NEW COMPLEX COMPOUNDS OF Fe(III) AND Cu(II) - WITH PHENOTHIAZINES DERIVATIVES

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Acest articol prezintă cateva noi combinaţii complexe mono şi dinucleare ale Fe(III) şi Cu(II) cu [N-[2–benzoil–amino–3–(10'–metil–phenotiazin–3'–il)–acriloil]–alanină ca ligand, L. Pentru aceştia s-au stabilit formulele, $FeL(H_2O)_2Cl_2]Cl$, $[Fe_2L(H_2O)_4Cl_5]Cl$, şi $[Cu_2L_2Cl_4]\cdot 2H_2O$ pe baza analizei chimice elementale, spectroscopiei IR şi UV-Vis, determinărilor magnetice şi analizei termice. Ligandul L acţionează bidentat, prin intermediul atomilor de N(amidic) şi O(carbonilic). Complecşii au geometrii octaedrice ($[FeL(H_2O)_2Cl_2]Cl$ şi $[Fe_2L(H_2O)_4Cl_5]Cl$), şi respectiv tetraedrică ($[Cu_2L_2Cl_4]\cdot 2H_2O$). În atmosferă de argon toţi trei compuşii se descompun în săruri în stări inferioare de oxidare ($FeCl_2$ şi CuCl) şi reziduuri cu carbon.

This paper presents some new mono and dinuclear complex compounds of Fe(III) and Cu(II) with [N-[2–benzoyl–amino–3–(10'–methyl–phenothiazin–3'–yl)–acriloyl]–alanine as ligand, L. For these, based on the elemental analysis data, IR and UV-Vis spectroscopy, magnetic measurements and thermostability were established the following formula: $[FeL(H_2O)_2Cl_2]Cl$, $[Fe_2L(H_2O)_4Cl_5]Cl$, and $[Cu_2L_2Cl_4]\cdot 2H_2O$. The ligand L acts as bidentate ligand, by intermediate of N(amidic) and O(carbonilic) atoms. The complex compounds have octahedral ($[FeL(H_2O)_2Cl_2]Cl$, and $[Fe_2L(H_2O)_4Cl_5]Cl$) and tetrahedral ($[Cu_2L_2Cl_4]\cdot 2H_2O$) distorted geometry. In argon atmosphere all three compounds are decomposed to salts of metals in low oxidation state ($FeCl_2$ and CuCl) and carbonaceous matter.

Keywords: phenothiazine derivatives, Fe(III), Cu(II) complexes, thermogravimetry

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1. Introduction

The literature points a large spectrum of practical applications of phenothiazines, the well-known areas being semiconductors, antioxidants, dyes, polymers and drugs [1]. The N-alkyl phenothiazines are biologically active compounds [2] capable of electron donation via the ring system and the metal complexing effect of phenothiazine derivatives may constitute the common cause of these interactions at the molecular level. The first coordination sphere of phenothiazine complex compounds is perhaps relevant for biological activity because these have an increased biological effect comparatively with the parent ligands [3,4]. Previously we described the complex compounds of Fe(III), Cu(II) with 3-thio-5-(-phenothiazinyl-ethylene)-1,3,4-triazole, 2-(N-phenothiazinyl-ethylene)-1,3,4-oxadiazole-5-phenothiazine [5,6].

This paper presents the isolation and characterization of some new mono and dinuclear complex compounds of Fe(III) and Cu(II) with [N-[2–benzoyl–amino–3–(10'–methyl–phenothiazin–3'–yl)–acriloyl]–alanine as ligand **L**, (fig.1).

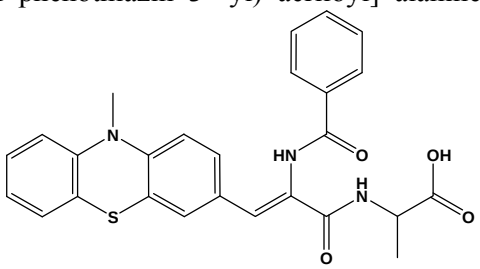


Fig. 1 L = $C_{26}H_{23}N_3O_4S$ - N-[2–benzoyl–amino–3–(10'–methyl–phenothiazin–3'–yl)–acriloyl]–alanine

Based on the elemental analysis data, IR and UV-Vis spectroscopy, magnetic measurements and thermostability we proposed for the complex compounds the following formulas: $[FeL(H_2O)_2Cl_2]Cl$, **1**, $[Fe_2L(H_2O)_4Cl_5]Cl$, **2** and $[Cu_2L_2Cl_4]\cdot 2H_2O$, **3.**

2. Experimental

Materials and Methods

Synthesis

The ligand was prepared as described in the literature [7].

The salts $FeCl_3\cdot 6H_2O$ and $CuCl_2\cdot 2H_2O$ were obtained from Merck and were used without further purification.

Analysis

Nitrogen content was analyzed by microcombustion Dumas. The metal content was determined by atomic absorption spectrometry (Perkin Elmer Analyst 400 spectrophotometter). Chlorine anion was determined gravimetrically, as AgCl.

The electronic spectra were recorded at the room temperature on a Jasco V560 in diffuse reflectance technique.

Vibration spectra were recorded with a Bruker Tensor 27 spectrophotometer in the wavenumbers range of 200-4000 cm^{-1}.

Molar electrical conductivities were determined in methanol or DMF solutions at 25°C with OK 102/1 Radelkis Conductometer.

Magnetic measurements were carried out using a Faraday balance at room temperature with $HgCo(NCS)_4$ as standard for calibration.

The thermal analysis of the compounds was followed with a Netzsch TG 449C STA Jupiter. Samples were placed in alumina crucible and heated with 10^o C min^{-1} from room temperature to 900^o C, under the flow of 20 mL min^{-1} dried argon.

Synthesis of complexes of N-[2–benzoyl–amino–3–(10'–methyl–phenothiazin–3'–yl)–acriloyl]–alanine, ***L***

All complexes have been synthesised according to the following general procedure: methanol solutions containing the metal salts $FeCl_3 \cdot 6H_2O$ / $CuCl_2 \cdot 2H_2O$ and the ligand L, were mixed with stirring in 1:1 (for $[FeL(H_2O)_2Cl_2]Cl$) or 2:1 (for $[Fe_2L(H_2O)_4Cl_5]Cl$ and $[Cu_2L_2Cl_4] \cdot 2H_2O$) molar ratio M:L**.** The resulting precipitates were separated by filtration and evaporation of the excess of solvent, washed with methanol-diethil ether mixture and dried on $(P_2O_5)_2$ in vacuum dessicator. The resulted powders were dark-green (complex **1** and **2**) or dark-brown (complex **3**) colored. The yields were around 72-75%.

1. $[FeL(H_2O)_2Cl_2]Cl$, M = 671,5 g/mol

Calculated for **$C_{26}H_{27}N_3O_6SCl_3Fe$**: C 46.46%, H 4.02%, N 6.25 %, O 14.31 %, S 4.76%, Cl 15.86%, Fe 8.34%

Found: N 6.98, Cl 16.45 %, Fe 8.72 %.

Molar electrical conductivity: 122 $\mu S \cdot cm^{-1} \cdot mol^{-1}$ *(methanol solution)* - nonelectrolyte

IR (cm^{-1}): $\nu_{N-H,}$ 3215, ν_{OH} = 3350-3150 (w), δ_{N-H} =1606 (m), ν_{C-N} =1515, $\delta_{CH2sym/asym,OH}$ = 1464 (m) ν_{M-N} = 275.

UV/Vis (kK): 12.55, 18.21, 21.37, 27.66

Magnetic susceptibility: $\chi_g = 1{,}8x10^{-6}$ cm^3/g (25ºC); μ_{eff} = 1.700 MB;

TG curve presents four decomposition steps, with residual mass 41.54% at 900^oC.

2. $[Fe_2L(H_2O)_4Cl_5]Cl$, M = 871 g/mol

Calculated for **$C_{26}H_{31}N_3O_8SCl_6Fe_2$**: C 35.86%, H 3.56%, N 4.84 %, O 14.71 %, S 3.68%, Cl 24.48%, Fe 12.87%

Found: N 5.05, Cl 24.74 %, Fe 12.58 %.
Molar electrical conductivity 76 $\mu S \cdot cm^{-1} \cdot mol^{-1}$ *(DMF solution)- 1:1 electrolyte*
IR (cm^{-1}): ν_{N-H} = 3225, ν_{OH} = 3450-3200 (w), ν_{CH2} = 2950 (s), δ_{N-H} =1612 (m), $\delta_{CH2sym/asym, OH}$ = 1451 (m), δ_{N-H} =1606 (m), ν_{C-N} = 1525, ν_{M-N} = 325.
UV/Vis (kK): 13.1, 18.09, 21.68, 27.77.
Magnetic susceptibility: $\chi_g = 0.8 \times 10^{-6}$ cm^3/g (26ºC); μ_{eff} = 1.644 MB;
TG curve presents three decomposition steps, with residual mass 34.32% at 900°C.

3. $[Cu_2L_2Cl_4] \cdot 2H_2O$, M = 1251 g/mol
Calculated for $C_{52}H_{50}N_6O_{10}S_2Cl_4Cu_2$: C 49.88%, H 3.99%, N 6.71 %, O 12.79 %, S 5.11%, Cl 11.33%, Cu 10.15%
Found: N 6.98, Cl 11.38 %, Cu 10.25 %.
Molar electrical conductivity 18 $\mu S \cdot cm^{-1} \cdot mol^{-1}$ *(DMF solution)* - nonelectrolyte
IR (cm^{-1}): ν_{N-H} =3235, δ_{N-H} =1615 (m), δ_{NH} = 1620 (m) ν_{C-N} = 1550, ν_{M-N} = 320.
UV/Vis (kK): 16.59, 17.76 (should)
RPE: g_x = 2.2330, g_y = 2.1714, g_z = 2.0446, $g_{z'}$ = 2.0446,
Magnetic susceptibility: $\chi_g = 0.4 \times 10^{-6}$ cm^3/g (25.5ºC); μ_{eff} = 1.639 MB;
TG curve presents four decomposition steps with residual mass 53.49% at 900°C.

3. Results and discussion

Starting from ligand [N-[2–benzoyl–amino–3–(10'–methyl–phenothiazin–3'–yl)–acriloyl]–alanine, **L** and Fe(III) or Cu(II) salts, three complexes have been prepared. The general formulas of these compounds, $[FeL(H_2O)_2Cl_2]Cl$ **1**, $[Fe_2L(H_2O)_4Cl_5]Cl$ **2**, and $[Cu_2L_2Cl_4] \cdot 2H_2O$ **3** are supported by elemental analysis, molar electrical conductivities data, IR, UV/VIS and EPR spectra, magnetic measurements and thermal analysis.

IR spectra

The infrared spectra of the investigated complexes can give insight especially on the co-ordination manner of **L**. For all complexes, **1-3** the ν_{N-H} stretching vibrations were shifted to lower frequencies in comparison with the free ligand (from 3250 cm^{-1} to 3215-3235 cm^{-1} for all the complexes), these bands being supperposed with ν_{OH} bands. For all complexes, **1-3** the ν_{C-N} and $\nu_{C=O}$ vibration frequencies were shifted from higher values (1510 cm^{-1} and respectively 1600 cm^{-1} for free ligand) to the lower values (around 1470 and respectively 1550 cm^{-1} for complexes **1-3**). These band shifts prove the participation of the N(amidic) and O(carbonilic) atoms at the coordination to metal ions. Also, the complex compounds **1** - **2** show a large band of the 3200 – 3400 cm^{-1} range which confirm the presence of the water molecules. The new band in the range of the 300 – 400 cm^{-1} area have been attributed to the M-N bounds formed during the coordination process [8].

In the range 1591-1600, 1568-1570, 925-939 and 731-744 cm^{-1} the specific phenothiazine bands appear.

UV-Vis spectra

The general aspect of the electronic spectra of the isolated complexes is in good agreement with literature data [9].

$[FeL(H_2O)_2Cl_2]Cl$, 1 and **$[Fe_2L(H_2O)_4Cl_5]Cl$, 2**

The electronic spectra of the $[FeL(H_2O)_2Cl_2]Cl]$, **1** and $[Fe_2L(H_2O)_4Cl_5]Cl$, **2** present a single large band at 19.53-17.54 kK (512-570 nm) and 25.51-24.04 kK (392-416 nm), respectively, which could be assigned to a spin forbidden *d-d* transition but also to a charge transfer transition specific for Fe^{3+} in octahedral surrounding. Generally these bands lie at fairly high energies and are superposed.

$[Cu_2L_2Cl_4]\cdot 2H_2O$, 3

The electronic spectrum of **$[Cu_2L_2Cl_4]$** presents a large band in the 13.3-17.76 kK (751.88 – 563.06 nm) range that can be assigned to the superposed *d-d* transitions for Cu^{2+} in tetrahedral distorted geometry.

Table 1

Electronic transition

Complex compounds	ע (kK)	Geometry proposed
1 $[FeL(H_2O)_2Cl_2]Cl$	19.53-17.54	Distorted octahedron
2 $[Fe_2L(H_2O)_4Cl_5]Cl$	25.51-24.04	Distorted octahedron
3 $[Cu_2L_2Cl_4]\cdot 2H_2O$	13.3-17.76	Distorted tetrahedron

EPR spectra

The polycrystalline EPR spectra at room temperature for the complex $[Cu_2L_2Cl_4]\cdot 2H_2O$, **3** presents a lower EPR signal with izotropic parameter g_{iso}=2.11, specific for four-coordinated Cu^{2+} ion with distorted tetrahedral geometry. The EPR spectrum and g_{iso} value for complex **3** show that this is dimer, by spin compensation of two Cu^{2+} (d^9) ions [10, 11].

Magnetic measurements

Table 2

Values of the magnetic moments calculated for compounds 1-3

Compound	μ_{eff} (MB)
$[FeL(H_2O)_2Cl_2]Cl$, **1**	1.7
$[Fe_2L(H_2O)_4Cl_5]Cl$, **2**	1.6
$[Cu_2L_2Cl_4]\cdot 2H_2O$, **3**	1.6

The magnetic moments of the compounds **1-3** (table 2) indicate the paramagnetic properties of metal ions Fe^{3+} and Cu^{2+}, for all of them the μ_{eff} being smaller than the theoretical expected values. Also for iron compounds **1** and **2** the μ_{eff} confirms the low spin d^5 state forced by strong field action of phenothiazine ligand, **L**.

Thermal analysis

The thermal analysis of the compounds **1-3** gave information about these compounds stability and suggested a decomposition pathway.

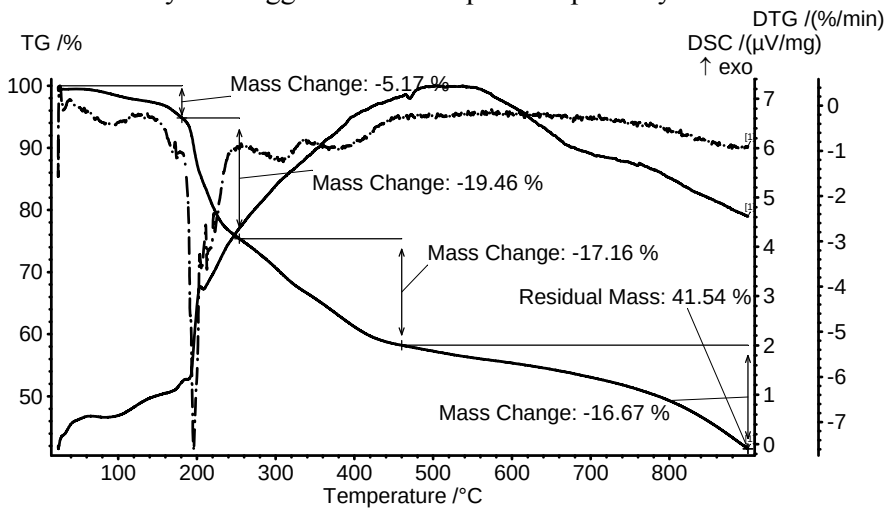
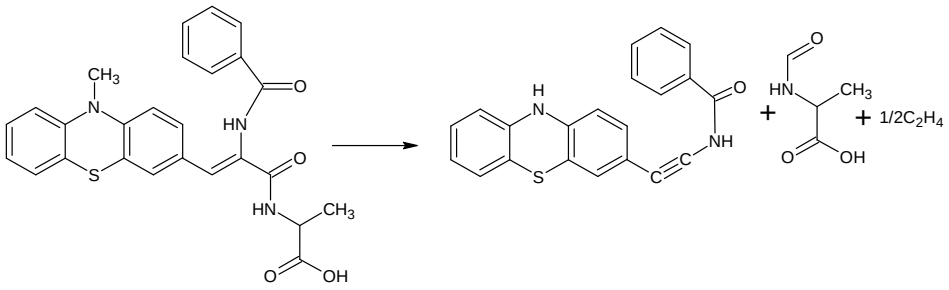


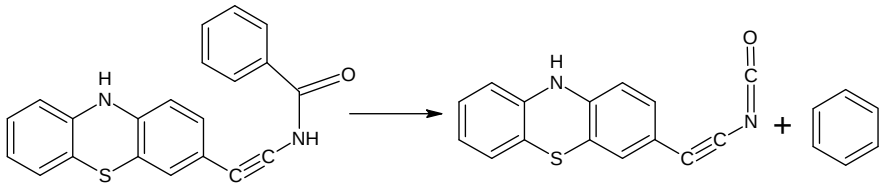
Fig. 2 TG-DSC for $[FeL(H_2O)_2Cl_2]Cl$

The thermal decomposition of **$[FeL(H_2O)_2Cl_2]Cl$, 1** takes place in four steps, until 900°C. In the first step, between 50-180°C, the compound is losing 2 water molecules from the coordination sphere, calculated mass loss 5.36% vs. 5.17% observed experimental. First water molecule is lost until 140°C, while second water molecule is lost between 140-180°C as one can see on the DTG curve. This process is slightly overlapped with the second decomposition step between 180-255°C which corresponds to the partial degradation of the side chain as seen in the following reaction (calculated mass loss being 19.50% vs. 19.46% observed experimental):



By studying the DTG curve it can be noticed that the second decomposition step consist from four superposing processes.

Third step of thermal decomposition is taking place between 255-460^{o}C and corresponds to the further degradation of the aromatic part of the side chain and reduction of Fe(III) to Fe(II) with elimination of chlorine [12]. On DTG curve can be observed two separate processes that are taking place in this temperature interval. The calculated mass loss is 16.90% while the experimental mass loss is 17.21%. The difference is probably due to some minor unaccounted decomposition processes that occur to the main phenothiazine nucleus.



While first and second steps have associated endothermic effects, the third decomposition step has associated a broad exothermic effect.

The final step of thermal decomposition takes place between 460-900^{o}C and corresponds to the total degradation of organic residue, part of the carbon atoms remaining as a product in the crucible. The final residue consists from 43.01% C, 11.47% S and 45.52% $FeCl_2$, calculated mass of it being 41.51% vs. experimental 41.54%. This decomposition step is associated with a weak endothermic effect. At 677^{o}C there is an inflexion point in DSC curve corresponding to the melting point of $FeCl_2$.

Thermal decomposition of **$[Fe_2L(H_2O)_4Cl_5]Cl$, 2** takes place in two steps until 450^{o}C, followed by a continuous mass loss until 900^{o}C.

The first step, associated with an endothermic effect, takes place between 140-260^{o}C and corresponds to the two water molecules loss. The calculated mass loss is 4.14% vs. 4.21% experimental one. Because both DSC and DTG curves show a small split of the peaks, we can assert that this water molecules are not equivalent.

More over, the fact that only two water molecules are lost until this temperature can be consider as a proof that the remaining two water molecules are functioning as bridge ligands.

The second step of decomposition is also the main one, taking place between 260-460^{o}C, with an experimental mass loss of 52.31%. This step is associated with both endo and exothermic effects. The main effect is an exothermic one, but at 275^{o}C, 318^{o}C, 340^{o}C and 386^{o}C we also observed endothermic effects, each of them corresponding to another overlapped decomposition process.

Due to the magnitude of the mass change, we cannot point out a specific mechanism of the compound decomposition. Taking in to the account the processes observed for compound **1** we can assume that the first, second and third process correspond to the degradation of the side chain and reduction of Fe(III) to Fe(II), while the last process corresponds to the phenothiazine moiety decomposition.

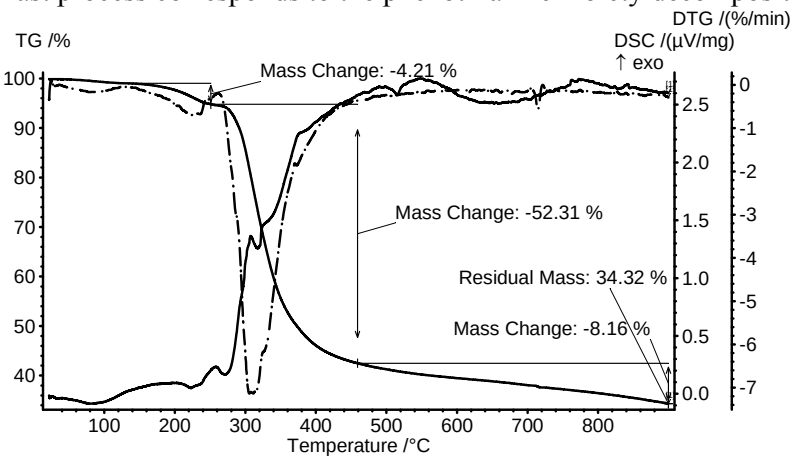


Fig. 3 TG-DSC for $[Fe_2L(H_2O)_4Cl_5]Cl$

There is no clear limit between second and the last decomposition step, which we have marked to take place between 460-900^{o}C. Practically there is a continuous mass loss in this last step, which also can be view as a continuation of the fourth process from previous decomposition step, namely the degradation of phenothiazine moiety. On the DSC curve the effect associated to this step is a weak exothermic one, but there can be seen also the endothermic effect associated with the melting of $FeCl_2$. The broadening of this effect is most probably due to formation of graphite intercalation compounds of iron chloride [13,14].

The residue consists from 27.43% C and 72.57% $FeCl_2$, calculated mass being 34.65% vs. 34.32% experimental. The difference in the residue composition points out also the different coordination mode of the ligand **L** in this compound vs. complex **1**.

The thermal decomposition of **$[Cu_2L_2Cl_4]\cdot 2H_2O$, 3** takes place in a similar manner with the compound **1**, the TG curves being much alike.

In the first decomposition step the compound is loosing two water molecules, weakly bounded in complex as the process ends at 150°C. The calculated mass loss is 2.87% vs. experimental one 2.28%. This step is coupled with a weak endothermic effect as we have expected.

Second decomposition step takes place between 150-240°C, and consists from at least 3 processes as seen on DTG curve. First one is associated with an exothermic effect and the others with endothermic effects. This step corresponds to the side chain degradation in a similar manner with processes described at compound **1**.

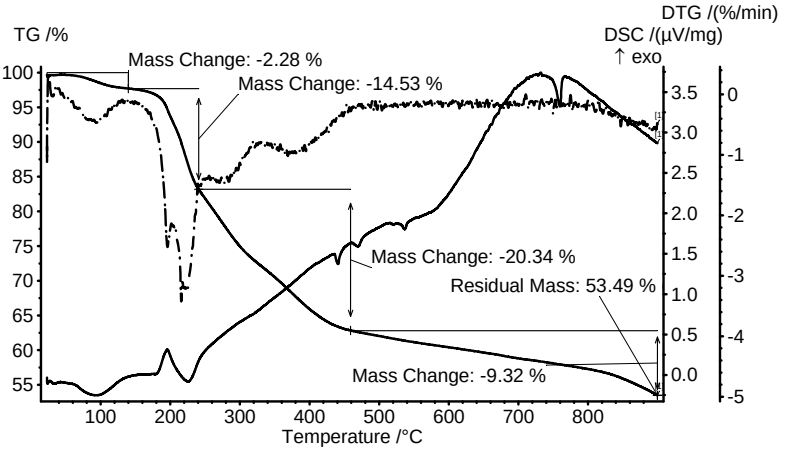


Fig. 4 TG-DSC for$[Cu_2L_2Cl_4]\cdot 2H_2O$

Third decomposition step takes place between 240-460°C and corresponds to the elimination of some chlorine and further decomposition of side chain. On the DTG curve we can observe two broad processes in this step.

On DSC curve there are two endothermic effects around 425°C a small one and at 500°C an even smaller one, corresponding to the melting of CuCl and $CuCl_2$ [15-17].

The last step between 460-900°C corresponds to the total degradation of organic residue in volatile components and carbonaceous matter, after 800°C the process observed being the graphitization of the products. The endothermic effect from 750°C could not be assigned and further investigations are needed.

4. Conclusions

This paper presents the isolation and characterization of some new mono and dinuclear complex compounds of Fe(III) and Cu(II) with [N-[2–benzoyl–amino–3–(10'–methyl–phenothiazin–3'–yl)–acriloyl]–alanine as ligand, **L.** Based on the elemental analysis data, IR, RPE and UV-Vis spectroscopy, magnetic measurements and thermal analysis we proposed for the complex compounds the following formulas: $[FeL(H_2O)_2Cl_2]Cl$, **1**, $[Fe_2L(H_2O)_4Cl_5]Cl$, **2** and

$[Cu_2L_2Cl_4]\cdot 2H_2O$, **3**. The ligand L acts as bidentate ligand, by intermediate of N(amidic) and O(carbonilic) atoms. The complexes have octahedral ($[FeL(H_2O)_2Cl_2]Cl$, **1** and $[Fe_2L(H_2O)_4Cl_5]Cl$, **2**) and tetrahedral distorted geometry ($[Cu_2L_2Cl_4]\cdot 2H_2O$, **3**). The magnetic measurements indicate the paramagnetic properties of Fe^{3+} and Cu^{2+} ions in compounds **1** - **3** and the strong field action of phenothiazine ligand, **L** (low spin, d^5 state for **1** and **2**). The thermal decomposition of the compounds **1** - **3** occurs in some different and complex steps, and in argon atmosphere all are decomposed in salts of metals in low oxidation state ($FeCl_2$ and CuCl) and carbonaceous matter.

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