

# Synthesis, structural characterization and thermal analysis of the cobalt(II) oxalate obtained through the reaction of 1,2-ethanediol with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

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Received: 20 January 2008 / Accepted: 8 December 2008 / Published online: 19 June 2009  
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**Abstract** The homopolynuclear coordination compound  $[\text{CoL} \cdot 2.5\text{H}_2\text{O}]_n$  with  $\text{L}=\text{C}_2\text{O}_4^{2-}$  was synthesized by a new unconventional method. It consist in the redox reaction between 1,2-ethanediol and cobalt nitrate in presence of nitric acid. The coordination compound was characterized by chemical analysis, electronic and vibrational spectra respectively, thermal analysis. In the coordination compound the Co(II) ion exists in a high spin octahedral configuration and oxalate anion acts as double-bridge ligand, tetradentate, similar as in  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  obtained by the classical method. Nonstoichiometric oxide,  $\text{Co}_3\text{O}_{4+0.25}$  with deficit in cobalt and normal spinel  $\text{Co}_3\text{O}_4$  where identified as thermal decomposition intermediates. As final product of decomposition, the oxide CoO was obtained.

**Keywords** 1,2-Ethanediol · Nitrate · Cobalt(II) oxalate · Nonstoichiometric mixed oxide · Normal spinel

## Introduction

The need of oxide systems with well-defined structure and properties, required by the modern technology in various fields (such as ceramic pigments, heterogeneous catalysis and electrocatalysis, electronics, drug industry, etc.), has determined the development of new unconventional methods for their synthesis. Among them, the thermal conversion of homo- and heteropolynuclear complexes with anions of carboxylic acids as ligands is to be mentioned [1–14].

In our previous papers [15–24] we reported an original route of synthesis coordination compounds, precursor of simple and mixed oxides. This consist in a redox reaction of diols (1,2-ethanediol, 1,2-propanediol or 1,3-propanediol) with some metallic nitrates, in the absence or presence of nitric acid. The oxidation of the diols leads to the formation glyoxylate, lactate, malonate or 3-hydroxypropionate anion, coordinated as ligands to the metallic cations. Such coordination compounds decompose at relatively low temperatures, forming the simple or mixed oxides and, evolving volatile products such as CO, CO<sub>2</sub>, H<sub>2</sub>O.

It is worth to mention here, that the synthesis method is a versatile one, being possible to obtain different precursors by ranging the experimental conditions. For example it is possible to conduct the oxidation of 1,2-ethanediol either oxalate or glyoxylate anion [25–27]. Such coordination compounds were already used in synthesis of metallic powders, alloys and oxide catalysts. The formation of homo- and heteropolynuclear glyoxylates of Co(II) and Ni(II) on a steel matrix and their thermal decomposition to nonstoichiometric oxides,  $\text{Co}_3\text{O}_{4+x}$  respectively  $\text{NiO}_{1+x}$ , made possible the obtaining of anodes with electrocatalytically active films for the oxygen evolution during electrolysis of alkaline solutions [25, 28]. On the other

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hand, after the cathodic prepolarization of the obtained nonstoichiometric oxides, cathodes with electrocatalytically active metallic films (Ni, Ni–Cu) for the hydrogen evolution at the electrolysis of alkaline solutions were obtained [25].

Because  $\text{Co}_3\text{O}_4$  represents an oxide with various applications [29–32], our present paper reports the synthesis of this oxide by the thermal decomposition of an oxalate coordination compound precursor, obtained during the reaction of 1,2-ethanediol with cobalt nitrate in the presence of nitric acid.

## Experimental

### Chemicals and methods

For the synthesis of the coordination compound,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Reactivul, Romanian company), with minimal purity of 99%, 1,2-ethanediol (Reactivul, Romanian company) with purity of 99% and 1 M nitric acid solution were used. The impurities from the reagents do not influence the synthesis and the purity of the obtained compound as they are removed in the subsequent purification step.

The water content was determined gravimetrically and the cobalt content was estimated using standard methods. Carbon and hydrogen were analyzed using a Carlo Erba 1108 elemental analyzer. The IR spectra (KBr pellets) of the compound and of the decomposition products were recorded on a Jasco FT-IR spectrophotometer, in the range  $400\text{--}4,000\text{ cm}^{-1}$ . The diffuse reflectance spectrum of the synthesized compound was recorded with a spectrophotometer Spekol 10 Carl Zeiss Jena using  $\text{MgO}$  as reference material. Simultaneous TG–DTA curves under non-isothermal conditions were obtained with a Derivatograph Q 1500 D Paulik–Paulik–Erdey in static air atmosphere between 25 and  $1,000\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Sample of  $\sim 60\text{ mg}$  was placed in Pt crucible with the diameter of 10 mm. As inert reference compound  $\alpha\text{-Al}_2\text{O}_3$  was used. The powder X-Ray diffraction patterns of the decomposition products were recorded at room temperature with a BRUKER D8 Advance diffractometer with zirconium filter, using  $\text{Mo K}_\alpha$  radiation ( $\lambda = 0.7093\text{ \AA}$ ). 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 method of the coordination compound is based on the oxidation reaction of 1,2-ethanediol in an alcohol–water system by cobalt nitrate and nitric acid with

the simultaneous isolation of the from the reaction system complex compound. A water solution containing diol,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and nitric acid in the molar ratio 1,2-ethanediol: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ : $\text{HNO}_3 = 1.5:1.5:1$  was used. This mixture was heated in a water bath for  $\sim 30\text{ min}$  at  $\sim 90\text{ }^\circ\text{C}$ . The reaction was considered completed when no gas evolution was observed. The solid reaction product was purified by refluxing from an acetone–water mixture. The solution was filtered and the solid pink product was washed with acetone and finally maintained in air until constant mass. The reaction yield was nearly quantitative.

## Results and discussion

### The synthesis and characterization of the coordination compound

The progress of the reaction between 1,2-ethanediol and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was investigated by IR spectroscopy. As the reaction advances the bands due to the nitrate ion respectively 1,2-ethanediol decreases in intensity, proving that both reactants are consumed. At the same time, the appearance and the increase of the intensity of the band assigned to  $\nu_{\text{asym}}\text{COO}^-$  vibration in the range of  $1,580\text{--}1,680\text{ cm}^{-1}$  is observed. This band is specific to the ligands that contain at least two oxygen atoms as donors such as the carboxylic anions [19, 25, 33, 34].

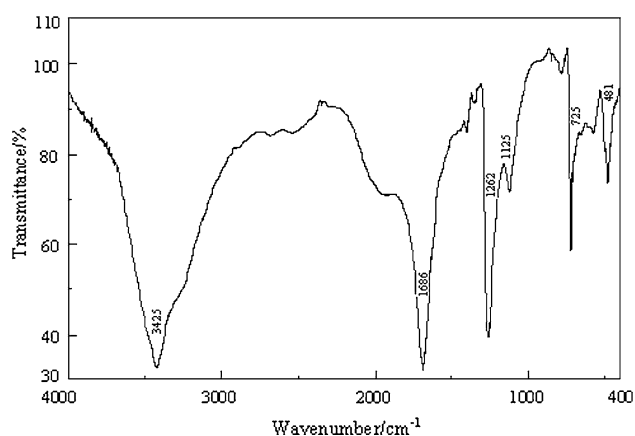
The elemental analysis results (Table 1) have indicated that the synthesized coordination compound has the  $\text{CoL} \cdot 2.5\text{H}_2\text{O}$  empirical chemical formula, where L is oxalate anion.

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 metallic cations, at the evaporation of the obtained solution,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  was isolated in a solid state. The elemental analysis confirms its presence: C experim./calc. (%) = 19.12/19.04 and H experim./calc. (%) = 4.68/4.76. The IR spectrum of isolated oxalic acid (Fig. 1) is similar with the one reported by literature [35; <http://www.chemistry.or.jp/journals/bcsj/bc-cont/bc70-10.html#ke70289cnt.html>].

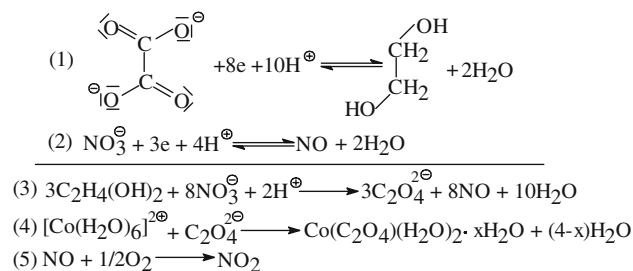
At the same time the resulted oxalic acid has been identified also by specific reactions: (a) the reaction with  $\text{KMnO}_4$  solution with the precipitation  $\text{MnO}_2$ , (b) the reaction with resorcin in sulphuric acid medium with the appearance of a blue ring, (c) the reaction with  $\text{CH}_3\text{COONa}$  followed by  $\text{CaCl}_2$  solution with the deposition of a very fine white precipitate of calcium oxalate, (d) the reaction with concentrated  $\text{H}_2\text{SO}_4$  with the burning of the carbon oxide generated during the reaction with a characteristic blue flame.

**Table 1** Composition and elemental analysis data

Compound (composition formula)	Co(II) (%)		C (%)		H (%)	
	Calc.	Experim.	Calc.	Experim.	Calc.	Experim.
CoL · 2.5H <sub>2</sub> O	30.70	31.20	12.50	12.76	2.60	2.45

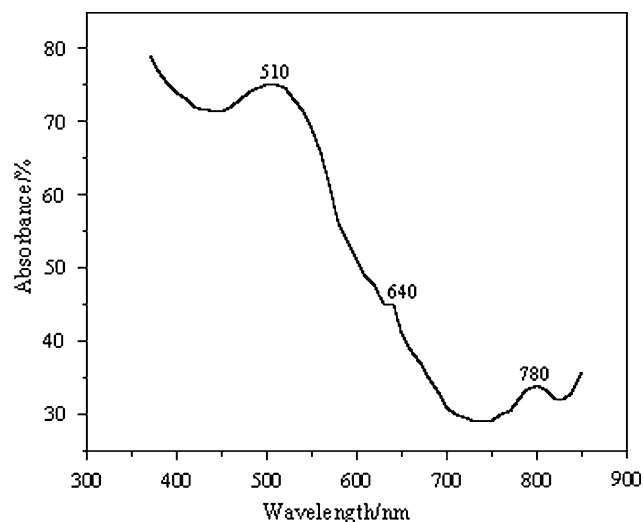

**Fig. 1** IR vibrational spectrum of the oxalic acid

These results as well as those previously reported [24, 25] concerning the oxidation of 1,2-ethanediol with metallic nitrates suggest that the oxidation of the 1,2-ethanediol with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  occurs, in distinct working conditions, to oxalate anion that is coordinated to Co(II). Thus, we suggest the following mechanism for the reaction between 1,2-ethanediol and  $\text{Co}(\text{NO}_3)_2$  in acid medium:



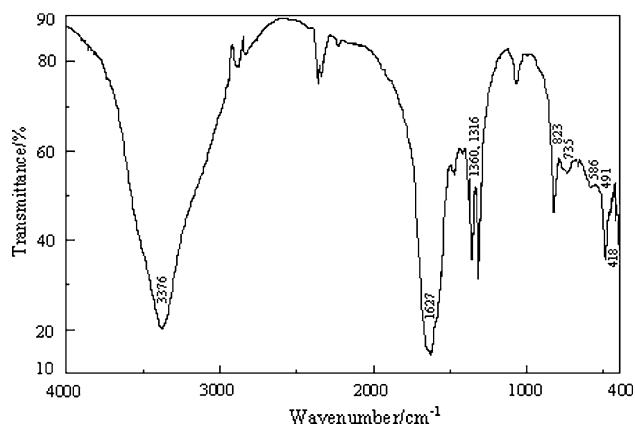
The diffuse reflectance spectrum of the coordination compound shows the presence of the characteristic bands of the Co(II) hexacoordinated ion in a high spin (pseudo)octahedral environment and high spin tetrahedral configuration (Fig. 2). The shape of the electronic spectrum, the width and asymmetry of the bands is a proof both for the deformation of octahedral coordination and, for the equilibrium between the octahedral configuration (predominant) and the tetrahedral stereochemistry of the Co(II).

The spectrum exhibit an absorption band at  $19,608 \text{ cm}^{-1}$  ( $\lambda = 510 \text{ nm}$ ) which may be assigned to the  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  ( $\nu_3$ ) transition, characteristic to Co(II) ion in a high spin octahedral configuration. The shoulder at about  $15,625 \text{ cm}^{-1}$  ( $\lambda = 640 \text{ nm}$ ) may be assigned to


**Fig. 2** Diffuse reflectance spectrum of the coordinative homopoly-nuclear compound  $[\text{CoL} \cdot 2.5\text{H}_2\text{O}]_n$ 

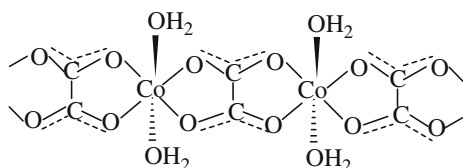
the  ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  ( $\nu_2$ ) transition. The results are in good agreement with those from the literature [11]. As a result, the Co(II) ion exists (predominant) in the fundamental state  $t_{2g}^5 e_g^2$ , high spin, both ligands,  $\text{C}_2\text{O}_4^{2-}$  and  $\text{H}_2\text{O}$  being of low field and of similar strength. The low intensity band at  $12,821 \text{ cm}^{-1}$  ( $\lambda = 780 \text{ nm}$ ) may be assigned to the  ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2$  transition, characteristic to Co(II) ion in a high spin tetrahedral configuration.

The IR spectrum of the coordination compound (Fig. 3), shows an intense and broad band in the range  $3,000\text{--}3,600 \text{ cm}^{-1}$  with a maximum at  $3,376 \text{ cm}^{-1}$ , due to the vibration  $\nu(\text{OH})$  from coordinated water as well as due to


**Fig. 3** IR vibrational spectrum of the homopoly-nuclear coordination compound  $[\text{CoL} \cdot 2.5\text{H}_2\text{O}]_n$

the strong hydrogen bonds between the water molecules and the oxalate ligand. A medium absorption band at  $823\text{ cm}^{-1}$ , respectively the weak absorption band at  $735\text{ cm}^{-1}$  confirms also the presence of water in the coordinated form [4, 36]. The weak absorption band at  $586\text{ cm}^{-1}$  is attributed to lattice water [37]. The absence of the bands in the range  $1,720\text{--}1,650\text{ cm}^{-1}$  attributed to of the vibration  $\nu_{\text{asym}}(\text{C}=\text{O})$  characteristic  $\text{C}_2\text{O}_4^{2-}$  bidentate bonded [38, 39], is a proof that the resonance of the carboxylate groups is realized and the four oxygen atoms are equivalent. Such behaviour is characteristic for the oxalate dianion acting as bridging ligand [40]. The intense band at  $1,627\text{ cm}^{-1}$  is attributed to the vibration  $\nu_{\text{asym}}(\text{OCO})$  and the its value shows that the Co(II)–carboxylate bond is preponderent ionic [34, 41]. The band at  $1,360\text{ cm}^{-1}$  is assigned to the vibration  $\nu_{\text{sym}}(\text{OCO})$  [42]. The difference  $\nu_{\text{asym}} - \nu_{\text{sym}}$ , higher than  $170\text{ cm}^{-1}$ , is evidence that the metal–carboxylate bond is really preponderantly ionic, and the carboxylate groups acts as a bidentate ligand [40]. At the same time, the value for  $\nu_{\text{sym}}(\text{OCO})$ ,  $1,360\text{ cm}^{-1}$ , and  $\delta(\text{OCO})$  found at  $1,316\text{ cm}^{-1}$ , are in agreement with the position of the corresponding absorption in the oxalate-bridged Co(II) complex [43]. The very sharp and medium band at  $491\text{ cm}^{-1}$  is attributed to the vibration  $\nu(\text{Co}–\text{O})$  and  $\nu(\text{C}–\text{C})$ . The band at  $418\text{ cm}^{-1}$  is due to  $\nu(\text{Co}–\text{O})$  and/or ring deformation.

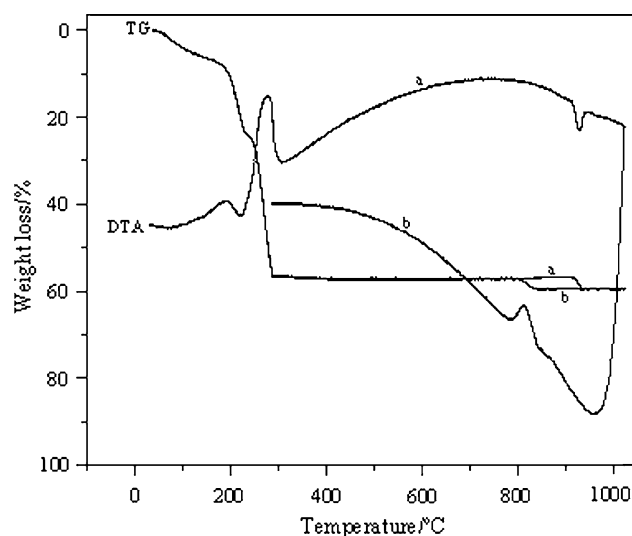
In agreement with the presented empirical formula, a polymeric structure of the obtained coordinated compound may be advanced, structure that presents cobalt(II) in a (pseudo)octahedral stereochemistry and a bridging anion as ligand:



#### Thermal behaviour of the coordination compound

The profiles of TG and DTA curves obtained for the thermal decomposition of compound in static air atmosphere respectively on cooling of the final decomposition product are shown in Fig. 4.

The first step of the thermal decomposition ( $45\text{--}125\text{ }^\circ\text{C}$ ), represents the removal of the lattice water (mass loss (%), found/calc. =  $4.9/4.69$ ), behaviour in agreement with the literature data [37]. The second decomposition step, that occurs in the temperature range  $125\text{--}228\text{ }^\circ\text{C}$  (mass loss (%), found/calc. =  $19/18.75$ ) indicates the complete elimination of the remaining two coordinated molecules of water. The IR studies revealed that the calcinated species isolated in furnace at  $200\text{ }^\circ\text{C}$  were practically anhydrous



**Fig. 4** Thermal analytical curves (TG and DTA) for the coordination compound decomposition in static air at the heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  (a—heating in air; b—cooling in air)

and the coordinated oxalate group was retained as tetradentate ligand as in  $\text{CoC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$  precursor.

The anhydrous cobalt oxalate decomposed exothermically, in the third step ( $228\text{--}293\text{ }^\circ\text{C}$ ). The mass loss found for this decomposition process,  $33.24\%$ , suggests that the intermediate product found after this decomposition step is the nonstoichiometric mixed oxide  $\text{Co}_3\text{O}_{4+x}$  with  $x = 0.25$ . Such an assumption is proved either by the existence of the fourth decomposition step, where a continuous mass loss attributed to oxygen evolving is registered and, by the data reported earlier by literature [25, 44–46].

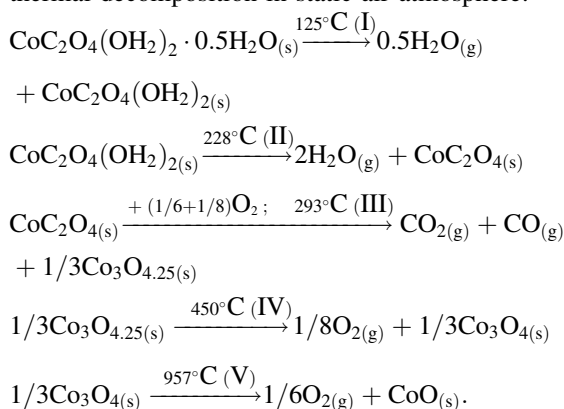
The nonstoichiometric mixed oxide, as semiconductor of p type, may be formulated as  $\text{Co}_{\text{tet}}^{2+} [\text{Co}_{2-x}^{3+} \text{Co}_{3x/4}^{4+} \diamond_{x/4}]_{\text{oct}} \text{O}_4$ , where  $\diamond$  is the hole of electrons [44]. Therefore, during the strong exothermic decomposition third step a partially oxidation of Co(II) to Co(III) and, of the formed Co(III) to Co(IV) occurs.  $\text{Co}_3\text{O}_{4+x}$  may be obtained only if the height of the sample in the crucible is small, facilitating an intimate and profoundness contact between air and the conversion's product. The literature data mention that for the voluminous samples, the intermediate product of conversion is  $\text{Co}_3\text{O}_4$  [38, 47–49].

The formation of a normal spinel,  $\text{Co}_{\text{tet}}^{2+} [\text{Co}_{\text{oct}}^{3+}]_2 \text{O}_4$ , after the fourth decomposition step implies the disappearance of hole of electrons, the reduction of  $\text{Co}^{4+}$  at  $\text{Co}^{3+}$  and, oxygen evolution. This oxide is thermally stable up to  $928\text{ }^\circ\text{C}$ . The next decomposition step ( $928\text{--}967\text{ }^\circ\text{C}$ ), characterized by a small endothermic DTA peak at  $950\text{ }^\circ\text{C}$ , and a mass loss of  $2.6\%$  represents the formation of CoO (theoretical mass loss  $2.78\%$ ). The temperature range of

$\text{Co}_{\text{tet}}^{2+}[\text{Co}_{\text{oct}}^{3+}]_2\text{O}_4$  to CoO conversion is similar with the reported one [44, 46, 50].

The nearly same result was obtained in the following mode: the product obtained after an independent decomposition of the compound in the furnace at 300 °C was dissolved in hydrochloric acid, in order to determine the  $\text{Co}^{4+}$  respectively  $\text{Co}^{3+}$  reduction to  $\text{Co}^{2+}$  by the chloride ion. The  $\text{Co}^{2+}$  content found through atomic absorption spectroscopy was 72.3%. A cobalt content of 73.8% was found for the oxide isolated at 600 °C, result closed to the theoretical value of cobalt content in  $\text{Co}_3\text{O}_4$  (calc. 73.41%). The results are in good agreement with the result from the thermogravimetric analysis, indicating that in the nonstoichiometric mixed oxide,  $\text{Co}_3\text{O}_{4+x}$ ,  $x$  is  $\cong 0.22$ .

The above study suggests the following sequence for thermal decomposition in static air atmosphere:



On air cooling, the TG curve showed a mass gain (2.6%) in the temperature range 821–843 °C accompanied by a small

exothermic peak at 828 °C, process which was attributed to the oxidation of CoO to  $\text{Co}_3\text{O}_4$  [50]. In the following temperature range, 821–293 °C the TG curve of the cooling is practically superposed with the one obtained during the heating.

#### Oxide characterization

In Fig. 5 are presented the XRD patterns of the products obtained after an independent calcinations in the furnace at 300 °C respectively 600 °C in static air atmosphere.

For both products the XRD patterns show the presence of the characteristic peaks of cobalt mixed oxides. In the case of the oxide obtained at 300 °C the lines are of the small as intensity which indicates the presence of nonstoichiometric mixed oxide in agreement with the literature data [46].

At the same time the lattice parameter is 8.07 Å for the oxide obtained at 300 °C and 8.08 Å in the case of the product obtained at 600 °C. Because the ionic radius of  $\text{Co}^{3+}$  is 0.64 Å but 0.48 Å for  $\text{Co}^{4+}$  the increase of the lattice parameter by the transformation of  $\text{Co}_3\text{O}_{4+x}$  in  $\text{Co}_3\text{O}_4$  may be explained.

The IR spectrum (Fig. 6) of the product obtained at 600 °C exhibits only the band characteristic of  $\text{Co}_3\text{O}_4$ ,  $\nu_1$ [665  $\text{cm}^{-1}$ ] and  $\nu_2$ [574  $\text{cm}^{-1}$ ], due to the vibrations of  $[\text{Co}^{\text{II}}\text{O}_4]$  respectively  $[\text{Co}^{\text{III}}\text{O}_6]$  polyhedra in accord with literature data [35, 51].

The IR spectrum of the product obtained at 1,000 °C (Fig. 7) and after quenching indicates the presence of CoO. A broad band in the range 400–500  $\text{cm}^{-1}$  (with the

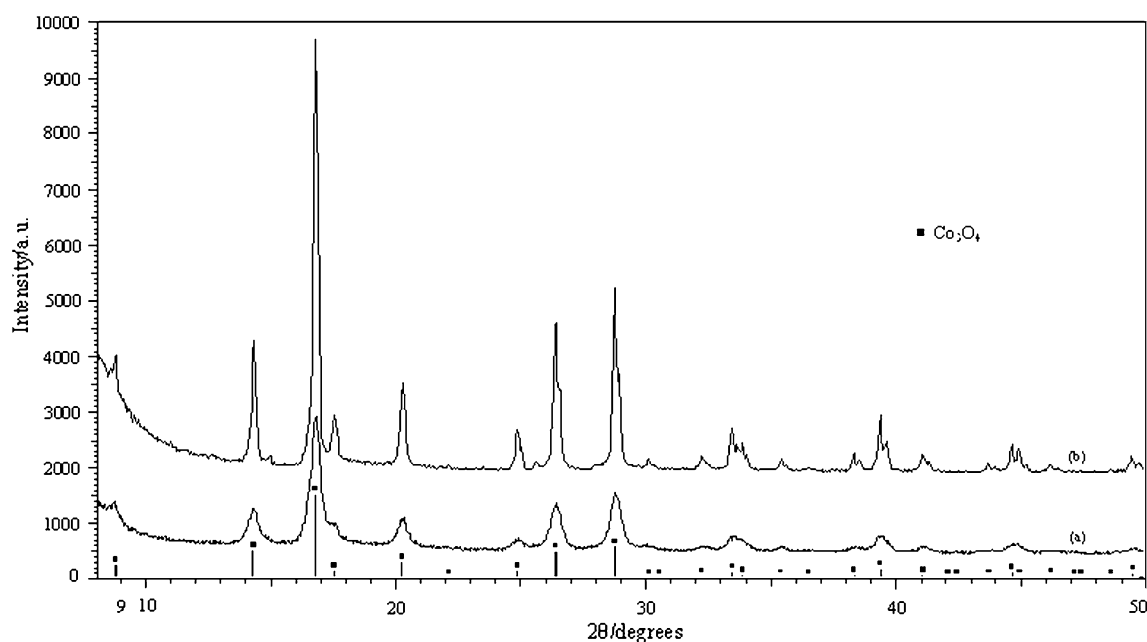


Fig. 5 The XRD of the products obtained at 300 °C (a) respectively at 600 °C (b)

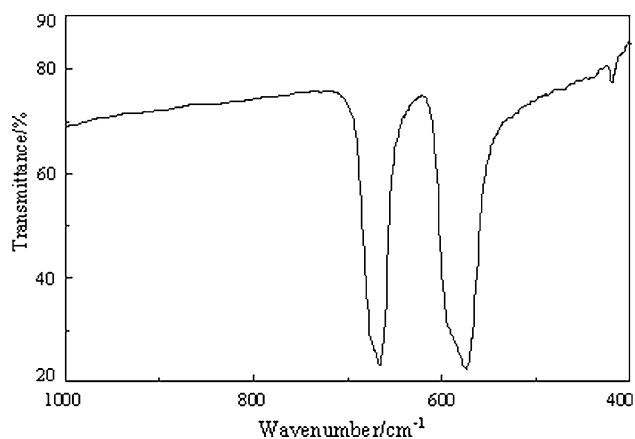


Fig. 6 IR vibrational spectrum of the product obtained at 600 °C

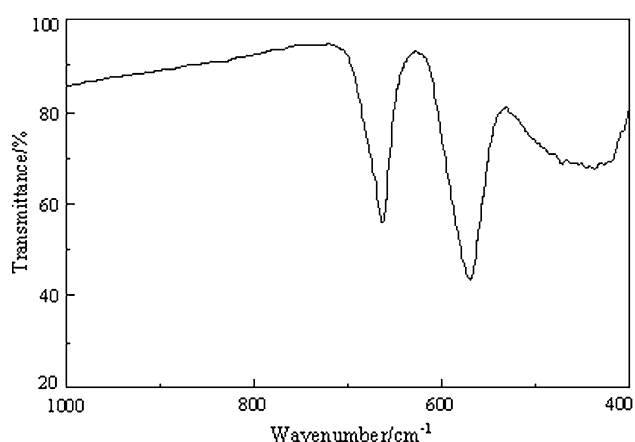


Fig. 7 IR vibrational spectrum of the product obtained at 1,000 °C

maximum at  $419\text{ cm}^{-1}$ ) assigned to the vibration  $\nu(\text{Co(II)}-\text{O})$  characteristic for Co(II) in octahedral environment,  $[\text{Co}^{\text{II}}\text{O}_6]$  [25, 35] is identified. At the same time, the band  $\nu_1[\text{Co}^{\text{II}}\text{O}_4]$  decreases in intensity comparative with the band  $\nu_2[\text{Co}^{\text{III}}\text{O}_6]$ , due to the partial oxidation of CoO to  $\text{Co}_3\text{O}_4$ .

The X-ray diffraction patterns for the same oxide (Fig. 8) show the presence of well crystallized products,  $\text{Co}_3\text{O}_4$  and CoO (traces) were identified in using JCPDS 43-1003 and respectively JCPDS 42-1300.

## Conclusions

A new synthesis method of the homopolynuclear coordination compound  $[\text{CoL} \cdot 2.5\text{H}_2\text{O}]_n \text{L}=\text{C}_2\text{O}_4^{2-}$  based on the oxidation reaction of 1,2-ethanediol in an alcohol–water system by cobalt nitrate and nitric acid and the simultaneous isolation of the complex compound in the reaction system is presented.

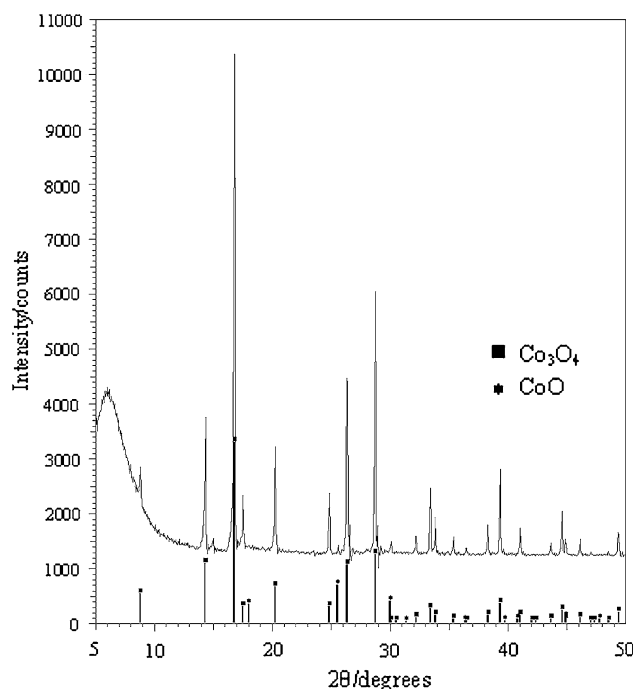


Fig. 8 The XRD of the product obtained at 1,000 °C

The coordination compound is characterized by a (pseudo)octahedral configuration of the cobalt(II) ion and the oxalate anion functions as double-bridge ligand (tetradentate). During the thermal conversion in air, depending on temperature, the products are nonstoichiometric spinel,  $\text{Co}_3\text{O}_{4+0.25}$ , normal spinel,  $\text{Co}_3\text{O}_4$  or CoO.

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