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Article

COORDINATION COMPOUNDS OBTAINED THROUGH OXIDATION OF DIOLS WITH METAL NITRATES

PART I. SYNTHESIS - STRUCTURE RELATIONSHIP FOR AQUEOUS ETHYLENE GLYCOL - METAL NITRATE SYSTEMS[*]

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ABSTRACT

The oxidation of ethylene glycol with Ni(II) and Fe(III) nitrates was investigated. The Ni(II)/Fe(III) heteropolynuclear coordination compound, which contains the oxidation product of ethylene glycol as ligand, was prepared, and its thermal and spectroscopic properties were established. The synthesis reaction occurs, under strict working conditions, with the oxidation of ethylene glycol to glyoxylic acid, coordinated to nickel and iron cations as glyoxylate dianion, with simultaneous isolation of the corresponding complex compound. After its treatment with R-H cationite and the retention of the metal cations, the ligand was isolated and identified. The resulting acid compound (glyoxylic acid) was characterized by measuring its physical constants, by specific reactions and by

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[*] Dedicated to Prof.Dr. Carol Csunderlik, in memoriam
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using spectroscopic methods. The structural and thermal analysis (TG, DTG and DSC) of the heteropolynuclear coordination compound, which is a precursor of a mixed oxide, are presented. This mixed oxide (spinel) obtained through thermolysis was characterized by FTIR, X-ray spectroscopy and elemental analysis.

Keywords: heteropolynuclear coordination compounds, glyoxylate, metal nitrates, thermal analysis, FTIR, X-ray spectroscopy.

1. INTRODUCTION

The usage of diols and their oxidation products as ligands is a well-established field in the coordination compounds chemistry. Knetsch and Groeneveld, for example, have synthesized and studied a number of coordination compounds with diols as ligands [1]. Also, the oxidation of 1,2-ethanediol, 1,2-propanediol and 1,3-propanediol with metal nitrates have been described [2-10]. The coordination compounds synthesized in this manner contain glyoxylate, oxalate, lactate and 3-hydroxypropionate anions as ligands.

The thermal conversion of homo- and heteropolynuclear complexes with carboxylic acid anions as ligands has been carried out, producing metal oxide systems with irreducible structure and properties, which are required by the modern technologies implemented in diverse industrial areas, such as heterogeneous catalysis, electrocatalysis, electronic engineering, physical supports (carriers, brackets) for information storage and processing, ceramic pigments, and drug industry [11-13]. These complexes decompose at relatively low temperatures with the formation of simple or mixed oxides, and of various volatile products (CO, CO_2, H_2, H_2O).

Depending on the working conditions, the reaction of ethylene glycol (EG) with copper(II) nitrate occurs with the oxidation of the former, with the possibility of forming the glyoxylate [11] or the oxalate anion [2,11b].

The colloidal crystal templating process is used to generate three-dimensionally ordered MFe_2O_4 (in which M = Co, Mn, Ni, Zn) macroporous structures [14]. Gao et al. [15] synthesized the $NiFe_2O_4$ mesoporous spinel with well-defined pore sizes (2.5-16.2 nm) by oxalate decomposition, which is useful for adsorption of acid orange 7. The preparation process for three-dimensional porous materials always uses the template method, which includes two steps: infiltration and template removal [16]. A simple way of producing 3D porous materials is required in the field of adsorbents.

Magnetic separation is considered an effective technique for separating adsorbents from wastewater, and magnetic adsorbents have been widely investigated in recent times [17-19]. At room temperature, the spinel ferrite (MFe_2O_4, where M is a d-block metal) shows a typical ferromagnetic property and is widely used as magnetic carrier in adsorbents to accomplish the magnetic separation [20,21]. For example, the magnetic microsphere containing ferrite is used for the adsorption of organic dye [17], bromide-coated ferrites are used for the preconcentration of phenolic compounds [18], while a magnetic polymer nanosphere adsorbent is used for dye molecules removal [19]. The composite adsorbents generally lose some adsorption capacity or ferromagnetism, but applying the spinel ferrite as adsorbent directly solves this problem, because of the intrinsic good adsorption and magnetic separation properties. Another application of $NiFe_2O_4$ as adsorbent was to treat wastewater [22].

In the last decades the thermal decomposition of heteropolynuclear coordination compounds, used as precursors, was frequently used for the generation of nanoferrites. This process represents a predictable and versatile unconventional method, having the advantage of controlling the quality (both the composition and the microstructure) of the final products' features by selecting suitable ligands.

The determination of the forming conditions for non-stoichiometric oxides of cobalt and nickel led to an original method of producing anodes covered with active electrocatalytic films for evolving oxygen during alkaline solutions electrolysis [23].

The spinel ferrites and the mixed oxides of spinel type in general show great promise in modern electronic technologies, as microwave absorbers, chemical sensors and catalysts, and also in biomedical applications. The ferrites' fine particle nature is essential for all these applications, being generally achieved by soft chemistry synthesis methods, like low temperature range decomposition of suitable precursors [24-32].

This paper, which is the first part of a series of papers, shows the results obtained during investigation of EG's oxidation with iron(III) and nickel(II) nitrates, in weak acidic media (pH around 2.5). The obtained coordination compound was studied regarding its composition and physical-chemical properties. It was shown that it can also be a precursor for nickel ferrite ($NiFe_2O_4$), which can thus be obtained at relatively low temperatures.

2. METHODS

2.1. Chemicals and analysis methods

EG, nickel(II) nitrate hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$ and ferric nitrate nonahydrate $Fe(NO_3)_3 \cdot 9H_2O$, all reagent grade, were employed as starting materials. The subsequent purification step assured the removal of reagent impurities.

The metal content was determined by atomic absorption spectrometry, while carbon and hydrogen were quantified with the help of a Carlo Erba 1108 elemental analyzer.

The TG, DTG and DSC curves (25-1000°C temperature range), corresponding to the decomposition of the heteropolynuclear coordination compound, were registered in a static air atmosphere using a 10 $K \cdot min^{-1}$ heating rate, on a Simultaneous TG-DTA/DSC 409 PC apparatus produced by Netzsch-Gerätebau GmbH (Germany).

The coordination compound was also characterized by chemical analysis, Fourier transform infrared spectroscopy (FTIR) and electronic spectroscopy (using diffuse reflectance technique).

The FTIR spectra (KBr pellets) were registered on a Jasco FT/IR-410 spectrometer in the 400-4000 cm^{-1} domain.

The electronic spectrum was registered through the diffuse reflectance technique with a Spekol 10 spectrophotometer from Carl Zeiss Jena (reference material: MgO).

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

A Bruker D8 Advance diffractometer, equipped with a graphite monochromator, was used to register the XRD patterns on the diffracted beam with Mo K_α radiation ($\lambda = 0.70930$ Å). The X-ray power was set at 40 KV and 30 mA. The powder samples were grounded, if required, to reduce the granulation, after which they were pressed in the specimen holder. The XRD patterns were registered over a range of 2θ angles beginning from 5° to 50°. The crystalline phases were identified using the JCPDS-ICDD files. The diffraction data were acquired and processed using the "Diffrac Plus" software.

2.2. Synthesis of the heteropolynuclear coordination compound

The method developed for the synthesis of the coordination compound is based on the oxidation of EG in a diol-water system by using the nickel(II) and ferric nitrates, with simultaneous isolation of the coordination compound from the reaction system.

An aqueous solution of nickel(II) nitrate, ferric nitrate and EG (1:2:2 molar ratio) was gradually heated in a thermostat until 90°C. When the gas evolution ceased the reaction was considered complete. The obtained powdery solid was purified by refluxing in an acetone-water mixture. The solution was filtered and the obtained beige solid was washed with acetone and exposed to air until constant mass (yield 85% based on EG).

The metal nitrates are completely consumed during the preparation of the coordination compound. This is easily verified by treating a sample with concentrated sulfuric acid, when no brown vapors release was noticed. Also, a negative ring reaction was observed, i.e. no intensely brown colored $[Fe(OH_2)_5NO]SO_4$ was produced in the reaction with $FeSO_4$ and sulfuric acid. The Braccio reaction was negative as well (no NO_3^- or NO_2^- anions were detected using the antipyrine test, which means that the oxidizing action of the nitrate did not lead to its reduction to nitrite).

In order to isolate and identify the ligand present in the coordination compound, its aqueous suspension thus obtained through the reaction of EG with metal nitrates (in the absence of other reagents), was treated with R-H cationite. The resulting acidic solution obtained after the retention of the metal cations was lyophilized and a white crystalline solid, with a 98°C melting point, highly soluble in water but with a poor solubility in alcohols or ethylic ether, was produced.

3. RESULTS AND DISCUSSIONS

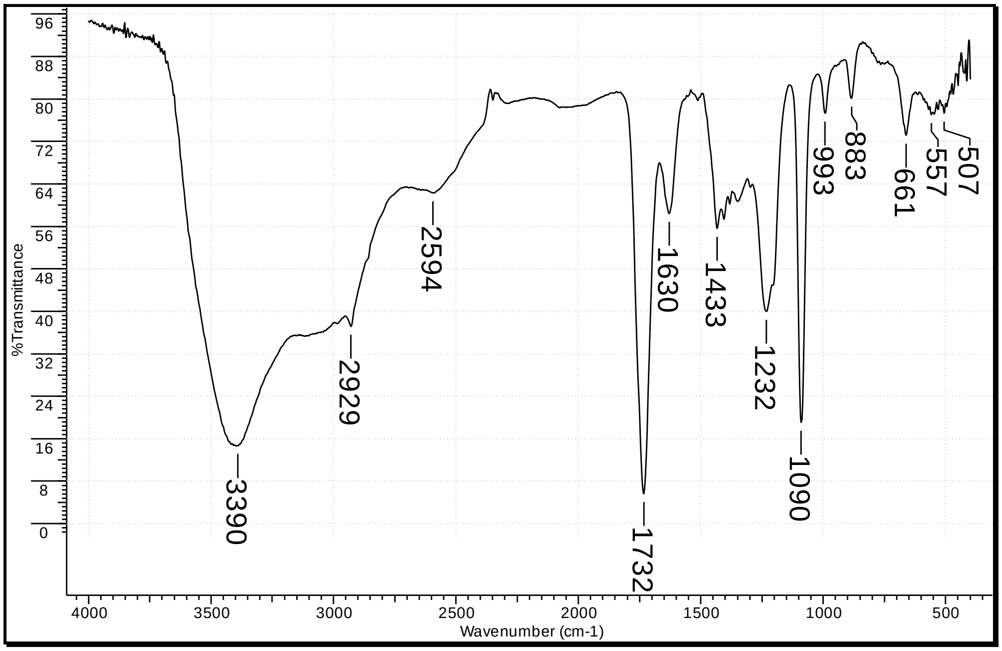
The progress of the reaction between nickel(II) nitrate, ferric nitrate and EG was first investigated by FTIR spectroscopy. As the reaction advances, the intensity of the nitrate bands decreases, proving that this ion is consumed.

Simultaneously, the appearance and the increase in intensity of one band in the range of 1580-1680 cm^{-1} ($\nu_{asym}(COO^-)$) is observed. This band appears for ligands that contain two oxygen atoms as donors, like carboxylic acid anions [33].

After the cations retention on R-H cationite (Purolite C-100 resin), the ligand was identified in its protonated form as glyoxylic acid by using specific reactions and by studying the physical properties of the lyophilization product.

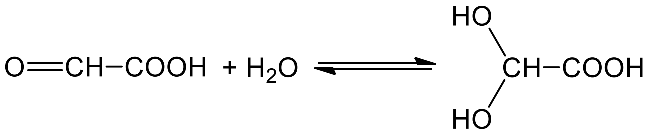
The FTIR spectrum of the glyoxylic acid is given in Figure 1.

Figure 1: FTIR spectrum of glyoxylic acid



In the FTIR spectrum from Figure 1, the characteristic bands for both forms of glyoxylic acid, which coexist in equilibrium in the presence of water (Figure 2), can be spotted.

Figure 2: Glyoxylic acid (left) and hydrated glyoxylic acid (right)



Chemical Formula: $C_2H_2O_3$
Molecular Weight: 74.0

Chemical Formula: $C_2H_4O_4$
Molecular Weight: 92.1

The broad band in the 3200 - 3600 cm^{-1} domain, with the maximum at 3390 cm^{-1}, is assigned to the stretching of the two different types of O-H bonds: the one in the carboxyl group and the alcohol type which comes from the hydrated aldehyde group (structure at right in Figure 2). The 1732 cm^{-1} sharp band is attributed to the ν(C=O) vibration. The 1630 cm^{-1}

band is assigned to the carboxylate asymmetric vibration. The 1381 cm^{-1} band is assigned to the ν_{sym}(OCO) vibration. The 1232 cm^{-1} band could arise from the coupling between a ν(CO) vibration and a δ(OH) vibration. The 1090 cm^{-1} and 993 cm^{-1} bands are attributed to the $CH(OH)_2$ geminal diol (hydrated aldehyde). The 661 cm^{-1} band is attributed to the γ(OCO) bending vibration [33].

The chemical analysis of the lyophilization product was done through specific redox, color and precipitation reactions: with metallic zinc (glycolic acid is obtained), with Ag_2O (metallic silver was obtained), with indole or pyrogallol in concentrated H_2SO_4 (a red or, respectively, blue color occurred), with resorcinol (the lactone of 2,4,2',4'-tetrahydroxydiphenylacetic acid is formed in the presence of sulfuric acid; the oxygen then oxidizes the lactone in alkaline conditions and a blue-violet color appeared); also, precipitates are obtained in the reactions with both 4-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine.

The physical properties (white, crystalline, water-soluble solid, with poor solubility in alcohol or ether, and with a melting point of 98°C) correspond to those found in literature [11,34].

The elemental analysis results (Table 1), as well as the FTIR studies, have indicated that the synthesized coordination compound should have the empirical chemical formula: $NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2\cdot1.5H_2O$.

Table 1: Elemental analysis data for the coordination compound

Empirical formula	%C		%H		%Fe		%Ni	
$NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2\cdot1.5H_2O$	found	calcd.	found	calcd.	found	calcd.	found	calcd.
	9.05	9.28	3.49	3.70	21.62	21.58	10.71	11.34

These results, as well as those previously reported [6-8,11] concerning the oxidation of diols with ferric nitrate, respectively nickel(II) nitrate, suggest that the simultaneous oxidation of EG with these nitrates gives, in the specified working conditions, the glyoxylate anion, coordinated to both Ni(II) and Fe(III) cations.

In consequence, we propose the following mechanism for the reaction between EG and these metal nitrates, in the absence of other reagents:

$$C_2H_3O_4^- + 6e^- + 7H^+ \rightleftharpoons C_2H_4(OH)_2 + 2H_2O \quad (1)$$

$$NO_3^- + 3e^- + 4H^+ \rightarrow NO + 2H_2O \quad (2)$$

$$C_2H_4(OH)_2 + 2NO_3^- + H^+ \rightleftharpoons C_2H_3O_4^- + 2NO + 2H_2O \quad (3)$$

$$[Fe(OH_2)_6]_3^+ + 2H_2O \rightleftharpoons [Fe(OH)_2(OH_2)_4]^+ + 2H_3O^+ \quad (4)$$

$$[Ni(OH_2)_6]^{2+} \rightleftharpoons [Ni(OH_2)_6]^{2+} \text{ (hydrolysis does not occur in the specified conditions)}$$

By summing Eqs. (3) and (4) and considering the interaction between the ligand and the metal cations, one obtains:

$$2C_2H_4(OH)_2 + (4NO_3^- + [Ni(OH_2)_6]^{2+} + 2[Fe(OH)_2(OH_2)_4]^+) + xH_2O \longrightarrow NiFe_2(C_2H_2O_4)_2(OH)_4 \cdot xH_2O + 18H_2O + 4NO \quad (5)$$

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

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad (6)$$

It can be noticed that the presence of protons, involved in equilibrium 3, is necessary to potentiate the oxidation activity of NO_3^- ions.

The proposed formula for the complex compound and the information regarding its structure are going to be further confirmed by the following results.

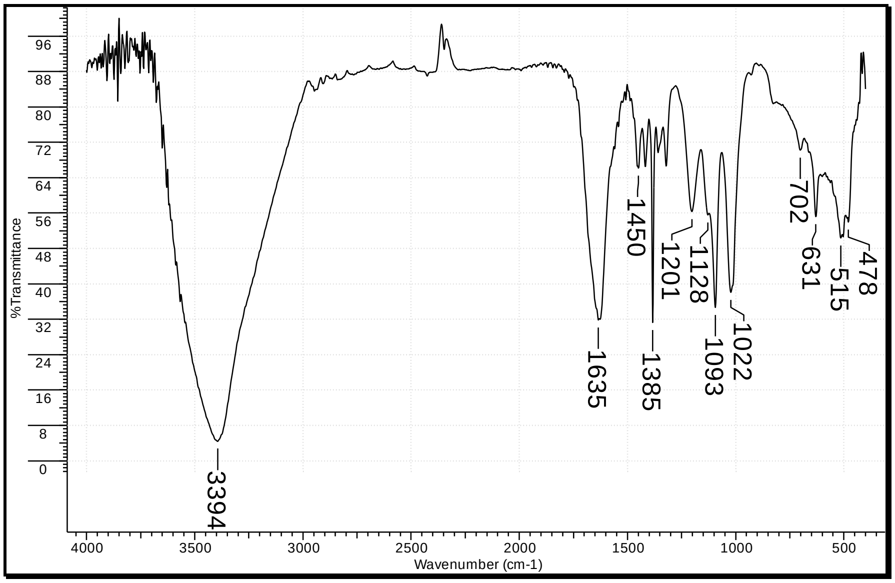
The diffuse reflectance spectrum of the coordination compound illustrates the characteristic bands for the hexacoordinated nickel(II) and ferric ions in a (pseudo)octahedral environment.

The absorption band at 26,316 cm^{-1} (with $\lambda = 380$ nm) can be attributed to the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (ν_3) transition, which is characteristic to the nickel(II) ion in a high spin octahedral configuration. The band at 13,158 cm^{-1} (with $\lambda = 760$ nm) can be assigned to the $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (ν_2) transition. The obtained results agree with the literature [6-10].

Accordingly, the nickel(II) ion is in fundamental state $t_{2g}^6 e_g^2$, high spin, the ligands being of low field and of similar strength. At 920 nm, the reflectance spectrum reveals the characteristic band of iron(III) in a high spin octahedral configuration and also the forbidden spin transition bands in the same configuration for iron(III) ($t_{2g}^3 e_g^2$) ions (ν3) [11].

In order to obtain more data regarding the structure of the synthesized complex compound and the ligand coordination, the FTIR spectrum was recorded (Figure 3).

Figure 3: FTIR spectrum of the heteropolynuclear coordination compound



The characteristic FTIR bands (in cm^{-1}) for the complex and the corresponding assignments are shown in Table 2.

Table 2: Characteristic FTIR absorption bands for $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]n\cdot1.5nH_2O$

Wavenumber [cm^{-1}]	Assignment
3394 vs,b	ν(OH), hydrogen bonding
1635 s	ν_{asym}(C=O), δ(H_2O*)
1560 m,sh	lattice water
1385 s	ν_{sym}(CO)+ν(CC)
1321 m	ν_{sym}(CO)+δ(O-C=O)
1093 s	ν(CO)
827 w	δ(O-C=O)+ν(FeO,NiO)
702 w	ρ(H_2O*)
631 m	lattice water
563 m	ρ(H_2O*)
515 m	ν(FeO,NiO)+ν(CC)

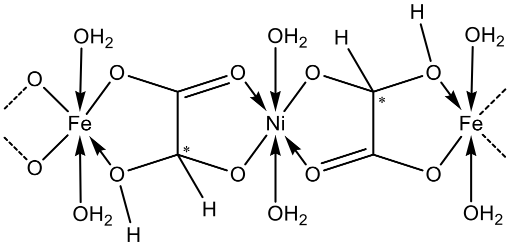
s-strong; b-broad; m-medium; w-weak; sh-shoulder; *coordinated water

The broad band from the 3200-3600 cm^{-1} range, with the maximum at 3394 cm^{-1}, is assigned to the hydrogen bonds formed between the water molecules and the hydroxyl groups [9-11]. The 1635 cm^{-1} intense band is assigned to the carboxylate asymmetric vibration, the value also showing that the carboxylate group resonance is maintained during complex formation and that the metal-carboxylate bond has a predominantly ionic character [33].

The band with maximum at 1385 cm^{-1} is attributed to the ν_{sym}(CO) vibration. Because the ν_{asym}-ν_{sym} value is higher than 170 cm^{-1}, the metal-carboxylate bond seems to be mainly ionic, and the carboxylate group must act as a bidentate ligand [33]. Moreover, the existence of the two bands for ν_{sym}(CO) can be explained through the octahedral deformation. The 1321 cm^{-1} band confirms that the carboxylate group is behaving as a bidentate ligand [23,33]. The band at 1093 cm^{-1} is assigned to the C-OH vibration. The 1022 cm^{-1} strong intensity band is assigned to the hydroxyl bridge group vibration, while the band at 827 cm^{-1} is assigned to the δ(OCO) vibration.

The complex combination is insoluble in water, ethanol or ether, although concentrated HCl or H_2SO_4 are able to destroy its structure. These properties, as well as the previous discussed data, confirm a polynuclear structure corresponding to the formula: $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]n\cdot1.5nH_2O$.

In accordance with the empirical formula, the (pseudo)octahedral stereochemistry of Ni(II) and Fe(III) and the structure of the bridging glyoxylate dianion, the heteropolynuclear coordination compound must have the following structure:



The thermal analysis methods were invoked to establish the conditions in which the $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]n\cdot 1.5nH_2O$ coordination compound is decomposed to $NiFe_2O_4$. The recorded TG, DTG and DSC curves suggest six steps:

I (*20-160°C*): $NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2\cdot 1.5H_2O_{(s)} \xrightarrow{-1.5H_2O} NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2$

II, **III** (*160-310°C*): $NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2 \xrightarrow{-6H_2O} NiFe_2(C_2H_2O_4)_2O_2$

IV (*310-450°C*): $NiFe_2(C_2H_2O_4)_2O_2 \xrightarrow{-CO_2;-H_2O} NiFe_2(C_2H_2O_4)CO_3$

V (*450-700°C*): $NiFe_2(C_2H_2O_4)CO_3 \xrightarrow{-H_2;-CO} NiFe_2(CO_3)_2$

VI (*700-765°C*): $NiFe_2(CO_3)_2 \xrightarrow{-2CO} NiFe_2O_{4(s)}$

In the 20-310°C temperature range, $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]_n\cdot 1.5nH_2O$ displays two dehydration DSC peaks, one endothermic (broad) and one exothermic (maximum at 263°C), for the two stages of water loss. The TG mass losses correspond to $1.5H_2O$ (process I) and, respectively, $6H_2O$ (process II-III).

The exothermic effects found in steps IV and V (maxima at 360°C and 516°C) are due to ligand combustion which leads to the spinel formation.

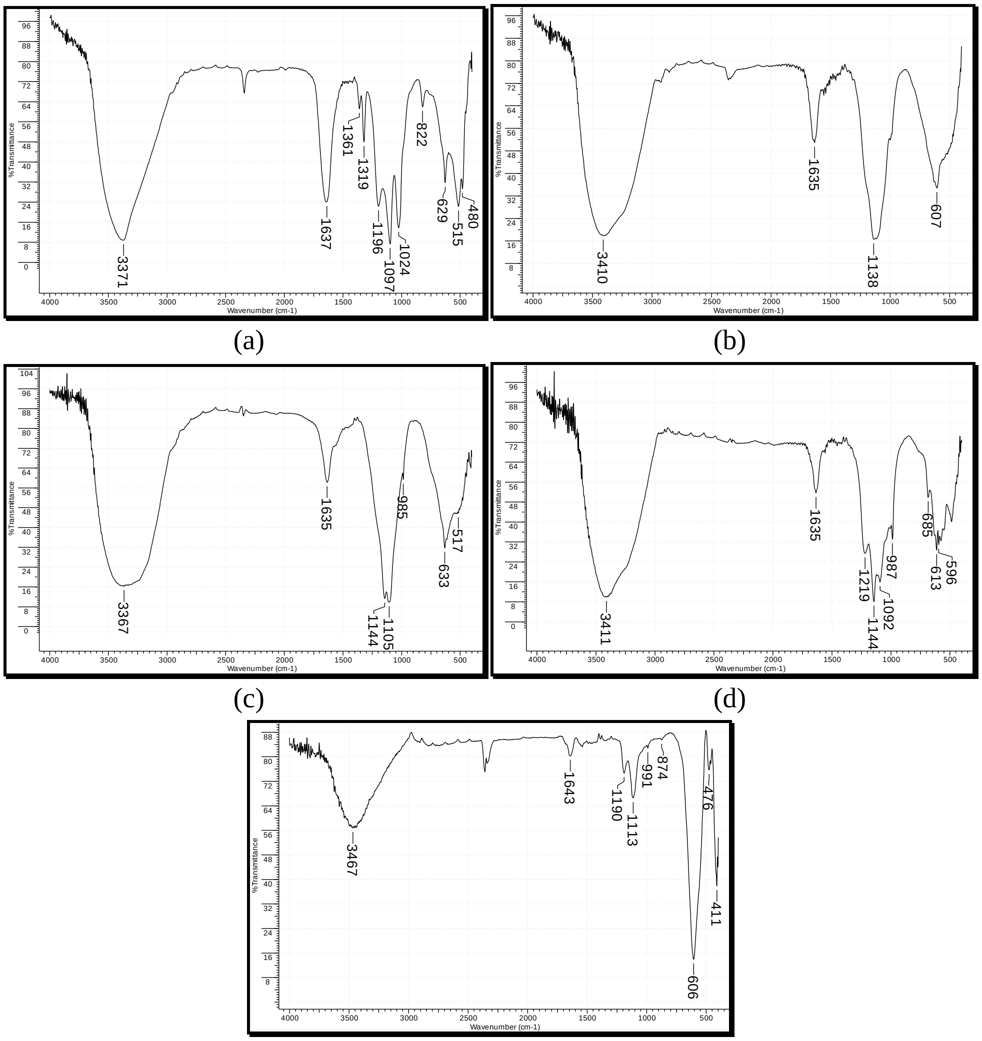
The spinel $NiFe_2O_4$ [14-19], obtained at the temperature of 765°C, is the main decomposition component.

In order to support the proposed conversion mechanism, the thermal decomposition of the synthesized heteropolynuclear coordination compound was followed by the analysis of the residues by FTIR and XRD spectroscopy. In Figure 4, the FTIR spectra are shown for different decomposition temperatures.

By analyzing the FTIR spectrum recorded for the residue obtained after decomposition of the coordination compound in air at 300°C (Figure 4a), the band at 1637 cm^{-1} can be noticed. This band is assigned to the ν(C=O) asymmetric vibration in the carboxylate, while the bands with maxima at 1361 and 1319 cm^{-1} are attributed to the ν_{sym}(O–C=O) vibration. The 1196, 1097 and 1024 cm^{-1} sharp bands are attributed to the ν(C–O) vibration from the former hydrated aldehyde. The band with maximum at 629 cm^{-1} is assigned to the δ(OCO) vibration. The 1732 cm^{-1} band, which corresponds to the ν(C=O) vibration from the aldehyde group, was not detected. The broad band at 3371 cm^{-1} is assigned to the ν(O–H) stretching vibration.

The decrease in intensity of the band at 1635 cm^{-1} (Figure 4b) was observed along with the emergence of the 607 cm^{-1} band, assigned to the ν(Fe–O) vibration, typical to iron oxides. The FTIR spectra recorded after calcination at 450°C (Figure 4c) is very similar to the one registered at 400°C.

Figure 4: FTIR spectra of residues obtained after decomposition of the coordination compound in air at: **(a)** 300°C; **(b)** 400°C; **(c)** 450°C; **(d)** 600°C and **(e)** 800°C



(a) (b)

(c) (d)

(e)

The FTIR spectrum of the residue obtained at 600°C (Figure 4d) reveals a significant decrease in the intensity of the band at 1635 cm^{-1}, indicating an advanced decomposition of the metal-glyoxylate complex. The bands at 613 and 577 cm^{-1} are typical to hematite [35]. The bands at 553 and 596 cm^{-1} are assigned to the stretching vibration of tetrahedrally coordinated Fe^{3+}–O^{2-} bond [36] and tetrahedrally Fe^{3+}–O^{2-} groups from the inverse spinel [37]. The 488 cm^{-1} band is assigned to the Ni–O octahedral metal stretching [38].

By analyzing the FTIR spectrum for the final conversion product (Figure 4e), the characteristic bands for the $NiFe_2O_4$ spinel, as found in the literature data [33,34,39], are revealed. The significant decrease of the 1643, 1190 and 1113 cm^{-1} bands proves that the decomposition of the complex compound and the carbonates led to their almost complete disappearance. Also, the most intense band centered at 606 cm^{-1} was attributes to the tetrahedral metal-oxygen bond stretching vibration from the inverse spinel ferrites [37].

As a final argument for the formation of the desired compound, the XRD patterns of the decomposition products, taken at different temperatures, show the appearance and increase in intensity of the characteristic peaks for the $NiFe_2O_4$ spinel, as found in the literature [40,41]. The studied samples seem to be relatively well crystallized.

4. CONCLUSIONS

An original method for synthesizing the coordination compound having the glyoxylate dianion as ligand, based on the oxidation reaction of EG in a diol-water system by nickel(II) and ferric nitrates, with the simultaneous isolation of the coordination compound, was developed.

The complex compound synthesized by this new synthetic method is a heteropolynuclear combination with the formula $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]_n \cdot 1.5nH_2O$. It was investigated by elemental and thermal analysis, electronic and FTIR spectroscopy. All the experimental studies lead to the conclusion that the coordination compound is characterized by a (pseudo)octahedral configuration of the cations.

The $NiFe_2O_4$ spinel, obtained by thermal conversion of the heteropolynuclear coordination compound, is the main degradation product.

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