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STRUCTURAL INVESTIGATIONS AND THERMAL ANALYSIS OF THE COMPLEX COMPOUND OBTAINED THROUGH THE REACTION OF 1,3-PROPANEDIOL WITH $Ni(NO_3)_2 \cdot 6H_2O$

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ABSTRACT. In this paper the authors present the results of an investigation concerning the reaction between 1,3-propanediol and $Ni(NO_3)_2 \cdot 6H_2O$, leading to a complex containing as ligand the β-hydroxypropionate anion (L). The obtained solid homopolynuclear combination, $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$, has been investigated by thermal analysis, electronic and IR spectroscopy and magnetic methods. Nickel oxide obtained by thermolysis of this coordinative compound was characterized by IR and X-ray spectroscopy.

Keywords*:* 1,3-propanediol; nitrate; homopolynuclear combination; β-hydroxypropionate; thermal analysis.

INTRODUCTION

The thermal conversion of homo- and hetero-polynuclear complexes with anions of carboxylic acids as ligands have been carried out to 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 stockade and processing of information, drug industry)[1-4]. Such ligands include the anions glyoxylate, malonate, succynate and lactate. These complexes have been obtained by the oxidation reaction between some diols and metal nitrates, under different reaction conditions [5-9]. In a recent paper [10] we have reported the results of the study of the oxidation reaction between 1,3-propanediol and $M(NO_3)_2 \cdot 6H_2O$ (M: Co, Ni), in the presence of dilute nitric acid solution. Ni and Co complex combinations synthesized in this way contain malonate anion as ligand.

The determination of the formation conditions of nonstoichiometric oxides of Ni and Co led to a original method for obtaining anodes with

electrocatalytically active films for the oxygen evolution at the electrolysis of alkaline solutions [8, 9].

This paper presents the results obtained at the investigation of 1,3-propanediol oxidation with $Ni(NO_3)_2.6H_2O$, in a weak acid medium, due to the hydrolysis of the metal nitrate. The obtained coordination compound was investigated with respect to the composition and physical-chemical properties. It will be shown that it can be a precursor for the NiO obtaining at relatively low temperature.

EXPERIMENTAL

For the synthesis of the coordination compound, $Ni(NO_3)_2.6H_2O$, "Reactivul" – Bucharest, with minimal purity of 98%, and 1,3-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 elaborated method of synthesis of the complex compound is based on the oxidation reaction of 1,3-propanediol in an alcohol-water system by nickel nitrate and the simultaneous isolation of the complex compound in the reaction system.

A solution of water + diol + $Ni(NO_3)_2 \cdot 6H_2O$ in the molar ratio: 1,3-propanediol : $Ni(NO_3)_2 \cdot 6H_2O$ = 3:2 was prepared. This mixture was heated gradually during 20 h in a thermostat up to 120^0 C. The reaction was considered completed when no more gas evolution was observed.

Refluxing from acetone-water mixture purified the solid reaction product. After that the solution was filtered and the solid product was washed with acetone and finally was maintained in air until constant mass.

The evolution of the reaction between 1,3-propanediol and $Ni(NO_3)_2.6H_2O$ was investigated by IR spectroscopy. As the reaction advances the bands due to nitrate ion decreases in intensity, proving that the nitrate ion is consumed in reaction [11]. In the same time, the appearance and the increase of the band intensity in the range 1580 – 1680 cm^{-1} (ν_{as} COO^-) is observed, which is specific to complexes ligands which contain at least two oxygen atoms as donors such as the carboxylic anions of the acids.

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 β-hydroxypropionate anion.

The heating curves (TG, DTG, DTA) corresponding to the decomposition of the coordination compound were recorded on a Q-1500D MOM-Budapest type Paulik-Paulik-Erdey derivatograph, in static air atmosphere and the temperature range 20 – 500^0C, at heating rates: 1.25 $K \cdot min^{-1}$, 2.5 $K \cdot min^{-1}$, 5 $K \cdot min^{-1}$ and 10 $K \cdot min^{-1}$; reference material: α-Al_2O_3.

The coordination compound was also characterized by the following methods: chemical analyses, IR-spectroscopy, electronic 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 400 – 4000 cm^{-1}.

Table 1.

Composition and elemental analysis data

Compound (compound formula)	Ni(II) %		C %		H %	
	calc.	exper.	calc.	exper.	calc.	exper.
$Ni(OH)L(H_2O)\cdot 0.25H_2O$	31.35	31.10	19.23	19.40	4.54	4.73

The electronic 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 the nickel oxide obtained by thermal decomposition of the investigated coordination compound was performed by IR and X-ray spectroscopy. XR-diffractogrames were recorded on a DRON 3 diffractometer.

RESULTS AND DISCUSSION

The experimental results as well as those previously reported [5] concerning the oxidation of 1,2-propanediol with M(II) nitrate (M= Ni, Co) suggest that the oxidation of the 1,3-propanediol with $Ni(NO_3)_2\cdot 6H_2O$ occurs at one primary hydroxyl, which is oxidized to carboxylate ion. Consequently, we suggest the following mechanism for the reaction between 1,3-propanediol and $Ni(NO_3)_2$:

a) $HO\text{-}CH_2\text{-}CH_2\text{-}COO^- + 4e + 5\,H^+ \rightleftharpoons HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH + H_2O$

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

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c) $3HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH + 4NO_3^- + H^+ \rightleftharpoons 3HO\text{-}CH_2\text{-}CH_2\text{-}COO^- + 4NO + 5H_2O$

d) $[Ni(H_2O)_x]^{2+} + H_2O \rightleftharpoons [Ni(OH)(OH_2)_{x-1}]^+ + H_3O^+$

(1) $C_3H_5O_3^- + [Ni(OH)(OH_2)_{x-1}]^+ \rightarrow Ni(OH)C_3H_5O_3\cdot yH_2O + (x\text{-}1\text{-}y)H_2O$

Ni(II)-β-hydroxypropionate

(2) $NO + 1/2\,O_2 \rightarrow NO_2$

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 the hydrated Ni(II) 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.

Electronic reflexion spectrum of Ni(II)- β-hydroxypropionate

The electronic spectrum of the coordination compound shows the presence of two characteristic bands due to the Ni(II) hexacoordinated ion.

Table 2 shows the wave numbers, which correspond to the diffuse reflectance spectral bands together with their assignments. The results are in good agreement with those from the literature [12].

Table 2.

Diffuse reflectance spectral data of the investigated compound

ν_1 [cm^{-1}]	ν_2 [cm^{-1}]	ν_3 [cm^{-1}]
-	15873 $^3T_{1g}(F) \leftarrow {}^3A_{2g}$	26316 $^3T_{1g}(P) \leftarrow {}^3A_{2g}$

In order to calculate the electronic parameters 10 Dq, B and β, we followed the classical procedure, employing König's formula [13]. Table 3 shows the calculated electronic parameters. The values of the spectral parameters show that the coordinated ligands at Ni(II), H_2O, HO^-, L, are in the spectrometric series of Ni(II) of close strength [12].

Table 3.

Calculated electronic parameters

10 Dq (kK)	B (kK)	β
9.804	0.816	0.78

The value of the effective magnetic moment 3.15 MB, is also in accordance with the octahedral configuration of the 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 electronic spectrum of band ν_2. Therefore the Ni(II) ion is to be found in the state of maximal spin $t_{2g}^6 e_g^2$ ($^3A_{2g}$).

The electronic spectrum suggests a pseudooctahedral 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)-β-hydroxypropionate

The infrared spectrum (Table 4) and the green color of the complex verified the above supposition.

Table 4.

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

ν (OH) [cm^{-1}]	ν_{as} (COO) [cm^{-1}]	ν_s (COO) [cm^{-1}]	ν_s (CO)+ δ(OCO) [cm^{-1}]	ν (C-OH) [cm^{-1}]	ν (OH bridge) [cm^{-1}]	δ(OCO) +ν(MO) [cm^{-1}]	ρ_w (H_2O) [cm^{-1}]
3300	1600	1420 1380	1310	1118 1088	1047	800	670

The intensive and large band in the range 3200 – 3600 cm^{-1} with maximum at ≈ 3300 cm^{-1} is attributed to the formation of the hydrogen bonds between water molecules and the alcoholic hydroxyl [14, 15].

The intensive band at 1600 cm^{-1} is attributed to asymetrical vibration of the carboxylate ion and the values show that the resonance from the carboxylate group is maintained during complex formation, metal-carboxylate bond being prevalent on the ionic one [16].

The low intensity band with maximum at 1420 cm^{-1} is attributed to symmetric vibration ν_s(COO). As the difference between ν_{as} - ν_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 [16, 17]. Also, the existence of the two bands for ν_s(COO) could be explained through the octahedral deformation [18].

The band at 1310 cm^{-1} confirms that the carboxylate group is acting as a bidentate ligand [19].

Two bands are present at 1118 cm^{-1} and 1088 cm^{-1}, both attributed to C-OH vibration.

The band at 1047 cm^{-1} is attributed to the vibration of the OH bridge group [20].

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 [19].

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 Serov et al. [21].

In accordance with Nagase et al. [22], the 480 cm^{-1} band, obtained for the investigated complex, can be attributed to ν(MO)-oxygen vibration belonging to the COO^- group from the anion.

The obtained compound is insoluble in water, ethanol and ether, but it is hardly destroyed 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: $[Ni_2(OH)_2 L_2(H_2O)_2 \cdot 0.5H_2O]_n$.

Thermal analysis of Ni(II)-β-hydroxypropionate

In order to confirm the composition and the configuration of the coordination compound ($[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$) as well as to establish the conversions to NiO which promote catalytic activity, the thermal analysis methods have been used. The thermogram corresponding to the decomposition of the $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ in static air atmosphere, at a heating rate of 2,5 K/min is shown in figure 1.

Similar thermograms have also been obtained for the other heating rates.One may observe that through the progressive heating of the studied complex three processes (noted I, II, III) take place with volatile products forming. The process I is endothermic, while the processes II and III are exothermic. We consider the apparent conversion degree of $[Ni_2(OH)_2L_2 (H_2O)_2 \cdot 0.5H_2O]_n$ as being given by the expression:

$$\alpha = \frac{\%\Delta m}{\%\Delta m_t} \tag{1}$$

in which:$\%\Delta m$ represents the percentage of the mass loss at a certain temperature and $\%\Delta m_t$ - the percentage of the total mass loss.

The TG curve in (α,T) coordinates for the heating rate β = 2.5 K/min is shown in figure 2.

Similar curves have also been obtained for the other heating rates.

Figure 3 shows the curves $\ln(d\alpha/dt) \equiv \ln\beta(d\alpha/dt)$ as a function of T, corresponding to the 4 heating rates (t represents the time; $d\alpha/dt$ - the decomposition rate; β - the heating rate, expressed in K/s). In the drawing of the curves in figure 3, the local heating rates have been used, calculated for temperature intervals of maximum 50°C. The curves in this figure are equivalent to the DTG - curves.

The figures 2 and 3 reconfirm the fact that at the progressive heating of $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ three main decomposition processes take place. Table 5 gives the main parameters of the processes I, II, and III.

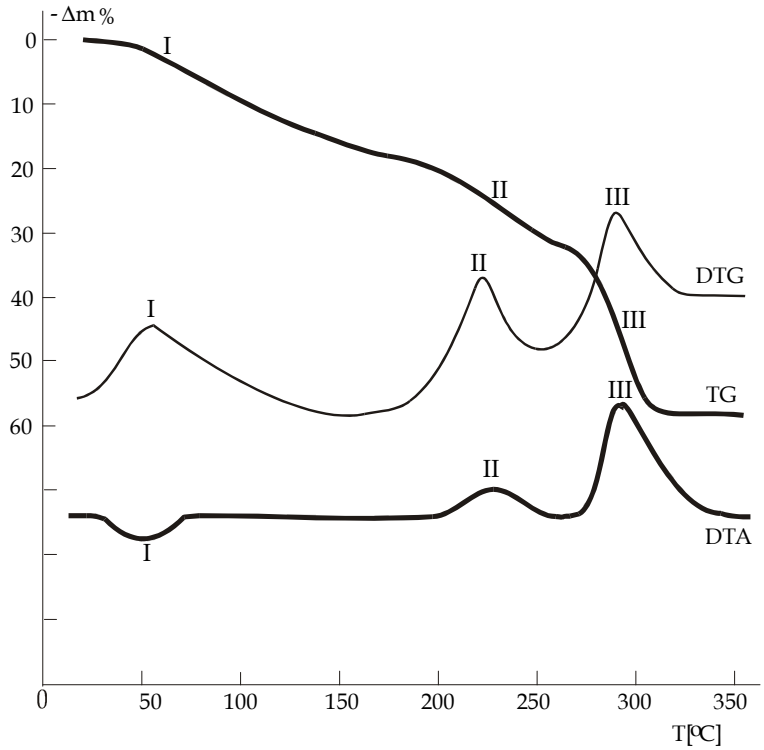

Fig. 1. Thermal analytical curves for the complex combination $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$

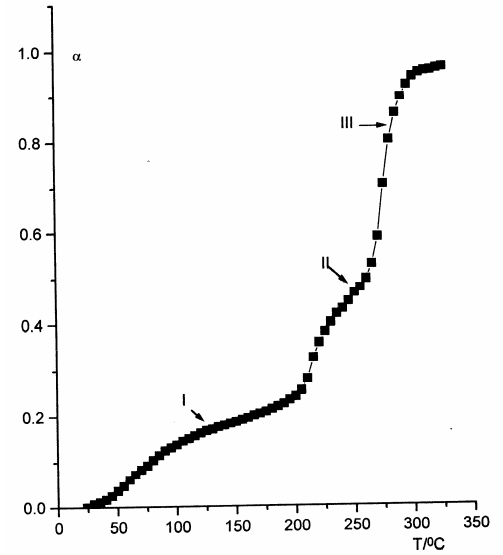

Fig. 2. α - curve as a function of T at the heating rate β = 2.5 K/min.

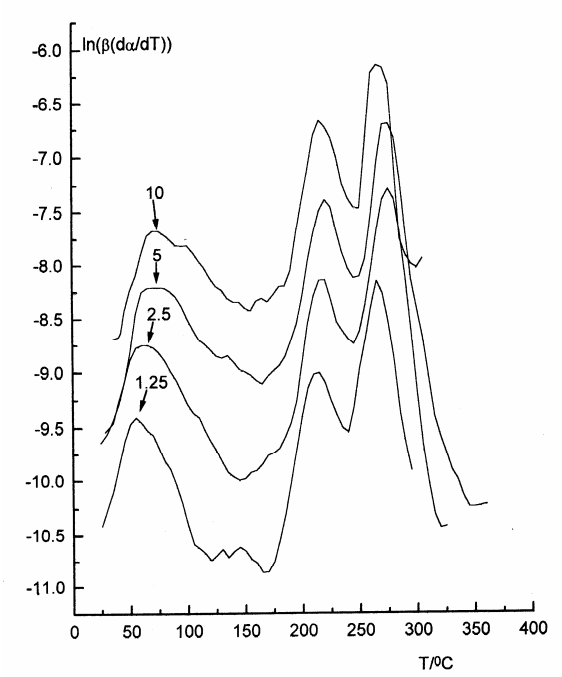

Fig. 3. lnβ(dα/dt) - curves as a function of T at the heating rates for which the thermograms have been recorded.

Table 5.

Characteristic parameters of the processes I, II, and III.

β K/min	Process I ΔT °C	%Δm_1	T_{DTA} °C	T_{DTG} °C
1,25	25-170	12.0	-	55
2,5	24-175	12.9	56	58
5	28-180	13.1	65	56
10	28-200	13.1	80	72
β	**Process II**			
K/min	**ΔT °C**	**%Δm_2**	**T_{DTA} °C**	**T_{DTG} °C**
1,25	170-245	16,1	-	213
2,5	175-255	16,6	235	217
5	180-250	15,3	230	215
10	200-255	13,9	240	217

β	Process III			
K/min	ΔT °C	%Δm_3	T_{DTA} °C	T_{DTG} °C
1,25	245-295	32,9	272	266
2,5	255-305	32,5	280	275
5	250-315	35,4	275	275
10	255-305	36,0	273	267

ΔT - represents the temperature interval in which the process takes place;

$\%\Delta m_i$ - the percentage of the mass loss in the process i (i = 1,2,3);

T_{DTA} - the temperature minimum (for the process I) or the maximum (for the processes II and III) DTA;

T_{DTG} - the temperature of the DTG - maximum;

$\%\Delta m_t$ - the percentage of the total mass-loss.

It must be specified that the delimitation between the processes pointed out in the thermograms is only approximate, which explains the differences of the corresponding mass-losses at different heating rates. Nevertheless, these differences are not very high

($12\% \le \%\Delta m_I \le 13{,}1\%$; $13{,}9\% \le \%\Delta m_{II} \le 16{,}6\%$; $32{,}5\% \le \%\Delta m_{III} \le 36\%$).

The total mass-loss also varies between 61,0% and 63,8%, which may be explained through the unavoidable errors in such determinations. Finally, one may observe, that with the exception of process II, the T_{DTA} values are close to those of T_{DTG}. The process II is characterized through a flat exothermic DTA - peak, which leads to errors in the evaluation of T_{DTA}.

Based on the obtained results, we suggest the following steps for the decomposition of the complex (at the heating rate β = 2.5 K/min):

$$[Ni_2(OH)_2(HO\text{-}CH_2CH_2COO^-)_2(H_2O)_2\cdot 0.5H_2O] \xrightarrow{I\,(24\text{-}175^\circ C)\ -2.5\,H_2O}$$

$$[Ni_2(OH)_2(HO\text{-}CH_2CH_2COO^-)_2] \xrightarrow{II\,(175\text{-}255^\circ C)\ -\ H_2O\ -\ CO_2}$$

$$[Ni_2O(C_5H_{10}O_4)]$$

$$\xrightarrow{III\,(255\text{-}305^\circ C)\ +\ 6\,O_2\ -\ 4\,H_2O\ -\ 6\,CO_2} 2\ NiO$$

Data from table 6 confirm the proposed conversion mechanism.

Table 6.

Mass-loss at the thermal conversion in air of the complex compound, at the heating rate β = 2.5 K/min

Step	I	II	III	I - III
Δm % (calculated)	12.00	16.50	31.50	60.10
Δm % (experimental)	12.90	16.60	32.50	61.90

Ni(II) oxide was the only component of the conversion products as it was proved by X-Ray diffraction, the obtained wave length being in agreement with ASTM 4-835.

Analysing the obtained results, one can observe that the calculated mass-losses are - within the experimental errors - in good agreement with the experimental ones, which supports the proposed formula for the complex compound.

The kinetic analysis of the nonisothermic data has been carried out through the isoconversional method, independently proposed by Flynn and Wall and by Ozawa [23], being based on the expression:

$$\ln \beta = \ln F(\alpha) + \ln \frac{AE}{R} - 2.315 - 1.052 \frac{E}{RT}$$

in which β represents the heating rate, F(α) - the conversion function, E - the activation energy, A - the preexponential factor, T - the thermodynamic temperature and R - the universal gas constant.

According to this relation, at α = constant, the dependence of lnβ as a function of 1/T should be a straight line; from its slope one may evaluate the activation energy, and from the ordinate at the origine - the preexponential factor.

The Flynn-Wall-Ozawa diagrams obtained for the decomposition of $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ are shown in the figures 4 and 5.

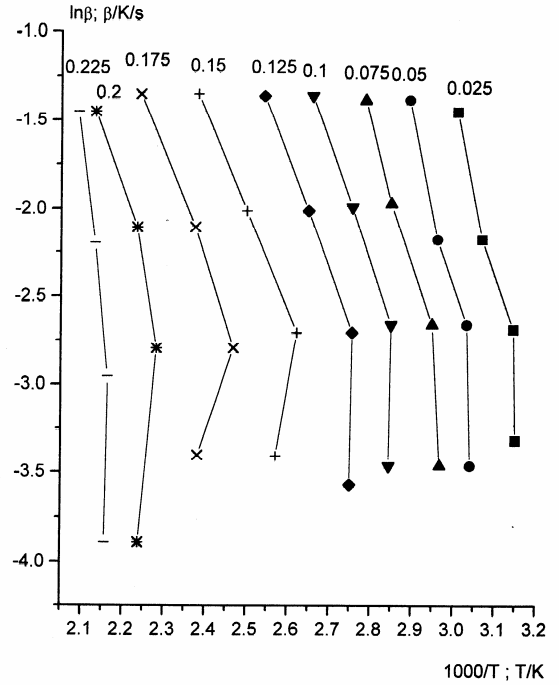

Fig. 4. Flynn-Wall-Ozawa diagram for the decomposition of

$[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$, $0{,}025 \leq \alpha \leq 0{,}225$.

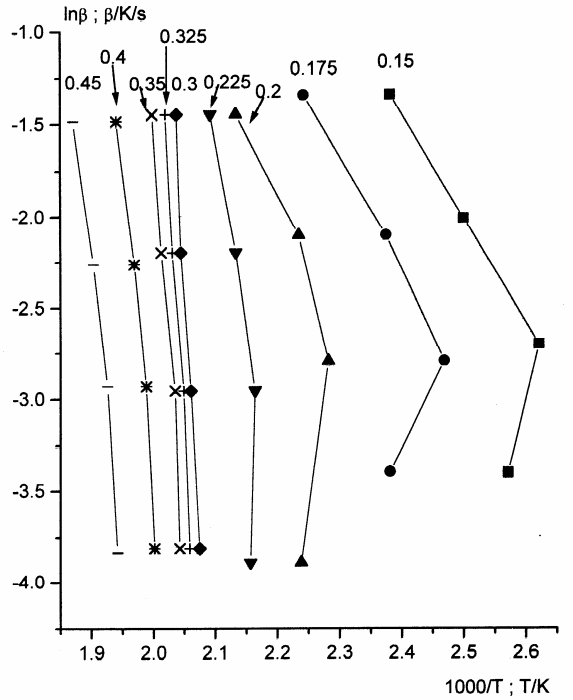

Fig. 5. Flynn-Wall-Ozawa diagram for the decomposition of $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$, $0{,}15 \leq \alpha \leq 0{,}45$.

One may establish that for all the considered α values, the curves $\ln\beta$ as a function of 1/T are not linear, which ascertains that the mechanisms of the decomposition steps of the investigated complex compound suffer modifications with the heating rate and the conversion degree. The use of other differential or integral methods for the evaluation of the kinetic parameters presumes the knowing of the conversion function.

Simplifying assumptions with respect to the analytical form of the conversion function lead to incorrect values for the activation parameters (E and A).

CONCLUSIONS

The coordination compound reported in this paper is a homopolynuclear combination having the formula $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$.

The thermal conversion product obtained at $\approx 300^0$C is NiO.

The kinetic analysis of the nonisothermic data has been carried out through the isoconversional method. The complex character of the processes

I, II, and III of the decomposition of $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ makes the evaluation of their kinetic parameters impossible.

REFERENCES

1. M. Lalia-Kantouri, G. A. Katsoulos, C.C. Hadgi-Kostas and A. D. Magri, *J. Thermal Anal.,* 1989. 35. 2411.
2. T. V. Albu, S. Plostinaru, L. Patron and E. Segal, *J. Thermal Anal.,* 1997. 50. 425.
3. O. Carp, E. Segal, M. Brezeanu, R. Barjega and N. Stanica, *J. Thermal Anal.,*1997. 50. 125.
4. Pocol, L. Patron, O. Carp, M. Brezeanu, E. Segal, N. Stanica and D. Crisan, *J. Thermal Anal.,*1999. 55. 143.
5. M.Bîrzescu, M. Niculescu, M. Ştefănescu and N. Vaszilcsin, *Chem. Bull. "Politehnica" Univ. Timisoara*, 1995. 40. 83.
6. N.Vaszilcsin, M.Birzescu, M.Stefanescu and M.Niculescu, *Bulg.Chem.Comm.*, 1996/1997. 29. 293.
7. M. Niculescu, N. Vaszilcsin, C. Muntean, C.M. Davidescu and M. Bîrzescu, *Chem.Bull. "Politehnica" Univ. Timisoara*, 1998. 43(57). 259.
8. Radoi, M. Birzescu, Fr. Golumbioschi and M. Stefanescu, *Rev. Chim. (Bucharest)*, 1985. 36. 832.
9. Fr. Golumbioschi, M. Birzescu, M. Stefanescu and M. Nemes, *Proc. Applied Electrochemistry Symp.,* Timisoara, 1985, p.399.
10. M. Niculescu, N. Vaszilcsin A.Magda and M. Medeleanu, *Chem. Bull. "Politehnica" Univ. Timisoara,* 1998. 43(57). 149.
11. B. M. Antti, *Acta Chem. Scand.,* 1973. 27. 3513.
12. Fischinger, A. Sarapu and A. Companion, *Can. J. Chem.,* 1969. 47. 2629.
13. E. Konig, *Structure and Bonding,* 1972. 9. 175.
14. P. Spacu, L. Patron, S. Plostinaru, A. Contescu and N. Stanica, *Rev. Roumaine Chim.,* 1989. 34. 1275.
15. M. Brezeanu, L. Patron, O. Carp, M. Andruch and N. Stanica, *Rev. Roumaine Chim.,* 1991. 36. 545.
16. K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc.,* 1961. 83. 4528.
17. P. V. Khadikar, *J. Thermal Anal.,* 1987. 32. 737.
18. Burbaciuc and V. P. Sokolov, *Zh. Obsc. Himii,* 1974. 44. 1626.
19. O. Ilie, *PhD Theses, Politechnical Institute of Bucharest,* 1985.
20. M. Maneva, N. Petroff and M. Pankova, *J. Thermal Anal.,*1990. 36. 577.
21. V. A. Sarov, T. M. Jdanovsky and E. A. Nikonanko, *Z. Neorg. Himii,* 1979. 24. 1489.
22. K. Nagase, K. Sato and N. Tanaka, *Bull. Chem. Soc. Japan,* 1975. 48. 439.
23. E. Segal and D. Fătu, *Introduction in nonisothermal kinetics*, Editura Academiei, Bucureşti, 1981.