



*Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary*

SYNTHESIS AND CHARACTERIZATION OF THE POLYNUCLEAR COORDINATION COMPOUND OBTAINED THROUGH THE REACTION OF 1,3-PROPANEDIOL WITH $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

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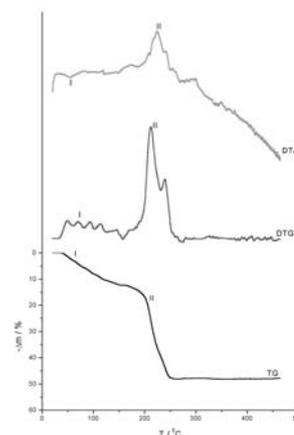
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Received February 26, 2013

This work presents the experimental results of the synthesis and the characterization of a new copper(II)-polynuclear coordination compound having as ligands the oxidation product of 1,3-propanediol. The reaction between 1,3-propanediol and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ occurs with the oxidation of 1,3-propanediol to 3-hydroxypropionate anion, under some working conditions. The synthesized coordination compound, having as ligand 3-hydroxypropionate anion, was characterized by chemical analysis, electronic and vibrational spectra, magnetic measurements and thermal analysis. Copper oxide obtained by thermolysis of this coordination compound was characterized by IR spectroscopy and X-ray powder diffraction (XRD).



INTRODUCTION

Knetsch and co-workers have synthesized and studied several metallic complex compounds having as ligand 1,3-propanediol.¹⁻³

In our previous papers,⁴⁻⁶ we have reported the results of the study of the oxidation reaction between 1,3-propanediol and $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (M:

Co, Ni), in dilute nitric acid solution. Ni and Co complex combinations synthesized in this way contain 3-hydroxypropionate anion as ligand.

The determination of the formation conditions of nonstoichiometric oxides of Ni and Co led to an original method for obtaining anodes with electrocatalytically active films for the oxygen evolution at the electrolysis of alkaline solutions.⁷

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This paper presents the results obtained at the investigation of 1,3-propanediol oxidation with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in a weak acid medium. The obtained coordination compound was investigated regarding the composition and physical-chemical properties. It will be shown that it can be a precursor for the copper oxide obtaining at relatively low temperature.

EXPERIMENTAL

Materials and methods

For the synthesis of the coordination compound, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, "Reactivul" – Bucharest, with minimal purity of 99%, and 1,3-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 compound obtained as they are removed in the subsequent purification step.

The heating curves (TG, DTG, DTA) 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 and the temperature range 20 – 450 °C, at heating rate 2.5 °C min⁻¹; reference material: $\alpha\text{-Al}_2\text{O}_3$.

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

The IR spectrum (KBr pellets) was recorded on a Nicolet FT-IR Spectrophotometer, in the range 400 – 4000 cm⁻¹.

The electronic spectrum was recorded by diffuse reflectance technique using a spectrophotometer SPEKOL 10 Carl Zeiss Jena and MgO as a reference material.

The magnetic measurements were performed according to Faraday's method, at room temperature, using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a standard.

The characterization of copper oxide obtained by thermal decomposition of the investigated coordination compound was performed by IR spectroscopy and X-ray powder diffraction (XRD). X-Ray diffraction data were recorded on a DRON-3X-Ray diffractometer with CoK_α radiation.

Synthesis of the coordination compound

The elaborated method of synthesis of the coordination compound is based on the oxidation reaction of 1,3-propanediol in an alcohol-water system by copper nitrate and the simultaneous isolation of the complex compound in the reaction system.

A solution of water + diol + $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ + nitric acid in the molar ratio: 1,3-propanediol : $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$: HNO_3 = 3 : 2 : 0.001 was prepared. This mixture was heated

gradually during 10 h in a thermostat up to 120 °C. The reaction was considered completed when no more gas evolution was observed.

The solid reaction product was purified by refluxing from an acetone-water mixture. After that, the solution was filtered and the solid product was washed with acetone and finally maintained in air until constant mass. The yield was 70% (based on the 1,3-propanediol).

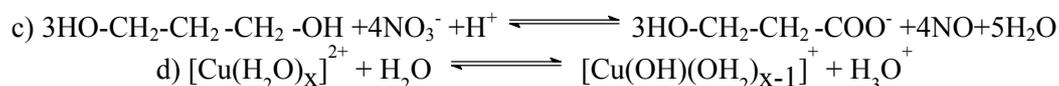
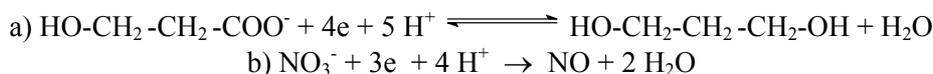
RESULTS AND DISCUSSION

The evolution of the reaction between 1,3-propanediol and copper(II) nitrate was investigated by IR spectroscopy. As the reaction advances, the bands due to nitrate ion decrease in intensity, proving that the nitrate ion is consumed in reaction.⁸ In the same time, the appearance and the increase of the band intensity in the range 1580 – 1680 cm⁻¹ ($\nu_{\text{as}} \text{COO}^-$) is observed, which is specific to complex ligands which contain at least two oxygen atoms as donors such as the carboxylic anions of the acids.⁹

The elemental analysis data (Table 1) as well as the IR investigation confirm the following empirical chemical formula for the coordination compound: $\text{Cu}(\text{OH})\text{L}(\text{H}_2\text{O})_{0.5}$, where L is the 3-hydroxypropionate anion ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{COO}^-$).

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 3-hydroxypropionic acid has been identified by specific reactions (the reaction with cerium(IV) and ammonium nitrate, the reaction with guajacol (monomethyl ether of pyrocatechine, $\text{HO}-\text{O}-\text{OCH}_3$), in the presence of sulfuric acid, the reaction with sodium mono hydrogencarbonate, the reaction with KMnO_4 solution). The physical properties (syrupy liquid, strongly acid, highly soluble in water, ethylic alcohol, ethylic ether) are in good agreement with those from the literature.¹⁰

These results as well as those previously reported¹¹ concerning the oxidation of 1,2-propanediol with M(II) nitrate (M= Ni, Co, Cu) suggest the following mechanism for the reaction between 1,3-propanediol and $\text{Cu}(\text{NO}_3)_2$:



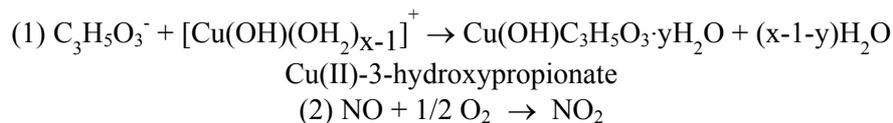


Table 1

Composition and elemental analysis data

Compound (composition formula)	Cu(II) %		C %		H %	
	calc.	exper.	calc.	exper.	calc.	exper.
$\text{Cu}(\text{OH})\text{L}(\text{H}_2\text{O})_{0.5}$	35.57	35.50	20.17	19.90	3.92	3.85

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 the hydrolysis of the Cu(II) hydrated cation, as shown in the d) step.

The oxidation of the 1,3-propanediol occurring simultaneously with the coordination of the oxidation product by the complex generator determines the shifting of the equilibrium towards oxidation, leading thus to the formation of the polynuclear coordination product.

The suggested formula of the coordination compound as well as information concerning its structure is going to be confirmed by the results which will be presented in the following.

Diffuse reflectance spectrum of Cu(II)-hydroxypropionate

The diffuse reflectance spectrum of the coordination compound shows the presence of the characteristic bands of the Cu(II) hexacoordinated ion (octahedral distorted geometry) (Fig. 1).

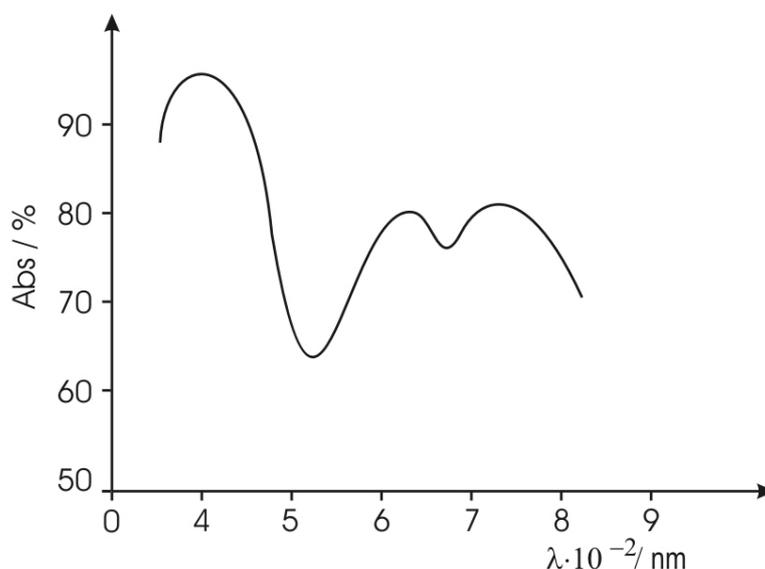


Fig. 1 – Diffuse reflectance spectrum of the coordination homopolynuclear compound $[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$.

In the electronic spectra of $[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$, instead of a single absorption band due to ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$, as a rule one may observe three bands (the lowering of symmetry, achieved by elongation of the octahedron, in order to suppress orbital degeneration, has as result that instead of a single transition there are usually three).

Elongation of the axial bonds can determine the passing from the octahedral symmetry to the tetragonal pyramid or square-planar coordination.¹²

IR vibrational spectrum of Cu(II)-hydroxypropionate

The presence of hexacoordinated Cu(II) atoms in a distorted octahedral environment is also verified by the infrared spectrum of polynuclear coordination compound, $[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$ (L = 3-hydroxypropionate anion (hydracrylate)) (Fig. 2).

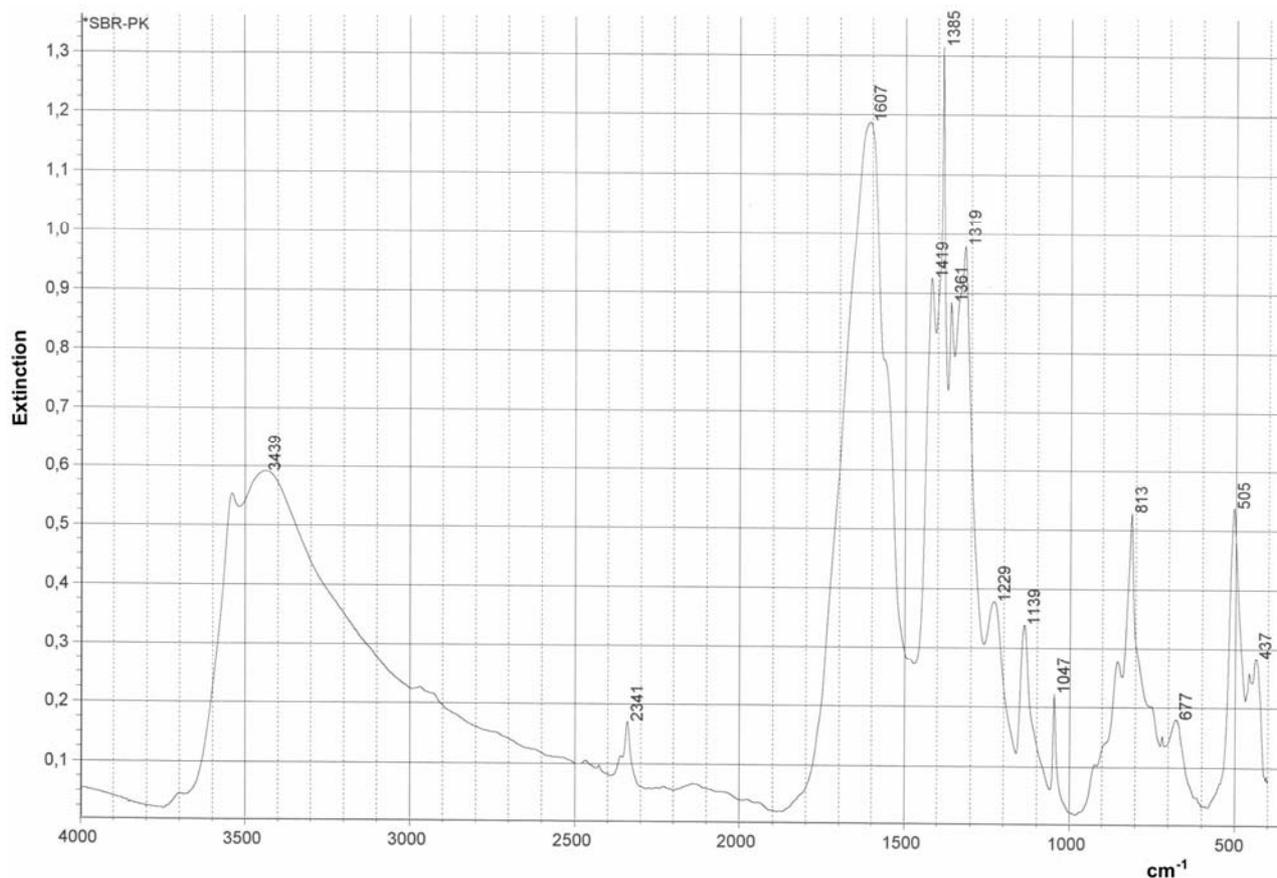


Fig. 2 – IR spectrum of the homopolynuclear coordination compound $[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$.

Table 2

Characteristic absorption bands in IR for Cu(II)-3-hydroxypropionate and the corresponding assignments

$\nu(\text{OH})$ (cm^{-1})	$\nu_{\text{as}}(\text{COO})$ (cm^{-1})	$\nu_{\text{sim}}(\text{COO})$ (cm^{-1})	$\nu_{\text{sim}}(\text{CO}) +$ $\delta(\text{OCO})$ (cm^{-1})	$\nu(\text{C-OH})$ (cm^{-1})	$\nu(\text{OH}_{\text{bridge}})$ (cm^{-1})	$\delta(\text{OCO}) +$ $\nu(\text{Cu-O})$ (cm^{-1})	$\rho(\text{H}_2\text{O})$ (cm^{-1})	$\nu(\text{Cu-O})$ (cm^{-1})
3439	1607	1419 1385	1361 1319	1139	1047	813	677	505

Table 2 shows the characteristic bands in IR (cm^{-1}) for the coordination compound and the corresponding assignments.

The intense and large band in the range $3200 - 3600 \text{ cm}^{-1}$ with maximum at 3439 cm^{-1} is attributed to the formation of the hydrogen bonds between water molecules and the alcoholic hydroxyl.^{13,14}

The intense band at 1647 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 upon the ionic one.¹⁵

The bands with maximum at 1419 cm^{-1} and 1385 cm^{-1} are attributed to the symmetric vibration $\nu_{\text{s}}(\text{COO})$. As the difference between $\nu_{\text{as}} - \nu_{\text{s}}$ is higher than 170 cm^{-1} one may say that the metal-carboxylate bond is mostly ionic, and the carboxylate group acts as a bidentate ligand.^{15,16}

Also, the existence of the two bands for $\nu_{\text{s}}(\text{COO})$ could be explained through the octahedral deformation.¹⁷

The band at 1319 cm^{-1} confirms that carboxylate group is acting as bidentate ligand.¹⁸

The band at 1047 cm^{-1} is attributed to the vibration of the OH bridge group.¹⁹ In accordance with Nagase *et al.*,²⁰ the 505 cm^{-1} band, obtained for the investigated complex can be attributed to the $\nu(\text{Cu-O})$ -oxygen vibration belonging to the COO^- group from the 3-hydroxypropionate anion.

Magnetic measurements

In table 3 the values of rectified magnetic molar susceptibility (χ_{M}) and effective magnetic moment (μ_{ef}) for $[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$ are presented.

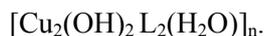
Table 3

Values of corrected magnetic molar susceptibility (χ_M) and effective magnetic moment for $[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$

Coordination homopolynuclear compound	$\chi_M \cdot 10^6 (\text{m}^3 \text{mol}^{-1} \text{K})$	$\mu_{\text{eff}}(\text{e}) (\mu_B)$	$\mu_{\text{spin}} (\mu_B)$
$[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$	1.19	1.67	1.73

The smaller value of the effective magnetic moment (experimentally determined $\mu_{\text{eff}}(\text{e})=1.67 \mu_B$) than that of the theoretical value of the magnetic moment "spin only" ($\mu_{\text{spin}}=1.73 \mu_B$) is due to a very weak superexchange interaction of ferromagnetic type through the oxygen atom of OH bridge.

The obtained solid emerald green 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:



Thermal conversion of Cu(II)-hydroxypropionate

In order to confirm the composition and the stereochemistry of the coordination compound, $[\text{Cu}_2(\text{OH})_2\text{L}_2(\text{H}_2\text{O})]_n$, as well as to establish the steps of conversion to CuO, the thermal analytical methods (TG, DTG, DTA) have been used (Fig. 3).^{21,22}

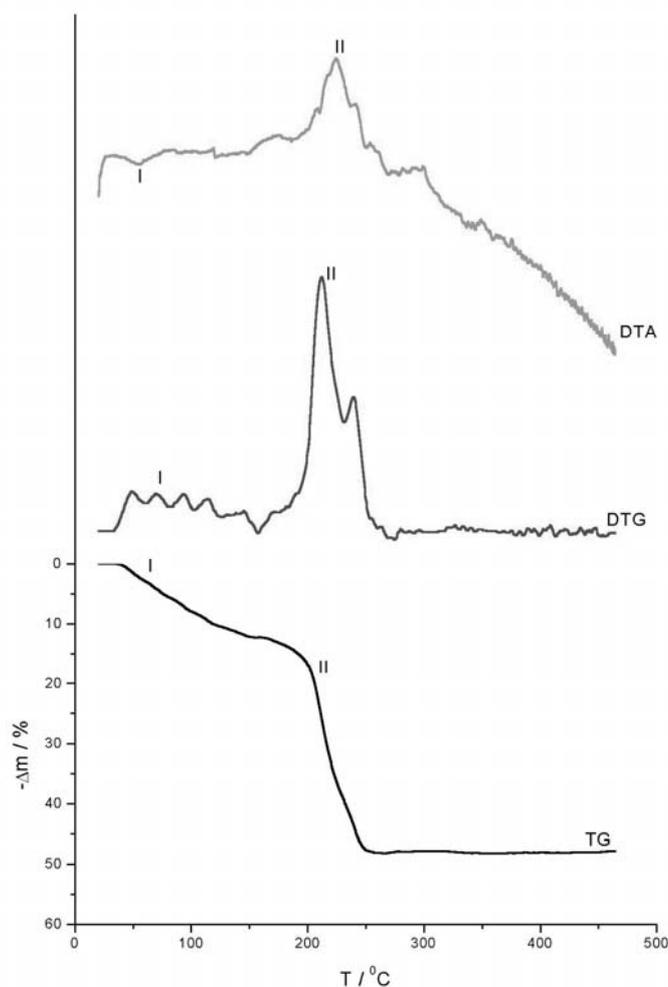
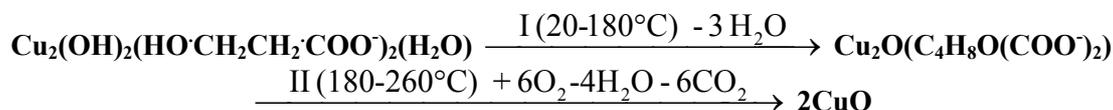


Fig. 3 – Thermal analytical curves for the coordination compound decomposition in static air atmosphere at the heating rate of $2.5 \text{ }^\circ\text{C min}^{-1}$.

The study of TG, DTG and DTA curves, recorded on a Q – 1500D MOM-Budapest type derivatograph, in a static air atmosphere in the temperature range of 20 – 450 °C, heating rate of

2.5 °C/min, suggests that at progressive heating of the coordinative compound the following steps occur:



The IR spectrum of the conversion product obtained at 450 °C exhibits only the bands characteristic for copper(II) oxide (534.28 cm⁻¹ and 420.48 cm⁻¹) being in agreement with the literature data.²³

The X-ray diffraction patterns show the characteristic peaks for CuO (tenorite) in accordance with JCPDS 48-1548.²⁴

CONCLUSIONS

The synthesis of the homopolynuclear coordination compound, unnotified in the scientific literature, was carried out by an original method, based on the oxidation reaction of 1,3-propanediol in aqueous–alcoholic system with Cu(II) nitrate. Under the working conditions (concentration, temperature, acidity), the nitrate ion – weak oxidizer – which does not break the hydrocarbonate chain, oxidizes 1,3-propanediol to 3-hydroxypropionic acid (3-hydroxypropionate as ligand). The oxidation product is coordinated at the Cu(II) cation, simultaneously with the precipitation of the homopolynuclear coordination compound [Cu₂(OH)₂ L₂(H₂O)]_n, which was studied both by chemical analysis methods and physical measurements.

REFERENCES

1. D. Knetsch and W.L. Groeneveld, *Inorg. Chim. Acta*, **1973**, 7, 81-87.
2. D. Knetsch and W.L. Groeneveld, *Rec. Trav. Chim.*, **1973**, 92, 855-864.
3. D. Knetsch and W.L. Groeneveld, *Inorg. Nucl. Chem. Letters*, **1976**, 12, 27-32.
4. M. Niculescu, N. Vaszilcsin, A. Magda and M. Medeleanu, *Chem. Bull. "Politehnica" Univ. Timisoara*, **1998**, 43, 149-153.
5. M. Niculescu, N. Vaszilcsin and P. Budrugaec, *Stud. Univ. Babeş-Bolyai, Chemia*, **1999**, XLIV 1-2, 275-286.
6. M. Niculescu, N. Vaszilcsin, C.M. Davidescu, P. Negrea, M. Birzescu and P. Budrugaec, *Rev. Roum. Chim.*, **2003**, 48(12), 997-1006.
7. I. Radoi, M. Birzescu, Fr. Golumbioschi and M. Stefanescu, *Rev. Chim. (Bucharest)*, **1985**, 36, 832-835.
8. B.M. Antti, *Acta Chem. Scand.*, **1973**, 27, 3513-3522.
9. K. Nakamoto, „Infrared and Raman spectra of inorganic and coordination compounds”, 5th Ed., K. Nakamoto, John Wiley & Sons, New York, 1997, p. 59-62.
10. a) R.L. Shriner, C.K.F. Hermann, T.C. Morrill, “The systematic identification of organic compounds”, 7th Ed., John Wiley & Sons, Inc., New York, 1998, p. 213-225, 264-265, 270, 304-313.
b) M. Avramov-Ivric, J.M. Léger, B. Beden, F. Hahn and C. Lamy, *J. Electroanal. Chem.*, **1993**, 351, 285-296.
11. M. Niculescu, R. Dumitru, A. Magda, G. Bandur and E. Şisu, *Rev. Chim. (Bucharest)*, **2007**, 58, 932-936.
12. C. Lepadatu and M. Andruh, “Forma moleculelor anorganice”, Editura Academiei Române, Bucureşti, 1998, p. 257-259.
13. P. Spacu, L. Patron, S. Plostinaru, A. Contescu and N. Stanica, *Rev. Roum. Chim.*, **1989**, 34, 1275-1281.
14. M. Brezeanu, L. Patron, O. Carp, M. Andruh and N. Stanica, *Rev. Roum. Chim.*, **1991**, 36, 545-551.
15. K. Nakamoto, Y. Morimoto and A.E. Martell, *J. Am. Chem. Soc.*, **1961**, 83, 4528-4532.
16. P. V. Khadikar, *J. Thermal Anal.*, **1987**, 32, 737-748.
17. I. Burbaciu and V.P. Sokolov, *Zh. Obsc. Chim.*, **1974**, XLIV, 1626-1632.
18. R.M. Silverstein, F.X. Webster and D.Kiemle, “Spectroscopic Identification of Organic Compounds”, John Wiley & Sons, Ltd., New York, 2005, p.72.
19. M. Maneva, N. Petroff and M. Pankova, *J. Thermal Anal.*, **1990**, 36, 577-587.
20. K. Nagase, K. Sato and N. Tanaka, *Bull. Chem. Soc. Japan*, **1975**, 48, 439-449.
21. M. Posposil, *J. Thermal Anal.*, **1990**, 36, 489-502.
22. M. Niculescu, N. Vaszilcsin, M. Birzescu, P. Budrugaec and E. Segal, *J. Therm. Anal. Cal.*, **2001**, 65, 881-889.
23. F.B. Freeman, D.S. Lee and A.L. Rozek: “Infrared spectra and characteristic frequencies ~ 700 – 300 cm⁻¹”, Interscience Publishers John Wiley & Sons, New York – London – Sydney, 1968.
24. M. Birzescu, M. Niculescu, R. Dumitru, P. Budrugaec and E. Segal, *J. Therm. Anal. Cal.*, **2008**, 94, 297-303.