Synthesis and Characterization of Some New Premetalated Dyes Based on Cu(II)

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The new complex combinations on Cu(II) were synthesized, using sodium salts of disulphonic acids as ligands: sodium(E)-2-((1-hydroxy-4-sulfonatonaphtalen-2-yl)diazenyl)-6-methoxybenzo[d]thiazole and sodium(E)-2-((2-hydroxy-6-sulfonatonaphtalen-1-yl)diazenyl)-6-methoxybenzo[d]thiazole, both having the group -6-methoxibenzo[d]tiazol sulphonated in 5 and 7 positions, mixed in both isomeric forms, denominated in this work as HL^1 *and respectively* HL^2 *ligand. The aqueous insoluble complexes, obtained by precipitation from the interaction of the two ligands with* Cu^{2+} *ion, were previously dried till constant mass at 105°C and then characterized by: chemical elemental analysis (Cu, C, H, N, S şi Na), FTIR, SEM-EDX, XRD and thermal analysis in dynamic system. Their crystalline structure was investigated by electronic microscopy and X- ray difraction and the thermal derivatogrames revealed their stability till 150°C. The studies show that Cu(II) central atoms are tetracoordinated with square plan (*dsp^2 *hybridization) and respectively tetrahedral structures (hybridization* sp^3*), corresponding to the two types of ligands,* HL^1 *for* T_d *geometry and* HL^2 *for the* D_{4h} *and corespond to the following molecular formulae:* $[Cu(C_{18}H_{10}N_3S_3O_8Na_2)(H_2O)Cl]\cdot 2HCl$ *and* $[Cu(C_{18}H_{10}N_3S_3O_8Na_2)_2]\cdot 4HCl$*. These complexes were synthesized for applications in wool fibers dyeing processes, having the advantage of reduced toxicity compared with other commonly used complexes .*

Keywords: premetalated dyes, organic ligands, SEM-EDX, FTIR, XRD, thermal derivatographic

Until now, a series of acid dyes with structures capable to coordinate transition metals, to be used in wool dyeing, were presented in the scientific literature [1-3]. Among the Cu(II) complexes utilised as wool dyes, we mention those based on 2-diazo dye and another one based on anthraquinone amino sulfonic acid derivatives [4], 2-Pyridylmethylene-1-Amino-2-Naphthol [5] or different Schiff bases [6]. The tinctorial fastness related to the action of various external factors (light, hydrothermal treatments etc), of a large number of dyeing processes performed with acid dyes are significantlly improved by treatment with some transition metalic salts, procedure which introduces a metallic ion in the dye molecule which is followed by complex formation as premetalated dyes type. A certaian number of high stable, poorly soluble complexses are known and used as pigments in dyeing processes [7], with minimal environmental impact, but not usable as premetalated dyes. The premetalated dyes with chrome are most used in practice but their main disadvantage is water and environment contamination with ireversible effects due to their partial solubility in aqueous systems, therefore difficult to be controled [8, 9]. The work presented in this paper aims the use of other salts as complexation reagents, which leads to the obtaining of more stable and lower toxicity premetalated dyes, so the wastewaters have a much lower load pollution in case of using the sodium salts of some disulphonic acids which contain the complexing active centres of OH-naphtalen and diazenyl type, as ligands [10]. In consequence complexed dyes with divalent copper were studied, the syntheses and characterization of these compounds being presented in this work.

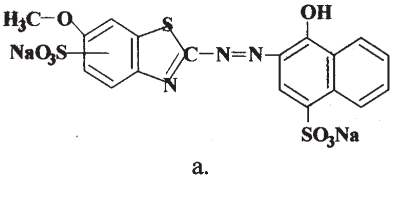
Experimental part

Materials and methods

In the first stage the synthesis of the copper complexed by precipitation was performed, using as ligand two acid dyes, from series sodium salts of the disulphonic dyes, type : (*E*)-2-((1-hidroxi-4-sulfonatonaftalen-2-il)diazenil)-6-methoxibenzo[*d*]tiazol and (*E*)-2-((2-hidroxi-6-sulfonatonaftalen-1-il)diazenil)-6-metoxibenzo[*d*]tiazol respectively , both having the group 6-methoxibenzo [*d*]tiazol sulphonated in 5 or 7 position. Both ligands, denominated as HL^1 and respectively HL^2, are presented in the form of two position isomers [11-13], soluble in water with their structure presented in fig.1. a and b.

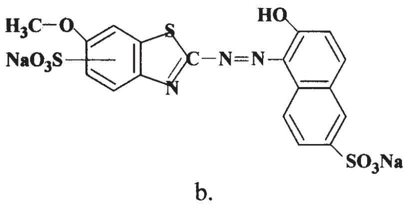
The sulphonic group position (by both ligands structures) in the structure of both ligands conferes them more different Lewis basicity and Brönsted acidity, HL^1being more Lewis basic and respectively more Brönsted acidic than HL^2, but slightly different for the position isomers derived from the same ligand [14-15].

Copper chloride (Merck Chem.) was used to provide divalent copper ions in aqueus solution as complexation reagent.



a.

Fig. 1. Structural formulas: a - HL^1



b.

Fig. 1. Structural formulas: b - HL²

The syntheses of the hard soluble complexes were realised at two different combination ratio M:L of 1:1 and respectively 1:2. In the first case, the precipitation was achieved using two 250 mL glass flasks, in which were introduced separately 50 mL of aqueous solutions of two acid dyes HL^1 and HL^2, (10^{-2} $M \cdot L^{-1}$ concentration), then 50 mL aqueos solution of the $CuCl_2$ 10^{-2} $M \cdot L^{-1}$ were dropwise added in each of the above mentioned flasks containing the aqueous solutions of acid dyes, under mild stirring, at room temperature. The complete homogenisation of the microdisperse system is achieved after about one hour of stirring followed by repeated centrifugation and washing with an echimolecular mixture 1:1 of water: ethilyc alcohol, and further drying till constant weight for about 4 h at 105°C. In the second case, for 1:2 combination ratio M:L, in other two 250 mL flasks, 100 mL of aqueous solutions of the two acid dyes (HL^1 şi HL^2) was added in each flask, then 50 mL aqueos solution of the $CuCl_2$ 10^{-2} $M \cdot L^{-1}$ were dropwise added under the same conditions. The precipitates formation, homogenization and separation from the microdisperse system were achieved in the same conditions as mentioned above. In all experiments bidistilated water was used for the solution preparation.

The chemical reaction which occur in the aqueous solution between the two acid dyes and Cu^{2+} ions, conducting to the Cu(II) complexes, are:

$$CuCl_2 + C_{18}H_{11}N_3S_3O_8Na_2 \cdot 3HCl + H_2O \rightarrow$$
$$[Cu(C_{18}H_{10}N_3S_3O_8Na_2)(H_2O)Cl] \cdot 2HCl + 2HCl$$

$$CuCl_2 + 2C_{18}H_{11}N_3S_3O_8Na_2 \cdot 3HCl \rightarrow$$
$$[Cu(C_{18}H_{10}N_3S_3O_8Na_2)_2] \cdot 4HCl + HCl$$

In the other experiments, the four synthesized complexes, as premetalated dyes, derived from the HL^1 and respectively HL^2 ligands were denominated as follows: CuL^1_1 and CuL^2_1 for the 1:1 molar ratio and respectively CuL^1_2 şi CuL^2_2 for 1:2 molar ratio of Cu:L.

All the four premetalated dyes were dried at 105°C till constant weight and then transfered in sealed weighing vials stored in a dessicator featured with an active $CaCl_2$ layer.

Each content, was sampled for chemical elemental analysis, FTIR, SEM-EDX, RDX and thermal derivatography.

The content of carbon and hydrogen was achieved by Pregl's method, and the nitrogen, sulphur and respectively chlorine content was performed using Kjeldhal and Schoneger methods [16-18].

The sintetized coordinative compounds were analysed in order to determine the morphological and chemical structure by Scanning Electronic Microscopy (SEM) coupled with Energy-Dispersive X-ray Spectroscopy (EDX), Fourier Transform IR Spectroscopy coupled with a microscope, in reflection mode (micro-FTIR), XRD and Thermal Analysis.

SEM microscopy were recorded with TESCAN model VEGA II LSH, coupled with EDX (X-ray detector from Brüker) at 30 KV, obtaining images and elemental composition.

Micro-FT-IR spectra were obtained with a Tensor 27 spectrometer, coupled with a Hyperion microscope 1000 (150X) from Brüker, Germany. The OPUS embedded software was used for obtaining the spectra. Spectral measurements were made in reflection mode. Measuring range was 4000-600cm^{-1}, the resolution being 4 cm^{-1}.

XRD spectra were carried out on BM26B beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) with a Frelon CCD camera, the measurements being made in transmission mode. The modulus of the scattering vector s (s = 2sin(theta/lambda) was calibrated using several diffractions orders of silver behenate.

The thermal analysis was conducted on a Linseis STA PT1600, from 20 to 1000°C with a heating ratio of 10°C/min. The TG, DTA and DTG curves were processed in order to evaluate the thermal decomposition processes. Also, worked with MOM Budapest Paulik-Erdey-Erdey, activated energy and reaction order were evaluated by Freeman-Caroll method [23].

Results and discussions

The qualitative highlighting of the constituents of each complexed dye was realised by EDX, based on the obtained spectra of the four premetalated dyes species (fig. 2.a, 2.b, 2c, and respectively 3.a, 3.b and 3.c), compared with the free dye spectrum.

These data were corroborated with quantitative elemental analysis (table 1).

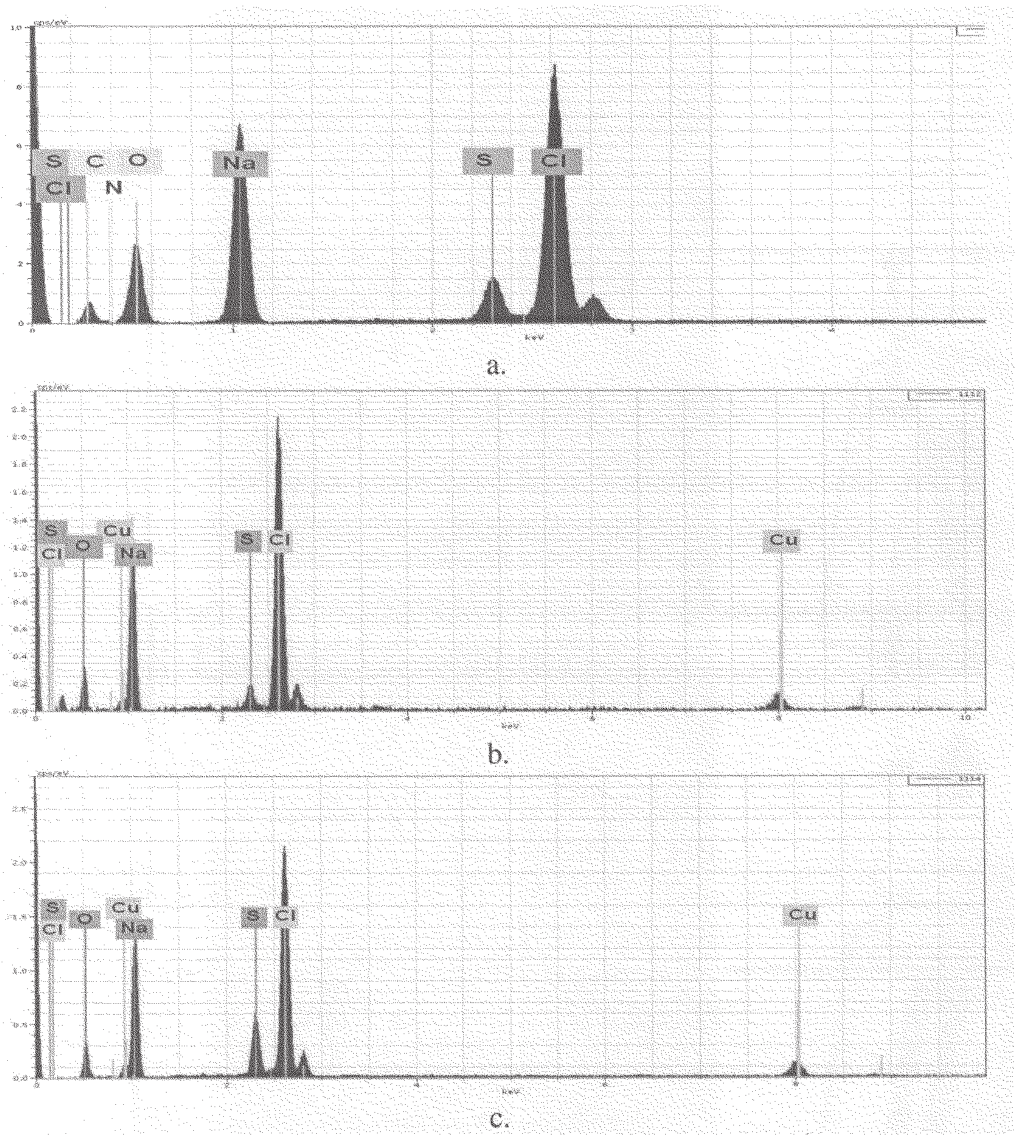
Its worth to mention that the elemental chemical analysis data of the premetalated dyes, using both HL^1 and HL^2 ligands, should be identical, small differences falling within experimental errors.

The recorded FT-IR spectra for the dyes analyzed before and after complexation with Cu^{2+} ions, at 1:1 and 1:2 molar ratio Cu:HL are shown in the figures 4.a, 4.b, 5.a and 5.b.

According to the FT-IR spectra (fig. 4) of HL^1 free ligand and corresponding copper complexes (1:1 and 1:2 molar ratio), the assigned band of the different water types and OH groups from complex is splitted in two for CuL^1_1(spectrum 1) (3445 cm^{-1} and 3358 cm^{-1}), showing on the one side the ligand involvement by OH group and water use as ligand [19]. This spliting could also be attributed to the presence af the intermolecular hydrogen bonds which can lead to formation of the molecular associations[20]. For the other complex species CuL^1_2 (spectrum 2) the corresponding band of the -OH groups is wide and slightly displaced, which could be attributed to a possible lower number of hydrogen bonds, as the molar ratio increases.

The absorbtion band assigned to the –N=N– bonds is slighly displaced at 1634 cm^{-1} compared to the free dye recorded spectrum, displacement which can be attributed to complexation with copper ions. In the CuL^1_2 case, the vibration band attributed to –N=N– bond appears as a splitted peak with wavelength of 1634 cm^{-1} and 1591 cm^{-1}, behavior presumably as a result of the two dye molecules participation in complexation process [14-16, 19-22].

The dye complexation with metallic ions leads to the fromation of the Me←N and respectively Me – O bonds. This bonds show low intensity absorbtion bands. The peak attributed to Cu← N bond is present at 515 cm-1, the band corresponding to the deformation vibrations while the

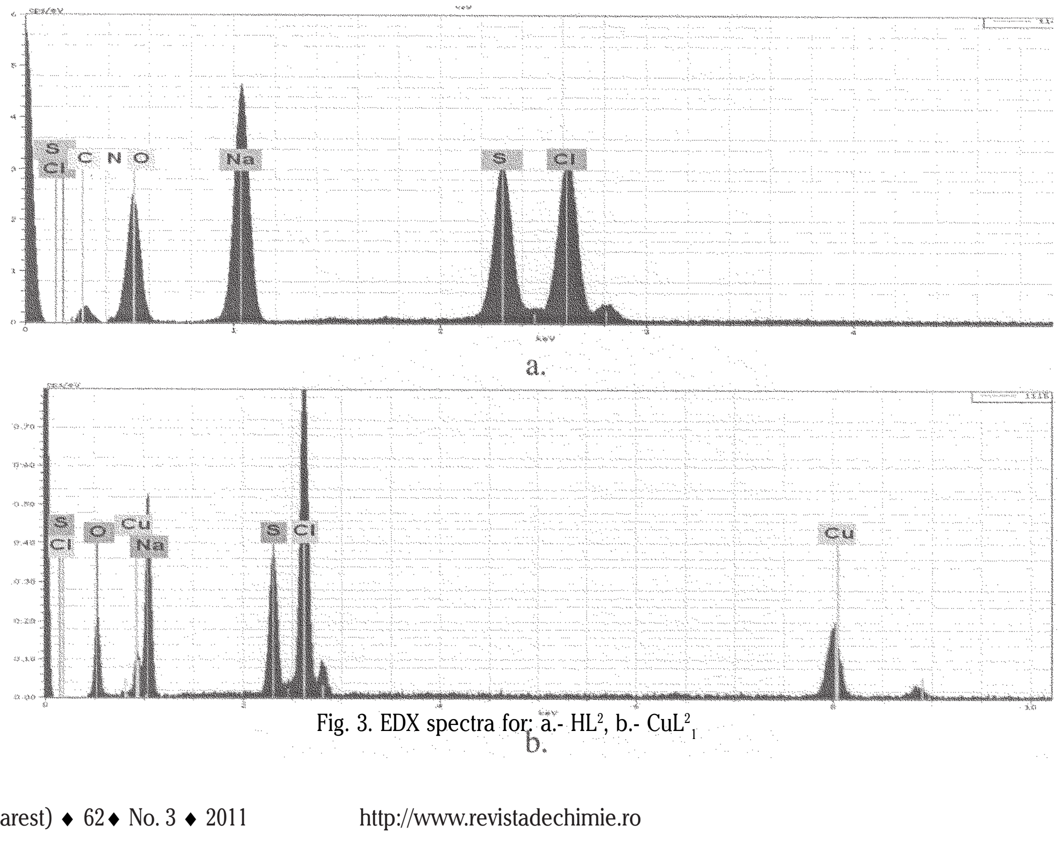


a.

b.

c.

Fig. 2. EDX spectra for: a.- HL^1, b.- CuL^1_1, c.- CuL^1_2



a.

Fig. 3. EDX spectra for: a.- HL^2, b.- CuL^2_1

b.

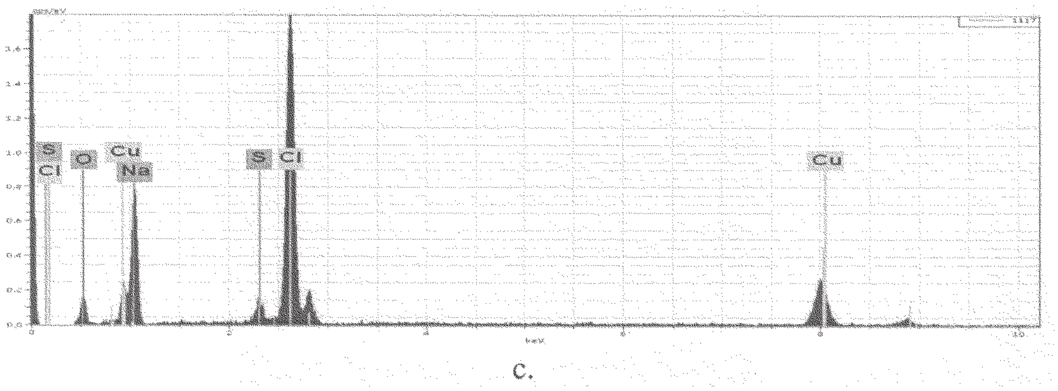


Fig. 3. EDX spectra for: c.- CuL^2_2

Table 1

CHEMICAL ELEMENTAL ANALYSIS OF PREMETALATED DYES

Compound	CuL^1_1		CuL^1_2		CuL^2_1		CuL^2_2	
Element	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
C %	32,95	32.71	33.59	33.41	32,95	32.72	33.59	33.39
H%	1.83	1.77	1.86	1.82	1.83	1.75	1.86	1.83
N%	6.40	6.31	6.53	6.84	6.40	6.35	6.53	6.81
S%	14.64	14.41	14.93	14.86	14.64	14.43	14.93	14.89
Na%	7.01	6.82	7.15	7.11	7.01	6.88	7.15	7.14
Cu%	9.76	9.45	4.97	4.89	9.76	9.51	4.97	4,91

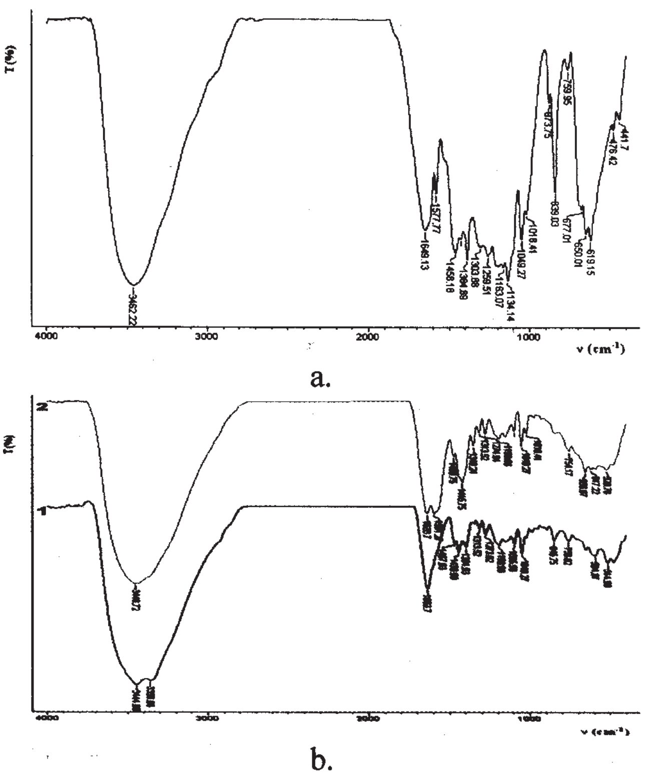


Fig. 4. FTIR spectra: a - for HL^2, b - for CuL^1_1(1) and CuL^1_2 (2)

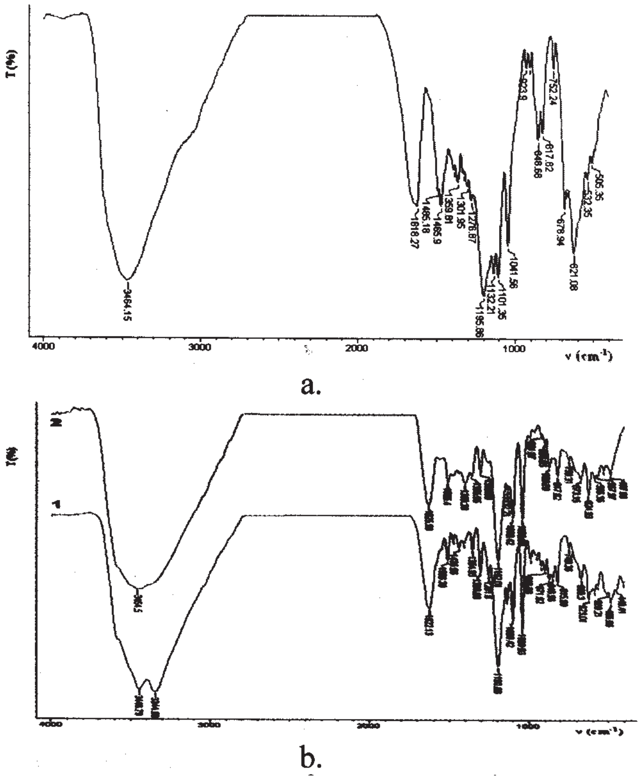
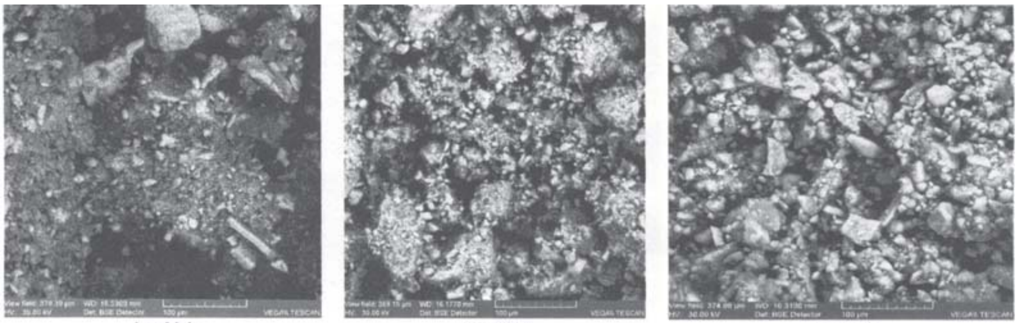


Fig. 5. FTIR spectra: a. - for HL^2, b. - for CuL^2_1(1) and Cu L^2_2(2)

attributed peak of the Cu–O bond appears at 478 cm-1, also corresponding to deformation vibrations [19-22].

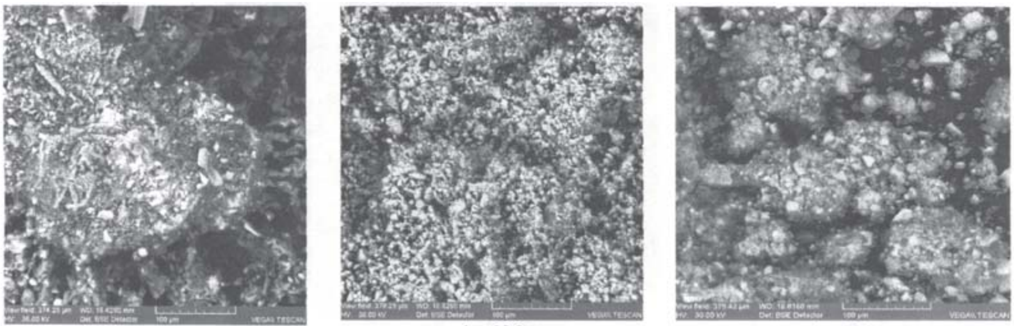
The recorded spectra for the HL^2 ligand, and complexed with copper ion are shown in figure 5.

In the case of dye HL^2 complexed at 1:1 molar ratio Cu:HL^2 the corresponding band of different type of water and OH naphtolyc group is splitted in two, having wavelengths at 3447 cm^{-1} and 3344 cm^{-1} [19-22]. This splitting can be assigned by the same interactions as in the previous mentioned case of the HL^1. In the case of the Cu:HL at 1:2 molar ratio, the corresponding band of the waters and -OH naphtolyc groups from the both dyes (HL^1 şi HL^2) occurs as a large peak, well individualized and slighly displaced at 3454 cm^{-1} [19-22]. This behaviour is a consequence of the decreasing number of hydrogen bonds as the complexation ratio increasing. The absorbtion band attributed to –N=N– bonds occurs slightly moved from 1618 cm^{-1} to 1622 cm^{-1} for the Cu:HL ratio of 1:1 complexed dye and respectively to 1625 cm^{-1} for the Cu:HL^2 ratio 1:2 complexed dye [20, 21].



1×600 a. 1×600 b. 1×600 c.

Fig.6. morphological structure :
a - HL^1, b - CuL^1_1, c - CuL^1_2



1×600 a. 1×600 b. 1×600 c.

Fig.7. Morphological structure:
a - HL^2, b - CuL^2_1 ,c - CuL^2_2

The differences between spectra of both dyes, which are position isomers, is due to the one side solvation phenomenon, that occur as a result of the inductive and electomere effects given by the sulphonic groups and also by the ($N \rightarrow H^+Cl^-$) association and interaction which often is shielding each other [22]. The absorbtion band attributed to naphthenic nuclei are slightly displaced at 1251 cm^{-1} in the case of the dye complexed with copper at 1:1 molar ratio. For the complexed dye with copper at 1:2 molar ratio this band is no more available due the changing of the complexation ratio.

Another cause of such behaviour could be attributed to the fact that the HL^2 ligand is an isomer of the HL^1 ligand. This phenomenon leads to flipping vibrations, with the effect of position changing of the -OH naphtolyc groups and in consequence, dissapearance or appearance of the characteristic absorbtion bands [19-22]. The Me ←N and Me–O bonds for premetalated complexes species derived from HL^2 also show absorbtion bands with low intensity. So, the attributed peaks of the Cu ← N bond, corresponding to deformation vibrations, appear at 509 cm^{-1} in the 1:1 molar ratio complexed dye, respectively at 567 cm^{-1} for the 1:2 molar ratio. The attributed peaks of the Cu–O can be observed at 486 cm^{-1} and 489 cm^{-1} for 1:1 and respectively 1:2 molar ratio [19-22].

Microstructure and morphology of the synthesized metallic complexes were analyzed by electronic microscopy SEM and XRD, the recorded imges and diffractometry are shown in the figures 6, 7 and 8.

From the recorded images, can be observed that the dye samples, in both states, uncomplexed and complexed with Cu^{2+} ions at both molar ratio, are in the form of relatively crowded particles , in various sizes and with shape irregularities. If initialy, both ligands HL^1 and HL^2 present a amorpho-crystalline structure, as a result of the complexation process, the structure of the premetalated dyes, is changing with increasing of the molar ratio Cu : HL, leading to crystalinity increasing.

X- ray diffractometry (fig.8) revealed a good crystallinity of the premetalated complexes CuL^1_2 and CuL^2_2, framed in the P2 symmetry group or space symmetry.

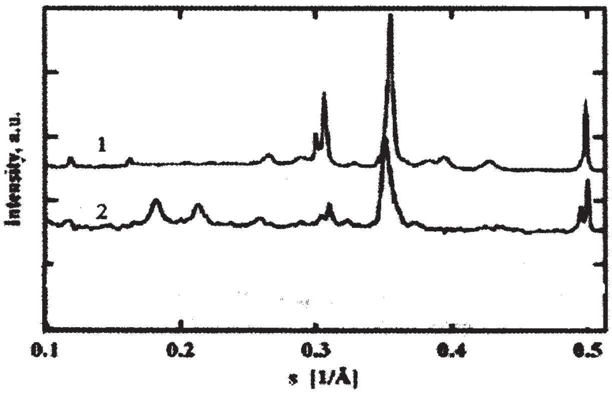
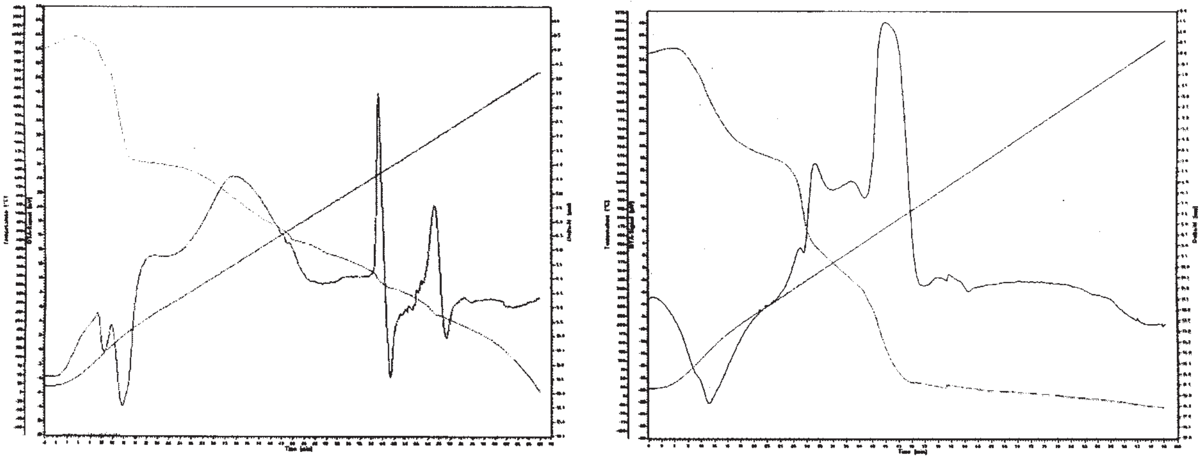


Fig. 8. X-ray diffractometry for: CuL^1_2 (1)and for CuL^2_2 (2)

The derivatograms of dyes and formed complexes (fig. 9, 10), mark out a large amount of hygroscopic water, physically bonded by hydrogen bridges to both dyes, also the synthesized premetalated dyes, especially in case of Cu:HL at 1:1 molar ratio, which besides the two types of water also contain coordination water.

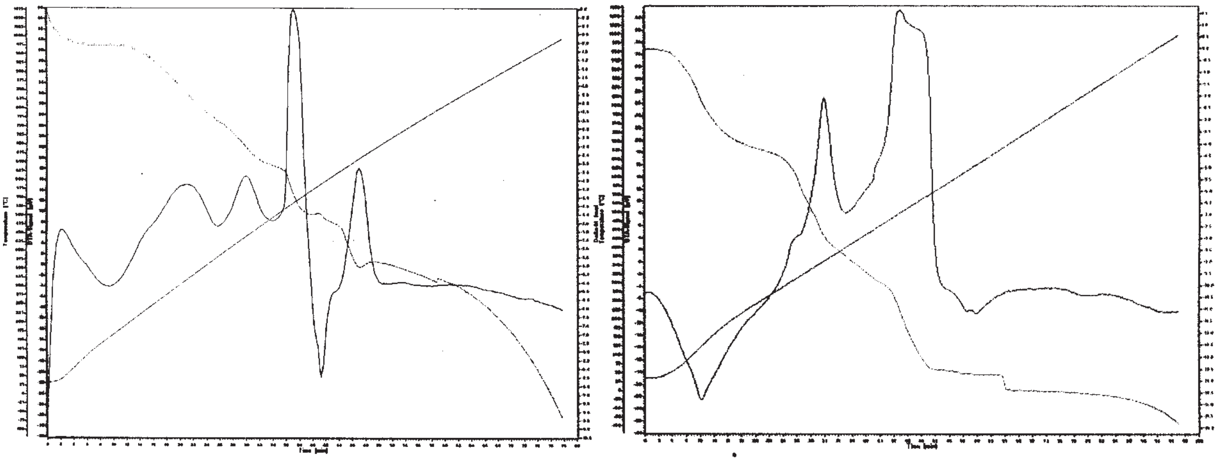
In the first step the complexation water is reduced with about 11-12% in 75-130°C range. HCl both from dye and complex and also the coordination water from the complex is lost in 150-370°C range, being a clear behaviour difference in this area between the ligand and complex. Also, thermal decomposition of the dyes is starting after 150°C while the complexes are decomposing after 320°C.

The derivatogrames of the ligands and synthesized complexes obtained from thermal decomposition using Linseis STA PT1600 technique and MOM-Budapest, Paulik-Paulik- Erdey type, demonstrates a several stage process. It is useful to emphasize on the very good accuracy of the Linseis technique, which provide high resolution, sensitivity and reproductibility compared to MOM-Budapest. Further, the first technique allows the activation energy and order reaction evaluation is automatically software generated and the second one by the Freeman-Carroll method [23]. The values of reaction order and activation energy for thermal decomposition of the studied compounds are summarised in table 2. In all stages of thermal decomposition reactions the calculated reaction order is



a. b.

Fig. 9. Derivagrams of studied compounds: a. – HL^1, b - CuL^1_1

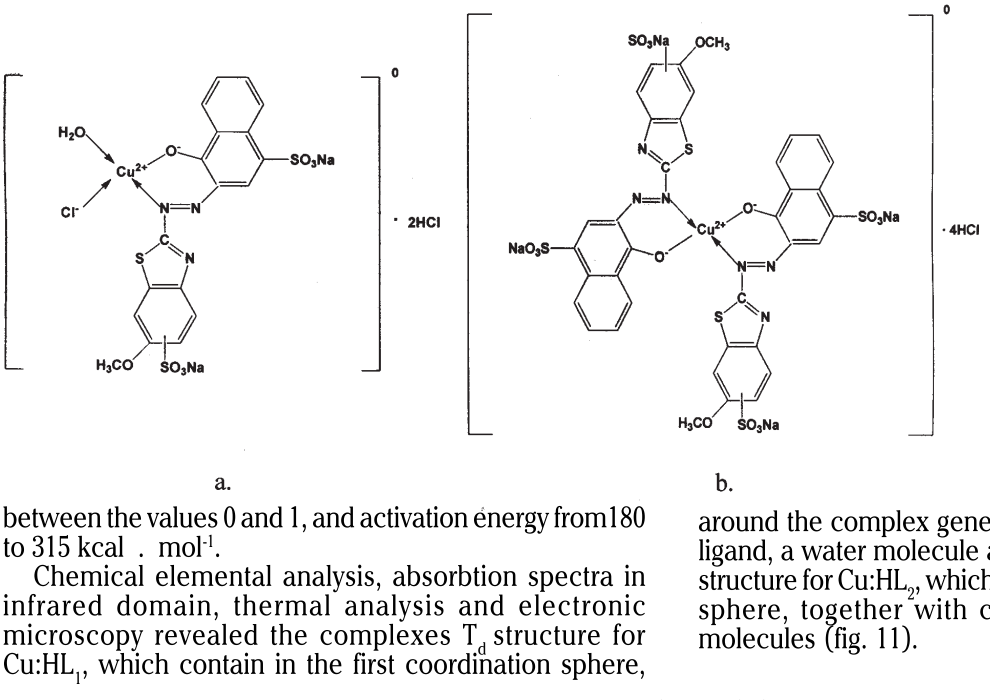


a. b.

Fig. 10. Derivagrams of studied compounds: a. - HL^2, b.- CuL^2_1

Table 2
THERMAL DECOMPOSITION STAGES, REACTION ORDER AND ACTIVATION ENERGY FOR THE STUDIED COMPOUNDS OBTAINED BY FREEMAN-CARROLL METHOD

Compus	Stage I				Stage II			
	T_i (°C)	T_f (°C)	n	E_a ($kcal \cdot mol^{-1}$)	T_i (°C)	T_f (°C)	n	E_a ($kcal \cdot mol^{-1}$)
CuL^1_1	70	295	0.96	189.3	295	490	0.85	270.3
CuL^1_2	92	470	0.83	179.4	470	580	0.88	195.7
CuL^2_1	85	150	0.91	190,7	150	420	0.93	250.67
CuL^2_2	75	290	0.89	205.6	290	580	0.90	315.2



a. b.

Fig. 11. The proposed structural formula for obtained complexes: a - CuL^1_1, b - CuL^1_2 * HCl is coordinated at tertiary group =N- as quaternary nitrogen chloride $=NH^+Cl^-$, which is considerated in the second coordinated sphere

between the values 0 and 1, and activation energy from180 to 315 kcal . mol^{-1}.

Chemical elemental analysis, absorbtion spectra in infrared domain, thermal analysis and electronic microscopy revealed the complexes T_d structure for $Cu:HL_1$, which contain in the first coordination sphere, around the complex generator Cu(II), a dye molecule as ligand, a water molecule and one chloride anion and D_{4h} structure for $Cu:HL_2$, which contain in the first coordination sphere, together with central atom Cu(II), two dye molecules (fig. 11).

In both cases, dyes molecules have the free centres in noncoordinated =N- type, shielded by HCl which is found in the second coordination sphere and which gives a partial solubility involved in the dyeing wool processes. At Cu:HL molar ratio of 1:1, the central atom form with the ligands two coordinative bonds (one with the water and the other by - N=N - center) and two polarized covalent (through $-O^-$ naphtolyc center and respectively by Cl^-), resulting a chelate internal complex. For Cu:HL molar ratio of 1:2, central atom form - N=N - centres and covalently polarizated by $-O^-$ naphtolyc of each ligand, also resulting a internal chelate complex, but with plane geometry (D_{4h}).

The presence of HCl in premetalated dyes structure comes from the acid dyes, HCl being trapped at each tertiary nitrogen ($=N^-$) as the chloride salt form of quaternary nitrogen ($=NH^+Cl^-$), only for the groups which are not interacting with Cu(II) central atom.

These groups ($=NH^+Cl^-$) show for the HCl a thermal stability below chloride anion stability as coordinated ligand to the Cu(II), in consequence this groups are considered as belonging to the second coordinative sphere. Their elimination is achieved in the same area with hygroscopic water (110-150°C), prior to water and chloride anion which is behaving as ligands in the first coordination sphere (360-400°C).

Conclusions

In summary, four new premetalated dyes, from two isomeric ligands by interaction with Cu^{2+} ion in molar ratios M:HL of 1:1 and 1:2. have been prepared.

The new obtained complexes were characterized in solid state by chemical elemental analysis, SEM-EDX, XRD, FTIR and Thermal derivatography. By corroborating data from elemental analysis, SEM-EDX and FTIR the following molecular formula: $[Cu(C_{18}H_{10}N_3S_3O_8Na_2)(H_2O)Cl]\cdot 2HCl$ and $[Cu(C_{18}H_{10}N_3S_3O_8Na_2)_2]\cdot 4HCl$. These formulae are confirmed by thermal analysis in dynamic conditions, where the decomposition steps corespond to the nature of ligands from first coordination sphere. In addition, as a result of the above presented studies, can be concluded that the Cu(II) central atoms are tetracoordinated, and in function of the ligand nature they can adopt in the first case of 1:1 molar ratio M:HL (T_d) tetrahedral structures, with sp^3 hybridization, and in the second case, square plan structures (D_{4h}), with dsp^2 hybridization. Based on SEM imaging and X –ray diffraction technique, the premetalated dyes are in the form of relatively crowed particles, with variable dimensional characteristics and irregular shape and highly crystalline. The synthesized complexes are stable up to 150°C, then their decomposition take places in a several stages, specific of the ligands in the first coordination sphere.

A particular behaviour was encontered at the HCl groups, set at the tertiar nitrogen groups($=N^-$) as a chloride salt form a quaternary nitrogen ($=NH^+Cl^-$), which is eliminated together with the hygroscopic water (110-150°C), both being in the second coordination sphere, compared with coordination water and chloride anion, coordinated at Cu(II) central atom, which are in the first sphere and therefore eliminated at higher temperatures (360-400°C).

Aknowledgments: This paper was elaborated with the support of BRAIN project Doctoral scholarships as an investment in intelligence, financed by the European Social Found and Romanian Government. Special Thanks to Linseis Germany for supporting with consumables for the thermal analysis. Also, the authors are thankful to Prof. D. Ivanov, Institut de Sciences des Matériaux de Mulhouse, France and Prof. Crişan Popescu, DWI an der RWTH Aachen ev, Chair of Textile and Macromolecular Chemistry of RWTH Aachen University, Germany.

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Manuscript received: 25.01.2011