



## SYNTHESIS-STRUCTURE RELATIONSHIP IN THE AQUEOUS ETHYLENE GLYCOL-IRON(III) NITRATE SYSTEM

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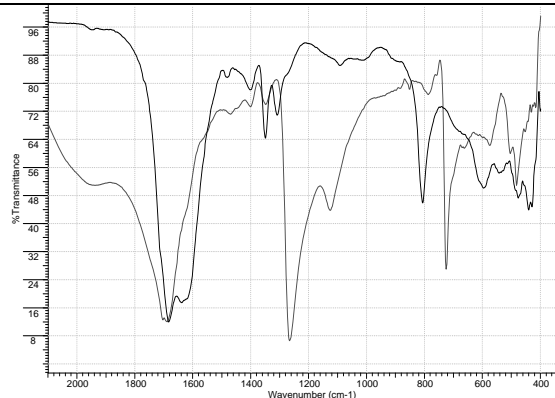
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The preparation of iron(III) polyoxalate from an aqueous ethylene glycol-iron(III) nitrate system was presented from the synthesis-structure relationship viewpoint. Under specific working conditions, the reaction between ethylene glycol and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  proceeds with the oxidation of the former to oxalate anion. The synthesized homopolynuclear coordination compound, which contains the oxalate anion as ligand, was characterized by physical-chemical analysis, electronic spectroscopy and Fourier transform infrared spectroscopy.



### INTRODUCTION

Mono- and polynuclear coordination compounds with carboxylic acids and their derivatives as ligands have occupied a core position in coordinative chemistry, starting with the nineteenth century and until present day. Besides their theoretical importance, they have found applications in diverse fields, like chemical industry (heterogeneous chemical catalysis, electrocatalysis, preparation of oxidic systems with special properties, ceramic

pigments), electrical engineering, information technology and medicine.<sup>1-29</sup>

The classical preparation method of such coordination compounds consists in reacting an aqueous solutions of proper metal salt with carboxylic acids or alkaline carboxylates. Depending on the cation nature and for specific pH values, established with or without adding alkaline hydroxides, precipitation of the complexes takes place.<sup>30-32</sup>

However, the requirements for oxidic systems with reproducible structures and

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properties, imposed by the modern technique, has determined the development of new, unconventional methods for their preparation.

In this context, starting with the '80s, a new preparation method for complexes with glyoxylate anion as ligand was established.<sup>15,33</sup>

It is well known that, depending on the oxidation agent used and the working conditions applied, polyols can be oxidized to aldehydes, carboxylic acids or mixed-function compounds.<sup>34-</sup>

<sup>38</sup> Thus, ethylene glycol (EG) can be oxidized to glycolic aldehyde, glyoxal and glycolic, glyoxylic or oxalic acids. In strong acidic medium and with powerful oxidizers, oxidation of EG proceeds with degradation, involving C-C bond breaking and producing formic aldehyde, formic acid and carbon dioxide.<sup>39-41</sup> The preparation of just one of these oxidation compounds is a tricky task, involving well established working conditions: an adequate oxidizer, proper reagent concentrations, acidity and temperature/heating speed.<sup>41</sup>

Bencze *et al.*<sup>42</sup> have shown that by mild oxidation of EG with aqueous nitric acid, glyoxylic acid is produced.

Knetsch and Groeneveld<sup>43</sup> have obtained the compound  $\text{Cu}(\text{EG})_2(\text{NO}_3)_2$  during the evaporative concentration of the solution containing 0.01 mol  $[\text{Cu}(\text{OH}_2)_6](\text{NO}_3)_2$  dissolved in 0.02 mol EG. This compound is very hygroscopic and rapidly decomposes, forming  $\text{NO}_2$ . This process has not been further investigated by the two authors.

Bîrzescu and Brezeanu<sup>15</sup> have further established that a redox reaction occurs between EG and  $\text{NO}_3^-$  ion even during the evaporation of the previously mentioned solution.

Bîrzescu and co-workers<sup>15,20,22,28,44</sup> have synthesized and characterized a series of homo- and heteropolynuclear glyoxylates and oxalates by a new method. This was based on the oxidation of EG to glyoxylate anion,  $\text{C}_2\text{H}_2\text{O}_4^{2-}$ , or oxalate anion,  $\text{C}_2\text{O}_4^{2-}$ , in aqueous solution and during heating, by some metal nitrates, with simultaneous solid state isolation of the corresponding coordination compounds. The yield of this synthesis exceeds 90%.

The thermal conversion of homopolynuclear M(II) glyoxylates,  $[\text{M}(\text{C}_2\text{H}_2\text{O}_4)(\text{OH}_2)_2]_n$  ( $\text{M}^{\text{II}} = \text{Mn}, \text{Co}, \text{Ni}$ ) and  $[\text{Cu}(\text{C}_2\text{H}_2\text{O}_4)]_n \cdot 0.5n\text{H}_2\text{O}$ , has allowed the establishment of preparation conditions for nonstoichiometric oxides in which the metal functions in diverse oxidation states:  $\alpha\text{-Mn}_2\text{O}_{3-x}$ ,  $\text{Co}_3\text{O}_{4+x}$ ,  $\text{NiO}_{1+x}$ , respectively  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ . Preparation of these oxides takes place at relatively low temperatures (300-400°C) and with good reproducibility.<sup>15</sup>

The determination of forming conditions for nickel and cobalt nonstoichiometric oxides has allowed the elaboration of an original method for the construction of anodes with active electrocatalytic films, used in the process of oxygen discharge during alkaline solutions electrolysis.<sup>15,33</sup>

By thermal conversion in air of M(II)-M'(II) heteropolynuclear glyoxylates  $[\text{Co}_2\text{Ni}(\text{C}_2\text{H}_2\text{O}_4)_3(\text{OH}_2)_6]_n$ ,  $[\text{Co}_2\text{Cu}(\text{C}_2\text{H}_2\text{O}_4)_3(\text{OH}_2)_2]_n$  and  $[\text{NiCu}(\text{C}_2\text{H}_2\text{O}_4)_2(\text{OH}_2)_2]_n$ , the preparation conditions for the mixed oxides  $\text{NiCo}_2\text{O}_4$ ,  $\text{CuCo}_2\text{O}_4$ , respectively for the system  $\text{CuO}/\text{NiO}$ , were established.<sup>15,20,22,27,28</sup>

By thermal decomposition of Ni(II) and Ni(II)/Cu(II) glyoxylates, supported on iron, with the formation of the corresponding oxides, and by cathodic prepolarization, metallic films have been obtained for cathodes which possess high electrocatalytic activity in the process of hydrogen discharge from alkaline solutions.<sup>15,33</sup>

Starting with these premises, we set the goal of producing coordination compounds by selective oxidation reactions of some diols with d-block metal nitrates.

It was observed that, in contrast with the reaction of EG, in the case of more acidic and more reducing hydroxyl compounds (which translates in a higher reactivity in relation with different metal nitrates), the selective oxidation reactions of such polyols in the same conditions<sup>45</sup> raises serious difficulties. Restrictive reaction parameters must therefore be imposed, with the control of temperature regime, of solution acidity (depending on the nature of the diol and of the metallic cation which generates the complex, the preparation of polynuclear coordination compounds is made to a specific pH value), of diol/metal nitrate molar ratios and of reaction speed.

It can be stated that the reaction for coordination compound preparation takes place through a sustained attack, because the two reactant species, i.e. the reducing diol and the oxidant nitrate anion (or nitric acid), have affinity for each other, an electrons transfer taking place from the highest occupied energy level (HOMO) of the reducer to the lowest unoccupied energy level (LUMO) of the oxidizer.<sup>41,45,46</sup>

Both the nitrate anion, statistically and thus kinetically (higher concentration) favored, and the nitric acid, thermodynamically favored (stronger oxidizer) can function as oxidizers. The solution

acidity, owned to the metal nitrate hydrolysis or to the addition of an acidic compound in the reaction system, potentiates the oxidant character of the nitrate.<sup>45,46</sup>

The present paper belongs to a series devoted to the research of oxidic systems obtained by thermal decomposition of polynuclear coordination compounds. The main objective of such research is to highlight the importance of the precursor's nature in the synthesis of simple and mixed metal oxides with different properties and applications.

In this paper the synthesis and structural characterization (including electronic and vibrational spectra) of Fe(III) polyoxalate are described.

## EXPERIMENTAL

### Chemicals and methods

For the synthesis of the coordination compound,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , EG (99%) and 1.5 M  $\text{HNO}_3$ , all from "Reactivul" Bucharest, were used. The subsequent purification step applied to the coordination compound assures the removal of most reagent impurities and reaction byproducts, so the desired product is obtained in high purity.

The water content was determined gravimetrically and the iron content was estimated using standard methods. Carbon and hydrogen were analyzed using a Carlo Erba 1108 elemental analyzer. The diffuse reflectance spectrum of the synthesized compound was recorded with a Carl Zeiss Jena Spekol 10 spectrophotometer using MgO as reference material. The FTIR spectrum (KBr pellets) for the coordination compound was recorded on a Jasco FT/IR-410 spectrometer, in the 400-4000  $\text{cm}^{-1}$  range.

### Synthesis of the coordination compound

In light of the above discussion, our devised protocol for synthesizing the complex compound is based on the oxidation reaction of EG by iron(III) nitrate and nitric acid in an alcohol-water mixture, with simultaneous isolation of the coordination compound from the reaction system.

Thus, an aqueous solution of EG,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{HNO}_3$  (1.5:1.5:1 molar ratio) was heated in a water bath, gradually up to 90°C. The reaction was considered complete when the gas evolution ceased (total reaction time being under 10 h).

The solid reaction product was purified by refluxing from an acetone-water mixture. The solution was filtered and the brown-rust solid product was washed with acetone and

maintained in air until constant mass. A brown-rust powder was finally obtained.

## RESULTS AND DISCUSSION

The redox reaction between EG and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was investigated by FTIR spectroscopy. Monitoring the reaction using this analytical method is feasible due to the decreasing intensity of functional bands for both nitrate ion and EG during the reaction. At the same time a new band appears in the 1580-1720  $\text{cm}^{-1}$  range ( $\nu_{\text{asym}}(\text{OCO})$ ), with its intensity increasing as the reaction proceeds further. This band is specific to the oxygenated ligands which possess functional groups that act as electron donors, like carboxylate anions.<sup>15,20,47</sup>

The elemental analysis results (Table 1), as well as the FTIR investigation, have indicated that the synthesized coordination compound has the following empirical chemical formula:  $[\text{Fe}(\text{C}_2\text{O}_4)(\text{OH})(\text{OH}_2)]_n \cdot 0.3n\text{H}_2\text{O}$ .

In order to separate and identify the ligand, the complex compound has been treated with R-H cationite (Purolite C-100). After retention of the metal ions and evaporation of the obtained solution,  $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  was isolated as a solid. The C and H elemental analysis confirmed the proposed composition: C found 19.12% (calcd. 19.04%), H found 4.68 % (calcd. 4.76%).

At the same time, the oxalic acid obtained has been identified with specific reagents: aqueous  $\text{KMnO}_4$  (precipitates  $\text{MnO}_2$ ), resorcinol in sulfuric acid (a blue ring appears), aqueous  $\text{CH}_3\text{COONa}$  followed by  $\text{CaCl}_2$  solution (a very fine white solid of calcium oxalate is deposited), and concentrated  $\text{H}_2\text{SO}_4$  (the carbon oxide generated during this reaction burns with a characteristic blue flame).

The determined physical properties (white solid, rhombic-pyramidal crystals, highly soluble in water and ethanol, highly acidic) and the FTIR spectrum of oxalic acid (Fig. 1, band assignment given in Table 2) are in good agreement with those from the literature.<sup>47-49</sup>

Table 1

Calculated composition and elemental analysis data

Compound (composition formula)	%Fe		%C		%H	
	calcd.	found	calcd.	found	calcd.	found
$[\text{Fe}(\text{C}_2\text{O}_4)(\text{OH})(\text{OH}_2)]_n \cdot 0.3n\text{H}_2\text{O}$	30.31	30.53	13.03	12.81	1.95	1.93

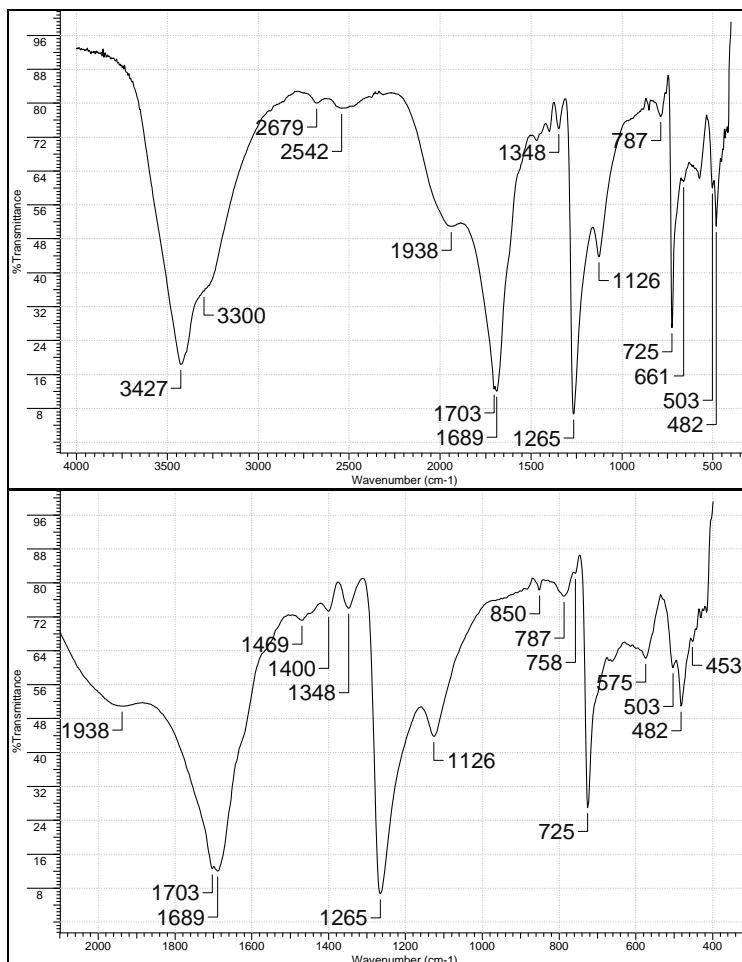


Fig. 1 – FTIR spectrum for the isolated oxalic acid: up, full scanned domain; down, 400-2000  $\text{cm}^{-1}$  range in detail.

Table 2

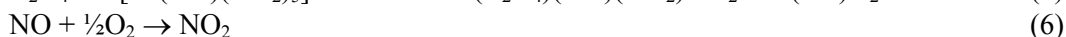
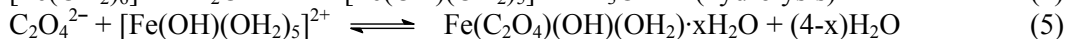
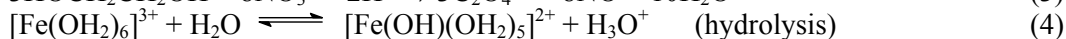
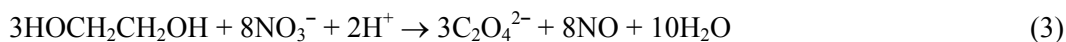
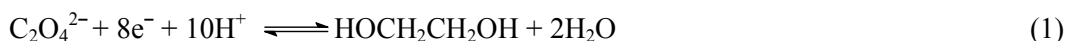
Characteristic FTIR absorption bands for the oxalic acid with the corresponding assignments

$\nu(\text{OH}), \nu(\text{H}_2\text{O})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})+\delta(\text{OH})$	$\nu(\text{C}-\text{OH})$	$\delta(\text{OCO})+\nu(\text{CC})$	$\gamma(\text{CCO})+\gamma(\text{OCO})$
3427 vs, br	1703 vs	1265 vs	1126 m	725 s	482s
3300 s, sh	1689 vs	1348 w			503m, sh

s – strong ( $\nu$  – very); br – broad; sh – shoulder; m – medium; w – weak

The current results, along with those previously reported in literature<sup>15,20</sup> concerning the oxidation of EG by metal nitrates, suggest that the oxidation of EG by  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  occurs, in some specific

reaction conditions, to oxalate anion.<sup>15,22,28</sup> Considering this, we suggest the following mechanism for the reaction between EG and  $\text{Fe}(\text{NO}_3)_3$  in acidic medium:



The oxidation of EG occurs simultaneously with the coordination of the oxidation product by the complex generator, determining the equilibrium shift towards oxidation and thus leading to the formation of the polynuclear coordination compound.

The suggested formula for the coordination compound, as well as the information concerning its structure, are going to be further confirmed by the following data.

### Diffuse reflectance spectrum of the polynuclear coordination compound

The diffuse reflectance spectrum of the coordination compound shows the characteristic bands for the Fe(III) hexacoordinated ion in a distorted octahedral environment (Fig. 2).

The reflectance spectrum reveals at ~350 nm the forbidden spin transition band  ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}(G)$ . The band located at ~460 nm (small shoulder) is due to the  $L \rightarrow Fe(III)$  charge transfer. The relatively low intensity bands that appear in the 700-1100 nm range are also attributed to Fe(III) ion in a high spin octahedral configuration,  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ .<sup>52</sup>

Accordingly, the Fe(III) ion exists in the fundamental state  $t_{2g}^3 e_g^2$ , high spin, the three

ligands ( $HO^-$ ,  $C_2O_4^{2-}$  and  $H_2O$ ) being of low field and of similar strength.

The overall shape of the electronic spectra, together with the width and asymmetry of the bands, are proof for the deformation of the octahedral coordination.

### Vibrational spectrum of Fe(III) polyoxalate

In order to obtain additional information regarding the structure of the synthesized compound and the ligands coordination, the FTIR spectrum was recorded for the product in the 400-4000  $cm^{-1}$  domain (Fig. 3).

Table 3 shows the characteristic FTIR bands for the synthesized coordination compound and the corresponding assignments.

The approximate description of vibrational modes was made following the IR absorption bands of iron(III) oxalate hexahydrate<sup>50</sup> and iron(III) oxalate tetrahydrate<sup>51</sup> from literature. It is clear at the very first glance that the spectra for the coordinative compound obtained does not resemble either the spectrum for the two iron(III) oxalate species (tetrahydrate and hexahydrate), and that it is also different from the spectrum of iron(II) oxalate dihydrate,<sup>50,51</sup> which confirms that it is a different compound.

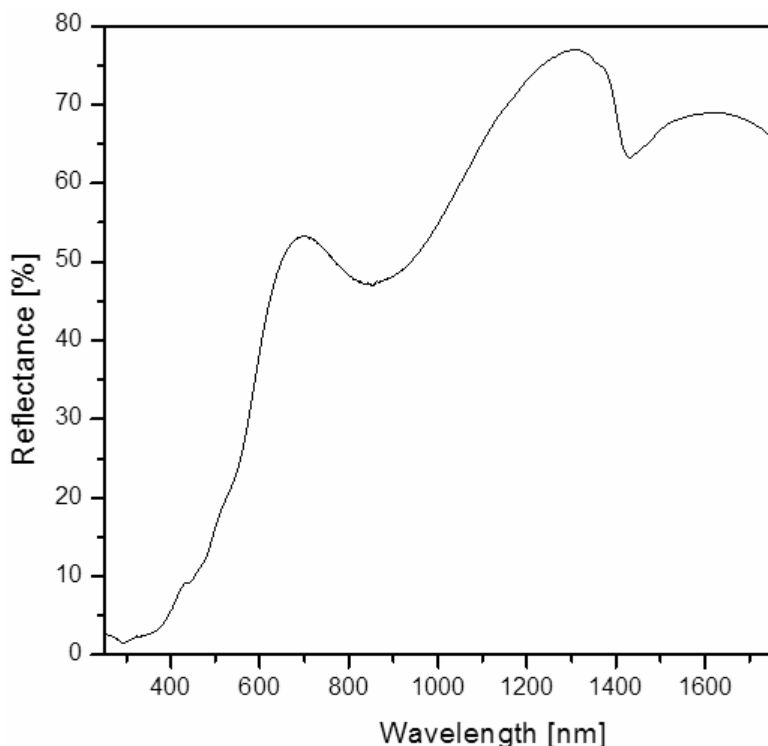


Fig. 2 – Diffuse reflectance spectrum for the synthesized coordination compound.

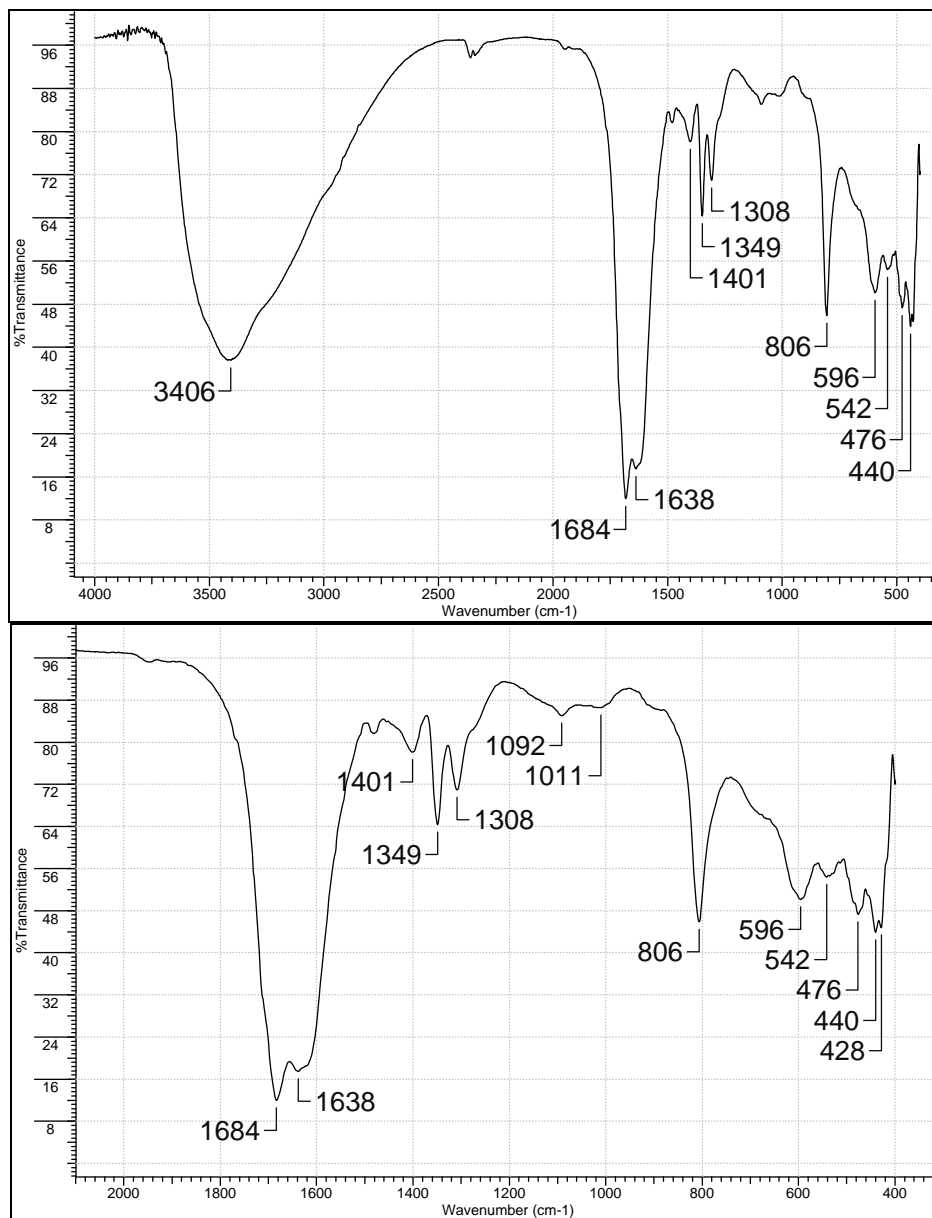


Fig. 3 – FTIR spectrum of the synthesized coordination compound: up, full scanned domain; down, 400-2000  $\text{cm}^{-1}$  range in detail.

Table 3

Characteristic FTIR absorption bands for Fe(III) polyoxalate and the corresponding assignments

Wavenumber [ $\text{cm}^{-1}$ ]	Assignment	Wavenumber [ $\text{cm}^{-1}$ ]	Assignment
3406 s, br	$\nu_{\text{asym}}(\text{OH}) + \nu_{\text{sym}}(\text{OH})$ , hydrogen bonding	806 m	$\nu(\text{CC}) + \delta_{\text{asym}}(\text{OCO})$
1684 vs, 1638 s	$\nu_{\text{asym}}(\text{OCO})$	596 m	lattice water + $\delta_{\text{sym}}(\text{OCO})$
1349 m, 1308 m	$\nu_{\text{sym}}(\text{OCO})$	542 m	$\rho(\text{H}_2\text{O}) + \nu(\text{FeO})$
		476 m, 440 m, 428 m	$\gamma(\text{OCO})$

s - strong (v - very); br - broad; m – medium

The intense and broad band with the maximum at  $3406\text{ cm}^{-1}$  appears due to the  $\nu(\text{OH})$  vibration of coordinated water molecules and hydroxyl groups, also being a proof for the strong hydrogen bonds between them and the oxalate ligand. The medium absorption band at  $806\text{ cm}^{-1}$  could also confirm the presence of water in the coordinated form.<sup>15,48</sup> The medium absorption band at  $596\text{ cm}^{-1}$  could be attributed to the lattice water,<sup>48</sup> while the medium intensity band at  $542$  could be attributed to the water vibrational mode ( $\rho$ ) or for one of the Fe-O stretching vibration. The intense bands at  $1684$  and  $1638\text{ cm}^{-1}$  are attributed to the  $\nu_{\text{asym}}(\text{OCO})$  vibration, and these probably overlap with the bending mode  $\delta(\text{HOH})$ , which should appear around  $1600\text{ cm}^{-1}$ .<sup>50</sup> The bands at  $1349\text{ cm}^{-1}$  and  $1308\text{ cm}^{-1}$  can be due to  $\nu_{\text{sym}}(\text{OCO})$  vibration, this values being in agreement with the position of the corresponding absorption in oxalate-bridged complexes.<sup>15,20,48</sup> The OCO deformations are

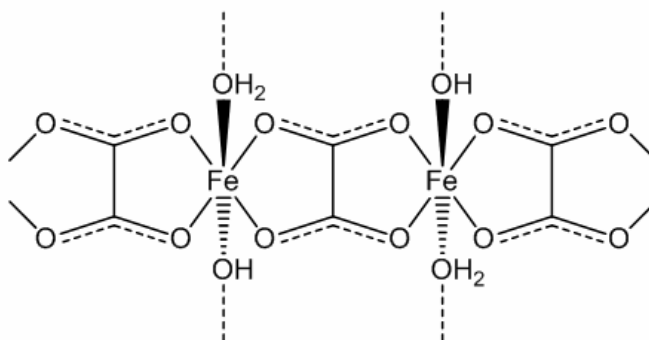
identified in the IR between  $428$  and  $476\text{ cm}^{-1}$ , according to Edwards *et al.*<sup>50</sup>

The synthesized brown-rust solid compound shows a remarkable stability, due to the very strong hydrogen bonds between adjacent layers, therefore it is practically insoluble in water and in common organic solvents. In pure state, its composition does not alter with time and it can only be destructured in a strongly acidic medium or by treatment with concentrated ammonia when it forms amino complexes.

These statements, as well as the above mentioned data suggest a polynuclear structure which corresponds to the following formula:



Consistent with elemental analysis, the distorted octahedral stereochemistry of Fe(III) and the bridging oxalate anion, the homopolynuclear coordination compound must have the following polymeric structure:



The *in situ* and *ex situ* thermal behavior of the polynuclear coordination compound, synthesized by the method described in the present work, will be presented in our future paper.

double bridge ligand and also tetradentate, all plead for a polynuclear structure. This is also confirmed by electronic and vibrational spectra, supplemented by elemental chemical analysis.

## CONCLUSIONS

The reaction between EG and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in the presence of nitric acid lead to a homopolynuclear coordination compound having a polynuclear structure which corresponds to the formula  $[\text{Fe}(\text{C}_2\text{O}_4)(\text{OH})(\text{OH}_2)]_n \cdot 0.3n\text{H}_2\text{O}$ . The oxalate anion ( $\text{C}_2\text{O}_4^{2-}$ ), which functions as ligand, was confirmed in the form of oxalic acid by determining its physical constants and by specific reactions. The composition formula and the unusual stability of the synthesized compound, the distorted octahedral stereochemistry of the Fe(III) cation and the fact that the oxalate anion is a

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