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# THERMAL AND STRUCTURAL INVESTIGATION OF THE REACTION BETWEEN 1,2-PROPANEDIOL AND $Ni(NO_3)_2{\cdot}6H_2O$

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## Abstract

The authors present the results of an investigation concerning the reaction between 1,2-propanediol and $Ni(NO_3)_2{\cdot}6H_2O$, leading to a complex containing as ligand the lactate anion (L), suggesting that the oxidation of 1,2-propanediol occurs at the primary hydroxyl group. The obtained solid homopolynuclear combination, $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$, has been investigated by thermal analysis, electron and IR spectroscopy, and magnetic methods. Nickel oxide obtained by thermolysis of this complex compound was characterized by IR, X-ray spectroscopy and elemental analysis. All the investigations lead to the conclusion that the complex compound is characterized by pseudooctahedral configuration of the nickel(II) ion. Thermal analysis of the homopolynuclear complex compound enabled to prove the thermal decomposition mechanism.

**Keywords:** homopolynuclear combination, hydroxylactate, nitrate, propanediol, thermal analysis

## Introduction

The necessity of obtaining oxide systems with irreducible structure and properties, required by the modern technology in various fields (heterogeneous catalysis, electrocatalysis, electronics, ceramic pigments, physical supports – carriers, brackets – for the stockage and processing of information, drug industry), has determined the advent of new unconventional methods for their synthesis. In this respect the thermal conversion of homo- and heteropolynuclear complexes with anions of carboxylic acids as ligands is to be mentioned [1–14]. Such ligands include the anions glyoxylate, malonate, succinate and lactate [15–20]. These compounds decompose at relatively low temperatures, forming simple or mixed oxides and volatile products (CO, $CO_2$, $H_2O$).

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Thermal conversion in air of M(II) (*M*=Ni, Co) homopolynuclear glyoxylates [15, 16] as well as Ni(II), Cu(II) heteropolynuclear glyoxylates [17] led to non-stoichiometric oxides of the corresponding metal.

The determination of the formation conditions of non-stoichiometric oxides of Ni and Co led to an original method for obtaining anodes with films electrocatalytically active for the oxygen evolution reaction in water and chloralkali electrolysis [18, 19].

Ni and Co complex compounds have been synthesized as result of the reaction between 1,3-propanediol and nitrates of these cations [20].

This paper presents the results obtained in the investigation of 1,2-propanediol oxidation with $Ni(NO_3)_2 \cdot 6H_2O$. The obtained complex compound was investigated from the composition and physical-chemical properties standpoints. It will be shown that it can be a precursor for NiO obtaining at relatively low temperature.

## Experimental

For the synthesis of the complex compound, $Ni(NO_3)_2 \cdot 6H_2O$, 'Reactivul' – Bucharest, with minimal purity of 98% and 1,2-propanediol, 'BDH Chemical Ltd. Poole' – England with purity of 97% were used. 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 thermoanalytical curves (TG, DTG, DTA) corresponding to the synthesis and the decomposition of the coordination compound were recorded on a Q-1500D MOM-Budapest type derivatograph, in static air atmosphere and in the temperature range of 20–500°C, at a heating rate of 5 K $min^{-1}$. The coordination compound was also characterized by the following methods: chemical analysis, IR spectroscopy, electron spectroscopy (diffuse reflectance technique) and magnetic methods. The IR spectrum was recorded on a Specord IR 75 Carl Zeiss Jena spectrometer using the technique of KBr pellets, in the range of 400–4000 $cm^{-1}$. The electron spectrum was recorded by diffuse reflectance technique using MgO as a reference material.

The magnetic measurements were performed according to Faraday's method, at room temperature, using $Hg[Co(NCS)_4]$ as a standard. The characterization of nickel oxide obtained by thermal decomposition of the investigated coordination compound was performed by IR and X-ray spectroscopy. X-ray diffractograms were recorded on DRON 3 diffractometer.

## Results and discussion

### *Synthesis of the coordination compound*

The elaborated method of the synthesis of the coordination compound is based on the oxidation reaction of 1,2-propanediol in alcohol–water system by nickel nitrate and the simultaneous isolation of the complex compound in the reaction system. A solution of water+alcohol+$Ni(NO_3)_2 \cdot 6H_2O$ in the molar ratio 1,2-propanediol: $Ni(NO_3)_2 \cdot$

$6H_2O$= 3:2 was prepared. This mixture was heated in a thermostat in the following steps of thermal treatment: 60°C (2 h); 70°C (2 h); 80°C (2 h); 90°C (2 h); 100°C (2 h); 110°C (2 h); 120°C (10 h). The end of the reaction corresponds to the end of the gas evolution.

The solid reaction product has been heated in an acetone – water mixture, filtered and washed with acetone. Finally, it was maintained in air until constant mass.

The thermal behaviour of an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ – 1,2-propanediol has been investigated. The heating of the solution put in a plate shaped platinum crucible has been performed in static air atmosphere at temperature between 20 and 500°C, using a heating rate of 5 K $min^{-1}$ and $\alpha$-$Al_2O_3$ as reference material. Figure 1 shows the thermoanalytical curves of the system $Ni(NO_3)_2 \cdot 6H_2O$ – 1,2-propanediol – $H_2O$. From the DTA curve one can see that at a temperature of about 130°C a peak is registered, which is attributed to the oxidation reaction of the diol with the nickel nitrate and the complex generation. Complex generation takes place practically in the temperature range of 100–150°C, when the TG and DTG curves show a mass loss corresponding to $NO_2$ elimination ($NO+\frac{1}{2}O_2 \rightarrow NO_2$) coupled with the simultaneous formation of the complex compound.

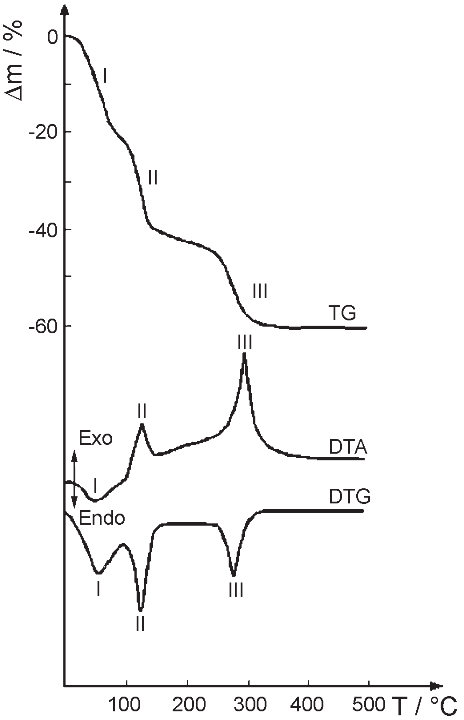


**Fig. 1** Thermoanalytical curves of the $Ni(NO_3)_2$ – 1,2-propanediol – $H_2O$ system

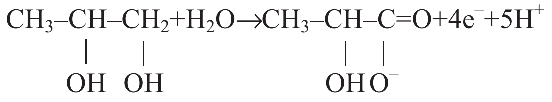
The evolution of the reaction between 1,2-propanediol and $Ni(NO_3)_2\cdot 6H_2O$ was also investigated by IR spectroscopy. As the reaction advances, the bands due to the nitrate ion decrease in intensity, proving that the nitrate ion is consumed in the reaction [21]. At the same time, the appearance and the increase of band intensity in the range of 1580–1680 $cm^{-1}$ ($\nu_{as}COO^-$) is observed, which is specific to the ligands of the complex compounds which contain at least two oxygen atoms as donors such as the carboxylic anions of the acids.

In order to separate and identify the ligand, the complex has been treated with RH cationite. After the retention of the metal cations, the resulted lactic acid has been identified by specific reactions (haloform reaction, reaction with $FeCl_3$ solution). The elemental analysis results (Table 1) as well as the IR investigation confirm the following empirical chemical formula for the coordination compound: $Ni(OH)L(H_2O)\cdot 0.25H_2O$, where *L* is the lactate anion.

**Table 1** Composition and elemental analysis data

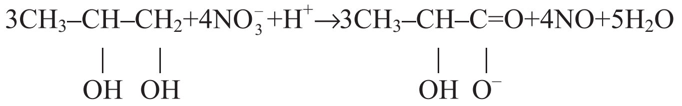
| Compound (compound formula) | Ni(II)/% | | C/% | | H/% | |
|---|---|---|---|---|---|---|
| | calc. | exp. | calc. | exp. | calc. | exp. |
| $Ni(OH)L(H_2O)\cdot 0.25H_2O$ | 31.35 | 31.10 | 19.23 | 19.30 | 4.54 | 4.63 |

These results as well as those previously reported [15, 16] concerning the oxidation of ethyleneglycol with M(II) nitrate (*M*=Ni, Co) suggest that the oxidation of the 1,2-propanediol with $Ni(NO_3)_2\cdot 6H_2O$ occurs at the primary hydroxyl group, which is more reactive and can be oxidized to carboxylate ion. The secondary hydroxyl has a lower reactivity and is not involved in the oxidative process under the reaction conditions. Consequently, we suggest the following mechanism for the reaction between 1,2-propanediol and $Ni(NO_3)_2$:



$$CH_3\text{–}\underset{\underset{OH}{|}}{CH}\text{–}\underset{\underset{OH}{|}}{CH_2}+H_2O\rightarrow CH_3\text{–}\underset{\underset{OH}{|}}{CH}\text{–}\underset{\underset{O^-}{|}}{C}{=}O+4e^-+5H^+ \qquad (a)$$

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



$$3CH_3\text{–}\underset{\underset{OH}{|}}{CH}\text{–}\underset{\underset{OH}{|}}{CH_2}+4NO_3^-+H^+\rightarrow 3CH_3\text{–}\underset{\underset{OH}{|}}{CH}\text{–}\underset{\underset{O^-}{|}}{C}{=}O+4NO+5H_2O \qquad (c)$$

$$[Ni(H_2O)_x]^{2+}+H_2O\rightarrow[Ni(OH)(H_2O)_{(x-1)}]^{+}+H_3O^{+} \qquad (d)$$

$$C_3H_5O_3^-+[Ni(OH)(H_2O)_{(x-1)}]^{+}\rightarrow Ni(OH)C_3H_5O_3\cdot yH_2O+(x-1-y)H_2O \qquad (1)$$

$$NO+½O_2\rightarrow NO_2 \qquad (2)$$

From this reactions one may notice the necessity of the presence of protons involved in the (c) stage in order to potentiate the oxidation activity of the nitrate ion. The necessary protons are generated by Ni(II) hydrated cation hydrolysis, as shown in the (d) process.

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.

### *Electron reflexion spectrum of Ni(II)-hydroxy-lactate*

The electron spectrum of the coordination compound shows the presence of two characteristic bands of the Ni(II) hexacoordinated ion. Table 2 shows the wavenumbers, which correspond to the diffuse reflectance spectral bands together with their assignments. The results are in good agreement with those from the literature [22].

**Table 2** Diffuse reflectance spectral data of the investigated compound

| $\nu_1$/cm$^{-1}$ | $\nu_2$/cm$^{-1}$ | $\nu_3$/cm$^{-1}$ |
|---|---|---|
| – | 15.152 $^3T_{1g}(F)\leftarrow{}^3A_{2g}$ | 26.316 $^3T_{1g}(P)\leftarrow{}^3A_{2g}$ |

In order to calculate the electron parameters 10 Dq, B and β, we followed the classical procedure, employing Kőnig's formula [23]. Table 3 shows the calculated electron parameters. The values of the spectral parameters are in agreement with those for the complex combination $NiL_2$ that shows that the coordinated ligands $H_2O$, $HO^-$, L, are in the spectrometric series of Ni(II) of close strength [22].

**Table 3** Calculated electron parameters

| 10 Dq/kK | B/kK | β |
|---|---|---|
| 9.18 | 0.93 | 0.89 |

The value of the effective magnetic moment 3.10 MB, is also in accordance with the octahedral configuration of Ni(II) ion – maximal spin, higher than that corresponding to the spin value (2.83 MB). The difference could be explained through the coupling spin-orbit, which is also found for the slight splitting in the electron spectrum of band $\nu_2$. Therefore the Ni(II) ion, in this compound, is in the state of maximal spin $t_{2g}^6 e_g^2(^3A_{2g})$.

The electron spectrum suggest a pseudo-octahedral configuration of the Ni(II) ion; water molecules from the apical position are coordinated at two Ni(II) ions from adjacent layers.

### *IR vibrational spectrum of Ni(II)-hydroxy-lactate and the green colour of the complex verified the above supposition*

The intensive and broad band in the range 3200–3600 cm$^{-1}$ with maximum at about 3400 cm$^{-1}$ is attributed to the formation of the hydrogen bonds between the water molecules and the alcoholic hydroxyl [24, 25]. The intensive band at 1610 cm$^{-1}$ is attributed to the asymmetrical vibration of the carboxylate ion and the values show that the resonance from the carboxylate group is maintained during complex formation, the metal-carboxylate bond is predominantly an ionic one [26]. The low intensity band with maximum at 1420 cm$^{-1}$ is attributed to symmetric vibration $\nu_s$(COO). As the difference between $\nu_{as}$–$\nu_s$ is greater 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 [26, 27]. Also, the existence of the two bands for $\nu_s$(COO) could be explained through the octahedral deformation [28]. The band at 1310 cm$^{-1}$ confirms that the carboxylate group is acting as a bidentate ligand [29].

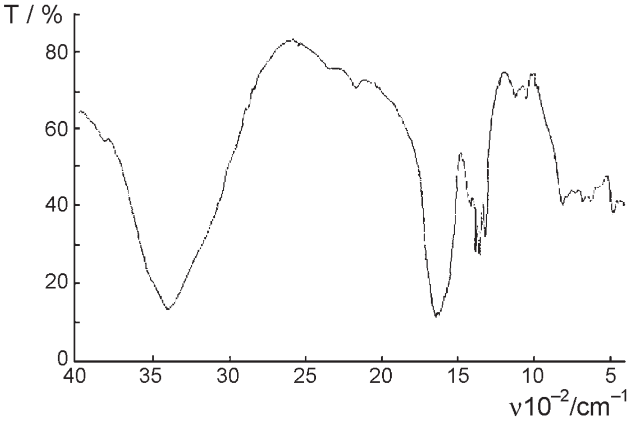


**Fig. 2** IR spectrum of the Ni(II)-hydroxy-lactate

**Table 4** Characteristic absorption bands in IR for Ni(II)-hydroxy-lactate and the corresponding assignments

| ν(OH) | $\nu_{as}$(COO) | $\nu_s$(COO) | $\nu_s$(CO)+ δ(OCO) | ν(C–OH) | ν(OH bridge) | δ(OCO) +ν(NiO) | $\rho_w$($H_2O$) |
|---|---|---|---|---|---|---|---|
| cm$^{-1}$ | | | | | | | |
| 3430 | 1610 | 1420<br>1380 | 1310 | 1128<br>1088 | 1047 | 800 | 670 |

In the vibrational spectrum of lactic acid [22] two bands are present at 1128 and 1088 cm$^{-1}$, both attributed to C–OH vibration. The fact that in the spectrum of this complex these bands appear at the same values and that they are not shifted towards lower number enables to presume that the OH alcoholic group does not take part in the coordination process. The band at 1047 cm$^{-1}$ is attributed to the vibration of the OH bridge group [30]. The band of mean intensity at 800 cm$^{-1}$ is attributed to the group of vibrations δ(OCO)+ ν(MO), the same as in the case of Fe(III), Ni(II) oxalate complexes [29].

The coordination of the two water molecules to the M(II) ion is further confirmed by the presence in the vibrational spectrum of the complex combination of the band at 670 cm$^{-1}$. This is in a good agreement with the results obtained by Sarov *et al.* [31].

In accordance with Nagase *et al.* [32], the 480 $cm^{-1}$ band, obtained for the investigated complex, can be attributed to ν(NiO)–oxygen vibration belonging to the $COO^-$ 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 $H_2SO_4$. These statements as well as the above mentioned data suggest a polynuclear structure which corresponds to the following formula: $[Ni_2(OH)_2L_2(H_2O)_2\cdot0.5H_2O]_n$.

*Thermal conversion of Ni(II)-hydroxy-lactate*

In order to confirm the composition and the configuration of the coordination compound ($[Ni_2(OH)_2L_2(H_2O)_2\cdot0.5H_2O]_n$) as well as to establish the conversions to NiO which promote catalytic activity, thermal analysis methods (TG, DTG, DTA) have been used [33, 34]. The obtained thermoanalytical curves, showed in Fig. 3, suggest the following steps which occur at the progressive heating of the coordination compound:

$$Ni_2(OH)_2(H_3CCH(OH)COO^-)_2(H_2O)_2\cdot0.5H_2O \xrightarrow{I(50-150\,°C)-2.5H_2O)}$$

$$Ni_2(OH)_2(H_3CCH(OH)COO^-)_2 \xrightarrow{II(150-250\,°C)-2H_2O)} Ni_2O(C_4H_8O(COO^-)_2$$

$$\xrightarrow{III(250-355°C)+6O_2-4H_2O-6CO_2)} 2NiO$$

Data from Table 5 confirm the proposed conversion mechanism.

Nickel(II) oxide was the only component of the conversion of the complex compound. By X-ray diffraction the lines 57 and 91 were emphasized, in accordance with ASTM 4-835. In the IR spectrum of residium the absorption bands at 460 and 650 $cm^{-1}$ appear, which are characteristic to the nickel(II) oxide. The composition of a residual sample determinated by elemental analysis (Ni: 78.5% and O: 21.5%) cor-

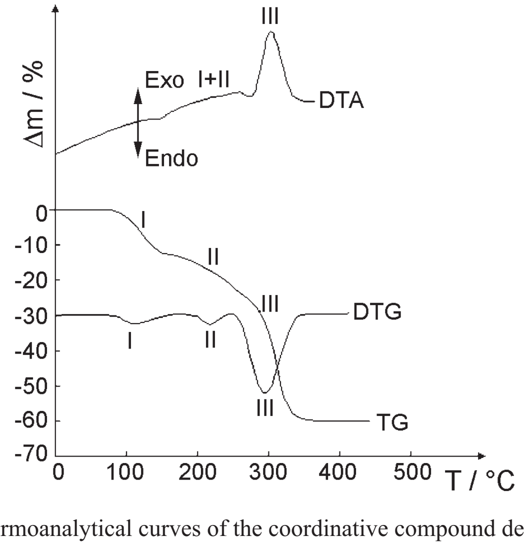


**Fig. 3** Thermoanalytical curves of the coordinative compound decomposition

responds to the NiO. There is no proof of evidence of the coke in the residual sample, in accordance with the proposed mechanism.

**Table 5** The mass loss during the thermal conversion in air of the investigated compound

| Step | I | II | III | I–III |
|---|---|---|---|---|
| $\Delta m$/% (calc.) | 12.02 | 9.61 | 38.46 | 60.09 |
| $\Delta m$/% (exp.) | 12.00 | 10.00 | 38.00 | 60.00 |

The ascending shape of the DTA curve in the range from step I to step III in which the loss of water takes place, could be attributed to the crystallization process and to the increase of the Ni(II)–ligand bond strength.

The strong exothermic effect that characterizes the 3rd step (DTA temperature maximum at 335°C) is due to the ligand combustion and respectively to the NiO oxidation to $NiO_{1+x}$. Above 355°C, $NiO_{1+x}$ loses the oxygen excess forming NiO.

In addition to all of these remarks, the following statements must be underlined:

– for the combination $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$ water is lost at a temperature above 110°C, which shows that some water molecules are coordinated to the metal(II) ion confirming our suppositions;

– the fact that one could not make a thermal separation between the loss of the two coordinated water molecules and of the crystallization water, could be explained by the existence of two ‘types of water’ involved in a strong hydrogen bond [35].

## Conclusions

The oxidation of 1,2-propanediol by Ni(II) nitrate was carried out at moderate temperature, at the primary hydroxyl, which is more reactive and can be oxidized to carboxylate ion. The secondary hydroxyl has a lower reactivity and it is not involved in the oxidation process under the reaction conditions.

The coordination compound synthesized by this method is a homopolynuclear combination having the formula $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$. This complex has been investigated by elemental analysis, thermal analysis (TG, DTG and DTA), electron and IR spectroscopy and magnetic methods. All the experimental investigations lead to the conclusion that the complex is characterized by a pseudooctahedral configuration of the nickel(II) ion. The thermal conversion product obtained at 355°C is NiO.

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