# Synthesis and Characterization of Some Metallic Combinations with Ligands Derived from Azo Dyes

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*Six new coordinated compounds of Fe(III) were synthesized using two isomeric ligands (HL1 and respectively HL2), each of them in other two isomeric forms: sodium(E)-2-((1-hydroxy-4-sulfonatonaphtalen-2-yl)diazenyl)-6-methoxybenzo[d]thiazole-5 and 7-sulfonate and sodium(E)-2-((2-hydroxy-6-sulfonatonaphtalen-1-yl)diazenyl)-6-methoxybenzo[d]thiazole-5 and 7-sulfonate. The new metallic coordinated compounds were characterized in solid state, using the following investigation methods: X-ray diffraction, infrared spectroscopy, SEM and ESR spectra. The constitutive elements of the new synthesized compounds were also analyzed from a qualitative (EDX analysis) and quantitative point of view. Finally, the thermal behaviour of the new compounds was studied, pointed out their thermal resistance up to 190 °C. The studies emphasized that the central Fe(III) atoms are six-coordinated and the complexed compounds had an octahedral structure.*

*Key words: Azo-dyes, ligands, iron(III) central atom, coordinated compounds*

In the previous reference papers [1 - 8] different processes for dyeing wool fibers were studied, using various acid dyes having high complexation capacity for heavy metal ions. One of the characteristic properties of the acid dyes is the tinctorial value, which could be enhanced towards external factors (as light, wet treatments, etc,) if the dyes are treated with metallic salts. As a result of this operation, the metallic ion is coordinated by the dye when a complexed compound is obtained, which could be used also for wool dyeing process. The chrome salts are the most used salts for complexation of the acid dyes in textile industrial practice, usually named chromatable dyes.

In recent researches are used other metallic salts such as complexing reagents, which lead to more stable complexed compounds, and as the consequence the wastewaters are less polluted [9-11] in comparison with dying process based on chromium salts. In this paper the synthesis and characterization of a new complexed dyes based on the iron salts are presented. These compounds with a complex coordinative structure were prepared in order to obtain acid dyes used in technological processes for dyeing wool fibers. The used ligands, $HL^1$ and respectively $HL^2$, are isomer compounds below the class of the acid dyes. Each of above mentioned compound is a mixture of other two position isomers concerning $-SO_3Na$ group, being impossible to be separated. However, these compounds were successfully tested for dying of the protein substrates [12-14], pointed out their high affinity for wool fibers. Starting from this promising property, of these dyes, keeping in the mind the dying possibility of the wool fibers using the iron complex of these, the syntheses and characterization of the new complexed compounds were investigated.

## Experimental part

### *Reagents*

The new synthesed dyes having the high complexation capacity, were provided from the Textile National Reseach Institute, Bucharest, Romania. These compounds were sodium(*E*)-2-((1-hydroxy-4-sulfonatonaphtalen-2-yl)diazenyl)-6-methoxybenzo[*d*]thiazole-5 or 7-sulfonate, denominated as ligand $HL^1$ and respectively sodium(E)-2-((2-hydroxy-6-sulfonatonaphtalen-1-yl)diazenyl)-6-methoxybenzo[d]thiazole- 5 or 7-sulfonate, denominated as ligand $HL^2$.The iron salts used for the complexation process was iron (III) chloride 99 %, being purchased from the Merk Company. All reagents were used without any purifcation.

### *Physical measurements*

The diffractograms were recorded using a SIEMENS D-500 equipment with data acquisition system and specialized software. The FTIR analysis was carried out by DIGILAB FTS 2000 equipment, using the method of KBr pellets. The ESR spectra were obtained on an I.F.A spectrometer, Bucharest. The electronic images were recorded using environmental scanning electron microscopes (ESEM) of Quanta 200, equipped with X-ray dispersion system for qualitative and quantitative analyses. Samples were covered by a 10 nm thin layer of molecular gold using the Emitech K550 equipment. The thermal decomposition was accomplished using a Q 1500 D MOM, Budapest equipment.

### *Synthesis of the complexes*

In order to synthesize the metallic complexes, the acid dyes in both isomeric forms (fig. 1.a.b) were used as the complexion reagent for Fe(III) ion, which are provided from the solution of iron(III) chloride. Synthesis was carried out in a glass vessel of 250 mL, in which the iron(III) solution was mixed with each solution of $HL^1$ and respectively $HL^2$. All the above mentioned solutions had a concentration of $10^{-2}$ mol . $L^{-1}$. The method was applied to three different molar ratios 1:1; 2:1; and 3:1.The above mention solutions were mixed under stirring, until the final solution becomes completely homogenous. After one hour of stirring, the

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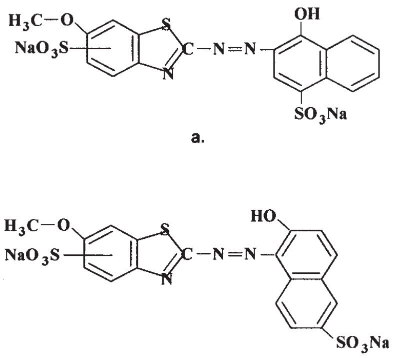


Fig. 1a. Structural formula of HL[1]
b. Structural formula of HL[2]

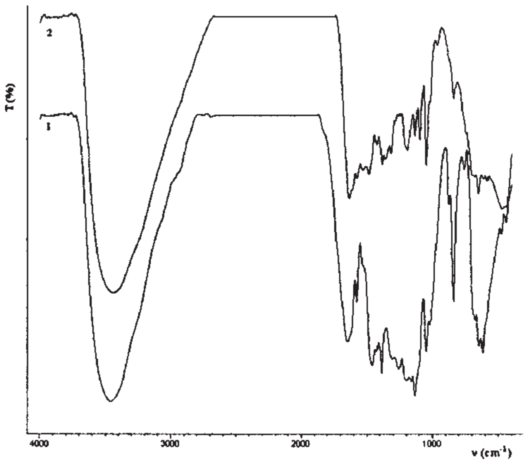


Fig. 2. FTIR Spectra for HL[1] (1) and FeL$^{1}_{2}$ (2)

**Table 1**
QUANTITATIVE ELEMENTAL CHEMICAL
ANALYSIS

| Compound | Found<br>(Calculated) | | | |
|---|---|---|---|---|
| | % C | % H | % N | % Fe |
| HL$^{1}$ | 40.13 (40,07) | 1.99 (2,04) | 7.83 (7,79) | - |
| FeL$^{1}_{1}$ | 29.47 (29,30) | 2.53 (2,44) | 5.61 (5,69) | 7,67 (7,59) |
| FeL$^{1}_{2}$ | 35.71 (35,83) | 1.88 (1,99) | 6.90 (6,96) | 4,73 (4,64) |
| FeL$^{1}_{3}$ | 38.81 (38,73) | 1.88 (1,79) | 7.60 (7,53) | 3.43 (3,34) |
| HL$^{2}$ | 39.98 (40,7) | 1.91 (2,04) | 7.67 (7,79) | - |
| FeL$^{2}_{1}$ | 29.89 (29,30) | 2.21 (2,44) | 5.73 (5,69) | 7.61 (7,59) |
| FeL$^{2}_{2}$ | 36.33 (35,83) | 1.81 (1,99) | 6.84 (6,96) | 4.76 (4,64) |
| FeL$^{2}_{3}$ | 39.57 (38,73) | 1.68 (1,79) | 7.49 (7,53) | 3.29 (3,34) |

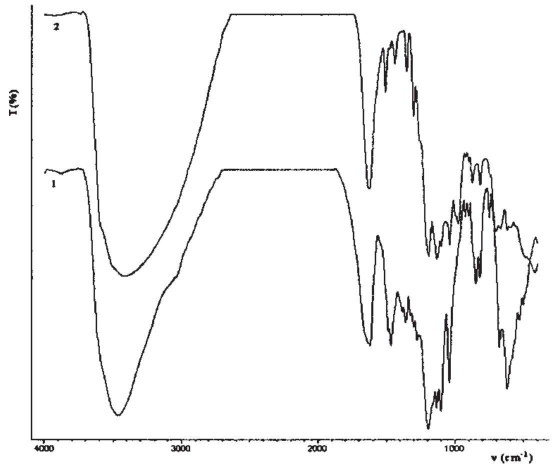


Fig. 3. FTIR Spectra for HL[2] (1) and FeL$^{2}_{2}$ (2)

obtained precipitates were separated by centrifugation, then washed repeatedly with water and respectively with ethanol. The obtained complexed compounds were dried in an oven until constant weight. In order to determine the content of carbon, hydrogen, nitrogen and iron, in the complexed compounds, was carried out an elemental chemical analysis.

## Results and discussion

The syntheses of the complexed compound could be described by the following reactions:

$$C_{18}H_{11}N_3S_3O_8Na_2+FeCl_3+4H_2O\rightarrow$$
$$[Fe(C_{18}H_{10}N_3S_3O_8Na_2)(H_2O)_4]^{2+} + 2Cl^- + (H^+ + Cl^-)$$

$$2C_{18}H_{11}N_3S_3O_8Na_2 + FeCl_3 + 2H_2O\rightarrow$$
$$[Fe(C_{18}H_{10}N_3S_3O_8Na_2)_2(H_2O)_2]^+ + Cl^- + 2(H^+ + Cl^-)$$

$$3C_{18}H_{11}N_3S_3O_8Na_2 + FeCl_3 \rightarrow [Fe(C_{18}H_{10}N_3S_3O_8Na_2)_3]$$
$$+ 3(H^+ + Cl^-)$$

Based on the quantitative elemental chemical analysis, the obtained results are presented in table 1.

It should be mentioned that a good concordance between the experimental contents and respectivly the calculated contents of the elements from the ligand (HL[1]) and respectively from the ligand (HL[2]) (within the limits of experimental errors) was observed. Also, the same good concordance was emphased for the corresponding obtained complexed compounds derived from each ligand (HL[1] and respectively HL[2]).

The recorded FTIR spectra for the analyzed compounds, before and after the interaction with iron salt are presented in figure 2 and respectively figure 3.

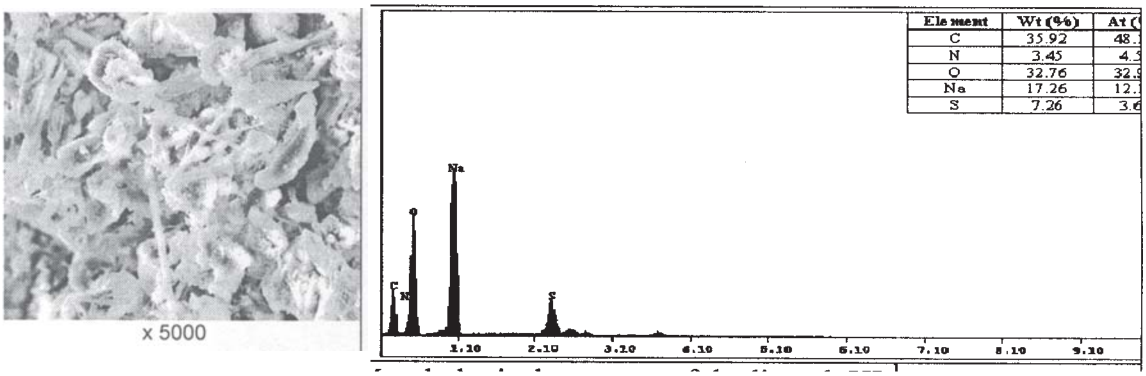
In figure 2 the recorded spectra of the ligand (HL[1]) and respectively the spectra of the corresponding complexed compound (FeL$^{1}_{2}$) at molar ratio 2:1 are presented. The absorption band assigned to the OH phenol groups appears at 3462 cm$^{-1}$, in the structure of (HL[1]) ligand. Concerning the metallic complex, the corresponding band from 3441 cm$^{-1}$ can be assigned to coordination water. The absorption band characteristic to – N = N – bonds is significantly modified due to the complexion process. As a result, the peak appears at 1634 cm$^{-1}$ and is slowly shifted and decreased in intensity in comparison with the one that appeared in the free ligand (HL[1]). This shift can be explained taking into consideration the presence of nitrogen atoms in coordinative bonds with metallic ions. The absorption band attributed to valence vibrations of the ether bonds appear at 1483 cm$^{-1}$ and is also slowly shifted and decreased in intensity, in comparison with absorption band corresponding to the free dye. The band assigned to $CH_3$ group corresponds to deformation vibrations and is present at 1381 cm$^{-1}$. Due to a higher number of dye molecules involved in the complexation process, a shift of the wavelength to smaller values can be observed. The peak corresponding to $SO_3^-$ groups appears at 1134 cm$^{-1}$ and the complexation process with metallic ions, did not determine any modifications. The absorption characteristic bands assigned to aromatic rings were recorded at 1192

| | $H_2O$ of coordination<br>ν | – N = N –<br>ν | – C – O – mix<br>ν | – $CH_3$<br>ν | – $SO_3$<br>ν | Aromatic rings<br>ν | Me → N<br>ν | Me – O<br>ν |
|---|---|---|---|---|---|---|---|---|
| $FeL^1_1 \cdot 4H2O$ | 3414 | 1624 | 1475 | 1357 | 1134 | 1215 and 1192 | 613 | 468 |
| $FeL^1_3$ | - | 1575 | 1417 | 1350 | 1134 | 1190 | 615 | 474 |
| $FeL^2_1 \cdot 4H_2O$ | 3431 | 1622 | 1506 | 1354 | 1134 | 1192 | 607 | 486 |
| $FeL^2_3$ | - | 1620 | 1508 | 1354 | 1134 | 1276 and 1190 | 624 | 487 |

**Table 2**
THE CHARACTERISTIC ABSORPTION BANDS OF THE SYNTHESIZED METALLIC COMPLEXES FOR MOLAR RATIOS 1:1 AND 3 :1

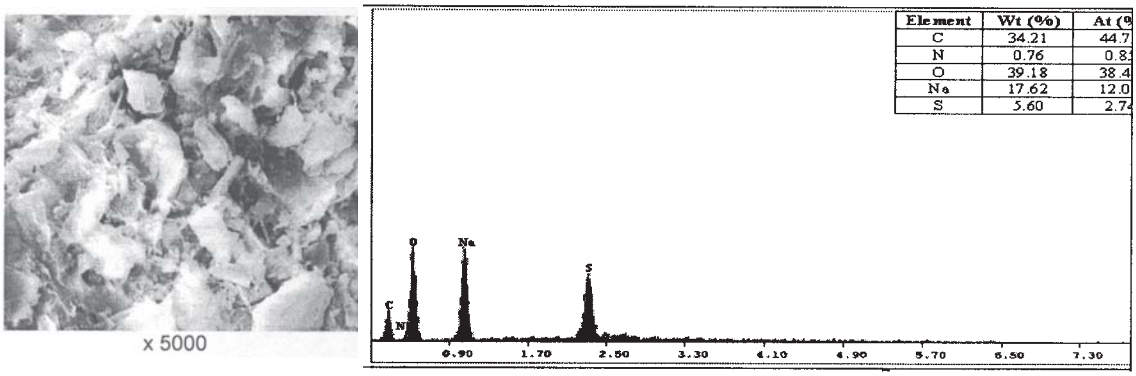
$cm^{-1}$ and 1240 $cm^{-1}$, which also did not present any significant modifications after the complexation process. The interaction process between the dye and metallic ions determines the formation of Fe → N and Fe- O bonds that show absorption bands of low intensity. The peaks assigned to Fe → N and Fe-O bonds appear at 615 $cm^{-1}$ and respectively 472 $cm^{-1}$ and correspond to the deformation vibrations.

The recorded FTIR spectra for the isomer ligand $HL^2$ and for the corresponding complex, at molar ratio 2:1 are presented in figure 3. From the FTIR data, it can be observed that for the free ligand $HL^2$, the band assigned to -OH phenol groups appear at 3464 $cm^{-1}$ and the vibration band assigned to –N = N – bond appears at 1624 $cm^{-1}$. For the same –N = N – bond corresponding to the complexed



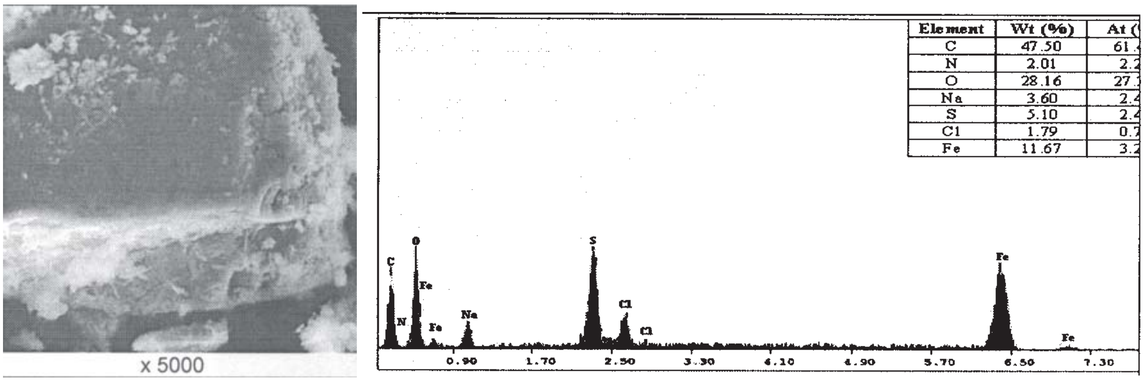
| Element | Wt (%) | At ( |
|---|---|---|
| C | 35.92 | 48. |
| N | 3.45 | 4. |
| O | 32.76 | 32. |
| Na | 17.26 | 12. |
| S | 7.26 | 3. |

Fig. 4. Morphological structure of the ligand $HL^1$



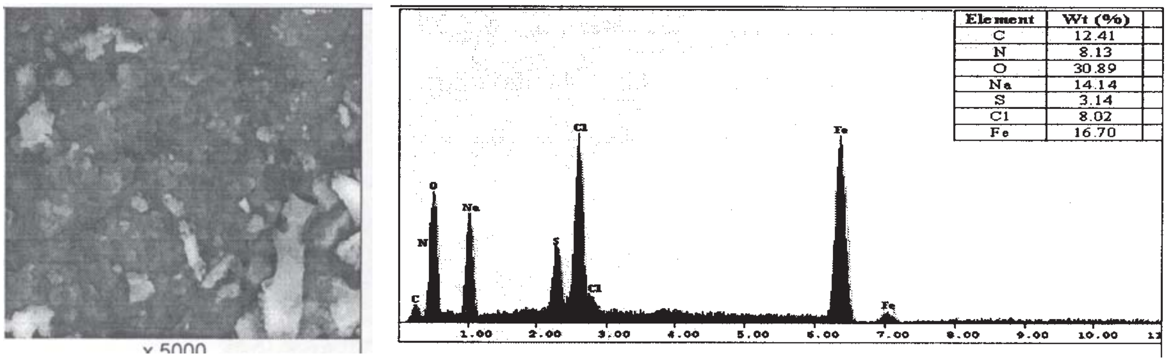
| Element | Wt (%) | At ( |
|---|---|---|
| C | 34.21 | 44.7 |
| N | 0.76 | 0.8 |
| O | 39.18 | 38.4 |
| Na | 17.62 | 12.0 |
| S | 5.60 | 2.7 |

Fig. 5. Morphological structure of the ligand $HL^2$



| Element | Wt (%) | At ( |
|---|---|---|
| C | 47.50 | 61. |
| N | 2.01 | 2.2 |
| O | 28.16 | 27. |
| Na | 3.60 | 2.4 |
| S | 5.10 | 2.4 |
| Cl | 1.79 | 0.7 |
| Fe | 11.67 | 3.2 |

Fig. 6. Morphological structure of the iron complex $FeL^1_2$



| Element | Wt (%) | |
|---|---|---|
| C | 12.41 | |
| N | 8.13 | |
| O | 30.89 | |
| Na | 14.14 | |
| S | 3.14 | |
| Cl | 8.02 | |
| Fe | 16.70 | |

Fig. 7. Morphological structure of the iron complex $FeL^2_2$

**Table 3**
THE CHARACTERISTIC TEMPERATURES OF THERMAL DECOMPOSITION STAGES, THE VALUES OF THE REACTION ORDER AND ACTIVATION ENERGIES OF THE CORRESPONDING REACTIONS (KJ/mol) FOR THE STUDIED COMPOUNDS

| Complex | Stage I | | | | Stage II | | | | Stage III | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_i$, $^0$C | $T_f$, $^0$C | n | E | $T_i$, $^0$C | $T_f$, $^0$C | n | E | $T_i$, $^0$C | $T_f$, $^0$C | n | E |
| $FeL^1_1 \cdot 4H_2O$ | 74 | 290 | 0,9 | 63.4 | 300 | 480 | 0.48 | 216.15 | - | - | - | - |
| $FeL^1_1 \cdot 2H_2O$ | 71 | 440 | 0,97 | 70,28 | 450 | 570 | 1,07 | 108,37 | - | - | - | - |
| $FeL^1_3$ | 90 | 500 | 1.6 | 87,97 | 510 | 600 | 1,69 | 175,52 | - | - | - | - |
| $FeL^2_1 \cdot 4H_2O$ | 80 | 140 | 1.5 | 47,22 | 150 | 430 | 1,15 | 40.4 | 440 | 810 | 0.5 | 41,63 |
| $FeL^2_2 \cdot 2H_2O$ | 74 | 460 | 0.34 | 74,25 | 470 | 880 | 1,13 | 56 | - | - | - | - |
| $FeL^2_3$ | 74 | 310 | 0.4 | 44,87 | 320 | 580 | 1.12 | 40,7 | - | - | - | - |

compound, a less intense band was observed due to the Fe- O bond formation, which is not significantly shifted even if two dye molecules are involved in the complexing process.

For the iron complex of the isomer ligand $HL^2$, a broad band at 3421 $cm^{-1}$ and other two less intensive at 3586 $cm^{-1}$ and 3508 $cm^{-1}$ are recorded and assigned to coordination water molecules. The peak corresponding to mixed ether groups appears at 1506 $cm^{-1}$ and is slowly shifted to the higher wavelengths values in the complexed compounds in comparison with the isomer ligand $HL^2$. The absorption bands characteristic to the groups $-CH_3$ and $SO_3^-$ appear at 1354 $cm^{-1}$, and respectively 1132 $cm^{-1}$ and are not highly modified due to the complex process with Fe(III) ions. The absorption bands assigned to aromatic rings for the iron complex are present at 1192 $cm^{-1}$ and 1257 $cm^{-1}$ being slowly shifted to lower wavelength values comparing to the free dye ligand $HL^2$. This shift could be explained by the complexing process of the dye with Fe(III) ions or by attributing to some vibrations that appear in the isomer compounds. The peaks assigned to Fe $\rightarrow$ N and Fe – O bonds appear at 621 $cm^{-1}$ and at 486 $cm^{-1}$ respectively, corresponding to deformation vibrations.

In the above two figures are presented the recorded spectra for the ligands ($HL^1$ and $HL^2$) and for the corresponding complexes at molar ratio 2:1 – $FeL^1_2$ and $FeL^2_2$. For each ligand $HL^1$ and respectively $HL^2$, were obtained other two complexes, corresponding to the molar ratios 1:1 and 3:1, which were spectrally characterized as is presented in table 2.

The SEM spectra for both ligands and corresponding iron complexes at 2:1 molar ration were presented in figures 4-7. As a consequence of the SEM images of both dyes and Fe(III) complexed compounds in different molar ratios, the studied samples were presented as relatively agglomerated particles of irregular shape and of various dimensions. Initially, both $HL^1$ and $HL^2$ ligands had an amorphous-crystalline structure with predominant cristalline zones; after the complexation process with Fe(III), the structures of the dyes were modified. As the molar ratio increases, the structure of the compounds become amorphous.

X-ray diffractogrammes have shown that the new synthesized compounds have an amorphous structure in concordance with the images recorded by SEM.

The main conclusion which could be drawn concerning the thermal decomposition process of the studied compounds is that this process takes place in several steps, according to the recorded derivatogrammes during this process (table 3).

In the first step of decomposition process, the coordination water is evaporated primarily, for the complexes 1:1, 2:1, 3:1, followed in the second step by the breakage of weaker chemical bonds from the studied complexes; finally solid products are obtained. The resulted gaseous products were not analyzed. The reaction order for the thermal decomposition reactions was calculated using the Freeman-Carroll method. In all decomposition steps, the values for the reaction order were ranged between 0.34 -1.69.

According to the reference literature [15, 16], the values of the reaction order for this type of decomposition reaction (when a solid compound decomposes in solids and gases) should be between 0 and 1. As the decomposition reaction advances, the gaseous compounds resulted from the thermal decomposition have to pass through a smaller layer of deposed solids. The dispersion degree of the system leads to the increasing value for the reaction order, very close to 1. For the thermal decomposition reactions, where the gaseous products pass through monomolecular layers, the reaction order is not influenced by the resistance of the solid reaction products.

ESR spectra of the studied coordinated compounds were recorded for solid samples using as standard sample a diphenyl picryl hydrozyl (DPPH), using an applied magnetic field of 3216.9 Gauss with a frequency of 9030 MHz.

Taking into account ESR spectra of the studied compounds,[17-19] the g factor, the intensity of Hx magnetic field and the number of odd electrons corresponding to a gram of analysis sample and respectively to a central atom of Fe(III), which coordinates the ligands, were calculated applying the method of graphical double integration (table 4).

Processing ESR spectra, analyzing the values of g factor and the number of odd electrons corresponding to a central atom of Fe(III), it can be drawn the conclusion that all coordinative compounds derived from both ligands ($HL^1$ and respectively $HL^2$) are paramagnetic due to the central Fe(III) atoms which contain in the electronic superior layer 5 odd electrons ($3d^5$). The g factor from the structure of

**Table 4**
VALUES OF THE SPECTROSCOPIC SPLITTING FACTOR (g), INTENSITY OF THE MAGNETIC FIELD CORRESPONDING TO THE SPECTRUM OF THE SAMPLE ($H_x$, GAUSS) AND ODD ELECTRON NUMBER OF THE CENTRAL ATOM (n) FOR THE EACH STUDIED COMPOUND.

| Compuond | g | $H_x$ | N |
|---|---|---|---|
| $FeL^1_1 \cdot 4H_2O$ | 2.0187 | 3238 | 4.92 |
| $FeL^1_2 \cdot 2H_2O$ | 2.0203 | 3240.6 | 4,88 |
| $FeL^1_3$ | 2,0211 | 3241.9 | 4.82 |
| $FeL^2_1 \cdot 4H_2O$ | 2.0196 | 3239.6 | 4.86 |
| $FeL^2_2 \cdot 2H_2O$ | 2.0219 | 3243.2 | 4.79 |
| $FeL^2_3$ | 2.0230 | 3244.9 | 4.75 |

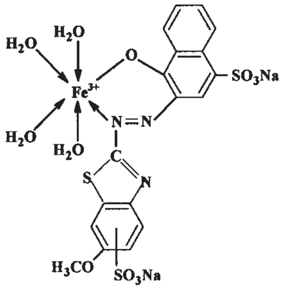


Fig. 8. Structural formula of FeL$^1$

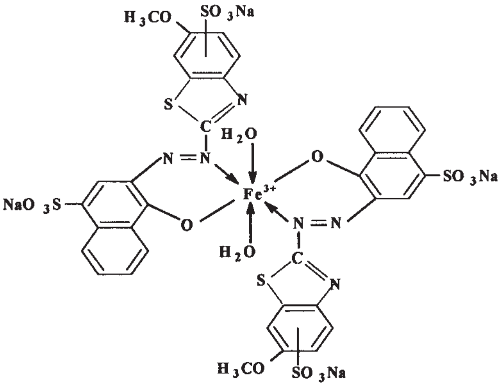


Fig. 9. Structural formula of FeL$^1_2$

central atom is different from the free electron g factor due to their contribution to the orbital momentum and covalence degree of the respective bonds in which the central atom is involved.

The elemental chemical analysis, the infrared spectra and the thermal-gravimetric analysis, concluded that the oxygen atoms are bonded with four water molecules and one ligand molecule. Concerning the FeL$^1_1$ complex, the central atom Fe(III) is hexa-coordinated by four water molecules, one nitrogen atom from the group -N = N- and one oxygen atom from the group –O(H) from the ligand HL$^1$ structure (fig. 8). Concerning the complex FeL$^1_2$ central atom is octa-coordinated by two nitrogen atoms from the group -N = N-, two oxygen atoms from the group –O(H) of the ligand and two water molecules (fig. 9). The octahedral structure of the complex HFeL$^1_3$ was proposed using the same arguments as in the previous examples, which include the formation of Fe → N, Fe - O bonds (fig. 10).

It is evident that the structures of complex compounds derived from ligand HL$^2$ were estabilished based on the same above mentioned arguments used in case of ligand HL$^1$.

## Conclusions

The obtaining of six new complexed compounds obtained as a result of the complexation reaction between two isomeric ligands (HL$^1$ and respectively HL$^2$) of a new textile dyes, and Fe(III) ions (in molar ratios 1:1, 2:1, 3:1 ligand / central atom) has been studied. The new metallic complexed combinations were characterized in solid state, using the following investigation methods: X-ray diffraction, infrared spectroscopy, SEM and ESR spectra. The constitutive elements of the new synthesized compounds were also analyzed from a qualitative (EDX analysis) and quantitative point of view. Finally, the thermal behaviour of the new compounds was studied.

These analyses have emphasized that Fe(III) central atoms are hexa-coordinated and the compounds have an octahedral structure; all compouds presented a thermal resistance up to the temperature value of 190 $^0$C and the

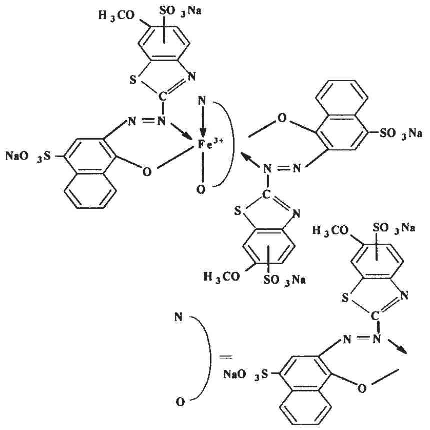


Fig. 10. Structural formula of FeL$^1_3$

decomposition reaction takes place in several steps. X-ray diffractogramms have shown that the new synthesized compounds have an amorphous structure in concordance with SEM spectra.

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