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

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Abstract

The results of an investigation concerning the reaction between 1,2-propanediol and $Co(NO_3)_2{\cdot}6H_2O$, leading to a complex containing the lactate anion (*L*) as ligand are presented. The obtained solid homopolynuclear coordination compound $[Co_2(OH)_2L_2(H_2O)_2{\cdot}0.5H_2O]_n$, has been investigated by thermal analysis, electronic and IR spectroscopy and magnetic methods. Cobalt oxide obtained by thermal decomposition of this coordinative compound was characterized by IR and X-ray spectroscopy.

Keywords: homopolynuclear coordination compound, hydroxylactate, nitrate, propanediol, thermal analysis

Introduction

In order to obtain 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) new methods for their synthesis are necessary.

In this respect it is to be mentioned the thermal conversion of homo- and heteropolynuclear complexes with anions of carboxylic acids as ligands [1–14]. Such ligands include the anions glyoxylate, malonate, succinate and lactate [15–22]. 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 as well as Ni(II), Cu(II) heteropolynuclear glyoxylates [23, 24] led to non-stoichiometric oxides of the corresponding metal.

This paper presents the results obtained at the investigation of 1,2-propanediol oxidation with $Co(NO_3)_2 \cdot 6H_2O$. The obtained coordination compound was investigated from the composition and physico-chemical properties standpoints. It will be shown that it can be a precursor for Co_3O_4 obtained at relatively low temperatures.

Experimental

For the synthesis of the coordination compound, $Co(NO_3)_2 \cdot 6H_2O$, '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 heating curves (TG, DTG, DTA) corresponding to the synthesis and the decomposition of the coordination compound were recorded on a Q-1500D MOM-Budapest derivatograph, in static air atmosphere and the temperature range 20–500°C, at a heating rate of 5°C min^{-1}.

The coordination compound was also characterized by the following methods: chemical analysis, IR spectroscopy, electronic spectroscopy (diffuse reflectance technique) and magnetic techniques.

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}.

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 cobalt 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 synthesis of the coordination compound worked out by us, is based on the oxidation reaction of 1,2-propanediol in alcohol-water system by cobalt nitrate and the simultaneous isolation of the complex compound in the reaction system.

A solution of water+diol+$Co(NO_3)_2 \cdot 6H_2O$ in the molar ratio 1,2-propanediol: $Co(NO_3)_2 \cdot 6H_2O$=3:2 was prepared. This mixture was heated during 20 h in a thermostat, gradually up to 130°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 brown product was washed with acetone and finally it was maintained in air until constant mass.

The thermal behaviour of an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$–1,2-propanediol has been investigated. The heating of solution in a plate shaped platinum crucible has been performed in static air atmosphere at temperatures, between 20 and 500°C, using a heating rate of 5°C min^{-1} and α-Al_2O_3 as reference material. The DTA curve recorded in air exhibits an exothermic peak located at 130°C. The TG and DTG curves recorded in the same conditions, show a mass loss in the temperature range 120–150°C. The DTA peak is assigned to oxidation processes. As far as the mentioned mass loss is concerned, it corresponds to NO_2 release ($NO+\frac{1}{2}O_2 \rightarrow NO_2$) coupled with the simultaneous complex formation.

The evolution of the reaction between 1,2-propanediol and $Co(NO_3)_2{\cdot}6H_2O$ was also investigated by IR spectroscopy.

As the reaction advances the bands in the 1700–1800 cm^{-1} region due to nitrate ion decreases in intensity, proving that nitrate ion is consumed in reaction [25].

At the same time, the appearance and the increase of band intensity in the range 1580–1650 cm^{-1} ($\nu_{as}COO^-$) 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.

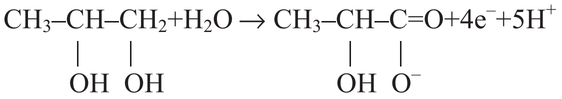
In order to separate and identify the ligand, the complex has been treated with RH cationite. After the retention of the metal cation, the resulted lactic acid has been identified by specific reactions (haloform reaction, reaction with $FeCl_3$ solution, reaction with $KMnO_4$ solution).

The elemental analysis results (Table 1) as well as the IR investigation confirm the following empirical chemical formula for the coordination compound: $Co(OH)L(H_2O){\cdot}0.25H_2O$, where *L* is the lactate anion.

Table 1 Composition and elemental analysis data

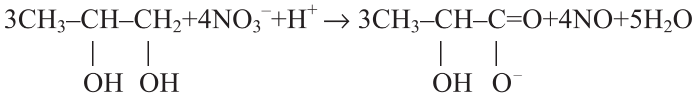
Compound (composition formula)	Co(II)/%		C/%		H/%	
	calc.	experim.	calc.	experim.	calc.	experim.
$Co(OH)L(H_2O){\cdot}0.25H_2O$	31.44	31.20	19.20	19.38	4.53	4.36

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 $Co(NO_3)_2{\cdot}6H_2O$ 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 $Co(NO_3)_2$:



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

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



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

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

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

$$NO+\tfrac{1}{2}O_2 \rightarrow NO_2 \qquad (2)$$

From these 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 necessary protons are generated by Co(II) hydrated cation hydrolysis, as shown in the d) step.

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.

Diffuse reflectance spectrum of Co(II)-hydroxy-lactate

The diffuse reflectance spectrum of the coordination compound shows the presence of the characteristic bands of the Co(II) hexacoordinated ion namely (Fig. 1).

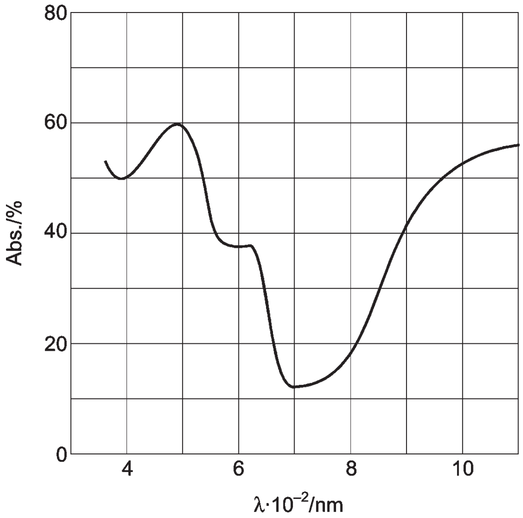


Fig. 1 Diffuse reflectance spectrum of Co(II)-hydroxy-lactate

The band due to the ν_3 transition could be distinguished:

$$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)\ (\lambda{=}495\ \text{nm})\ \text{Co(II) – high spin.}$$

The shoulder from ≈630 nm is due to the transition:

$$\nu_2\text{: } {}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$$

The results are in agreement with those from literature referring to Co(II) lactate [26].

Octahedral configuration of Co(II) – high spin is confirmed by the effective magnetic moment value (4.86 MB), higher than the corresponding to spin value (3.88 MB), suggesting a contribution of the orbital component, specific to complexes having fundamental term *T*.

Accordingly the Co(II) ion exists in the fundamental state $t_{2g}^5 e_g^2$, high spin, the three ligands OH, *L*, H_2O being of low field and of similar strength.

IR vibrational spectrum of Co(II)-hydroxy-lactate

The structure of synthesized complex and pseudo-octahedral configuration of the cobalt(II) ion are verified also by the infrared spectrum (Fig. 2).

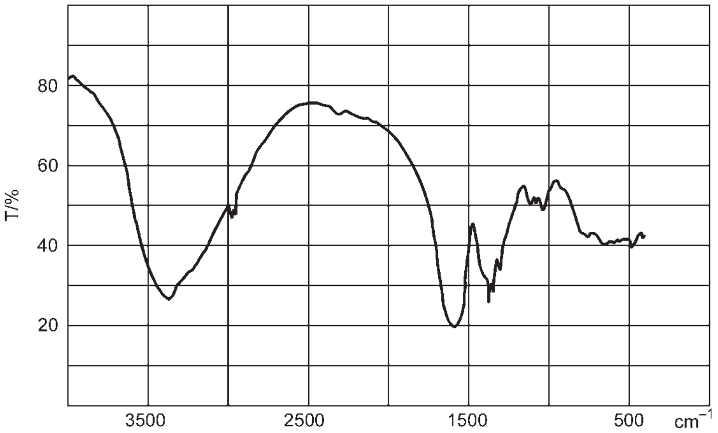


Fig. 2 IR vibrational spectrum of Co(II)-hydroxy-lactate

Table 2 shows the characteristic bands in IR (cm^{-1}) for solid and brown coloured complex and the corresponding assignments.

Table 2 Characteristic absorption bands in IR for Co(II)-hydroxy-lactate and the corresponding assignments

ν(OH)/	ν_{as} (COO$^-$)/	ν_s (COO$^-$)/	ν_s (CO)+ δ(OCO)/	ν(C–OH)/	ν(OH bridge)/	ν(OCO) +νMO)/	ρ_w(H_2O)/
			cm^{-1}				
3400	1595	1380, 1360	1300	1127, 1087	1040	780	670

The intensive and large band in the range 3200–3600 cm^{-1} with maximum at ≈3400 cm^{-1} is attributed to the formation of the hydrogen bonds between water molecules and the alcoholic hydroxyl [27, 28].

The intense band at 1595 cm^{-1} is attributed to asymmetrical vibration of the carboxylate ion and the value shows that the resonance from carboxylate group is maintained during complex formation, metal-carboxylate bond being prevailing an ionic one [29].

The low intensity band with maximum at 1380 cm^{-1} is attributed to the symmetric vibration $\nu_s(COO^-)$. As the difference between $\nu_{as}-\nu_s$ is higher 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 [29, 30]. Also, the existence of the two bands for $\nu_s(COO)$ could be explained through the octahedral deformation [31].

The band at 1300 cm^{-1} confirms that carboxylate group is acting as bidentate ligand [32].

In the vibrational spectrum of lactic acid [26] two bands are present at 1127 and 1087cm^{-1} both attributed to the C–OH vibration. The fact that in the spectrum of this complex these bands appear at the same values and that they are not shifting towards lower numbers permits to presume that OH alcoholic group does not take part in the coordination process.

The band at 1040 cm^{-1} is attributed to the vibration of the OH bridge group [33].

The band of mean intensity at 780 cm^{-1} is attributed to the group of vibrations $\delta(OCO)+\nu(MO)$ [32].

The coordination of the two water molecules to the Co(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.* [34].

In accordance with Nagase *et al.* [35], the 480 cm^{-1} band, obtained for the investigated complex can be attributed to the $\nu(MO)$-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:

$$[Co_2(OH)_2\,L_2(H_2O)_2 \cdot 0.5H_2O]_n$$

Thermal conversion of Co(II)-hydroxy-lactate

In order to confirm the composition and the configuration of the coordination compound ($[Co_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$) as well as to establish the steps of conversion to Co_3O_4, the thermal analytical methods (TG, DTG, DTA) have been used [36, 37]. The obtained TG, DTG and DTA curves, shown in Fig. 3, suggest the following steps which occur at the progressive heating of the coordination compound:

$$3[Co_2(OH)_2(H_3CCH(OH)COO^-)_2(H_2O)_2{\cdot}0.5H_2O] \xrightarrow{I\,(30-120\,^\circ C)-7.5H_2O}$$

$$\rightarrow 3[Co_2(OH)_2(H_3CCH(OH)COO^-)_2] \xrightarrow{II\,(120-200\,^\circ C)-6H_2O}$$

$$\rightarrow 3[Co_2O(C_4H_8O(COO^-)_2] \xrightarrow{III\,(200-380\,^\circ C)+17.5O_2-12H_2O-18CO_2}$$

$$\rightarrow 2Co_3O_4\ (\equiv 2CoO{\cdot}Co_2O_3)$$

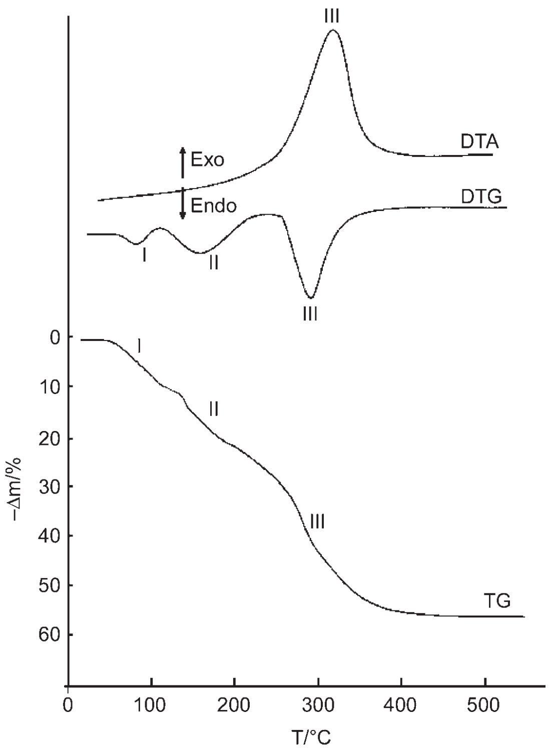


Fig. 3 TG, DTG and DTA curves of the coordinative compound decomposition

Data from Table 3 confirm the proposed conversion mechanism.

Table 3 The mass loss during the thermal conversion in air of the investigated compound

Step	I	II	III	I–III
Δm/% (calculated)	12.0	9.6	37.0	58.6
Δm/% (experimental)	12.5	10	35.5	58.0

The IR spectrum of the conversion product obtained at 500°C exhibits only the bands characteristic of the spinel Co_3O_4 namely: $\nu_1[Co^{III}O_6]$=665 cm^{-1} and $\nu_2[Co^{II}O_4]$= 570 cm^{-1} the results being in agreement with literature data [38].

The X-ray diffractogram confirms the formation of Co_3O_4.

As one can observe from Fig. 3, for the two losses of water (processes I and II), the DTA curve does not exhibit endothermic minima. This fact could be explained by the exothermic effect of a crystallization process caused by increasing the Co(II)-lactate bond strength.

The strong exothermic effect that characterizes III step is due to the ligand combustion (maximal at 300°C) and respectively to the partial oxidation of Co(II) to Co(III) by oxygen leading to the spinel formation [39].

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

– for the combination $[Co_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ water is lost at a temperature before 120°C which shows that some water molecules are coordinated to cobalt(II) ion confirming our supposition,

– the fact that one could not do a thermal separation between the loss of the two coordinated water molecules and of the crystallization water is explained by the fact that the two 'types of water' are involved in a strong hydrogen bond [40].

Conclusions

The oxidation of 1,2-propanediol by Co(II) nitrate was carried out at a moderate temperature, and 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 new method is a homopolynuclear combination with the formula $[Co_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$; this complex has been investigated by elemental analysis, thermal analysis (TG, DTG and DTA), electronic 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 cobalt(II) ion.

The thermal conversion product obtained at 500°C is Co_3O_4.

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