



*Dedicated to the memory of
Professor Eugen Segal (1933-2013)*

SYNTHESIS AND THERMAL ANALYSIS OF THE NICKEL(II) OXALATE OBTAINED THROUGH THE REACTION OF ETHYLENE GLYCOL WITH $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

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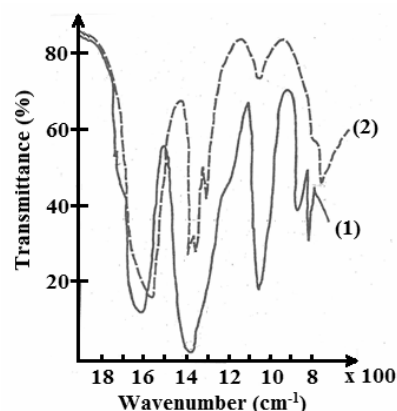
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Received April 29, 2014

This paper presents the experimental results of the synthesis and thermal analysis of the nickel(II) oxalate, a homopolynuclear coordination compound obtained through the RedOx reaction which took place between ethylene glycol and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

The reaction between ethylene glycol and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ occurs with the oxidation of ethylene glycol to the oxalate anion, $\text{C}_2\text{O}_4^{2-}$ (L) under the chosen experimental conditions. The synthesized homopolynuclear coordination compound, having as ligand the oxalate anion, was characterized by chemical analysis, magnetic measurements, electronic and vibrational spectra and thermal analysis. The thermal behaviour of the polynuclear coordination compound has been investigated by TG, DTG and DTA. Nickel oxide obtained by thermal decomposition of this compound was characterized by IR spectroscopy and X-ray diffraction (XRD).



INTRODUCTION

Oxidic systems can be obtained by various methods and are nowadays required in increasing quantities by the development of modern technology in various fields, from ceramic pigments, catalysis and electrocatalysis, electronics, physical supports-carriers, in device intended for the processing of

information and up to pharmaceutical industry. One of the synthetic pathways, with a rapid development is represented by the thermal conversion of homo- and heteropolynuclear metal complexes with anions of carboxylic acids as ligands.¹⁻¹⁴

In our previous studies and reported as papers¹⁵⁻²⁴ we have presented the results of the oxidation reactions between several diols such as ethylene

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glycol, 1,2-propanediol and 1,3-propanediol, respectively, and certain metallic nitrates. All the coordination compounds obtained by this synthetic pathway contain as ligands anions such as glyoxylate, lactate, oxalate or 3-hydroxypropionate. These coordination compounds, which contain relatively simplistic organic ligands have the main advantage over other coordinative metal complexes that they undergo thermal induced degradation to simple or mixed metallic oxides at relatively low temperatures, with the releasing of gaseous species such as carbon oxides or hydrocarbons (CO, CO₂, CH₄ etc.) and water (H₂O). These studies proved that via this new pathway it is possible to synthesize some coordination compounds with ligands consisting in carboxylate or hydroxycarboxilate anions. It was proved that by thermal treatment of these species at considerably low temperatures they were degraded to powders consisting in metals, alloys and/or oxidic structures, depending both by the structure of coordination compound or by the applied thermal treatment.

Literature^{15,20,24} mentions that the reaction between ethylene glycol and Ni(NO₃)₂·6H₂O occurs with the oxidation of ethylene glycol to glyoxylate anion or oxalate anion, depending the experimental conditions. Even if numerous investigations were previously carried in order to determine the thermal decomposition and as well the physico-chemical characterization of nickel oxalate, this paper is focused in both the synthesis of the a coordinative compound on Ni(II) with a well-known ligand, which was prepared “in situ” following a RedOx reaction.²⁵⁻²⁸ The properties and the applicability of NiO in different domains were presented in several studies published by different authors.²⁹⁻³²

The aim of this paper is represented by the investigation of the redox reaction that occur between ethylene glycol and Ni(NO₃)₂·6H₂O, in an strong acidic medium (at pH ~ 0.0). In order to determine and confirm the structure of the obtained compound, this was characterized by several techniques, including elemental analysis. The paper also describes the thermally-induced decomposition at relatively low temperature with the formation of a non-stoichiometric nickel oxide.

EXPERIMENTAL

Chemicals and methods

The synthesis of the coordination compound was carried out in aqueous medium, using analytical reagents used as

received, without further purification, namely: Ni(NO₃)₂·6H₂O (>99% “Reactivul” Bucharest), ethylene glycol (>99% “Reactivul” Bucharest), and nitric acid solution 2M. The impurities from the reagents do not influence the synthesis and purity of the obtained compound as they are removed in the subsequent purification step.

The water content was determined gravimetrically and the nickel content was estimated using standard methods. Carbon and hydrogen were analyzed using a Carlo Erba 1108 elemental analyzer. The FTIR spectra (as dispersion in KBr pellets, Specac Pellet Press) of the coordinative compound and the decomposition product were recorded on a Jasco-FT-IR 410 spectrophotometer, in the spectral range 400 – 4000 cm⁻¹, after a number of 16 acquisitions. The diffuse reflectance spectrum of the synthesized compound was recorded with a spectrophotometer Spekol 10 Carl Zeiss Jena using MgO as reference material.

The magnetic measurements were performed according to the Faraday’s method, at room temperature, using Hg[Co(NCS)₄] as a standard.

TG, DTG and DTA curves (in the range 20 – 1000 °C) corresponding to the decomposition of the coordination compound were recorded on a thermoanalyzer system Mettler TGA/SDTA 851/LF/1100. The measurements were conducted in dynamic air atmosphere at a flow of 0.05 L·min⁻¹, using the alumina plates crucibles of 150 µL and the mass samples were about 20 mg at a heating rate of 10 °C·min⁻¹.

The powder X-Ray diffraction patterns of the decomposition product were recorded at room temperature with a BRUKER D8 Advance diffractometer with graphite monochromator on the diffracted beam, using Cu K_α radiation (λ = 1,54056 Å). The X-Ray power was 40 KV and 30 mA. The crystalline phases were identified using JCPDS-ICDD files. The data were collected and processed with the Diffrac plus program package.

Synthesis of the coordination compound

The synthesis of the coordination compound took place via the redox reaction that occur between ethylene glycol and nitrate anion (from nickel nitrate and nitric acid) in an aqueous system, followed by the isolation of the complex compound from the system.

An homogenous mixture consisting in distilled water, alcohol, Ni(NO₃)₂·6H₂O and nitric acid in the molar ratio of ethylene glycol : Ni(NO₃)₂·6H₂O : HNO₃ equal to 1.5 : 1.5 : 1 was prepared. This mixture was subjected gradually to heat after placed in a water bath. The reaction was considered completed when the gas evolving stopped.

The final solid remained after heating was purified by suspending in a binary system consisting in acetone/distilled water and heated under reflux for an optimized period of time. The solution was filtered off under vacuum and the resulted solid product (coloured pink) was washed with acetone and finally maintained in air until constant mass was observed.

RESULTS AND DISCUSSION

The redox reaction between ethylene glycol and Ni(NO₃)₂·6H₂O was investigated by IR spectroscopy (Fig. 1). The analysis of this reaction by the use of FTIR spectroscopy can be realized due to the fact that modification of functional

bands with the advance of the reaction is evidenced in the spectra by decreasing the intensity of corresponding bands of nitrate ion and ethylene glycol respectively. At the same time, the appearance and the increase of the band intensity in the range of $1580\text{--}1680\text{ cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}^-$) is observed, which is specific to the oxygenated ligands that contain functional groups that act like donors, i.e. carboxylate anions.^{15,20,33}

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: $\text{NiL}\cdot 2.5\text{H}_2\text{O}$, where L is oxalate anion.

In order to separate and identify the ligand, the complex compound has been treated with R-H cationite (Purolite C-100). After the retention of the metal ions, at the evaporation of the obtained solution, was isolated in the solid state $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$. The elemental analysis confirms this composition: C (experim., 19.12 %, calc., 19.04 %) and H (experim., 4.68 %, calc., 4.76 %).

The physical properties (white solid, rhombic-pyramidal crystals, highly soluble in water, ethanol, strongly acid), the FTIR spectrum of oxalic acid (Fig. 2) are in good agreement with those from the literature^{33,34} and with the spectroscopic assignments (Table 2).

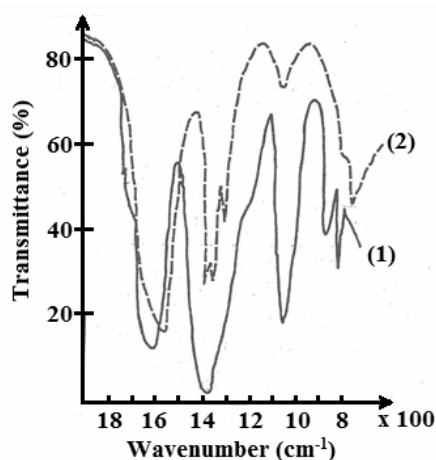


Fig. 1 – IR vibrational spectra (in the range $700\text{--}1900\text{ cm}^{-1}$) of the product of incomplete reaction between EG and nickel nitrate (1) and the homopolynuclear coordination compound $[\text{NiL}\cdot 2.5\text{H}_2\text{O}]_n$ (2).

Table 1

Composition and elemental analysis data

Compound (composition formula)	Ni(II) %		C %		H %	
	calc.	experim.	calc.	experim.	calc.	experim.
$\text{NiL}\cdot 2.5\text{H}_2\text{O}$	30.62	31.05	12.52	12.73	2.60	2.48

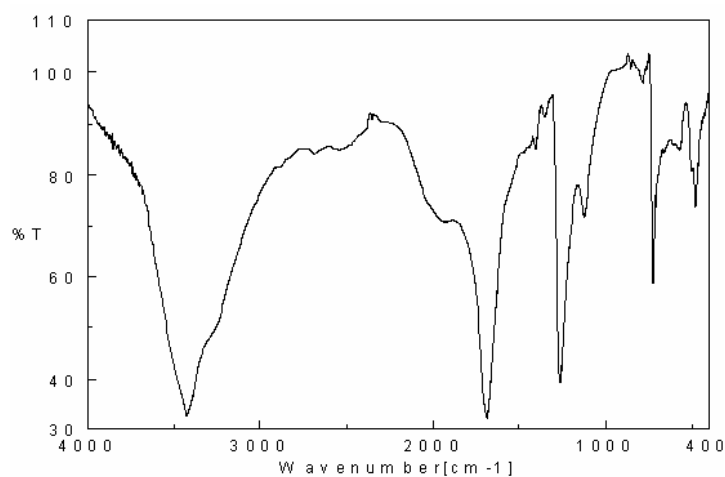


Fig. 2 – FTIR spectrum of the oxalic acid.

Table 2

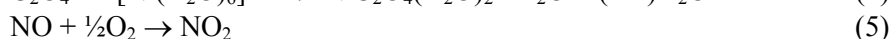
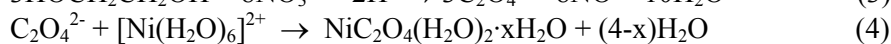
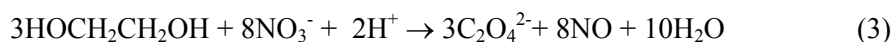
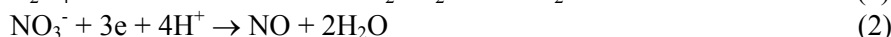
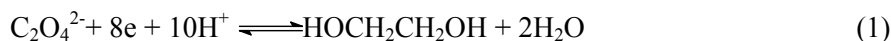
Characteristic absorption bands in IR for oxalic acid and the corresponding assignments

$\nu(\text{OH}), \nu(\text{H}_2\text{O})$	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{CO}) + \delta(\text{OCO})$	$\nu(\text{C-OH})$	$\delta(\text{OCO})$	$\delta(\text{CCO})$
3425 vs, br	1686 vs	1262 vs	1125 m	725 s	481s

s – strong (v – very); br – broad; m – medium.

These results as well as those previously reported^{15,20} concerning the oxidation of ethylene glycol with metallic nitrates suggest that the oxidation of the ethylene glycol with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ occurs, in some working

conditions, to the oxalate dianion.¹⁵ Following this, we suggest the following mechanism for the reaction between ethylene glycol and $\text{Ni}(\text{NO}_3)_2$ in acid medium:



The oxidation of the ethylene glycol occurring simultaneously with the coordination of the oxidation product by the complex generator determines the shifting of the equilibrium towards oxidation, leading thus to the formation of the polynuclear coordination product.

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 Ni(II)-oxalate

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

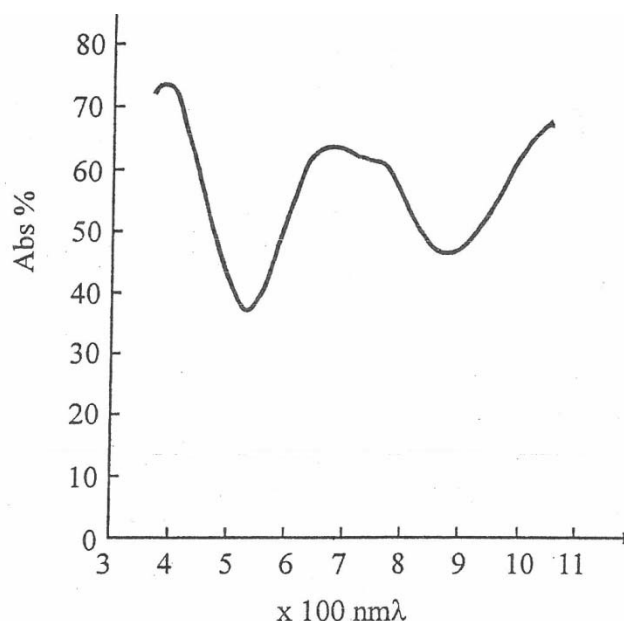


Fig. 3 – Diffuse reflectance spectrum of the coordinative homopolynuclear compound $[\text{NiL} \cdot 2.5\text{H}_2\text{O}]_n$.

Table 3

Calculated electronic parameters

Compound (composition formula)	10 Dq (kK)	B (kK)	β
NiC ₂ O ₄ (H ₂ O) ₂ ·0.5H ₂ O	9.180	0.930	0.89

The spectrum exhibit an absorption band at 26.315 cm⁻¹ ($\lambda = 380$ nm) which may be assigned to the ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(v_3)$ transition, characteristic to Ni(II) ion in a high spin octahedral configuration. The split band at about 15,150 cm⁻¹ ($\lambda = 665$ nm) may be assigned to the ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(v_2)$ transition.

In order to calculate the electronic parameters 10 Dq, B and β , we followed the classical procedure, employing König's formula.³⁵ Table 3 shows the calculated electronic parameters.

The values of the spectral parameters show that the coordinated ligands H₂O and C₂O₄²⁻ (L) are in the spectrometric series of Ni(II) of close strength.³⁶

Accordingly, the Ni(II) ion exists in the fundamental state $t_{2g}^6 e_g^2$, the two ligands L, H₂O being of low field and of similar strength.

The shape of the electronic spectra, the width and asymmetry of the bands is a proof not only for the deformation of octahedral coordination, but for the equilibrium between the octahedral configuration (predominant) and the tetrahedral stereochemistry of the Ni(II), as well.

IR vibrational spectrum of Ni(II)-oxalate

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).

Table 4 shows the characteristic bands in IR (cm⁻¹) for Ni(II)-oxalate, a green mustard powder, and the corresponding assignments.

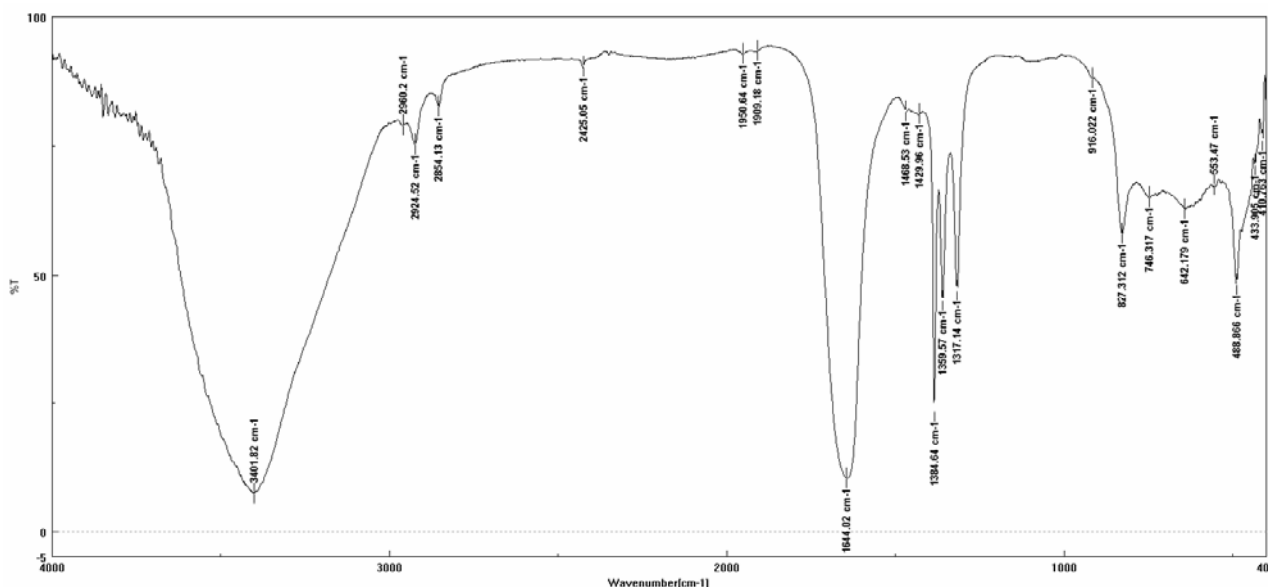
Fig. 4 – FTIR spectrum of the homopolynuclear coordination compound [NiL·2.5H₂O]_n.

Table 4

Characteristic absorption bands in IR for Ni(II)-oxalate and the corresponding assignments

Wavenumber [cm ⁻¹]	Assignment	Wavenumber [cm ⁻¹]	Assignment
3402 s, br	$\nu_{\text{asym}}(\text{OH}) + \nu_{\text{sym}}(\text{OH})$ or hydrogen bonding	827 m	coordinated water
1644 vs	$\nu_{\text{asym}}(\text{OCO})$	746 m	
1365 vs	$\nu_{\text{sym}}(\text{OCO})$	553 w	lattice water
1317 s	$\nu_{\text{sym}}(\text{CO}) + \delta(\text{OCO})$	488 m	$\nu(\text{Ni(II)-O}(\text{C}_2\text{O}_4)) + \nu(\text{C-C})$
		410 w	$\nu(\text{Ni-O})$ and/or ring deformation

s- strong (ν – very); br – broad; m – medium; w – weak.

Table 5

Magnetic moments and stereochemistry for the investigated compound

Compound (composition formula)	μ_{eff} (MB)	μ_{spin} (MB)	stereochemistry
$\text{NiC}_2\text{O}_4(\text{H}_2\text{O})_2 \cdot 0.5\text{H}_2\text{O}$	3.10	2.83	octahedral

The intense and broad band in the range $3000\text{--}3600\text{ cm}^{-1}$ with a maximum at 3402 cm^{-1} due to the vibration $\nu(\text{OH})$ from coordinated water as well as due to strong hydrogen bonds between water molecules and oxalate ligand. A medium absorption band at 827 cm^{-1} respectively the weak absorption band at 746 cm^{-1} confirms also the presence of water in the coordinated form.^{6,37} The weak absorption band at 553 cm^{-1} is attributed to lattice water.³⁸ The absence of the bands in the range $1720\text{--}1660\text{ cm}^{-1}$ attributed at vibration $\nu_{\text{asym}}(\text{C}=\text{O})$ in the case coordination compounds in which $\text{C}_2\text{O}_4^{2-}$ is bidentate ligand^{39,40} shows that in the synthesized coordination compound is realized the resonance of the carboxylate groups and the four oxygen atoms are equivalent, the oxalate dianion is bridging ligand.⁴¹ The intense band at 1644 cm^{-1} is attributed to the vibration $\nu_{\text{asym}}(\text{OCO})$ and the value shows that the Ni(II)-carboxylate bond is preponderant ionic. The band at 1365 cm^{-1} is due to vibration $\nu_{\text{sym}}(\text{OCO})$. At the same time, the value for $\nu_{\text{sym}}(\text{OCO})$, 1365 cm^{-1} , beside $\delta(\text{OCO})$ found at 1317 cm^{-1} , are in agreement with the position of corresponding absorption in oxalate-bridged complex.⁴² The broad band in the range $600\text{--}700\text{ cm}^{-1}$ is assigned to Ni-O stretching vibration mode. The very sharp and medium band at 488 cm^{-1} is attributed vibration $\nu(\text{Ni-O})$ and $\nu(\text{C-C})$. The band at 410 cm^{-1} is due to $\nu(\text{Ni-O})$ and/or ring deformation.

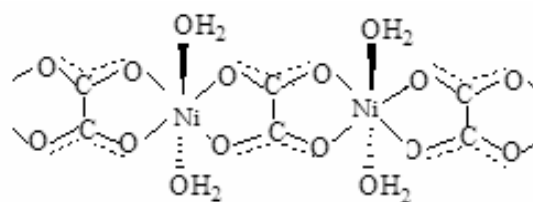
Magnetic measurements

Magnetic susceptibility measurements have been used to determine the presence and number of unpaired electrons, the geometry around the metal ions and the presence and magnitude of exchange interactions in the complexes. Magnetic moments have been determined for the Ni(II)- polynuclear

compounds. The results (Table 5) indicate octahedral coordination for Ni(II) ions.^{15,20} This supports our conclusions as obtained from electronic spectrum for this compound.

The (pseudo)octahedral stereochemistry of Ni(II) – high spin is confirmed by the effective magnetic moment value, higher than that corresponding to the spin value, suggesting a coupling spin-orbit for Ni(II)-oxalate.

In accord with empirical formula, the (pseudo)octahedral stereochemistry of the nickel(II) and the bridging oxalate anion, the homopolynuclear coordination compound has the following polynuclear polymeric structure:

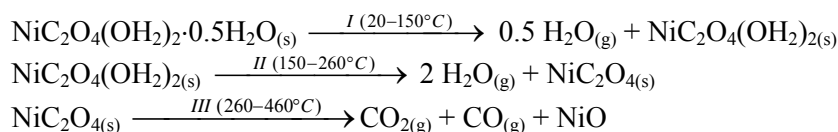


The polynuclear structure is due to the coordination of the water molecules at two metal ions from adjacent layers. The investigated compound has a high stability, due to the very strong hydrogen bonds; in water and in common organic solvents it is practically insoluble; it's not modifying its composition in time and it can only be decomposed in a strongly acid medium.

Thermal conversion of Ni(II)-oxalate

In order to confirm the composition and the structural formula of the coordination compound as well as to establish the steps of the conversion, the thermal analytical methods have been used.

The analysis of the obtained data (Fig. 5) suggests that the progressive heating of the coordination compound could imply the following processes:



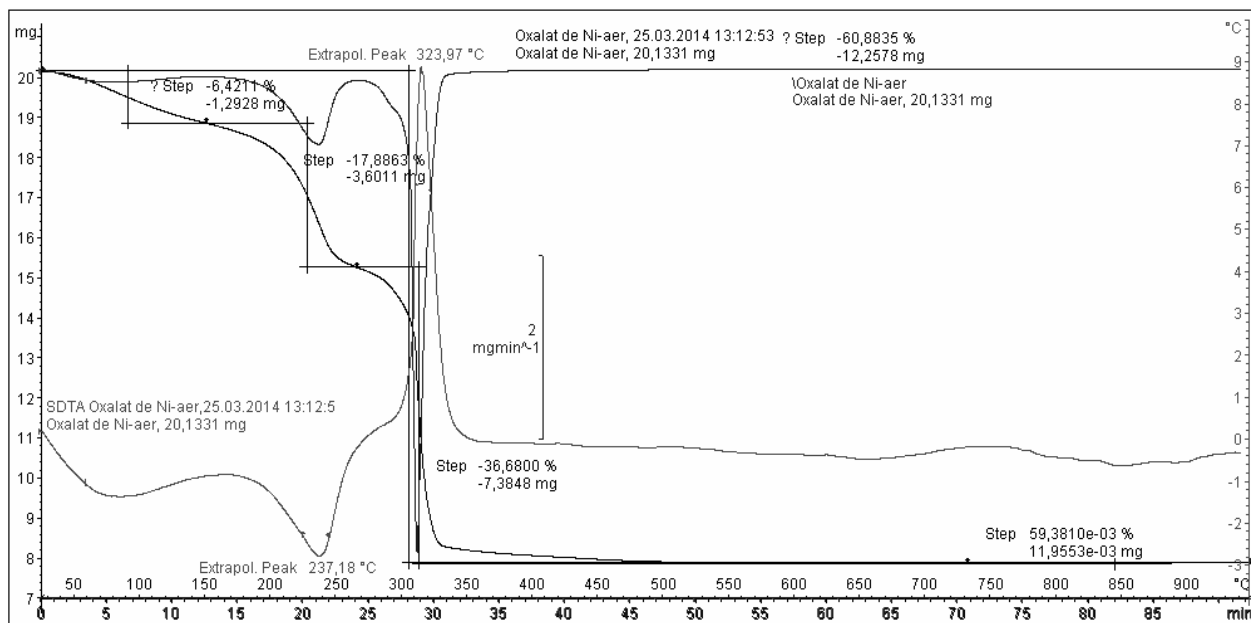


Fig. 5 – Thermal analytical curves (TG, DTG and DTA) for the decomposition in air of $[\text{NiL}\cdot 2.5\text{H}_2\text{O}]_n$.

Table 6

Weight loss of the sample during the thermal conversion in air of the polynuclear coordination compound $[\text{NiL}\cdot 2.5\text{H}_2\text{O}]_n$

Steps	I	II	III	I – III
$\Delta m / \%$ (calculated)	4.72	18.75	37.54	61.01
$\Delta m / \%$ (experimental)	6.42	17.89	36.68	60.88

The data shown in Table 6 confirms the proposed conversion mechanism.

The TG profile shows the removal in the first step of the lattice water at 150 °C followed, in the second step, by an inclined slope up to 237 °C (mass loss, found 17.89%) indicating the removal of about 1.90 coordinated molecules water (mass loss, calc., 17.81%). Complete dehydration compound is produced at 260 °C with 18.75% mass loss. An endothermic DTA peak between 180-250 °C (maximum at 237 °C) and a change on DTG in the same range correspond to the removal of two coordinated molecules of water. These results are in good agreement with those from the literature for $\text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ obtained through classical methods.^{43,44} The breakdown of anhydrous compound, NiC_2O_4 , in the third step, takes place within a very short temperature range (290-320 °C) as shown by a steep slope on TG at 310 °C with a mass loss of 36.68% (calc., 37.54%) which suggests that the product of the conversion is nonstoichiometric oxide NiO_{1+x} , where $x \approx 0.25$ and it showing a deficit in nickel. The formation of $\text{NiO}_{1.25}$ is accompanied by a very sharp exothermic DTA peak at 323.97 °C, then it is reduced beyond 450 °C with the formation of NiO. The good

agreement between the values of mass loss confirms the proposed conversion mechanism.

The FTIR spectrum of the thermal decomposition product (Fig. 6) shows two absorption bands at 440 și 660 cm^{-1} respectively, slightly shifted with respect to the characteristic bands of nickel(II) oxide mentioned in the literature (460 and 650 cm^{-1}) – the broadness of the band indicates that the NiO powder is nanocrystal.³¹

The XRD pattern of the NiO sample shows the presence of the characteristic peaks for NiO, in the range of 35 – 100° 2 θ , in accordance with JCPDS 47 – 1049.²⁴

CONCLUSIONS

A new elaborated method of synthesis of the homopolynuclear coordination compound having oxalate anion as ligand is based on the oxidation reaction of ethylene glycol in an alcohol-water system by nickel nitrate and nitric acid and the simultaneous isolation of the complex compound in the reaction system.

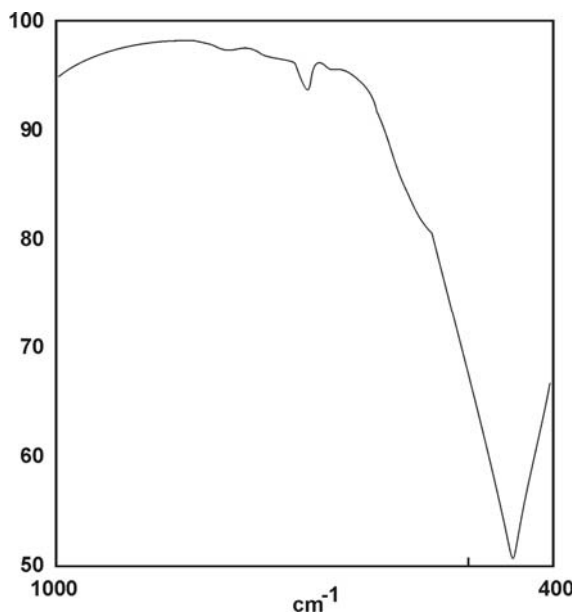


Fig. 6 – FTIR spectrum of the nickel(II) oxide.

The coordination compound synthesized by this new method is a homopolynuclear combination with the formula $[\text{NiL} \cdot 2.5\text{H}_2\text{O}]_n$ which has been 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 nickel(II) cation and oxalate anion functionated as double-bridge ligand (tetradentate). During the thermal conversion in air, depending of temperature, the product is non-stoichiometric nickel oxide.

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