THERMAL AND SPECTROSCOPIC STUDIES OF Ni(II)-Fe(III) HETEROPOLYNUCLEAR COORDINATION COMPOUND OBTAINED THROUGH THE REACTION OF 1,2-ETHANEDIOL WITH METALLIC NITRATES

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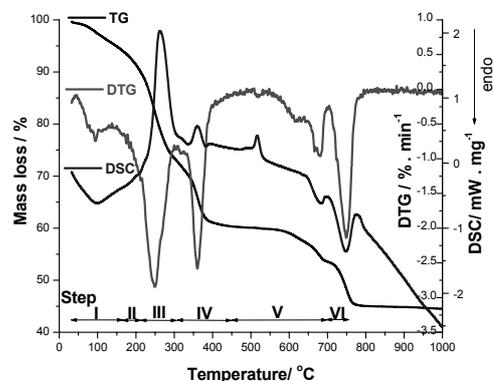
The oxidation reaction of 1,2-ethanediol (ethylene glycol, EG) with Ni(II) and Fe(III) metallic nitrates in aqueous solution was investigated.

Also, the paper presents the experimental results of the thermal and spectroscopic studies of the synthesized Ni(II)-Fe(III)-heteropolynuclear coordination compound having as ligand oxidation product of ethylene glycol.

Under specific working conditions, the reaction occurs with the oxidation of EG to glyoxylic acid, coordinated to the Ni(II) and Fe(III) cations as glyoxylate anion ($C_2H_2O_4^{2-}$, GA), with simultaneous isolation of heteropolynuclear coordination compound. In order to separate and identify the ligand, the synthesized coordination compound, having the composition formula is the main component of the conversion of the complex compound, $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$, has been treated with R-H cationite (Purolite C-100). After the retention of the metal cations, the glyoxylic acid was characterized by measuring the physical constants, by specific reactions and spectroscopic methods.

The structural investigations and thermal analysis of nickel ferriglyoxylate coordination compound, precursor of nickel ferrite are presented.

The thermal properties of the synthesized polynuclear coordination compound have been investigated by TG, DTG and DSC. The mixed oxide obtained through thermolysis was characterized by IR, X-ray spectroscopy and elemental analysis.

INTRODUCTION

Knetsch and Groeneveld[1] have synthesized and studied a number of complexes with diols as ligands.

In our previous papers[2-10] we have reported the results of the studies of the oxidation reactions between 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol and some metallic nitrates.

The coordination compounds synthesized in this way contain glyoxylate anion, oxalate anion, lactate anion and 3-hydroxypropionate anion as ligands.

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The thermal conversion of homo- and hetero-polynuclear complexes with anions of carboxylic acids as ligands has been carried out to oxide systems with irreductible structure and properties, required by the modern technology in various fields (heterogeneous catalysis, electrocatalysis, ceramic pigments, electronics, physical supports – carriers, brackets – for the stockage and processing of information, drug industry).[11-13]

These compounds decompose at relatively low temperatures, forming simple or mixed oxides and volatile products (CO, CO_2, H_2O).

The reaction between 1,2-ethanediol and $Cu(NO_3)_2 \cdot 3H_2O$ occurs with the oxidation of 1,2-ethanediol to glyoxylate anion[2,11] or oxalate anion,[8,11b] depending on the working conditions.

Colloidal crystal templating method is used to prepare three-dimensionally ordered macroporous MFe_2O_4 (M = Mn, Ni, Zn, Co).[14] Gao *et al.*[15] synthesize mesoporous spinel $NiFe_2O_4$ with well-defined pore size (2.5–16.2 nm) by oxalate decomposition process for adsorption acid orange 7. The preparation procedure of 3D porous materials is always template methods, which include the process of infiltration and templates removal.[16] A simple way of synthesizing 3D porous materials is necessary in the field of the adsorbents investigation.

Magnetic separation is considered as an effective technique of separating adsorbents from wastewater, and magnetic adsorbents are investigated widely, recently.[17-19] Spinel ferrite (MFe_2O_4, where M = transition metal) shows a typical ferromagnetic property at room temperature and it is wildly used as magnetic carrier in adsorbent to realize magnetic separation.[20,21] For instance, the magnetic microsphere containing ferrite is applied for the adsorption of organic dye,[17] bromide-coated ferrites are applied for the preconcentration of phenolic compounds[18] and magnetic polymer nanosphere adsorbent is applied for dye molecules removal.[19] However, the composite adsorbents always lose some adsorption capacity or ferromagnetism. Using the spinel ferrite as adsorbent directly can solve this problem, because it shows both good adsorption and magnetic separation properties. $NiFe_2O_4$ was used as adsorbent to treat wastewater.[22]

In the last years the thermal decomposition of solid heteropolynuclear coordination compounds, as precursors, has been widely used for synthesis of nanoferrites. It represents a versatile and predictable unconventional method, due to the possibility of controlling the quality (composition and microstructure) of the end products featuring, by selecting suitable ligands.

The determination of the forming conditions of non-stoichiometric oxides of Ni and Co led to an original method of obtaining anodes with active electrocatalytically films for the oxygen evolution at the electrolysis of alkaline solutions.[23]

The spinel ferrites, generally the mixed oxides of spinel type are showing great promise in modern electronic technologies, microwave absorber, chemical sensors, catalysts and biomedical applications. For all these applications the fine particle nature of the ferrite is crucial, being usually achieved by soft chemistry synthesis methods, respectively low temperature range decomposition of suited precursors.[24-32]

This paper presents the results obtained at the investigation of 1,2-ethanediol oxidation with $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, in a weak acid medium (pH ~ 2.5). The obtained coordination compound was investigated from the standpoint of the composition and physical-chemical properties. It will be shown that it can be a precursor for nickel ferrite, $NiFe_2O_4$, which is obtained at relatively low temperatures.

EXPERIMENTAL

Chemicals and methods

Chemical reagents of quality were used for the synthesis of coordination compoud. As starting materials, $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and 1,2-ethanediol were employed.

The impurities from the reagents do not influence the synthesis and the purity of the obtained compound as they are removed in the subsequent purification step.

The metal content was determined by the atomic absorbtion spectrophotometry. Carbon and hydrogen were analyzed using a Carlo Erba 1108 elemental analyzer.

TG, DTG and DSC curves (in the range 25–1000 ^{o}C) corresponding to the decomposition of the coordination compound were recorded on a Simultaneous TG-DTA/DSC Apparatus 409PC produced by NETZSCH GERATEBAU GMBH –Germany, in static air atmosphere at a heating rate of 10 K min^{-1}.

The coordination compound was also characterized by the following methods: chemical analyses, IR-spectroscopy and electronic spectroscopy (diffuse reflectance technique).

The IR spectrum (KBr pellets) was recorded on a Jasco 410 FT-IR Spectrophotometer, in the range 400–4000 cm^{-1}.

The electronic spectrum was recorded by diffuse reflectance technique using a spectrophotometer SPEKOL 10 Carl Zeiss Jena and MgO as a reference material.

The characterization of the nickel ferrite, $NiFe_2O_4$, obtained by thermal decomposition of heteropolynuclear coordination compound was performed by elemental analysis, IR spectroscopy and X-ray diffraction (XRD).

Powder X-Ray diffraction patterns of the samples were recorded on a BRUKER D8 Advance diffractometer with graphite monochromator on the diffracted beam, using Mo K$_\alpha$ radiation (λ = 0.70930 Å). The X-Ray power was 40 KV and 30 mA.

The powder samples were grounded in order to reduce the granulation (when necessary) and then pressed in the specimen holder.

The patterns were recorded over a range of 2θ angles from 5° to 50° and crystalline phases were identified using the Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD) files. The data were collected and processed with the DIFFRAC plus program package.

Synthesis of the coordination compound

The elaborated method of the synthesis of the complex compound is based on the oxidation reaction of 1,2-ethanediol in an alcohol-water system by Ni(II) and Fe(III) nitrates and the simultaneous isolation of the coordinative compound from the reaction system.

A solution of water + diol + $Fe(NO_3)_3 \cdot 9H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$ in the molar ratio: $Ni(NO_3)_2 \cdot 6H_2O$: $Fe(NO_3)_3 \cdot 9H_2O$: 1,2- ethanediol = 1 : 2 : 2 was prepared. This mixture was heated in a thermostat, gradually up to 90°C. The reaction was considered complete when no more gas evolution was observed.

The solid, powdery reaction product was purified by refluxing from an acetone-water mixture.

After that, the solution was filtered and the solid beige product was washed with acetone and finally maintained in air until constant mass. The yield was 85% (based on the 1,2-ethanediol). The metallic nitrate is entirely consumed during the obtaining process of the coordination compound. The phenomenon was marked by treating a sample with a concentrated sulphuric acid solution, when no release of brown vapors was observed. Besides, one observed a negative ring reaction (no intensely brown coloured $[Fe(H_2O)_5NO]SO_4$ was obtained in the reaction with $FeSO_4 + H_2SO_4$). The Braccio reaction was negative as well (nor NO_3^- or NO_2^- anion were shown by the antipyrine test, so the oxidizing action of the nitrate anion did not cause its reduction to nitrite anion).

In order to separate and identify the ligand, the aqueous suspension of the complex combination, obtained by the reaction between EG and metal nitrates in the absence of another reactant, was treated with R-H cationite. After the retention of the metal cations, the acidic solution resulted is lyophilized and a solid, white crystallin, highly water soluble product, with a poor solubility in alcohols and ethylic ether, with a 98 °C melting point was obtained.

RESULTS AND DISCUSSION

The evolution of the reaction between 1,2-ethanediol, $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ was investigated by IR spectroscopy. As the reaction advances, the bands due to the nitrate ion decrease in intensity, proving that the nitrate ion is consumed in the reaction.[33]

At the same time, the appearance and the increase of the band intensity in the range of 1580-1680 cm^{-1} ($\nu_{asym}COO^-$) is observed, which is specific to complex ligands that contain two oxygen atoms as donors such as the carboxylic anions of the acids.[34]

After the retention of the cations, the ligand was identified. The ligand, in a protonated form(glyoxylic acid), was identified by specific reactions and physical measurements. The physical properties of the lyophilization product lead to the conclusion that this one is the glyoxylic acid.

The infrared spectrum of glyoxylic acid was recorded in the range 400-4000 cm^{-1} (Fig. 1).
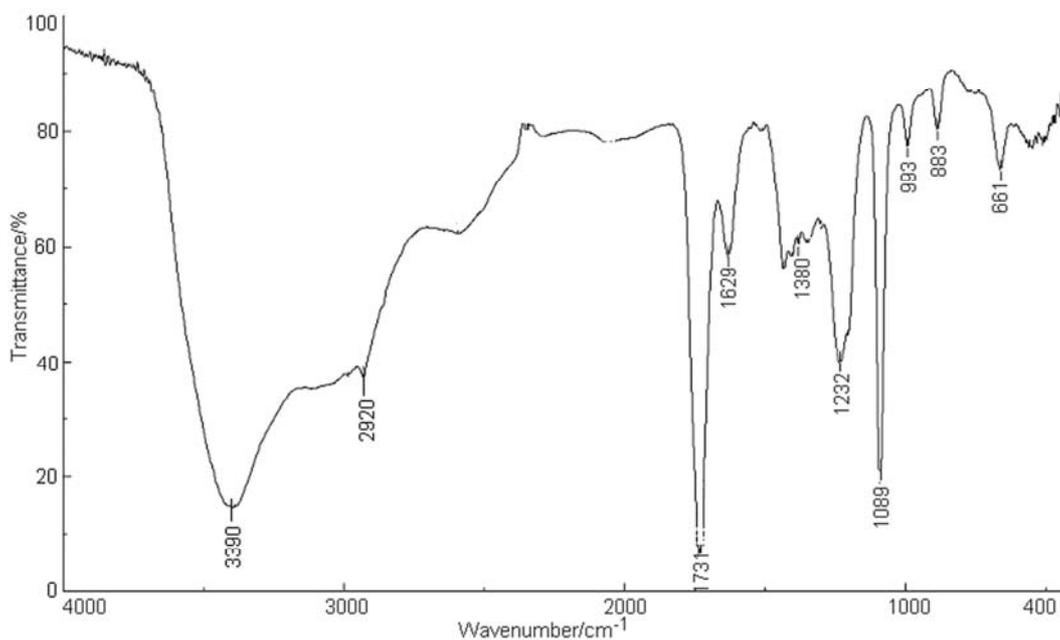

Fig. 1 – The infrared spectrum of glyoxylic acid.

In the infrared spectrum, one can observe the characteristic bands for the two forms of the glyoxylic acid, which exist in equilibrium (Fig. 2).
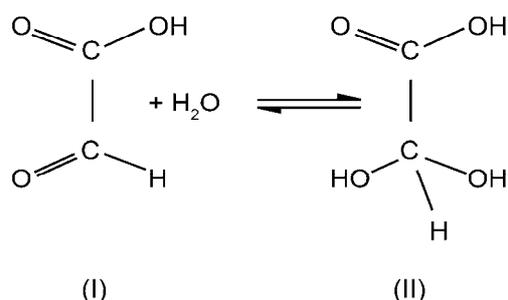

Fig. 2 – Glyoxylic acid (I) and hydrated glyoxylic acid (II).

The broad band in the range 3200-3600 cm^{-1} with a maximum at 3390 cm^{-1} is attributed to the stretching of the two different sorts of O-H bond – the one in the acid group and the simple "alcohol" type in the hydrated aldehyde group (II). The sharp band at 1731 cm^{-1} is assigned to the vibration ν(C=O). The band at 1629 cm^{-1} is attributed to the asymmetric vibration of the carboxylate group. The band with maximum at 1380 cm^{-1} is assigned to the symmetric vibration ν_{sym}(OCO). The band with maximum at 1232 cm^{-1} can be attributed to coupling between a stretching vibration, ν(CO) and a bending vibration, δ(OH). The two bands at 1089 cm^{-1} and 993 cm^{-1} are assigned to the hydrated aldehyde (gem-diol, CH(OH)$_2$). The band with maximum at 661 cm^{-1} is attributed to the bending vibration δ(OCO).[33,34]

Chemical identification of glyoxylic acid

The chemical investigation of the lyophilization product was carried out through specific reactions (redox reactions, colour reactions and precipitation reactions): the reaction with silver oxide, Ag$_2$O (metallic silver was obtained), the reaction with metallic zinc (glycolic acid was obtained), the reaction with indole or pyrogallol in concentrated sulphuric acid medium (a red or blue colour, respectively, occurred), the reaction with resorcin (the lactone of the 2,2',4,4'-tetraoxodyphenylacetic acid is formed in the presence of sulphuric acid; the oxygen oxidizes in basic medium the lactone and a blue violet color appeared); precipitates are obtained in the reactions with p-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine, respectively.

The physical properties (a white, crystalline, water-soluble solid, with a low solubility in alcohol or ether, and the melting point 98 °C) are in good agreement with the literature data.[11,35]

The elemental analysis results (Table 1) as well as the IR investigation have indicated that the synthesized coordination compound has the following empirical chemical formula: NiFe$_2$(C$_2$H$_2$O$_4$)$_2$(OH)$_4$(H$_2$O)$_4\cdot$1.5H$_2$O.

These results, as well as those previously reported[6-8,11] concerning the oxidation of the diols with Fe(III) nitrate respectively Ni(II) nitrate, suggest that the oxidation of the 1,2-ethanediol with Fe(NO$_3$)$_3\cdot$9H$_2$O and Ni(NO$_3$)$_2\cdot$6H$_2$O occurs, in some working conditions, to glyoxylate anion, coordinated to Fe(III) and Ni(II).
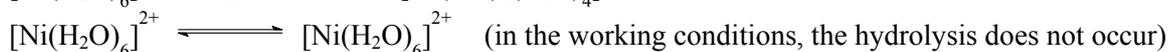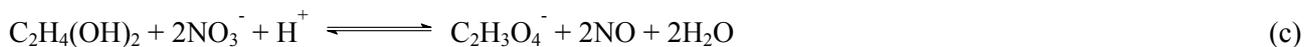
Table 1
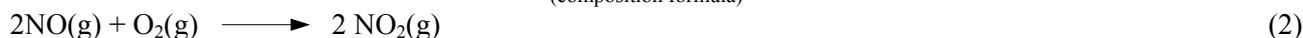
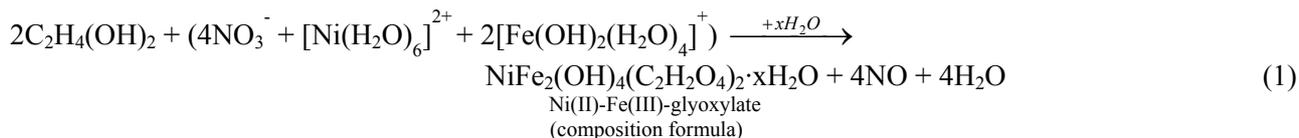The elemental analysis data of the coordination compound

Compound	C %		H %		Fe %		Ni %	
	found	calc.	found	calc.	found	calc.	found	calc.
NiFe$_2$L$_2$(OH)$_4$(H$_2$O)$_4\cdot$1.5H$_2$O	9.05	9.24	3.49	3.66	21.62	21.50	10.71	11.31

Consequently, we suggest the following mechanism for the reaction between 1,2-ethanediol and these metallic nitrates, in the absence of another reactant:

$$C_2H_3O_4^- + 6e + 7H^+ \rightleftharpoons C_2H_4(OH)_2 + 2H_2O \qquad (a)$$

$$NO_3^- + 3e + 4H^+ \longrightarrow NO + 2H_2O \qquad (b)$$

$$C_2H_4(OH)_2 + 2NO_3^- + H^+ \rightleftharpoons C_2H_3O_4^- + 2NO + 2H_2O \qquad (c)$$

$$[Fe(H_2O)_6]^{3+} + 2H_2O \rightleftharpoons [Fe(OH)_2(H_2O)_4]^+ + 2H_3O^+ \qquad (d)$$

$$[Ni(H_2O)_6]^{2+} \rightleftharpoons [Ni(H_2O)_6]^{2+} \quad \text{(in the working conditions, the hydrolysis does not occur)}$$

By totaling (c) + (d) and counting the interaction of ligands with metallic cations, one obtains:

$$2C_2H_4(OH)_2 + (4NO_3^- + [Ni(H_2O)_6]^{2+} + 2[Fe(OH)_2(H_2O)_4]^+) \xrightarrow{+xH_2O}$$

$$NiFe_2(OH)_4(C_2H_2O_4)_2 \cdot xH_2O + 4NO + 4H_2O \qquad (1)$$

Ni(II)-Fe(III)-glyoxylate
(composition formula)

$$2NO(g) + O_2(g) \longrightarrow 2 NO_2(g) \qquad (2)$$

Analyzing reactions, one may notice the necessity of the presence of protons involved in the c) stage in order to potentiate the oxidation activity of nitrate ion.

The suggested formula of the coordination compound as well as information concerning its structure is going to be confirmed by the results which will be presented in the following.

Diffuse reflectance spectrum of Fe(III)-Ni(II)-hydroxo-glyoxylate

The diffuse reflectance spectrum of the coordination compound shows the presence of the characteristic bands of the hexacoordinated Ni(II) and Fe(III) ions in a (pseudo)octahedral environment (Fig. 3).

The absorption band at 26,316 cm^{-1} (λ = 380 nm) may be assigned to the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (ν_3) transition, characteristic to the Ni(II) ion in a high spin octahedral configuration while the band at 13,158 cm^{-1} (λ = 760 nm) may be assigned to the $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (ν_2) transition. The results are in good agreement with those from the literature.[6-10,34]

Accordingly, Ni(II) ion in fundamental state $t_{2g}^6 e_g^2$, high spin, the three ligands OH, L, H$_2$O being of low field and similar strength. The reflectance spectra reveal also, at 920 nm the characteristic band of Fe(III) ion in a high spin octahedral configuration, the presence of the forbidden spin transition bands in an octahedral high spin configuration of the Fe^{3+} ($t_{2g}^3 e_g^2$) ions (ν_3).[11,34]

IR vibrational spectrum of Fe(III)-Ni(II)-hydroxo-glyoxylate

In order to obtain information regarding the structure of synthesized compound and the ligand coordination, the IR spectrum was recorded within the range 400-4000 cm^{-1} (Fig. 4).
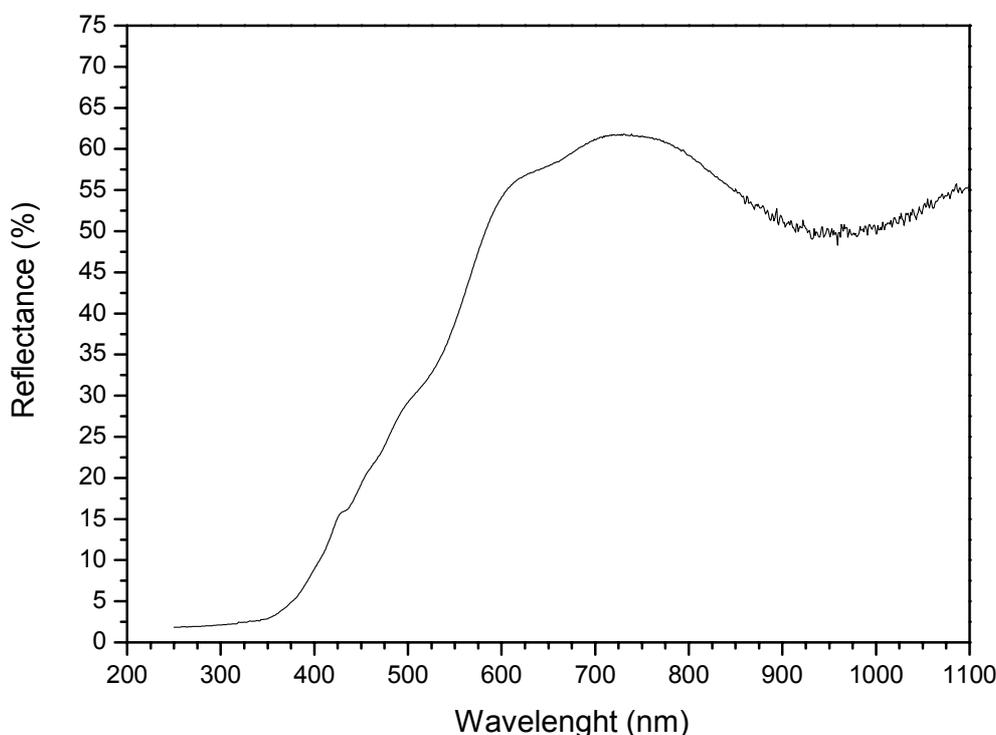

Fig. 3 – Diffuse reflectance spectrum of the coordinative heteropolynuclear compound is the main component of the conversion of the complex compound, NiFe$_2$(C$_2$H$_2$O$_4$)$_2$(OH)$_4$(H$_2$O)$_4 \cdot$1.5H$_2$O]$_n$.
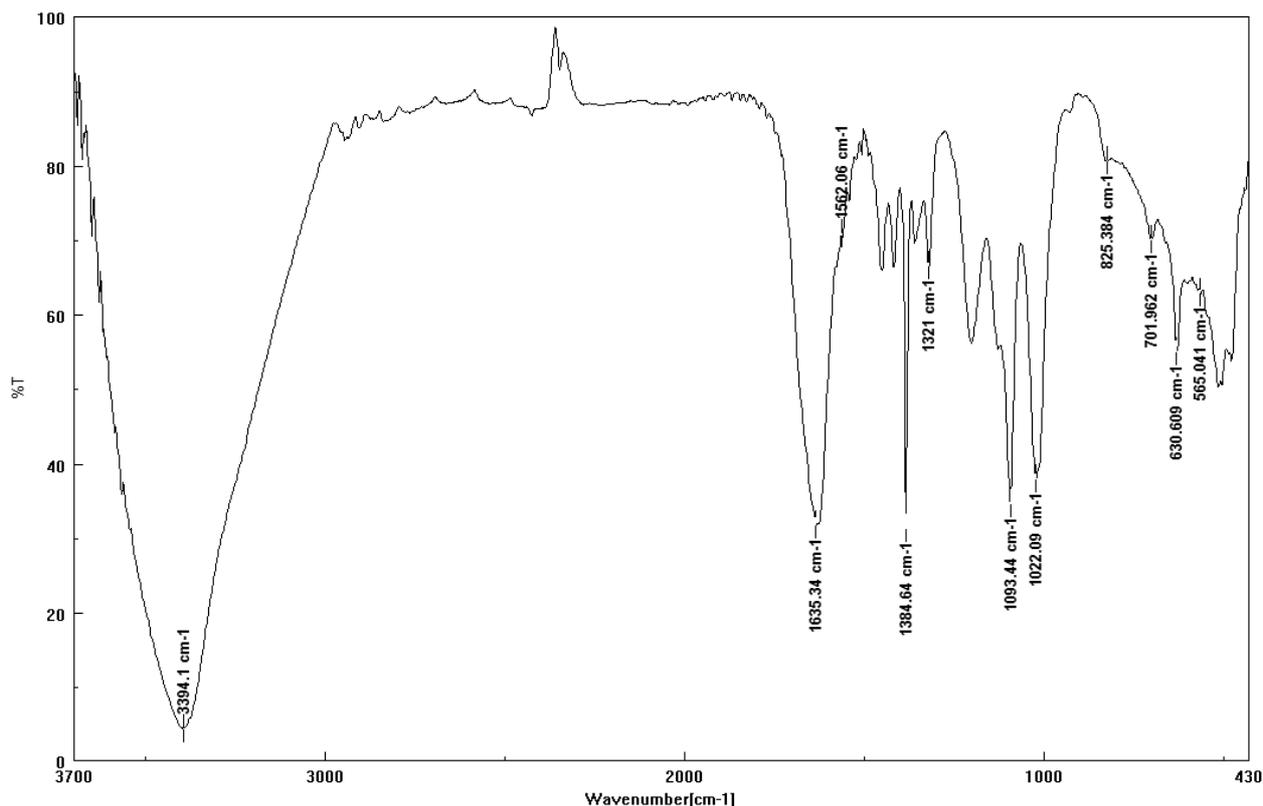
Fig. 4 – IR vibrational spectrum of the coordination heteropolynuclear compound $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$.

Table 2

Characteristic absorption bands in IR for coordinative heteropolynuclear compound
$[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$ and the corresponding assignments

$[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)]_n$	
Wavenumber [cm^{-1}]	Assignment
3394 s,b	$\nu(OH)$
1636 vs	$\nu_{asy}(OCO) + \delta(H_2O^*)$
1564 m, sh	lattice water
1384 s	$\nu_{sy}(OCO)$ and/or $\nu(C-C)$
1321 m	$\nu_{sy}(OCO)$ and/or $\delta_{sy}(OCO)$
1093 s	$\nu(C-O) + \delta(Fe-OH)$
825 w	$\delta_{asy}(OCO)$
702 w	$\rho(H_2O^*)$
630 m	lattice water
563 w	w (H_2O^*)

s – strong (v – very); b – broad; m – medium; w – weak, sh – shoulder; H_2O^* – coordinated water.

Table 2 shows the characteristic bands in IR (cm^{-1}) for solid and beige coloured complex and the corresponding assignments.

The broad band in the range 3200-3600 cm^{-1} with a maximum at 3394 cm^{-1} is attributed to the formation of the hydrogen bonds between water molecules and the alcoholic hydroxyl.[9-11,33]

The intense band at 1636 cm^{-1} is attributed to the asymmetrical vibration of the carboxylate ion and the value shows that the resonance from the carboxylate group is maintained during complex formation, the metal-carboxylate bond prevailing with respect to the ionic one.[34]

The band with maximum at 1384 cm^{-1} is attributed to the symmetric vibration $\nu_{sym}(COO^-)$. As the difference between $\nu_{asym} - \nu_{sym}$ is higher than 170 cm^{-1} one may say that the metal-carboxylate bond is really preponderantly ionic, and the carboxylate group acts as a bidentate ligand.[33,34] Also, the existence of the two bands for $\nu_{sym}(COO)$ can be explained through the octahedral deformation. The band at 1321 cm^{-1} confirms that

the carboxylate group is acting as a bidentate ligand.[23,34]

The band at 1128 cm^{-1} is attributed to the C-OH vibration. The band of mean intensity at 1022 cm^{-1} is attributed to the vibration of the OH bridge group. The band at 825 cm^{-1} is attributed to the vibration δ(OCO).[33]

The obtained compound is insoluble in water, ethanol and ether. It can be destroyed only by concentrated solutions of HCl or H_2SO_4. These statements as well as the above mentioned data suggest a polynuclear structure which corresponds to the following formula: $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$.

Thermal conversion of Fe(III)-Ni(II)-hydroxo-glyoxylate

In order to establish the conditions in which the coordination compound $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$ is decomposed to $NiFe_2O_4$, the thermal analysis methods (TG, DTG, DSC) were used.

The obtained TG, DTG and DSC curves, shown in Fig. 5, suggest six steps which occur at the progressive heating of the coordination compound:
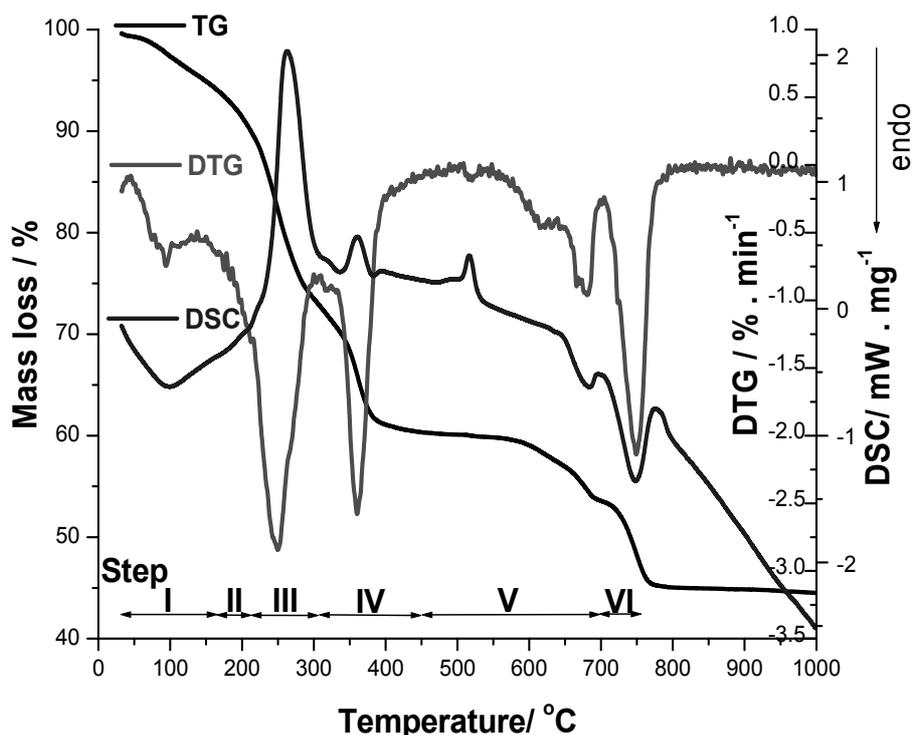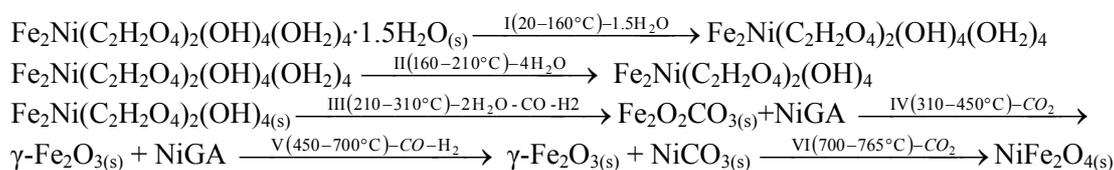
$$Fe_2Ni(C_2H_2O_4)_2(OH)_4(OH_2)_4 \cdot 1.5H_2O_{(s)} \xrightarrow{\text{I}(20-160°C)-1.5H_2O} Fe_2Ni(C_2H_2O_4)_2(OH)_4(OH_2)_4$$

$$Fe_2Ni(C_2H_2O_4)_2(OH)_4(OH_2)_4 \xrightarrow{\text{II}(160-210°C)-4H_2O} Fe_2Ni(C_2H_2O_4)_2(OH)_4$$

$$Fe_2Ni(C_2H_2O_4)_2(OH)_{4(s)} \xrightarrow{\text{III}(210-310°C)-2H_2O-CO-H2} Fe_2O_2CO_{3(s)}+NiGA \xrightarrow{\text{IV}(310-450°C)-CO_2}$$

$$\gamma\text{-}Fe_2O_{3(s)} + NiGA \xrightarrow{\text{V}(450-700°C)-CO-H_2} \gamma\text{-}Fe_2O_{3(s)} + NiCO_{3(s)} \xrightarrow{\text{VI}(700-765°C)-CO_2} NiFe_2O_{4(s)}$$

Fig. 5 – TG, DTG and DSC curves for the decomposition in air of $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$.

Table 3

The mass loss during the thermal conversion in air of the investigated compound

Step	I	II	III	IV	V	VI	I – VI
Δm % (calc.)	5.20	13.87	12.72	8.48	5.78	8.48	54.53
Δm % (experim.)	5.03	13.93	12.87	8.54	5.87	8.56	54.80

Data from Table 3 confirm the proposed conversion mechanism.

In the temperature range 20-210 ^{o}C, $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$ display two endothermic dehydration DSC peaks (broad), for the two losses of water (processes I and II). The TG mass losses correspond to 1.5 H_2O (process I) respectively 4H_2O (process II).

The strong exothermic effect that characterizes the III step (maximal at 263.4 °C) and the exothermic effects that characterize the IV and V steps (maximals at 360 °C and 516 °C) are due to ligand combustion leading to the spinel formation.

The spinel $NiFe_2O_4$,[14-19] obtained at 765 °C, is the main component of the conversion of the complex compound, $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$.

In order to confirm the proposed conversion mechanism, thermal decomposition of the synthesized heteropolynuclear coordination compound was followed by the analysis of the obtained residue by IR and XRD spectroscopy. In Fig. 6 are shown the IR spectra at different temperatures.
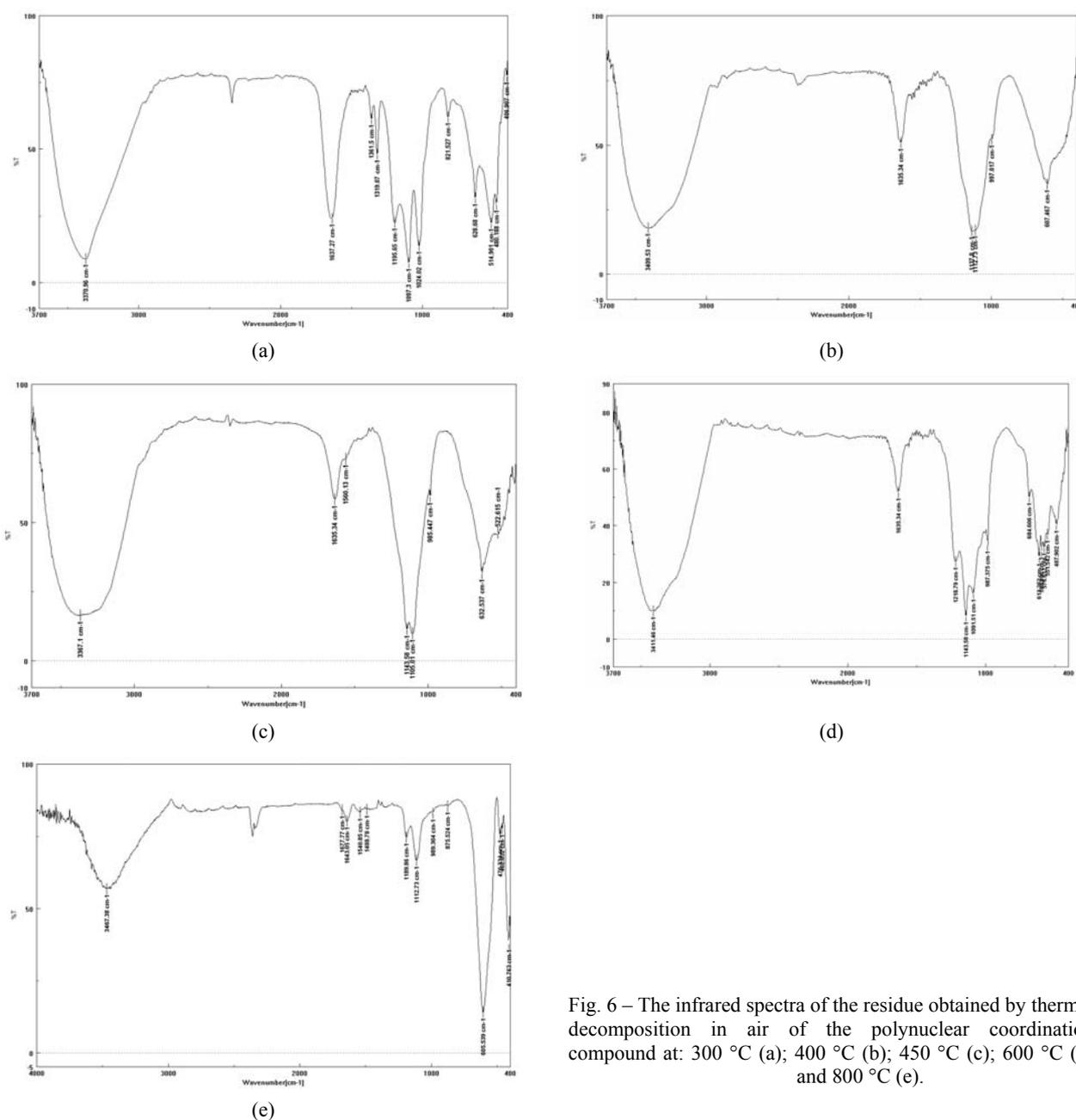

(a)

(b)

(c)

(d)

(e)

Fig. 6 – The infrared spectra of the residue obtained by thermal decomposition in air of the polynuclear coordination compound at: 300 °C (a); 400 °C (b); 450 °C (c); 600 °C (d) and 800 °C (e).
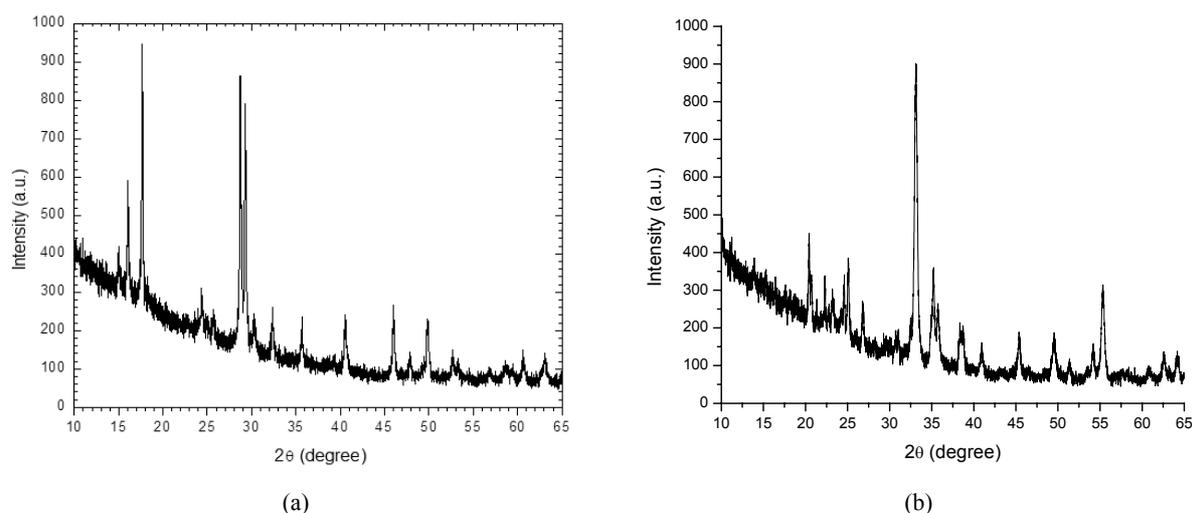
Fig. 7 – The XRD of the residue obtained by thermal conversion in air
of the polynuclear coordination compound at 300 °C (a) and 600 °C (b).

By the analysis of the FTIR spectrum recorded for the residue obtained by thermal decomposition in air of the polynuclear coordination compound at 300 °C (Fig. 6a), one can notice the presence of a band at 1637 cm^{-1}, which is attributed to the asymmetric vibration ν(C=O) of the carboxylate group and the bands with maximum at 1361 and 1319 cm^{-1} is assigned to the symmetric vibration ν_{sym}(O-C=O). The three sharped bands at 1195, 1097 and 1024 cm^{-1} and 993 cm^{-1} are assigned to stretching vibration, ν(C-O) from the hydrated aldehyde (gem-diol, CH(OH)$_2$). The band with maximum at 628 cm^{-1} is attributed to the bending vibration δ(OCO). It was not observed the band at 1731 cm^{-1} corresponding to the vibration ν(C=O) in aldehyde group. The broad band at 3370 cm^{-1} is attributed to the stretching vibration ν(O-H) from coordinated water in the complexes or adsorbed water.

The decrease in intensity of the band at 1637 cm^{-1} (Fig. 6b) was observed and the emergence of the band at 607 cm^{-1} assigned to stretching vibration ν(Fe-O) typical of iron oxides. It can be noticed that the IR spectra recorded after calcinations at 450 °C (Fig. 6c) is similar to the one recorded at 400 °C.

The infrared spectra of the residue obtained by thermal decomposition in air of the polynuclear coordination compound at: 600 °C (Fig. 6d) reveals a significant decrease of the intensity of the band at 1637 cm^{-1} that indicates an important decomposition of complex metal-glyoxylate. Two bands were observed at 613 and 577 cm^{-1}, typical of hematite.[36] The bands at 552 and 596 cm^{-1} are

assigned to stretching vibration of tetrahedrally coordinated Fe^{3+}—O^{2-} bond[37] and tetrahedrally groups Fe^{3+}—O^{2-} in inverse spinel.[38] The band at 488 cm^{-1} is attributed to octahedral metal stretching (Ni $\leftrightarrow$ O).[39]

The IR spectra (Fig. 6e) of the final conversion product obtained exhibits the bands characteristic for the spinel NiFe$_2$O$_4$ being in agreement with the literature data.[33-35,40] There was a significant decrease of the bands at 1643, 1190 and 1112 cm^{-1} that indicates both the decomposition of complex metal-glyoxylate and carbonates compounds close to extinction. Also the most intense band centred at 605 cm^{-1} was assigned to the stretching vibration of the tetrahedral metal oxygen bond in inverse spinel ferrites.[38]

Also, as a further proof for the formation of the desired compound, the X-ray diffraction patterns of the thermal decomposition products at different temperatures (Fig. 7) shows the appearance and increasing in intensity of the characteristic peaks for mixed spinel NiFe$_2$O$_4$, (nickel ferrite), in good agreement with the literature data.[41,42] As can be seen, the samples are relatively well crystallized.

CONCLUSIONS

A new elaborated method of synthesis of the complex compound having glyoxylate anion as ligand is based on the oxidation reaction of 1,2-ethanediol in an alcohol-water system by nickel(II) and iron(III) nitrates and the simultaneous isolation of the complex compound in the reaction system.

The coordination compound synthesized by this new method is a heteropolynuclear combination with the formula $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$; this complex was investigated by elemental analysis, thermal analysis (TG, DTG and DSC), electronic and IR spectroscopy. All the experimental investigations lead to the conclusion that the complex is characterized by a (pseudo)octahedral configuration of the metal ions.

The mixed spinel $NiFe_2O_4$ obtained by thermal decomposition of heteropolynuclear coordination compound is the main component of the conversion of the complex compound, namely $[NiFe_2(C_2H_2O_4)_2(OH)_4(H_2O)_4 \cdot 1.5H_2O]_n$.

In our future work, the results obtained in the investigation of the magnetic properties and the structural characterization of the coordination compound and their thermal decomposition products at different temperatures synthetized by the method described in the present paper will be presented.

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