



# Co(II)–Ni(II) heteropolynuclear coordination compound obtained through the reaction of 1,2-propanediol with metallic nitrates as precursor for mixed oxide of spinel type NiCo<sub>2</sub>O<sub>4</sub>

M. Niculescu<sup>a,\*</sup>, M. Birzescu<sup>a</sup>, Raluca Dumitru<sup>a</sup>, E. Şişu<sup>b,c</sup>, P. Budrugaec<sup>d</sup>

<sup>a</sup> University “Politehnica” of Timisoara, Faculty for Industrial Chemistry and Environmental Engineering, Piata Victoriei 2, 300223 Timisoara, Romania

<sup>b</sup> Chemistry Institute of Romanian Academy, Bdul Mihai Viteazul 24, 300223 Timisoara, Romania

<sup>c</sup> University of Medicine and Pharmacy “Victor Babes”, Pta Eftimie Murgu No. 2, 300041 Timisoara, Romania

<sup>d</sup> National Institute for Research and Development in Electrical Engineering ICPE, CA, Splaiul Unirii 313, 030138 Bucharest, Romania

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## ABSTRACT

In this paper the authors present the experimental results of the thermal analysis of heteropolynuclear coordination compound  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$ , where L is lactate anion, obtained by a new method, through the reaction of 1,2-propanediol with  $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (M: Co, Ni).

The reaction between 1,2-propanediol and  $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (M: Co, Ni) occurs with the oxidation of 1,2-propanediol to the lactate anion (L), coordinated to M(II).

The thermal properties of the synthesized polynuclear coordination compound,  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$ , have been investigated by TG, DTG and DTA.

The mixed oxide of spinel type, NiCo<sub>2</sub>O<sub>4</sub>, impurified with NiO, obtained by thermal decomposition of heteropolynuclear coordination compound was characterized by IR spectroscopy, X-ray powder diffraction (XRD) and elemental analysis.

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## 1. Introduction

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

In our previous papers [2–11] 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, lactate anion, malonate anion and 3-hydroxypropionate anion as ligands.

The thermal conversion of homo- and hetero-polynuclear complexes with anions of carboxylic acids as ligands has been carried out to oxide systems with irreducible 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) [12–22].

These compounds decompose at relatively low temperatures, forming simple or mixed oxides and volatile products (CO, CO<sub>2</sub>, H<sub>2</sub>O).

The reaction between 1,2-ethanediol and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  occurs with the oxidation of 1,2-ethanediol to glyoxylate anion [2,11] or oxalate anion, depending on the working conditions.

The determination of the forming conditions of nonstoichiometric 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].

Several studies about the properties of nickel cobaltite, NiCo<sub>2</sub>O<sub>4</sub>, and its applicability in electrochemistry have been performed by different authors [24–32].

For many years, the spinel NiCo<sub>2</sub>O<sub>4</sub> has been used as an electrocatalyst in electrochemical systems. It also possesses high electrical conductivity and low thermal stability for a compound of this structure [24–29]. A number of film deposition procedures have been developed for depositing the spinel phase of these films. These procedures comprise, but are not limited to, solution deposition processing, reactive sputter deposition, and pulsed laser ablation [28].

Also, the nickel cobaltite, NiCo<sub>2</sub>O<sub>4</sub>, has been synthesized by the thermal decomposition of carbonates, sol–gel methods, the decomposition of hydroxides, electrospinning technique [29–32]. Several papers present the structure and the properties of nickel cobaltite, NiCo<sub>2</sub>O<sub>4</sub> [24,27–32]. Films deposited on sapphire substrates exhibit a refractive index of about 1.7 and are relatively transparent in the wavelength region from 0.6 to 10.0 μm. They are also magnetic.

\* Corresponding author. Tel.: +40 256 404186; fax: +40 256 403060.

E-mail addresses: [mniculescu@yahoo.com](mailto:mniculescu@yahoo.com), [mircea.niculescu@chim.upt.ro](mailto:mircea.niculescu@chim.upt.ro) (M. Niculescu).

The electrical and spectroscopic properties of the oxides have been studied as a function of  $x = \text{Co}/(\text{Co} + \text{Ni})$  ratio [28].

This paper presents the results obtained at the investigation of 1,2-propanediol oxidation with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in a weak acid medium ( $\text{pH} \sim 3$ ). 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 cobaltite,  $\text{NiCo}_2\text{O}_4$ , which is obtained at relatively low temperatures.

## 2. Experimental procedures

### 2.1. Chemicals and methods

For the synthesis of the coordination compound,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  “Reactivul”, Bucharest, with minimal purity of 99%, 1,2-propanediol, “BDH Chemical Ltd. Poole “England with purity of 97 % and nitric acid solution 1 M ( $F = 1.000 \pm 0.002$ ) were used. 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.

TG, DTG and DTA curves (in the range 25–600 °C) corresponding to the decomposition of the coordination compound were recorded on a Simultaneous TGA/SDTA 851/LF/1100 Apparatus produced by METTLER, under an air flow of  $50 \text{ mL min}^{-1}$  at a heating rate of  $10 \text{ K min}^{-1}$ .

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 FT-IR spectrophotometer, in the range 400–4000  $\text{cm}^{-1}$ .

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 cobaltite,  $\text{NiCo}_2\text{O}_4$ , 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 ( $\lambda = 0.70930 \text{ \AA}$ ). 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  $2\theta$  angles from  $5^\circ$  to  $50^\circ$  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.

### 2.2. Synthesis of the coordination compound

The elaborated method of the synthesis of the complex compound is based on the oxidation reaction of 1,2-propanediol in an alcohol–water system by M(II) nitrates (M(II): Co(II), Ni(II)) and nitric acid and the simultaneous isolation of the complex compound from the reaction system.

A solution of water + diol +  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  +  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  + nitric acid in the molar ratio:  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:1,2\text{-propanediol}:\text{HNO}_3 = 1:2:4.5:0.001$  was prepared. This mixture was heated in a thermostat, gradually up to  $90^\circ\text{C}$ . The reaction was considered completed when no more gas evolution was observed.

**Table 1**  
Composition and elemental analysis data

Compound (composition formula)	$\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3$
Co(II)%	
Calculation	21.48
Experiment	21.92
Ni(II)%	
Calculation	10.70
Experiment	10.85
C%	
Calculation	19.69
Experiment	19.38
H%	
Calculation	4.37
Experiment	4.20

The solid 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 75% (based on the 1,2-propanediol).

## 3. Results and discussion

The evolution of the reaction between 1,2-propanediol,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was investigated by IR spectroscopy. As the reaction advances the bands due to the nitrate ion decreases in intensity, proving that the nitrate ion is consumed in the reaction [33].

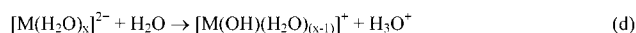
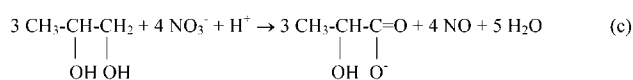
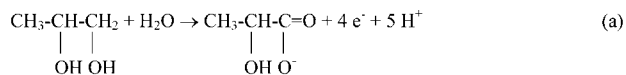
At the same time, the appearance and the increase of the band intensity in the range of 1580–1680  $\text{cm}^{-1}$  ( $\nu_{\text{asym}} \text{COO}^-$ ) is observed, which is specific to complex ligands that contain two oxygen atoms as donors such as the carboxylic anions of the acids [34].

In order to separate and identify the ligand, the complex has been treated with R–H cationite (Purolite C-100). After the retention of the metal cations, the resulted lactic acid has been identified by specific reactions (haloform reaction, reaction with  $\text{FeCl}_3$  solution, reaction with  $\text{KMnO}_4$  solution). The physical properties (syrupy liquid, strongly acid, highly soluble in water, ethylic alcohol, ethylic ether) are in good agreement with those from the literature [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:  $\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3$ , where L is lactate anion.

These results, as well as those previously reported [6–8] concerning the oxidation of 1,2-propanediol with Co(II) nitrate respectively Ni(II) nitrate, suggest that the oxidation of the 1,2-propanediol with  $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (M: Co, Ni) occurs, in some working conditions, to lactate anion, coordinated to M(II).

Consequently, we suggest the following mechanism for the reaction between 1,2-propanediol and  $\text{M}(\text{NO}_3)_2$  (M = Co, Ni):



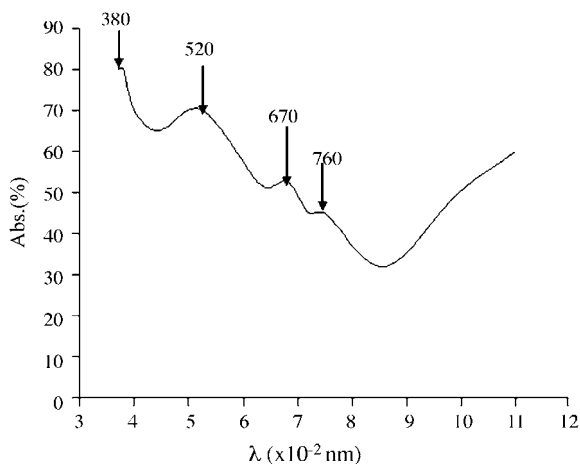
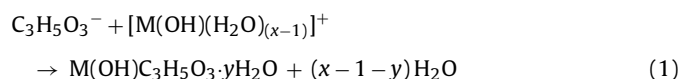


Fig. 1. Diffuse reflectance spectrum of Co(II)-Ni(II)-hydroxo-lactate.



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 are going to be confirmed by the results which will be presented in the following.

### 3.1. Diffuse reflectance spectrum of Co(II)-Ni(II)-hydroxo-lactate

The diffuse reflectance spectrum of the coordination compound shows the presence of the characteristic bands of the hexacoordinated Co(II) and Ni(II) ions in a (pseudo)octahedral environment (Fig. 1).

Table 2 shows the wave numbers, which correspond to the diffuse reflectance spectral bands with tentative assignments.

The spectrum exhibit an absorption band at 19,231  $\text{cm}^{-1}$  ( $\lambda = 520 \text{ nm}$ ) which may be assigned to the  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  ( $\nu_3$ ) transition, characteristic to the Co(II) ion in a high spin octahedral configuration. The band at 14,925  $\text{cm}^{-1}$  ( $\lambda = 670 \text{ nm}$ ) may be assigned to the  ${}^4\text{A}_{2g} \leftarrow {}^4\text{T}_{1g}(\text{F})$  ( $\nu_2$ ) transition. The absorption band at 26,316  $\text{cm}^{-1}$  ( $\lambda = 380 \text{ nm}$ ) may be assigned to the  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$  ( $\nu_3$ ) transition, characteristic to the Ni(II) ion in a high spin octahedral configuration while the band at 13,158  $\text{cm}^{-1}$  ( $\lambda = 760 \text{ nm}$ ) may be assigned to the  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$  ( $\nu_2$ ) transition. The results are in good agreement with those from the literature [36].

Accordingly, the Co(II) ion exists in the fundamental state  $t_{2g}^5 e_g^2$ , high spin, respectively Ni(II) ion in the fundamental state  $t_{2g}^6 e_g^2$ , high spin, the three ligands OH, L,  $\text{H}_2\text{O}$  being of low field and of similar strength.

Table 2

Diffuse reflectance spectral data of the investigated compound

Compound (composition formula)	Co(II)		Ni(II)	
	Wavenumber ( $\text{cm}^{-1}$ )	Transition identification	Wavenumber ( $\text{cm}^{-1}$ )	Transition identification
[Co <sub>2</sub> NiL <sub>3</sub> (OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sub>n</sub>	19,231	${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$	26,316	${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$
	14,925	${}^4\text{A}_{2g} \leftarrow {}^4\text{T}_{1g}(\text{F})$	13,158	${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$

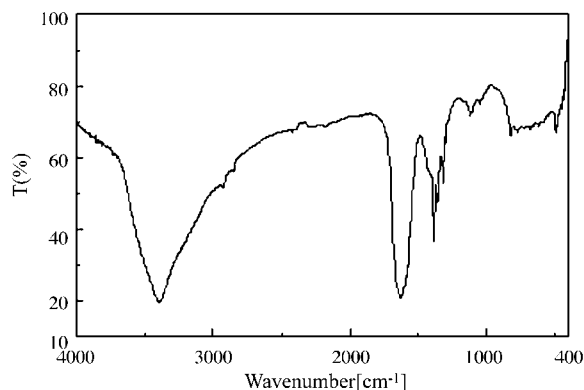


Fig. 2. IR vibrational spectrum of the heteropolynuclear coordination compound [Co<sub>2</sub>NiL<sub>3</sub>(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>.

Table 3

Characteristic absorption bands in IR for Co(II)-Ni(II)-hydroxo-lactate and the corresponding assignments

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
3397 s, b	$\nu(\text{OH}), \nu(\text{H}_2\text{O})$
1627 vs	$\nu_{\text{asym}}(\text{COO}^-) + \delta_{\text{sym}}(\text{HOH})$
1384 vs	
1360 s	$\nu_{\text{sym}}(\text{COO}^-)$
1317 m	$\nu_{\text{sym}}(\text{CO}) + \delta(\text{OCO})$
1127 w	$\nu(\text{C-OH})$
1049 w	$\nu(\text{OH bridge})$
824 w	$\delta(\text{OCO})$
490 w	$\nu(\text{M-O})$

s: high intensity ( $\nu$ : very); b: broad; m: medium; w: weak.

### 3.2. IR vibrational spectrum of Co(II)-Ni(II)-hydroxo-lactate

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  $\text{cm}^{-1}$  (Fig. 2).

Table 3 shows the characteristic bands in IR ( $\text{cm}^{-1}$ ) for solid and brown coloured complex and the corresponding assignments.

The broad band in the range 3200–3600  $\text{cm}^{-1}$  with a maximum at 3397  $\text{cm}^{-1}$  is attributed to the formation of the hydrogen bonds between water molecules and the alcoholic hydroxyl [17,37].

The intense band at 1627  $\text{cm}^{-1}$  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]. At same time the band may correspond also to the deformation vibration of  $\text{H}_2\text{O}$ .

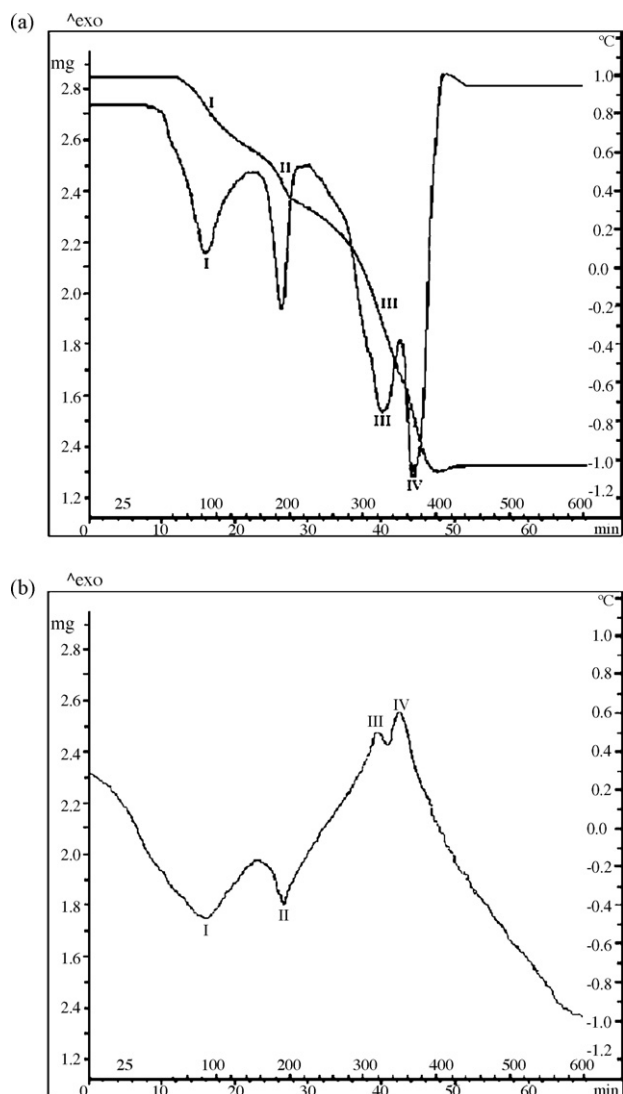
The band with maximum at 1384  $\text{cm}^{-1}$  is attributed to the symmetric vibration  $\nu_{\text{sym}}(\text{COO}^-)$ . As the difference between  $\nu_{\text{asym}} - \nu_{\text{sym}}$  is higher than 170  $\text{cm}^{-1}$  one may say that the metal–carboxylate bond is really preponderantly ionic, and the carboxylate group acts as a bidentate ligand [34,38]. Also, the existence of the two bands for  $\nu_{\text{sym}}(\text{COO}^-)$  can be explained through the octahedral deformation. The band at 1317  $\text{cm}^{-1}$  confirms that the carboxylate group is acting as a bidentate ligand [34].

In the vibrational spectrum of lactic acid [36] the band at  $1127\text{ cm}^{-1}$  is attributed to the C–OH vibration. The fact that in the spectrum of this complex this bands appears at the same value and that it is not shifting towards lower number permits to presume that OH alcoholic group does not take part in the coordination process.

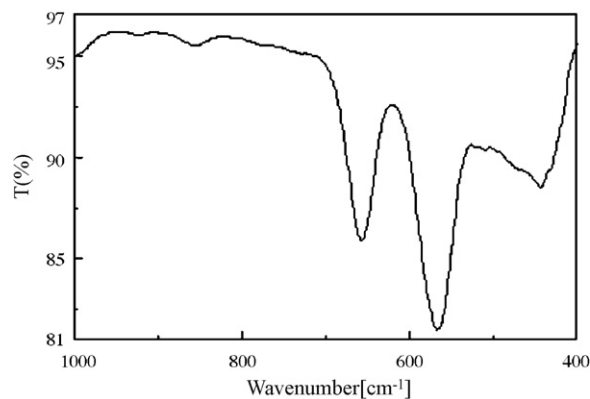
The band of mean intensity at  $1049\text{ cm}^{-1}$  is attributed to the vibration of the OH bridge group [39]. The band at  $824\text{ cm}^{-1}$  is attributed to the vibration  $\delta(\text{OCO})$  [34,38].

In accordance with Nagase et al. [40], the  $490\text{ cm}^{-1}$  band, obtained for the investigated complex can be attributed to the vibration  $\nu(\text{M–O})$ , the atom O belonging to the  $\text{COO}^-$  group from the lactate anion.

The obtained compound is insoluble in water, ethanol and ether. It can be destroyed only by concentrated solutions of HCl or  $\text{H}_2\text{SO}_4$ . These statements as well as the above mentioned data suggest a polynuclear structure which corresponds to the following formula:



**Fig. 3.** Thermal analytical curves for the coordination compound decomposition in air atmosphere at the heating rate of  $10\text{ K min}^{-1}$ : (a) TG and DTG; (b) DTA.



**Fig. 4.** IR vibrational spectrum of the conversion product obtained at  $600\text{ °C}$ .

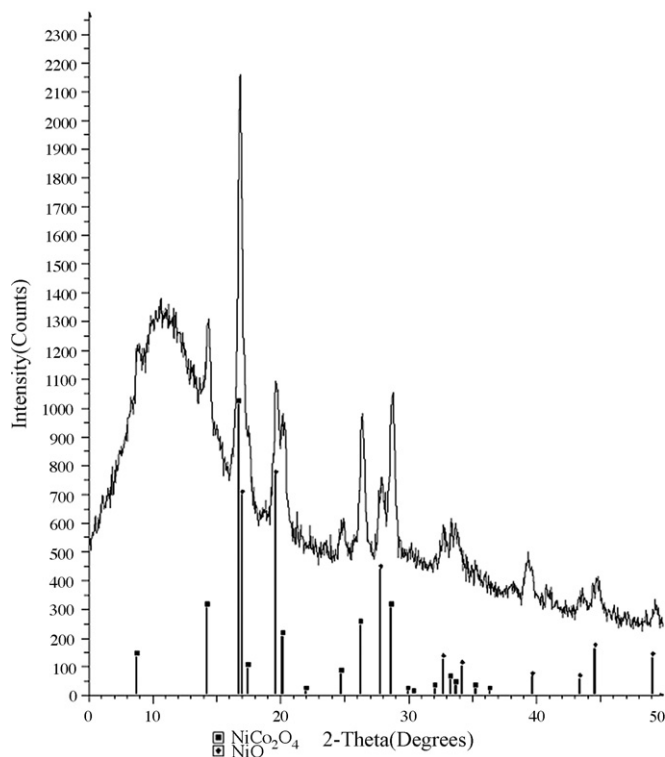
### 3.3. Thermal conversion of *Co(II)*–*Ni(II)*–hydroxo–lactate

In order to establish the conditions in which the coordination compound  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$  is decomposed to  $\text{NiCo}_2\text{O}_4$ , the thermal analysis methods (TG, DTG, DTA) were used [41].

The obtained TG, DTG and DTA curves, shown in Fig. 3, suggest four steps which occur at the progressive heating of the coordination compound.

In the temperature range  $25\text{--}240\text{ °C}$ ,  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$  display two endothermic dehydration DTA peaks (broad), for the two losses of water (processes I and II). The TG weight losses correspond to  $3\text{H}_2\text{O}$  (process I) respectively  $2\text{H}_2\text{O}$  (process II).

The strong exothermic effect that characterizes the III and IV steps (maximals at  $325$  and  $365\text{ °C}$ ) is due to ligand combustion respectively to the oxidation of *Co(II)* to *Co(III)* by oxygen leading to the spinel formation [31,42].



**Fig. 5.** The XRD of the solid product obtained by thermal conversion in air of the polynuclear coordination compound  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$ .

The spinel  $\text{NiCo}_2\text{O}_4$ , obtained at  $600^\circ\text{C}$ , is the main component of the conversion of the complex compound,  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$ .

The composition of a residual sample determined by elemental analysis (Ni: 24.49 %; Co: 48.89 %; O: 26.60 %) corresponds to this one.

The residue was identified by IR and XRD.

The IR spectrum (Fig. 4) of the conversion product obtained at  $600^\circ\text{C}$  exhibits the bands characteristic for the spinel  $\text{NiCo}_2\text{O}_4$  ( $\nu_1[\text{Ni}^{\text{II}}\text{O}_4] = 658\text{ cm}^{-1}$  and  $\nu_2[\text{Co}^{\text{III}}\text{O}_6] = 565\text{ cm}^{-1}$ ) being in agreement with the literature data [31,43–45].

The low intensity band at  $450\text{ cm}^{-1}$ , characteristic for NiO, revealed that the product of thermal decomposition of the coordination compound is a nonstoichiometric metal oxide [44,45].

The X-ray diffraction patterns (Fig. 5) show the presence of the characteristic peaks for  $\text{NiCo}_2\text{O}_4$  (nickel cobaltite), in accordance with JCPDS 73-1702.

As can be seen, the sample is relatively well crystallized [29,31].

Peaks of NiO were found in the XRD pattern (JCPDS 47-1049), indicating that  $\text{NiCo}_2\text{O}_4$  obtained via this method consists of impurified phase [32].

#### 4. Conclusions

A new elaborated method of synthesis of the complex compound having lactate anion as ligand is based on the oxidation reaction of 1,2-propanediol in an alcohol–water system by nickel nitrate, cobalt nitrate and nitric acid 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  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$ ; this complex was investigated by elemental analysis, thermal analysis (TG, DTG and DTA), 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(II) ions.

The spinel  $\text{NiCo}_2\text{O}_4$  obtained by thermal decomposition of heteropolynuclear coordination compound,  $[\text{Co}_2\text{NiL}_3(\text{OH})_3(\text{H}_2\text{O})_3]_n$  is a nonstoichiometric oxide impurified with NiO.

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