Thermal and Kinetic Studies of the Polynuclear Coordination Compound Obtained Through the Reaction of 1,3-propanediol with $Ni(NO_3)_2 . 6 H_2O$

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Our paper presents the experimental results of the thermal analysis of Ni(II)-polynuclear coordination compound having as ligand 3-hydroxypropionate anion (L), which is oxidation product of 1,3-propanediol. The reaction between 1,3-propanediol and $Ni(NO_3)_2 \times 6H_2O$ occurs, under specific working conditions, with the oxidation of 1,3-propanediol to the 3-hydroxypropionate anion ($HO-CH_2-CH_2-COO^-$). The thermal properties of the synthesized polynuclear coordination compound have been investigated by TG, DTG and DTA. The kinetic analysis of the nonisothermal data has been carried out through the isoconversional method. The simple oxide obtained through thermolysis was characterized by IR, X-ray spectroscopy, scanning electron microscopy (SEM) and elemental analysis.

Keywords: 1,3-propanediol; $Ni(NO_3)_2 . 6H_2O$; polynuclear coordination compound, 3-hydroxypropionate, thermal analysis

The thermal conversion of homo- and hetero-polynuclear coordination compounds 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 [1-14].

These compounds decompose at relatively low temperatures, forming simple or mixed oxides and volatile products (CO, CO_2, H_2O).

In our previous papers [15-17] we have reported the results of the study of the oxidation reaction between 1,3-propanediol and $M(NO_3)_2 \times 6H_2O$ (M: Co, Ni), in dilute nitric acid solution. Ni and Co complex combinations synthesized in this original way contain 3-hydroxypropionate anion as ligand.

The present work is included in a series [15-26] devoted to the use of oxidation of diols with metallic nitrates for obtaining coordination compounds, which decompose at relatively low temperature, forming simple or mixed oxides. It represents the completion of the characterization of the polynuclear coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$, having as ligand 3-hydroxypropionate anion (L), performed in our previous papers with the thermal properties of this coordination compound.

Experimental part

The thermal properties of the synthesized polynuclear coordination compound, $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$, was performed in static air atmosphere and also under a nitrogen flow.

Thermal analysis measurements (in the range 20 – 350 °C) 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 at heating rates of:

1.25 K min^{-1}, 2.5 K min^{-1}, 5 K min^{-1} and 10 K min^{-1}; reference material: α-Al_2O_3. Also, thermal analysis measurements were performed by using a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments, Inc.).

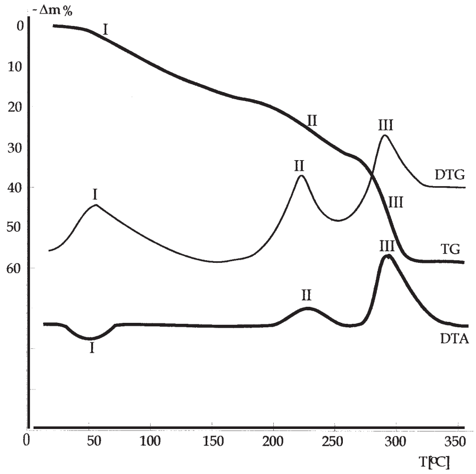

Fig.1. Thermal analytical curves for the coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$

The sample was heated from 20 to 500 °C at a heating rate of 10 K min^{-1} under a nitrogen flow of 60 mL min^{-1}.

Results and discussions

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^{-1} is shown in figure 1.

Similar thermograms have also been obtained for the other heating rates [15].

One may observe that through the progressive heating of the studied complex three processes (noted I, II, III) take place with volatile products formation.

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:

$$\alpha = \frac{\%\Delta m}{\%\Delta m_t} \quad (1)$$

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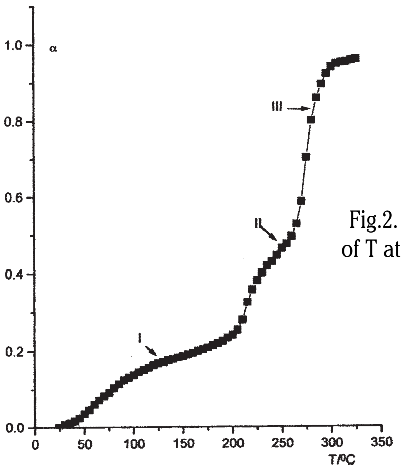

Fig.2. α - curve as a function of T at the heating rate β = 2.5 K min^{-1}

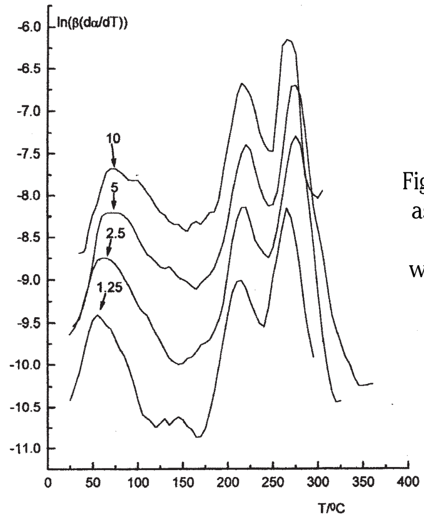

Fig.3. lnβ(dα/dt) - curves as a function of T at the heating rates for which the thermograms have been recorded

Table 1
CHARACTERISTIC PARAMETERS OF THE PROCESSES I, II, AND III

β [K/min]	Process I				Process II				Process III				%Δm$_t$
	ΔT [°C]	%Δm$_1$	T$_{DTA}$ [°C]	T$_{DTG}$ [°C]	ΔT [°C]	%Δm$_2$	T$_{DTA}$ [°C]	T$_{DTG}$ [°C]	ΔT [°C]	%Δm$_3$	T$_{DTA}$ [°C]	T$_{DTG}$ [°C]	
1,25	25-170	12.0	-	55	170-245	16.1	-	213	245-295	32.9	272	266	61.0
2,5	24-175	12.9	56	58	175-255	16.6	235	217	255-305	32.5	280	275	61.9
5	28-180	13.1	65	56	180-250	15.3	230	215	250-315	35.4	275	275	63.8
10	28-200	13.1	80	72	200-255	13.9	240	217	255-305	36.0	273	267	63.0

ΔT - represents the temperature interval in which the process takes place;
%Δm$_i$ - 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;
%Δm$_t$ - the percentage of the total mass-loss.

in which:

%Δm represents the percentage of the mass loss at a certain temperature and %Δm$_t$ - the percentage of the total mass loss.

The TG curve in (α,T) coordinates for the heating rate β = 2.5 K min^{-1} is shown in figure 2.

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

Figure 3 shows the curves lnβ(dα/dt) as a function of T, corresponding to the 4 heating rates (t represents the time; dα/dt - the decomposition rate;β - the heating rate, expressed in K·s^{-1}). 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 1 gives the main parameters of the processes I, II, and III.

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

$$(12\% \leq \%\,\Delta m_I \leq 13.1;\ 13.9 \leq \%\Delta m_{II} \leq 16.6\%;\ 32.5\% \leq \%\Delta m_{III} \leq 36\%).$$

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^{-1}):

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

$$[Ni_2(OH)_2(HO\text{-}CH_2CH_2COO^-)_2] \xrightarrow{II\,(175\text{-}255°C)\,-\,H_2O\,-\,CO_2} [Ni_2O(C_5H_{10}O_4)]$$

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

Data from table 2 confirm the proposed conversion mechanism.

Table 2
MASS-LOSS AT THE THERMAL CONVERSION IN AIR OF THE COMPLEX COMPOUND, AT THE HEATING RATE β = 2.5 K·min^{-1}

Step	I	II	III	I - III
Δm % (calculated)	12.0	16.5	31.5	60.1
Δm % (experimental)	12.9	16.6	32.5	61.9

Ni(II) oxide was the only component of the conversion products.

Analyzing the obtained results, one can notice 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, 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 origin - 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.

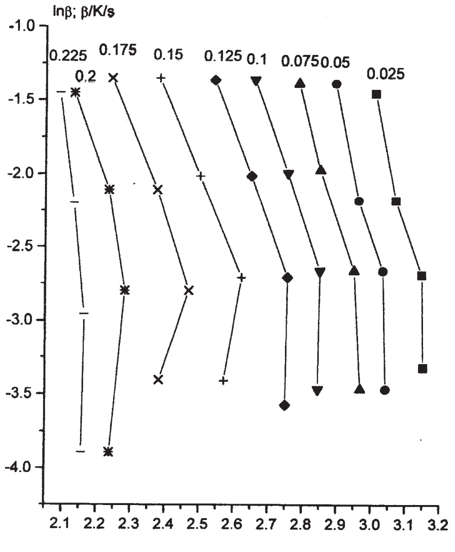

Fig.4. Flynn-Wall-Ozawa diagram for the decomposition of $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$, 0,025 ≤ a ≤ 0,225

One may establish that for all the considered α values, the curves lnβ 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 knowledge of the conversion function.

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

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 by only simple thermal analysis.

The thermal conversion product obtained at ~ 350°C is NiO.

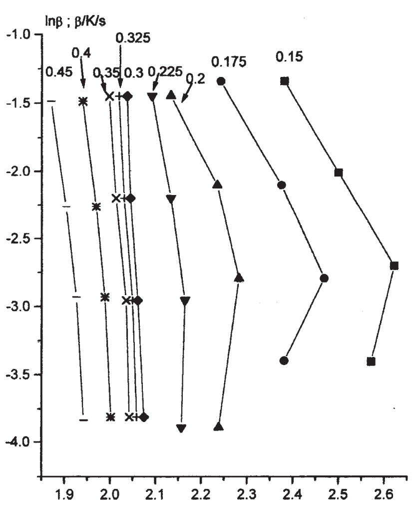

Fig.5. Flynn-Wall-Ozawa diagram for the decomposition of $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$, 0,15 ≤ α ≤ 0,45

The infrared spectrum of this thermal decomposition product (fig. 6) shows two absorption bands at 440 and 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}).

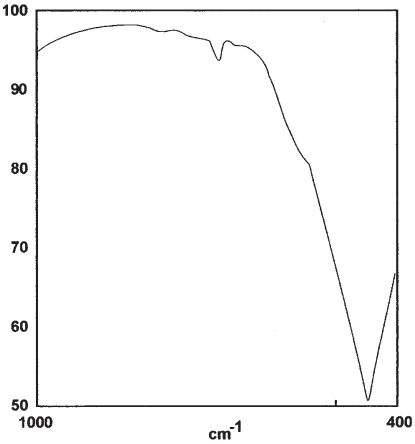

Fig. 6. IR vibrational spectrum of nickel (II) oxide

Nickel oxide obtained by the thermal conversion in air of the synthesized coordination compound $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$ is a product with very different crystalline morphology. The particles exhibit irregular shapes and their size is widely distributed between 10 nm and 5μm. The crystalline structure of obtained NiO was evaluated by X-ray diffraction (XRD) and its microstructure was examined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis. The XRD pattern of the NiO sample (fig. 7) shows the presence of the characteristic peaks for NiO, in the range of 35 – $100^0 2\theta$, in accordance with JCPDS 47 – 1049.

As it can be seen, the sample is relatively well crystallized.

A quantitative elementary analysis of very small areas using the EDX technique revealed that the product of thermal decomposition of the complex is a non-stoichiometric oxide.

Thermal behaviour of the coordination compound was also studied under a nitrogen flow of 60 mL min^{-1}, in the temperature range of 20-500°C with a heating rate of 10°C min^{-1} (fig. 8).

The obtained residue (decomposition product) in this case is metallic Ni.

In the temperature range of 20-50°C the crystallization water ($0.5H_2O$) is lost. In the V step, the thermal

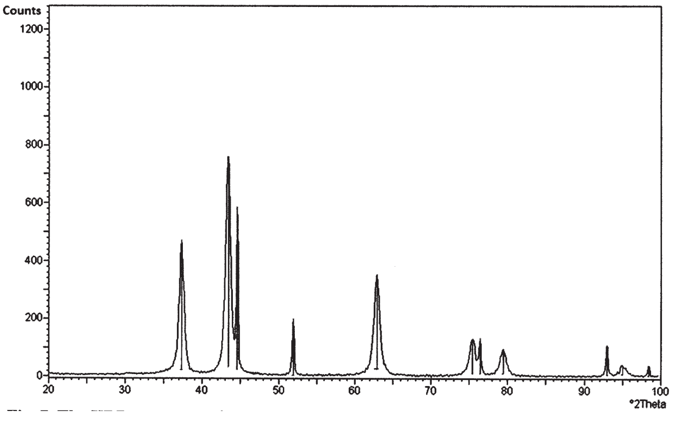

Fig. 7. The XRD spectrum of the solid product obtained by thermal conversion in air of the polynuclear coordination compound $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$

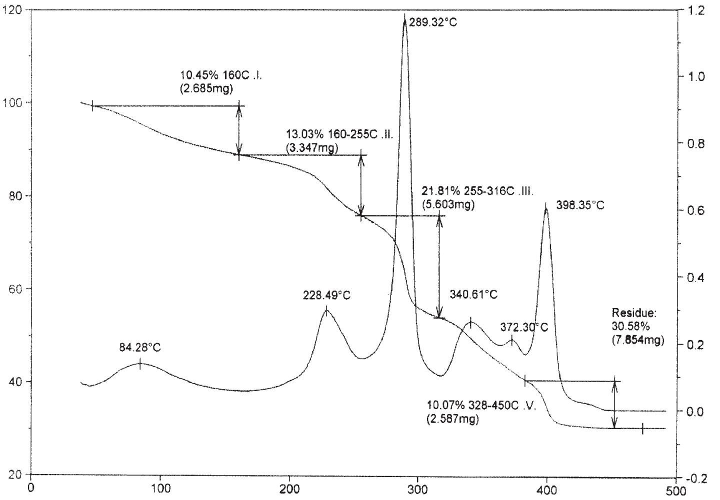

Fig.8. Thermal analytical curves for the coordination compound decomposition in nitrogen atmosphere at the heating rate of 10 K min^{-1}

Table 3

THE MASS LOSS DURING THE THERMAL CONVERSION IN NITROGEN OF THE INVESTIGATED COMPOUND

Step	I	II	III	IV	V	I - V
Δm % (calc.)	**9.84**	**14.01**	**21.54**	**14.13**	**9.02**	**68.54**
Δm % (experim.)	**10.45**	**13.03**	**21.81**	**14.06**	**10.07**	**69.42**

decomposition of the intermediates by redox reactions leads to gaseous products including a mixture of (CO, H_2O, C_nH_m).

The thermal analytical curves, showed in figure 8, suggest the following decomposition steps which occur during the progressive heating of the coordination compound:

$$2[Ni_2(OH)_2(HOCH_2CH_2COO^-)_2(H_2O)_2] \xrightarrow{I\,(50\text{-}160°C)\ -4\,H_2O}$$

$$2[Ni_2(OH)_2(HOCH_2CH_2COO^-)_2] \xrightarrow{II\,(160\text{-}255°C)\ -6\,H_2O}$$

$$2[Ni_2O(OC_3H_3O^-)_2)] \xrightarrow{III\,(255\text{-}316°C)\ -2CO_2\ -2{,}5CO}$$

$$[Ni_4O_2(C_{7.5}H_{12}O_{1,5})] \xrightarrow{IV\,(316\text{-}382°C)\ -2\,CO\ -1{,}85\,C_2H_2}$$

$$[Ni_4O_{1.5}C_{1.8}H_{8.3}] \xrightarrow{V\,(382\text{-}450°C)\ -x\,CO\ -y\,H_2O\ -z\,C_nH_m} 4\,Ni$$

(where: x + zn = 1,8; x + y = 1,5; 2y + zm = 8,3)

Thermal behaviour of the coordination compound in nitrogen proves the complexity of the thermal decomposition mechanism.

Data from table 3 confirm the proposed conversion mechanism.

Analyzing the thermoanalytical curves, obtained in nitrogen, we may conclude that the thermal decomposition process of the investigated polynuclear coordination compound is very complex. The effective decomposition of the synthesized compound take place in the temperature range of 250 - 400 °C by a multiple stage redox process.

Under such circumstances the evaluation of the kinetic parameters for certain steps of the decomposition have no relevance, and a more complex process analysis including derivation of species kinetic curves is necessary in this respect.

Conclusions

Analyzing the thermoanalytical curves, obtained both in air and nitrogen, we may conclude that the thermal decomposition processes of the investigated polynuclear coordinative compound presents a high complexity. The kinetic analysis of the nonisothermic data has been carried out through the isoconversional method. The complex character of the processes of the decomposition of $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$ makes the determination of their kinetic parameters practically impossible by simple thermo-gravimetric measurements.

Under such circumstances, the evaluation of the kinetic parameters for certain steps of the decomposition of $[Ni_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$ (with L = 3-hydroxy-propionate) is beyond the scope of this paper. Our study proves experimentally the existence of at least three successive decomposition steps of this organo-metallic compound, the first being endothermic while the last two exothermic. We consider that such suppositions hold also for other compounds presenting a high structural complexity.

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