New Complexes of Mn(II), Fe(III) and Co(II)

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Several new complexes were synthesized and studied. These complexes consists of Mn(II), Fe(III) and Co(II) respectively with ligand derived from 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone. Their characterization was performed by using methods such as chemical analysis, thermogravimetry, IR absorption spectroscopy, Mössbauer spectroscopy and X-ray diffraction. The novel complexes crystallize in monoclinic systems with central atoms, such as Mn(II), Fe(III) and Co(II), hexacoordinated in octahedral structures. The obtaining reactions of these complexes can be used in gravimetric determination of Mn(II), Fe(III) and Co(II) with an error of ± 0.25%.

Keywords: 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone, precipitating reagent, gravimetric determination

The compounds presented in this paper belong to the category of complexes achieved by bonding the central atom, such as Mn(II), Fe(III) and Co(II). with functional groups of $\rangle C = O$ and $O(H)$ bound to the benzene ring in α position. All of them can be applied in gravimetry [1-6].

In this paper are described the synthesis of several new compounds and their characterization performed by applying methods such as chemical analysis, thermogravimetry, IR absorption spectroscopy, Electron Spin Resonance (ESR) Spectroscopy, Mössbauer spectroscopy and X-ray diffraction.

The new compounds were obtained in ethanol-water medium through the reaction of 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone ligand with salts such as $MnCl_2$, $FeCl_3$ and $CoCl_2$ respectively, in the molar ratio (ligand:central atom)=2:1 in case of Mn(II) and Co(II), and 3:1 ratio in case of Fe(III). The performed studies emphasized that the central atoms are hexacoordinated through oxygen atoms derived from $>C = O$ and O(H) groups in the ligand and (coordination) water molecules.

Processing the ESR spectra of these compounds, it resulted that the central atoms Mn(II), Fe(III) and Co(II) are paramagnetic.

Mössbauer spectrograms show that the iron atoms in the novel complex is in the third oxidation state with high spin (S = 5/2) and octahedral coordination.

All the studied complexes crystallize in the monoclinic system having very close values for *a* and *c* elemental cell parameters. However, these values are much different and lower than *b* parameter.

The obtaining reactions of the studied compounds can be applied for determining quantitatively the respective cations. Moreover, their gravimetric factor values are very low ($f_{Mn} = 0.0538$, $f_{Fe} = 0.0384$, $f_{Co} = 0.0574$).

Experimental part

Experimental investigations were carried out using 10^{-1} M solutions of $MnCl_2 \times 6H_2O$, $FeCl_3 \times 6H_2O$ and $CoCl_2 \times 6H_2O$ Merck , and a ligand derived from 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone (Merck A.R.). The synthesis of the coordination compounds was performed according to the method described in references [2,4] using as solvent water for inorganic salts, and a mixture of ethylic alcohol and water in a ratio of 1:1 (in volumes) for 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone.

The obtaining reactions of the new compounds were achieved by mixing and stirring at room temperature, for 60 min, the mixtures composed of 100 mL from one of each 10^{-1} M solutions of $MnCl_2 \times 6H_2O$, $FeCl_3 \times 6H_2O$ and $CoCl_2 \times 6H_2O$, and 200 mL of 10^{-1} M solution of 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone ligand. In case of Fe(III) cation, the mixture was composed of 100 mL of 10^{-1} M solution of $FeCl_3 \times 6H_2O$, and 300 mL of 10^{-1} M solution of 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone ligand.

The reaction products are light pink-colored precipitates when contain Mn(II), brown precipitates when contain Fe(III), and light pink precipitates when contain Co(II). The precipitates were separated by filtration, washed on a funnel vacuum nozzle, and then dried at 105°C until a constant weight was reached. Under these conditions, 100% efficiencies were achieved. The contents of C, H, S and Mn(II), Fe(III) or Co(II) were determined for each obtained compound.

The thermal analysis and parameter determination of thermal decomposition reactions were performed using the derivatograms recorded by a Q1500D (MOM Budapesta) derivatograph.

A quantity of 100 mg of each synthesized compound were introduced into a ceramic crucible and then heated up to 1000°C, at a heating rate of 10°C/min. The recorder was set at the following values: TG - 500μV, DTG-2.5 mV and T-500 μV. Al_2O_3 calcinated at 1200°C was used as reference material.

ESR spectra of the studied coordinated compounds were recorded for solid samples on an IFA Bucharest spectrometer using diphenyl picryl hydrozyl (DPPH) as reference and a magnetic field of 3216.9 Gauss with a frequency of 9030 MHz. Thus, the number of electrons corresponding to a central atom and to one gram of analysis sample as well as the *g* factor were calculated according to the directions available in literature [6, 8]. For this purpose, it was employed the graphical method of double integration and then the relationship, $N_x = N_e \, . \, A_x / A_e$ where:

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Table 1

ELEMENTAL COMPOSITION OF STUDIED COMPOUNDS (%)

Complex	C		H		S		M	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
MnL_2	44.68	44.35	2.94	3.16	6.27	6.39	5.38	5.48
FeL_3	47.16	47.30	2.69	2.83	6.62	6.78	3.85	3.92
CoL_2	44.50	44.72	2.93	2.81	6.24	6.43	5.75	5.89

Table 2

CHARACTERISTIC TEMPERATURES OF THERMAL DECOMPOSING STAGES, REACTION ORDERS, ACTIVATION ENERGIES (KJ/mol) OF THE REACTIONS OF THE STUDIED COMPOUNDS

Complex	Stage I				Stage II			
	T_i°, C	T_f°, C	n	E	T_i°, C	T_f°, C	n	E
Mn	205	345	0.80	148.2	345	560	0.92	260.2
Fe	200	350	0.75	135.8	350	545	0.85	238.7
Co	190	340	0.85	127.6	340	550	0.90	226.8

N_x and N_e (= 2.81×10^{-19} odd electrons/mL) represent the number of odd electrons of the analyzed sample and reference respectively, A_x and A_e – areas of ESR spectra of the analyzed sample and reference respectively. The spectroscopic splitting factor was calculated with the relationship, $g = g_e \cdot H_x / H_e$ where: g and g_e (= 2.0055) are spectroscopic splitting factor of the analyzed sample and reference respectively, H_x and H_e = 3216.9 *Gauss* magnetic field of the spectrum center of the analyzed sample and reference respectively.

The two relationships can be applied only when both spectral curves (analyzed sample and reference) are of the same type (Gauss or Lorentz). For all the investigated compounds and reference employed, ESR spectral curves are of the Lorentz type.

The absorption spectra in the IR range (200 to 4000 cm^{-1}) were recorded using a FTIR 660 Plus spectrometer and KBr pellet technique.

Mössbauer spectra of the compound containing Fe(III) were recorded with an electrodynamic spectrometer with an uniform accelerated motion of the source. As source, ^{57}Co isotope in Cr matrix was used. The values of isomer shift were measured as against the reference of sodium nitroprusside that present a doublet with values of ΔEa and σ of 1.76 and 0.165 mm/s respectively. The experimental investigations were carried out at room temperature (300 K) and at liquid nitrogen temperature (80 K). Mössbauer spectra of the investigated compounds were processed by means of an EC-1033 computer provided with specialized software.

X-ray diffractogram recordings of the studied compounds were achieved for solid samples in the angular range of 2θ between 5 and 60^0, and a step of 0.1°/s, at room temperature by means of a Siemens D-500 diffractometer using Cu (K_α) radiation filtered by Ni. The anode voltage was 40 KV, while the anodic current was 1000 mA. The diffractometer is provided with data acquisition system and specialized software. Thus, the index of diffractograms and data processing were performed with TREOR, DIFRAC-AT, CRYSTAL softwares according to the direction in literature [9,10].

Results and discussions

Considering the combination ratio of the central atoms, Mn(II), Fe(III) or Co(II), with 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone, and the chemical analyses of the studied compounds related to the content of C, H, S and Mn(II), Fe(III) or Co(II), it results that two anions provided by the ligand correspond to each central atom of Mn(II) or Co(II), and three molecules of ligand correspond to each Fe(III) central atom.

The elemental composition of the studied compounds determined with an error of ±0.25% is presented in table 1. The new compounds present the following formulas: $Mn(C_{19}H_{13}O_2S_2Br_2)_2\times2H_2O$, $Fe(C_{19}H_{13}O_2SBr_2)_3$, $Co(C_{19}H_{13}O_2SBr_2)_2\times2H_2O$. Here in further, these complexes will be noted as MnL_2, FeL_3 and CoL_2, while the ligand will be mentioned as HL.

Based on the derivatograms of the studied compounds, the characteristic temperature values of the thermal decomposing stages were established. The reaction order and activation energy values of thermal decomposing reactions are calculated according to Freeman-Carrol method [7], and are shown in table 2.

The thermal behaviour of two of the investigated complexes consist in eliminating in the first stage the two water molecules retained as coordination water, at 165°C in case of MnL_2, and at 160°C for CoL_2. FeL_3 complex does not contain water. The elimination of the coordination water from MnL_2 and CoL_2 complexes is followed by two decomposing stages resulting in some intermediary instable products that pass at the end of the process in more stable products such as gases and oxides of the respective metals.

FeL_3 complex decomposes in two stages (table 2), in the final stage resulting Fe_2O_3 and gas products that could not be identified.

In the case of the coordination compounds, especially chelate like the compounds studied in this paper, the thermal stability decreases with the increase of alkalinity of the central atom MnL_2, FeL_3, CoL_2 [11-16].

Thermal decompositions of the studied compounds are gas-solid systems generally characterized by reaction orders with values ranged between 0 and 1. Thermal decomposing reaction is not favored by transport phenomena of the volatile compounds through the heated solid layer, vaporization phenomenon of volatile components. If these phenomena would not exist, the layer of complexes obeyed to thermal decomposing will present the thickness of a molecule, and the reaction order will be 1. In fact, the layer of substance obeyed to thermal decomposing is much thicker, and could reach a few millimeters. However, it gets thinner and thinner as the reaction takes place resulting in an increase of the dispersion degree. As the thermal decomposition advances stage by stage, the increase of the dispersion degree is more pronounced due to the chemical reaction generating the volatile components. This generates thinner layers

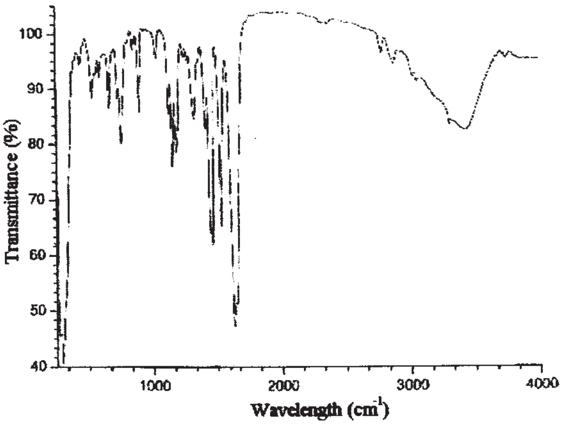

Fig. 1. IR absorption spectrum of MnL_2 complex.

through which the gases pass and consequently the reaction order is higher and higher tending to unity in agreement with the data presented in this paper (table 2) and by other authors [6, 11, 14-16].

In the investigation of the absorption spectra the main purpose was to see if there are bends corresponding to bonds like O-M and O→M, these originating in the interaction of functional groups OH and $>C=O$ in the respective ligand.

In the frequency range of 450-1500 cm^{-1} occur both bends corresponding to the valence vibrations of bonds like C-C, C-O, Mn-O, Fe-O, Co-O, and bends corresponding to the deformation vibrations of other bonds.

Regarding the ligand used in the synthesis of the studied compounds, the absorption bends within the range 1220-1290 cm^{-1} are assigned to the stretch vibrations of C-O bonds in the phenolic group in concordance with some works reported in literature [18,19].

The absorption of OH phenol groups in orto position in the 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone ligand is located at 1285 and 3275 cm^{-1}, and disappears in the investigated complexes. The bends with frequencies 490, 475 and 465 cm^{-1} are assigned to the stretch frequencies ν_{Mn-O}, ν_{Fe-O} and ν_{Co-O} respectively (table 3).

Table 3

SPECTRAL BANDS IN IR RANGE CHARACTERISTIC TO THE STUDIED COMPLEXES AND LIGAND (cm^{-1}).

Compound	ν_{H_2O}	$\nu_{C=0}$	$\delta_{\phi OH}$	ν_{ϕ}	ν_{M-O}
HL	-	1705	1285	1595	-
MnL_2	3420-3410	1660	-	1580	490
FeL_3	-	1640	-	1570	475
CoL_2	3380-3360	1630	-	1565	465

The bends of vibration frequencies of C-O group observed in the region 1230-1290 cm^{-1} on the ligand spectrum are shifted to higher wavelengths, and become less intense in the spectra of the studied compounds.

The stretch (valence) vibrations of the carbonyl corresponds to an intense, characteristic bend with a maximum located at 1705 cm^{-1} in the ligand, while in the studied compounds occurs at 1660-1630 cm^{-1}. This represents an argument on the coordination of central atoms with the oxygen atom in carbonyl group:
$M \leftarrow O=C<$ (fig. 1, table 3).

The presence of water molecules coordinated by the central atoms Mn ← OH_2 and Co ← OH_2 in the studied compounds generates symmetric and asymmetric stretch vibrations at 3420-3410 cm^{-1} respectively 3380-3260 cm^{-1}, and deformation vibrations at 1620-1625 respectively 1600-1610 cm^{-1} in concordance with studies reported by other authors [6,14,15,20].

Processing the ESR spectra, it results that the studied complexes have paramagnetic properties. The spectroscopic splitting factor takes values between 2.0194-2.0242, hence it is higher than that of the free electron (2.0023) due to the contribution of the orbital momentum and covalence degree of the respective bond where the central atoms Mn(II), Fe(III) and Co(II) are involved (table 4). This is in agreement with the works in literature related to the same central atoms [6,14-16,19-21].

Table 4

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

Compound	g	H_x	N
MnL_2	2.0219	3243.1	4.90
FeL_3	2.0194	3239.1	4.89
CoL_2	2.0242	3246.8	2.92

Based on the Mössbauer spectra it can be stated that the central atom of iron in FeL_3 complex present a IIIrd oxidation state with high spin ($S=5/2$) which point out a relatively ionic character of Fe-O bond. In figure 2 is presented the Mössbauer spectrogram of FeL_3 complex.

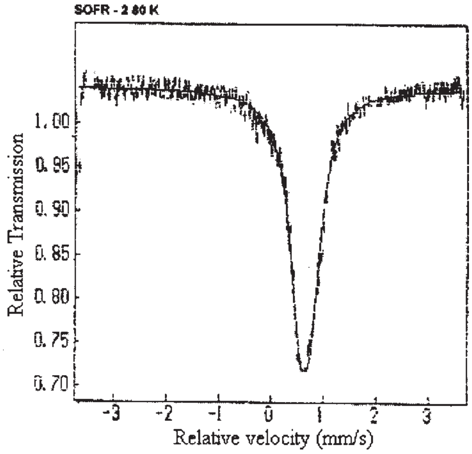

Fig. 2. Mössbauer spectrogram of FeL_3 complex recorded at a temperature of 300 K

Table 5

VALUES OF MÖSSBAUER PARAMETERS OF FeL_3 COMPLEX.

T (K)	δ (mm/s)	ΔE_Q (mm/s)	Γ (mm/s)
300	0.90	0.85	0.72

Considering the value of E_Q parameter (table 5), it can be inferred that the central atom Fe(III) presents an octahedral encompassment with a disposal of the electrons in concordance to the crystalline field in two sublevels: t^3_{2g} and e^2_g.

Due to the symmetrical electronic configuration $3d^5$ of Fe(III) central atom, it was not observed a quadrupol splitting in case of octahedral coordination only through the oxygen atoms provided by the ligand. For this complex, it was noticed a dependence on the temperature of a higher isomer shift than the normal one that is 0.05 mm/s at 100°C, phenomena observed also at other complexes [22,23]. This increase of the isomer shift is in agreement with the Doppler effect of the second order (degree). We speculate that as the temperature increases from 80 to 300 K, at the same time as the oscillations of Fe(III) atoms in the crystalline network increase, it takes also place a shift of the electronic density of spin *s* within the ligand-central atom bond.

By indexing the X-ray diffractograms, it results that HL ligand and MnL_2 and CoL_2 complexes crystallizes in monoclinic system having the elemental cell parameters presented in table 6.

Table 6

PARAMETER VALUES OF ELEMENTAL CELLS OF HL LIGAND AND MnL_2 AND CoL_2 COMPLEXES

Elemental cell parameters	Values obtained by indexation		
	HL	MnL_2	CoL_2
a (Å)	12.9834	13.1947	9.1832
b (Å)	9.5743	5.8148	13.1214
c (Å)	9.7798	12.0675	8.3431
α	90°	90°	90°
β	90°	92.56°	103.40°
γ	90°	90°	90°
Elemental cell volume ($Å^3$)	1216.1654	925.8734	998.7454

Based on the indexation of diffractograms (figs. 3, 4, 5) of ligands and studied complexes, it results that the coordination process of Mn(II) and Co(II) central atoms is influenced by crystallographic characteristics of the ligand. This is characterized by the similarity of two of the elemental cell parameters of the complexes reported to those of the ligand.

Data resulted from the indexation of MnL_2 complex diffractogram point out close values of *a* and *c* parameters, yet the value of *b* parameter is much higher, which means that the central atom Mn(II) is coordinated by two ligand molecules in the *ab* plane on *b* crystallographic direction accompanied by the volume compression of the complex elemental cell. It is noted a slight distortion of the β angle due to a probable disposal of the two molecules of coordinated water at the central atom of Mn(II), one above and the other beneath the plan were are placed the ligands. However, it is preserved a slightly deformed octahedral symmetry of the central ion. Thus, it can be inferred that the central atom of Mn(II) is coordinated with the two water molecules in *ab* plane on *b* crystallographic direction accompanied by the volume compression of the complex elemental cell.

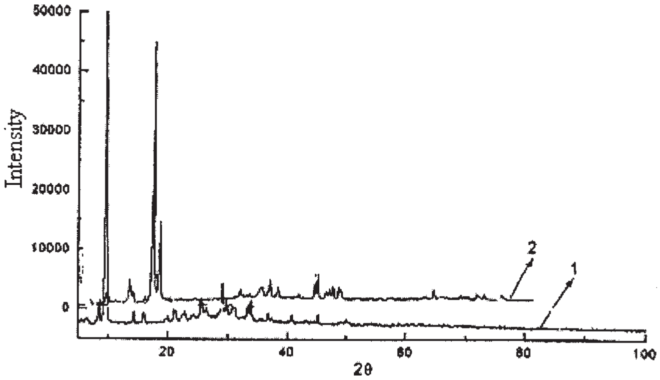

Fig. 3. Diffractograms of HL ligand (1) and MnL_2 complex (2).

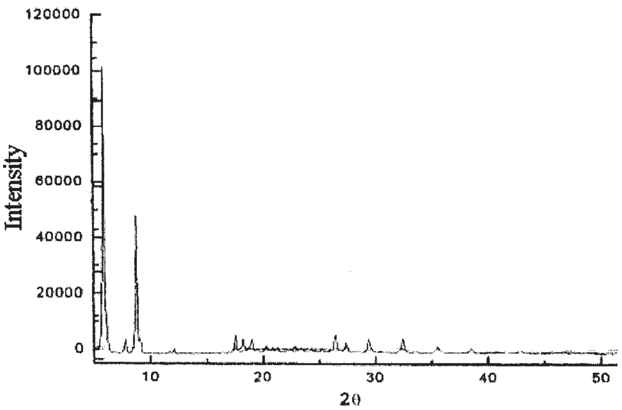

Fig. 4. $CoL_2.2H_2O$ complex (2) diffractogram

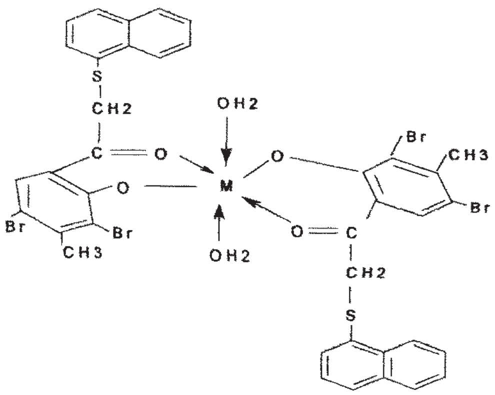

Fig. 5. Structure of complexes $M(C_{19}H_{13}O_2SBr_2)_2$. $2H_2O$ M=Mn(II), Co(II).

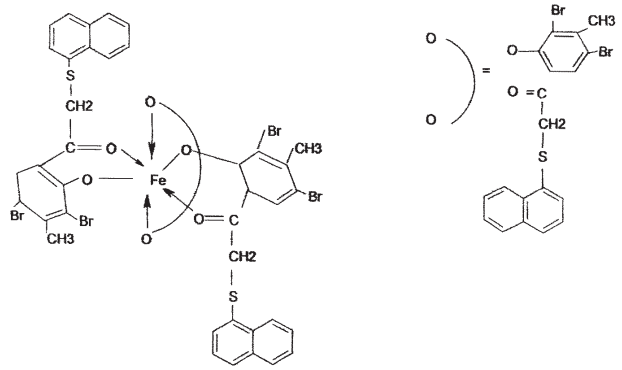

Fig. 6. Structure of complexes $Fe(C_{19}H_{13}O_2SBr_2)_3$.

In case of CoL_2 complex, the coordination of the ligand is achieved in the *ac* plane with a compression of its volume. It is noted a slight distortion of β angle that supports the idea that the water molecules are disposed on both sides of *ac* plane. FeL_3 complex presents a high amorphicity degree that does not allow the indexation of the diffractogram.

Experimental data obtained by chemical analysis, absorption spectra in the IR range, Mössbauer spectra, thermal analysis and X-ray diffraction point out that the central atoms of Mn(II), Fe(III), Co(II) are hexacoordinated in octahedral structures. In case of MnL_2 and CoL_2 complexes, the hexacoordination of Mn(II) and Co(II) central atoms is achieved through the oxygen atoms from the groups OH and >C=O provided by the ligand to which are added two more molecules of coordination water (fig. 6).

Conclusions

In this paper was presented the synthesis and study of some new complexes resulted from the reactions of Mn(II), Fe(III) and Co(II) with the 1-(3,5 dibromo, 2 - hydroxy, 4 methyl phenyl), 2 naphtyl sulfanyl ethanone ligand, of which formulae are $M(C_{19}H_{13}O_2SBr_2)_2 \times 2H_2O$ where M is Mn(II) or Co(II), and $Fe(C_{19}H_{13}O_2SBr_2)_3$.

The studies were performed applying modern methods like chemical analysis, thermogravimetry, absorption spectroscopy in the IR range, ESR spectroscopy, Mössbauer spectroscopy and X-ray diffraction. Complexes containing hexacoordinated central atoms of Mn(II) and Co(II) crystallize in monoclinic system. The obtaining reaction of the novel complexes can be employed in order to determine gravimetrically Mn(II), Fe(III) and Co(II).

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Manuscript received: 11.02.2009