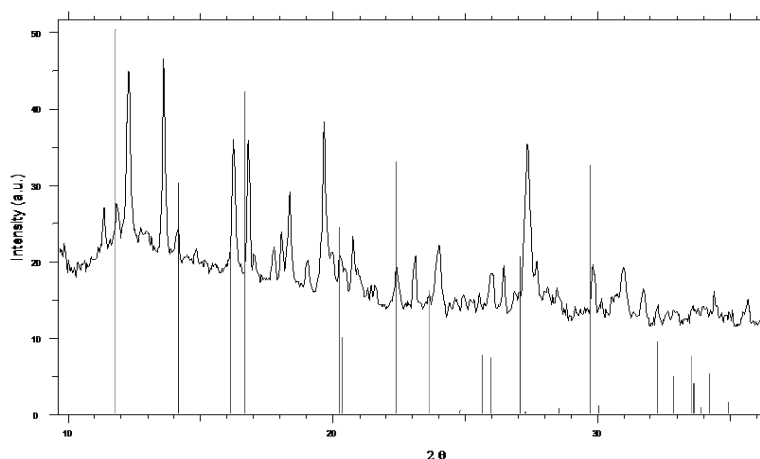


Fig. 4. X-ray diffractogram of Fe-II complex

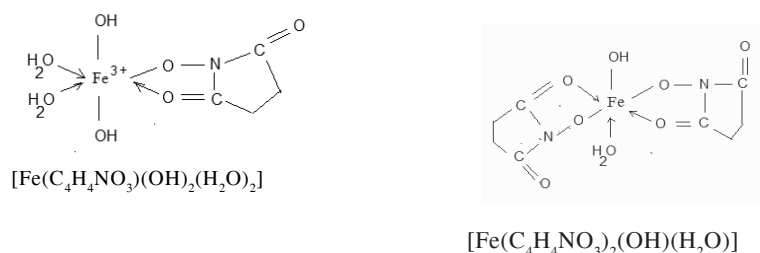
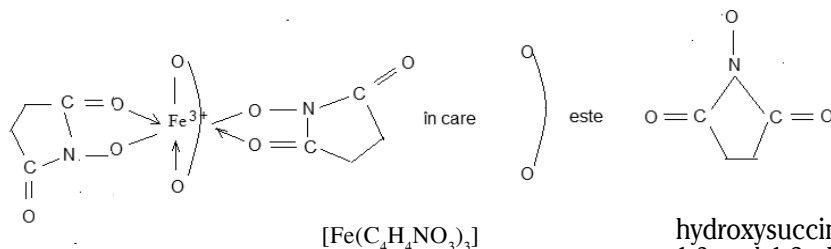


Fig. 5. Structural chemical formulae proposed for the studied complexes



X-Ray Diffraction

As a result of processing the diffractogram of N-hydroxysuccinimide ligand and Fe-I and Fe-II complexes it was deduced that the type of the crystalline network is triclinic. The Fe-III complex has a very high degree of amorphicity, which does not allow diffractogram indexing.

Table 8 presents values of parameters of crystalline networks for Fe-I and Fe-II compounds.

The Proposed Structure of the New Synthesized Complexes

Based on all experimental data discussed above, the following structures were proposed for the obtained and studied complexes (fig. 5):

Complexes obtained and characterized were then used in leather processing to test their tanning capacity.

Values of hydrothermal resistances of leathers treated according to [18], with previously synthesized products as well as the use of electron microscopy can provide the required information on the tanning capacity of the new tanning materials.

Hydrothermal resistances obtained for all leathers tanned with the new tanning compounds do not raise up to values of those treated with chromium(III) salts, but ensure very good behaviour to mechanical processing subsequent to tanning (splitting, trimming).

Conclusions

Syntheses of studied compounds were performed in aqueous medium, at room temperature with intermittent stirring for 60 min, and the soluble reaction products were separated by recrystallization.

Through the synthesis and study of three new complexes of Fe(III) resulting from the interaction of FeCl_3 with N-

hydroxysuccinimide, in central atom:ligand ratio of 1:1, 1:2 and 1:3, this paper proposes to solve several issues, among which: increasing the eco-efficiency of the leather industry, total or partial replacement of basic chromium salts in leather tanning technologies, and lowering the cost of chromium-free tanning auxiliaries.

The thermal analysis shows that thermal decompositions of synthesised compounds studied in the paper occurs at temperatures of 170-500°C confirming the fact that by complexing the central atom of Fe(III) with N-succinimide ligand more stable structures were obtained.

Processing RES spectra leads to the conclusion that all Fe(III) compounds have maximum spin corresponding to five odd electrons for each central atom.

As a result of processing and interpreting Mössbauer spectra, it is found that in all studied compounds, iron atoms have an oxidation state of 3, and high spin ($S = 5/2$), which indicates a relatively ionic nature of Fe-O and Fe-N bonds.

From the values of the E_Q parameter, quadrupole splitting, it can be deduced that the central atom of iron(III) is octahedrally surrounded in all studied compounds.

The infrared absorption spectra showed that in the case of coordination compounds with N-hydroxysuccinimide ligand, central atoms of iron are coordinated through oxygen atoms from N-O and C=O groups from the ligand, as well as through the OH group and water molecules.

Leathers processed with the new Fe(III) complexes have good quality (at least comparable to that of leathers tanned with chromium salts), and technologies applied are in accordance with European regulations on improving environmental performance compared to technologies and materials they replace.

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