



**COORDINATION COMPOUNDS OBTAINED IN THE
REACTION BETWEEN DIOLS AND METALLIC
NITRATES AS PRECURSORS OF SIMPLE AND MIXED
OXIDES**

Raluca Dumitru^{a*}, E. Segal^b

^aUniversity "Politehnica" of Timisoara, Faculty for Industrial Chemistry and Environmental Engineering, Piata Victoriei No. 2, Timisoara, RO-300006, ROMANIA

^bUniversity of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, 70606 Bd. Elisabeta 4-12, Bucharest, ROMANIA

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SUMMARY

The paper is dedicated to a new nonconventional method of synthesis which permits to obtain homopolynuclear, heteronuclear and heteropolynuclear coordination compounds. The coordination compounds were obtained through the oxidation of ethyleneglycole with nitrates of some type d metals. Through their thermal decomposition simple and mixed oxides with nanometric particle sizes were obtained.

Keywords: coordination compounds; oxalates; nitrate; ethyleneglycole; oxides.

INTRODUCTION

The mono and polynuclear coordination compounds with ligands as carboxylic acids and their derivatives exhibit a special interest due to their practical applications in various fields like chemical industry (heterogeneous catalysis, electrocatalysis the obtaining of oxidic systems with special properties, ceramic pigments), electrotechnics, information technology and, medicine [1-15].

The classical methods of obtaining such coordination compounds consisted in the treatment of aqueous solutions of metallic salts with carboxylic acids or their alkaline

carboxylates. The precipitation of the coordination compounds occurs according to the nature of the cation, for particular values of pH realized by adding or without adding alkaline hydroxides [15-28].

Due to the increasing importance of simple and mixed oxides in the contemporary technique as well as the dependence of their properties on the used precursors, new nonconventional methods of synthesis were developed.

As an example, this paper aims to present our results concerning the synthesis and characterization of some homo and heteronuclear as well as heteropolynuclear coordination compounds with oxalate anions as ligands.

According to the working conditions, particularly the oxidation agents in the reaction medium the polyols could be oxidized to aldehydes, carboxylic acids, compounds with mixed functions (hydroxi-acids, oxo-acids, hydroxi-aldehydes), [29-32]. Thus ethyleneglycole (EG) could be oxidized to: glycolic aldehyde, glyoxal, glycolic, glyoxilic and oxalic acids. In strong acid medium as well as with strong oxidants, the oxidation of ethyleneglycole is degradative, with the breaking of the bond C-C, the resulting products being formaldehyde, formic acid and carbon dioxide [33-36]. The obtaining of only one of the oxidation products is a difficult problem requiring strictly respected conditions as the presence of an oxidizing agent, given concentrations of reactants, acidity, reaction temperature as well as a suitable heating rate [37].

Bârzescu and coworkers [38, 39] showed that in the reaction between the nitrates of some metals and ethyleneglycole without another reactant, ethyleneglycole is oxidized to the glyoxilate dianion, $C_2H_2O_4^{2-}$, with the separation of metallic glyoxilates.

In the following we are going to present the results concerning the oxidation of ethyleneglycole by nitrates of some transitional metals (Cu, Co, Fe) and nitric acid in aqueous alcoholic solution.

RESULTS AND DISCUSSION

The synthesis method of the coordination compounds

The synthesis method of metallic oxalates $[CuC_2O_4 \cdot 0.3H_2O]_n$, $[CoC_2O_4 \cdot 2.5H_2O]_n$, $[Fe_2(C_2O_4)_3(OH)_4]$, $[Fe_2Co(C_2O_4)_3(OH)_2(OH_2)_4 \cdot 2H_2O]_n$ and $[Fe_2Co(C_2O_4)_4(OH)_6]$ is based on the oxidation of ethyleneglycole with metallic nitrates and nitric acid in aqueous solution, simultaneously with the obtaining in situ of the corresponding coordination compounds.

In order to separate and identify the ligand, the coordination 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 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 (Figure 1) is similar with the one reported in literature [40-42].

At the same time the resulted oxalic acid has been identified also by specific reactions: (a) the reaction with KMnO_4 solution with the precipitation of MnO_2 , (b) the reaction with resorcline in sulphuric acid medium with the appearance of a blue ring, (c) the reaction with CH_3COONa followed by CaCl_2 solution with the deposition of a very fine white precipitate of calcium oxalate, (d) the reaction with concentrated H_2SO_4 with the burning of the carbon monoxide generated during the reaction with a characteristic blue flame.

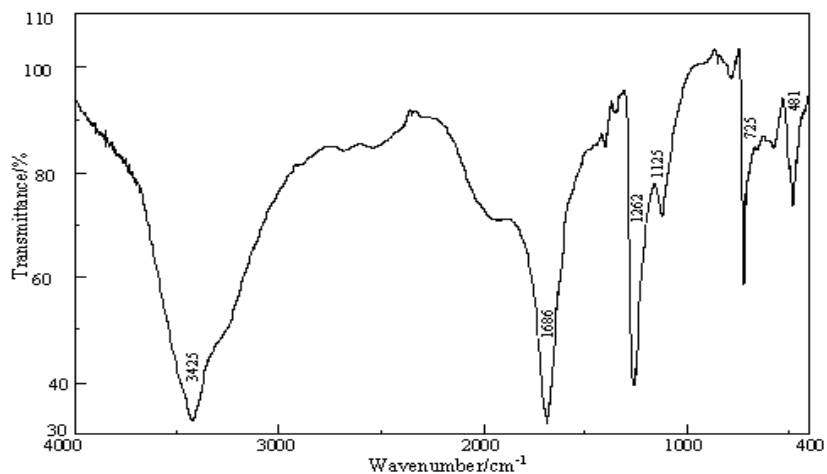


Figure 1. IR vibrational spectrum of the oxalic acid

1. Synthesis and characterization of the coordination compounds $[\text{CoL} \cdot 2,5\text{H}_2\text{O}]_n$ and $[\text{CuL} \cdot 0,3\text{H}_2\text{O}]_n$ (L = oxalate anion)

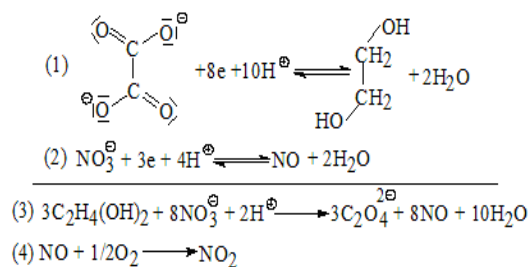
A water solution containing diol, $\text{M}(\text{NO}_3)_2$ and nitric acid in the molar ratio 1,2-ethanediol : $\text{M}(\text{NO}_3)_2$: HNO_3 = 1.5 : 1.5 : 1 was used. This mixture was heated in a water bath for ~30 minutes at ~90°C. The reaction was considered completed when no gas evolution was observed. The solid reaction product was purified by refluxing from an acetone-water mixture. The solution was filtered and the solid product was washed with acetone and finally

maintained in air until constant mass. The reaction yield was nearly quantitative.

The coordination compounds synthesised using this new method, polynuclear M(II) oxalates, were physico-chemically characterised (electronic reflexion spectra, IR spectra IR, thermal analysis, chemical analysis, X Ray diffraction) [42, 43].

The obtained compounds are solids practically insoluble in water and usual solvents (ethanol, diethyleter, benzene and acetone). In concentrated solutions of hydrochloric and sulphuric acid they exhibit quite low solubility being decomposed through the protonation of the ligand. This behaviour indicates a polymer structure. The synthesized compound are soluble in concentrated ammonia solutions generating M(II) ammino coordination compounds.

The investigation of the reaction between 1,2 ethanedyol and metallic nitrates in acid solutions led us to the following mechanism of dyol oxidation to oxalic acid (coordinated in deprotonated form, as oxalate anion at the metallic cation):



The identification of the ligand was performed through specific reactions, determination of the physical properties and IR spectroscopy. The analysis of diffuse reflectance and IR vibration spectra allowed us to establish that the oxalate dianion act as ligand in double bridge. As a consequence metal(II) oxalates ehhbit a homopolynuclear structure.

According to the composition formula, the (pseudo)octahedric stereochemistry of cobalt(II) as well as the anion oxalate ligand in double bridge, tetradentate, the following formula reflects the polymer polynuclear structure of the coordination compound homopolynuclear:

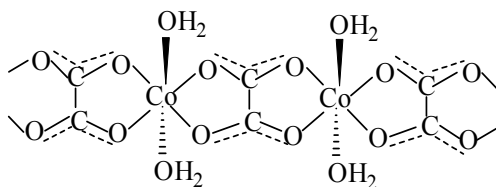
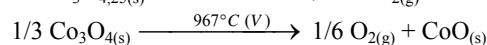
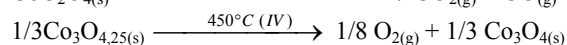
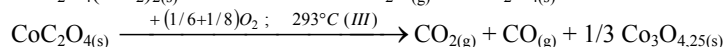
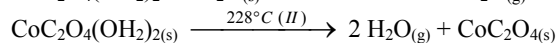
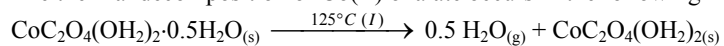


Figure 2. The structure of coordination polynuclear compound $[\text{CoL} \cdot 2.5\text{H}_2\text{O}]_n$

The thermal decomposition of Co(II) oxalate occurs in the following five steps:



A nonisothermal kinetic study of the decomposition in oxidizing atmosphere of cobalt(II) oxalate at four heating rates was performed (2.5 K min^{-1} ; 5 K min^{-1} ; 7.5 K min^{-1} and 10 K min^{-1}) [44].

The thermal stability of the compound $[\text{CoC}_2\text{O}_4(\text{OH}_2)_2 \cdot 0.5\text{H}_2\text{O}]_n$ was characterized by the kinetic parameters of the release of two water molecules according to the second reaction. Using the isoconversional methods of Friedman and Ozawa-Flynn-Wall, it was shown that the activation energy depends on the conversion degree thus indicating a complex process. For the kinetic analysis of this process we used the NETZSCH Thermokinetics Program. The best fitting of the nonisothermal and quasi-isothermal ($T = 150^\circ\text{C}$) data is given by the mechanism $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D$ with the kinetic models Bn-Bn-Bn (Bn = Prout-Tompkins model). The obtained kinetic parameters can be used for prediction of the thermal behaviour of the investigated system in conditions which differ from the used ones.

According to Kitagawa and coworkers [45] the copper(II) oxalate, could be characterized by the following polymer polynuclear structure:

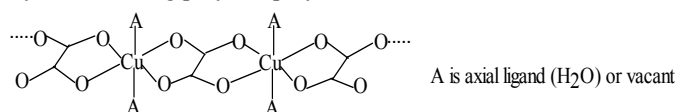


Figure 3. The structure of the coordination polynuclear compound $[\text{CuL} \cdot 0.3\text{H}_2\text{O}]_n$

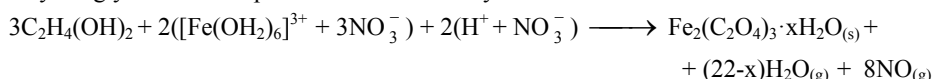
As the final product of the thermal analysis is copper(II) oxide, the breaking of the bond C–O occurs in the first step of the thermal decomposition.

The lower stability of copper(II) oxalate ($165\text{--}260^\circ\text{C}$) with respect to that of cobalt(II) ($228\text{--}293^\circ\text{C}$) could be assigned to the higher electronegativity of copper(II) which leads to the formation of a stronger bond, Cu – O with the weakening C – O [46, 47].

The analysis of the X-ray diffractograms, the values of the lattice parameters as well as the mean crystallite sizes of the decomposition products of the oxalates in air allowed us to conclude on their high degree of crystallinity which increases with the temperature increase.

2. Synthesis and characterization of the coordination compound $[\text{Fe}_2(\text{C}_2\text{O}_4)_3(\text{OH}_2)_4]$

Taking into account the good results obtained for the synthesis of M(II) oxalates through the reaction between nitrates and ethyleneglycole in the presence of nitric acid we extended the method to the M(III) nitrates [48]. As M(III) aquocations $[\text{M}(\text{OH}_2)_6]^{3+}$, exhibit higher acidity than M(II) ones and correspondingly a higher degree of hydrolysis, in order to diminish the hydrolysis we worked with nitric acid in excess and implicitly of ethyleneglycole with respect to the stoichiometry of the reaction:



The synthesized coordination compound was characterized by chemical analysis, electronic spectroscopy, IR spectroscopy and thermal analysis.

According to the composition formula the octahedral symmetry of the metallic ion and of the oxalate ligand in double bridge, tetradentate and bidentate, the obtained coordination compound should be characterized by the structure:

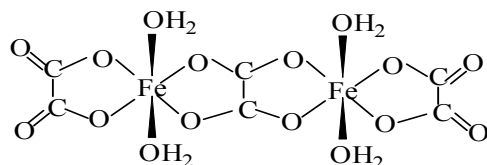
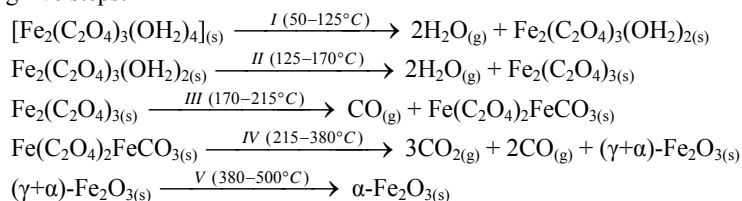


Figure 4. Structure of the homonuclear coordination compound $[\text{Fe}_2(\text{C}_2\text{O}_4)_3(\text{OH}_2)_4]$

The thermal decomposition of the coordination compound in static air occurs in the following five steps:



The final product of thermal decomposition is Fe_2O_3 under the two forms: $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) and $\alpha\text{-Fe}_2\text{O}_3$ (hematite). X-Ray diffraction and IR spectroscopy data have shown that the product of thermal decomposition obtained at 380°C contains a mixture of phases $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$, at temperatures lower than 400°C $\gamma\text{-Fe}_2\text{O}_3$ being the main compound.

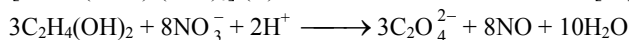
By calcining the solid product between 380°C and 600°C the change $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ was evidenced by X-Ray diffraction and confirmed by IR spectroscopy.

The SEM (scanning electron microscopy) images recorded on α -Fe₂O₃ have shown that the fine particles of oxide are porous aggregates with irregular forms.

The quantitative elemental analysis performed by EDX (Energy dispersive X-ray microanalysis) on the sample surface confirmed the composition for Fe₂O₃.

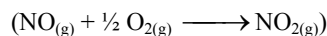
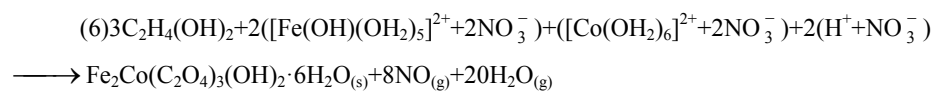
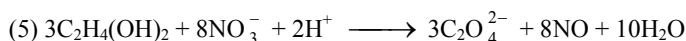
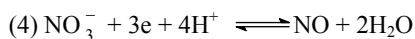
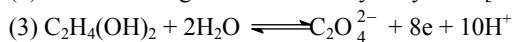
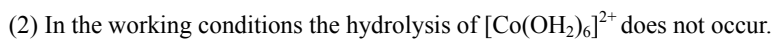
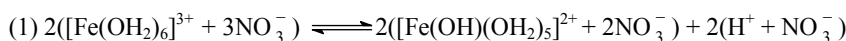
3. Synthesis and characterization of coordination compounds [Fe₂Co(C₂O₄)₃(OH)₂(OH₂)₄]·2H₂O (I) and [Fe₂Co(C₂O₄)₄(OH)₂] (II)

The obtaining of the coordination compounds [Fe₂Co(C₂O₄)₃(OH)₂(OH₂)₄]·2H₂O (I) and [Fe₂Co(C₂O₄)₄(OH)₂] (II) is based on the redox reaction [48]:

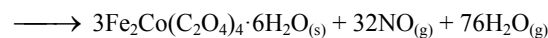
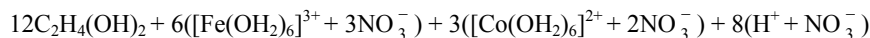


Consequently, we suggest the following mechanism for the synthesis of the two coordination compounds:

I) If the reaction occurs in the presence of nitric acid 1M the following steps are considered:



II) In excess of 1,2-ethandiole, and nitric acid 2M, the hydrolysis of [Fe(OH₂)₆]³⁺ is avoided. Thus reaction for the synthesis of the coordination compound II is:



The structures of these compounds were established taking into account the reflexion electronic spectra as well as IR spectra.

Taking into account the two different coordination modes for the anion C₂O₄²⁻ as well as the different solubilities in water, a polymer polynuclear structure was suggested for compound I and a trinuclear structure for the compound II. The structures were confirmed by thermal analysis.

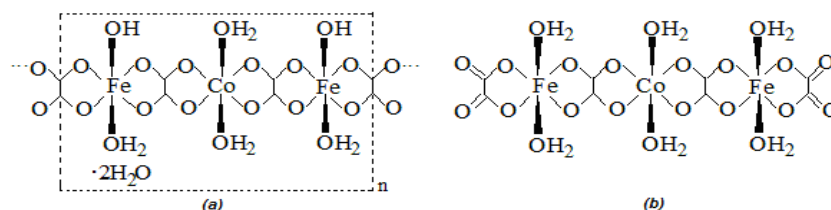


Figure 5. The structures of the polynuclear coordination compounds

(a)- $[\text{Fe}_2\text{Co}(\text{C}_2\text{O}_4)_3(\text{OH})_2(\text{OH}_2)_4 \cdot 2\text{H}_2\text{O}]_n$ (I) and (b)- $[\text{Fe}_2\text{Co}(\text{C}_2\text{O}_4)_4(\text{OH}_2)_6]$ (II)

The thermal decomposition of the two coordination compounds CoFe_2O_4 is obtained. For both compounds obtained by calcining at 350°C the values of crystallite sizes estimated from the TEM are very close to the values given by X-Ray diffraction images. This demonstrates the character of monocrystal of the mixed oxide particles.

The lattice parameter of CoFe_2O_4 obtained at 350°C is 8.369\AA for compound I and 8.343\AA for compound II. These values are similar to the values for a powder obtained by other chemical methods. The increase of temperature eliminates the lattice defects thus leading to big and more perfect crystals.

CONCLUSION

A new synthesis method of the coordination compounds homo and heteropolynuclear based on the oxidation reaction of 1,2-ethanediol in an alcohol-water system by metal nitrate and nitric acid and the simultaneous isolation of the complex compounds in the reaction system is presented.

The method proposed here opens new perspectives concerning the new chemistry of oxalate compounds as source for various oxide materials confirming both their accessibility and higher performance.

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