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Review

HOMOPOLYNUCLEAR COORDINATION COMPOUNDS WITH CARBOXYLATE ORGANIC LIGANDS

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Year 1982

Prof. Mihail Bîrzescu elaborates a new synthesis method for homopolynuclear carboxylic complex compounds of metals (II and III). This method is based on the oxidation of 1,2-etanediol (ethylene glycol, EG) by the nitrate (NO_3^-) ion generated from d-block metal nitrates (M = Cu, Ni, Co, Zn, Fe, Cr) with the simultaneous isolation of the complex compounds from the reaction system.

This type of combinations can be used as generators/precursors of simple or mixed oxides or metals with special properties.

At the beginning of his research **Prof. Mihail Bîrzescu** worked very hard to establish the conditions in which some metal nitrates could oxidize EG **in a unitary way** to the glyoxylate ($C_2H_2O_4^-$) anion. The isolation of copper glyoxylate ($CuC_2H_2O_4$) complex combination was the most difficult, because of the different oxidation states of copper.

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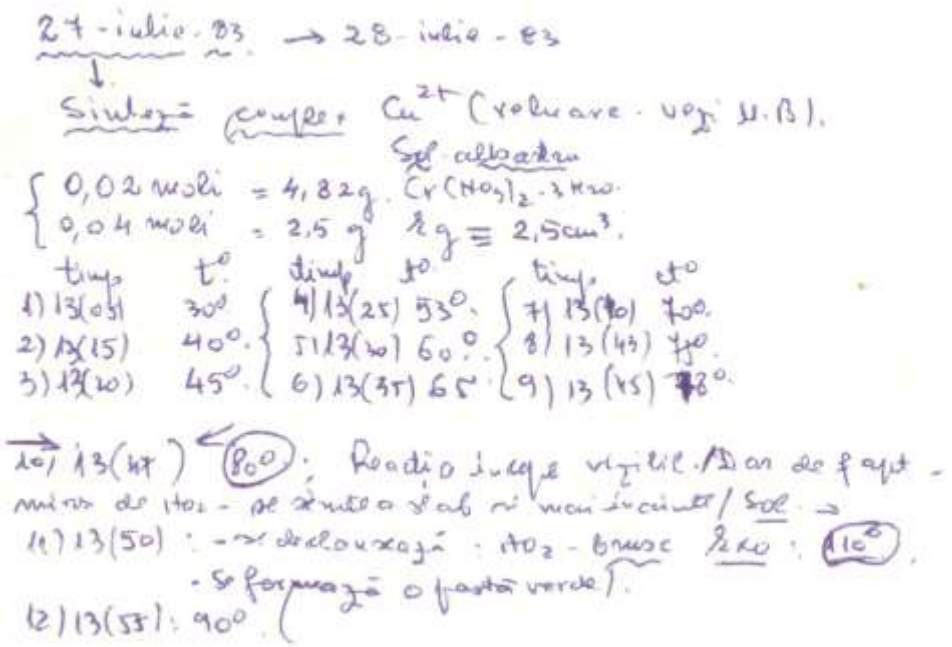


The chemical equation that lies at the base of the redox reaction is:

$$C_2H_4(OH)_2 + (2NO_3^- + [Cu(H_2O)_6]^{2+}) \rightarrow CuC_2H_2O_4 + 8H_2O + 2NO$$

copper glyoxylate

Apparently, this reaction does not imply the involvement of H_3O^+ ions, but their presence is necessary to force the nitrate ion to act as oxidant towards EG. The H_3O^+ ions necessary for the redox reaction to take place come from the hydrolysis of Cu(II) aquacation.

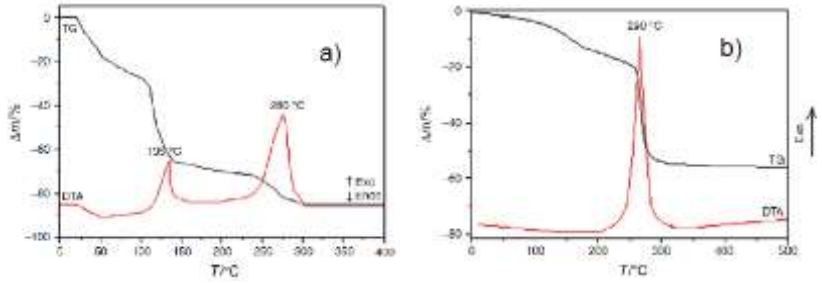
$$[Cu(H_2O)_6]^{2+} + H2O \Leftrightarrow [Cu(OH)(H_2O)_5]^+ + H_3O^+$$

The stabilization of glyoxylate ($C_2H_2O_4^{2-}$) dianion is favored by its interaction with Cu(II) ions (**chelation**).

Similarly, other M(II), M(III) or mixed M(II)-M(III) homopolynuclear carboxylic compounds were synthesized.

Prof. Mircea Ştefănescu studied the aerobic heating behavior for aqueous solutions of EG and Na(I), Co(II), Ni(II), Cu(II) and Fe(III) nitrates. The solutions were placed in platinum crucibles. The investigations used a MOM-Budapest derivatograph. For all nitrates except Na(I) nitrate it was established that after partial water loss the redox reaction between the two reactants, EG and NO_3^-, begins. The proof lies in the presence on the DTA curve of a first pronounced maximum, located under the temperature of 150°C (Figure 1a).

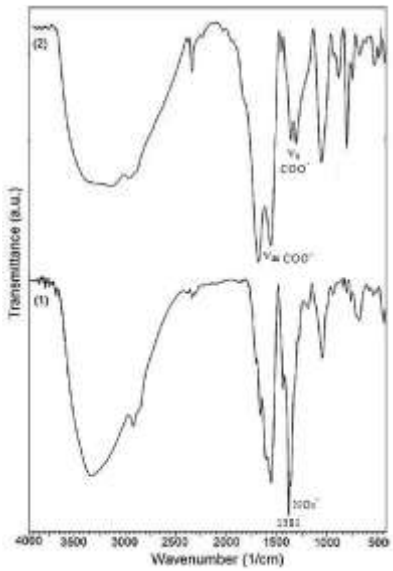
Figure 1: (a) $Ni(NO_3)_2$ – EG solution (redox reaction); **(b)** Ni(II) complex compound synthesized at 140°C (decomposition)



The exothermic effect is not found, though, in the case of M(II) nitrate solutions in the absence of EG. Thus, the exothermic effect cannot be assigned but to the EG oxidation by NO_3^- ion. The redox reaction begins at different temperatures, depending of the H3O+ ion concentration, which are produced following the metal aquacations hydrolysis.

The progress of the redox reaction was also followed with the help of the FT-IR spectroscopy (Figure 2).

Figure 2: The FT-IR spectra: **(1)** incomplete redox reaction (100°C); **(2)** complete redox reaction (140°C)



The presence of a band at 1381 cm^{-1} shows that the redox reaction is incomplete. If the redox reaction was completed, the vasim(COO^-) bands in the 1580-1650 cm^{-1} region and the vsim(COO^-) bands in the 1350-1400 cm^{-1} region appear for the reaction product, these being typical to complex combinations with carboxylate ligand.

The complex combinations which possess the **glyoxylate dianion ligand** were the center of numerous studies.

A series of papers were presented and analyzed at symposiums and conferences:

1. **Bîrzescu M.**, Ștefănescu M., Brezeanu M., Andruh M., "Combinații complexe ale Co(II) și Ni(II) conținând ligand anionul glioxilat" ("Co(II) and Ni(II) complex combinations containing the glyoxylate anion as ligand"), Conferința de Chimie și Inginerie Chimică, Bucharest, 22-23 October 1987.
2. **Bîrzescu M.**, Ștefănescu M., Brezeanu M., Andruh M., "Glioxilatul de Cu(II). Obținere și caracterizare" ("Cu(II) glyoxylate. Preparation and characterization"), Al III-lea Congres Național de Chimie, Bucharest, 21-24 September 1988.
3. **Bîrzescu M.**, Vaszilcsin N., Ștefănescu M., Niculescu M., "Catozi de cupru scheletați obținuți prin conversia termică a combinațiilor complexe Cu(II)-Al(III)-glioxilat" ("Cladding copper cathodes obtained through thermal conversion of Cu(II)-Al(III)-glyoxylate complex combinations"), Zilele Academice Timișene, Timișoara, 25-27 May 1995.
4. **Bîrzescu M.**, Ștefănescu M., Golmbioschi F., "Herstellung von Oxiden mit elektrokatalytisch aktiven Eigenschaften aus Metallkomplexen" ("Producing oxides with electrocatalytically active properties from metal complexes"), Simpozionul de Electrochimie Aplicată, Timișoara, 1985, p. 384.

Year 1990

Patent: Bîrzescu M., Cristea M., Ștefănescu M., Constantin G., "Procedeu de obținere a feritei de cobalt" ("Method of obtaining cobalt ferrite"), Nr. 102501/27.09.1990.

The newly proposed synthesis method was extended by **Prof. Mircea Niculescu** for the reaction between some metal nitrates and diverse diols, like 1,2- and 1,3-propanediol, with the obtaining of the corresponding complex combinations – **lactates and malonates**.

The fundamental studies regarding the synthesis and characterization of complex combinations with diol oxidation products as ligands led to the elaboration of a number of Ph.D. theses and published papers.

Ph.D. theses:

Mihail Bîrzescu – "Complecși cu etilenglicol și produșii săi de oxidare" ("Complex compounds with ethylene glycol and its oxidation products"), 1998, supervisor Acad.Prof.Dr.Doc. Maria Brezeanu;

Mircea Niculescu – "Combinații complexe cu liganzi produși de oxidare a diolilor" ("Complex combinations with diols oxidation products as ligands"), 2004, supervisor Prof.Dr.Ing. Ilie Julean;

Raluca Dumitru – "Compuși coordinativi obținuți în reacția dintre dioli și azotați metalici ca precursori pentru oxizi simpli și micști. Caracterizare și stabilitate termică" ("Coordination compounds obtained in the reaction between diols and metal nitrates as precursors for simple and mixed oxides. Characterization and thermal stability"), 2009, supervisor Acad.Prof.Dr.Doc. Eugen Segal.

Papers published in national and international journals:

1. **Bîrzescu M.**, Niculescu M., Ștefănescu M., Vaszilcsin N., "Studies on the reaction between 1,2-propanediol and some nitrates, Thermal and structural investigation", Buletinul

Ştiinţific al Universităţii Tehnice Timişoara (Chem. Bull. "Politehnica" Univ. (Timişoara)), 40 (1995) 83-89.

2. Niculescu M., Vaszilcsin N., **Bîrzescu M.**, Budrugeac P., Segal E., "Thermal and structural investigation of the reaction between 1,2-propanediol and Co(NO3)2·6H2O", J. Therm. Anal. Calorim., 65 (2001) 881-889.

3. Niculescu M., Vaszilcsin N., **Bîrzescu M.**, Budrugeac P., Segal E., "Thermal and structural investigation of the reaction between 1,2-propanediol and Ni(NO3)2·6H2O", J. Therm. Anal. Calorim., 63 (2001) 181-189.

4. Stefanescu M., Stefanescu O., Stoia M., Lazau C., "Thermal decomposition of some metal-organic precursors", J. Therm. Anal. Calorim., 88 (2007) 27-32.

5. **Bîrzescu M.**, Niculescu M., Dumitru R., Budrugeac P., Segal E., "Copper(II) oxalate obtained through the reaction of 1,2-ethanediol with Cu(NO3)2·3H2O", J. Therm. Anal. Calorim., 94 (2008) 297-303.

6. **Bîrzescu M.**, Niculescu M., Dumitru R., Carp O., Segal E., "Synthesis, structural characterization and thermal analysis of the cobalt(II) oxalate obtained through the reaction of 1,2-ethanediol with Co(NO3)2·6H2O", J. Therm. Anal. Calorim., 96 (2009) 979-986.

7. Niculescu M., **Bîrzescu M.**, Dumitru R., Sisu E., Budrugeac P., "Co(II)-Ni(II) heteropolynuclear coordination compound obtained through the reaction of 1,2-propanediol with metallic nitrates as precursor for mixed oxide of spinel type NiCo2O4", Thermochim. Acta, 493 (2009) 1-5.

8. Stefanescu O., Stefanescu M., "New Fe(III) malonate type complex combination for development of magnetic nanosized γ-Fe2O3", J. Organomet. Chem., 740 (2013) 50-55.

Besides the theoretical interest that the reactions which lie at the base of obtaining new polynuclear compounds present, the synthesized complex combinations constitute **precursors** for the preparation of simple or mixed oxides or metals with special properties.

It is worth mentioning that through the thermal conversion of M(III)-M'(II) complex combinations (M = Fe, Cr; M' = Ni, Co, Zn, Cu) a series of spinel oxidic systems **with magnetic and catalytic properties** were obtained, and these were the central focus for some Ph.D. theses:

Mircea Ștefănescu – "Considerațiuni asupra modului de formare a oxizilor micști din substanțe inițiale cu reactivitate crescută" ("Considerations over mixed oxides formation from highly reactive initial substances"), 1993, supervisor Prof.Dr. Zeno Simon;

Marcela Stoia – "Contribuții la obținerea de nanomateriale cu proprietăți magnetice, nedispersate și dispersate în matrici anorganice" ("Contributions to obtaining of nanomaterials with magnetic properties, undispersed and dispersed in inorganic matrices"), 2007, supervisor Prof.Dr.Ing. Ilie Julean;

Thomas Dippong – "Nanomateriale pe bază de cobalt nedispersate și dispersate în matrice de silice" ("Cobalt based nanomaterials undispersed and dispersed in silicon matrices"), 2008, supervisor Prof.Dr.Chem. Mircea Ștefănescu;

Oana Ștefănescu – "Metode noi de obținere a unor nanomateriale pe bază de γ-Fe2O3" ("Novel methods for obtaining new nanomaterials based on γ-Fe2O3"), 2010, supervisor Prof.Dr.Eng. Corneliu Davidescu;

Mirela Barbu – "Noi metode de sinteză a nanomaterialelor pe bază de MIICr2O4" ("Novel methods for synthesis of MIICr2O4 based nanomaterials"), 2012, supervisor Prof.Dr.Eng. Mircea Ștefănescu.

This field which was founded by **Prof. Mihail Bîrzescu**, chief of the "**Homo- and heteropolynuclear compounds with organic ligands**" research group, was developed and applied inside the Inorganic and Analytical Chemistry Group and, afterwards, inside the CAICAM department, by publishing of a large number of papers in specialized journals.

One of the applications of the synthesized complex combinations thermal conversion is the construction of **electrodes** made from oxidic films:

1. Rădoi I., **Bîrzescu M.**, Golumbioschi F., Ferentz A., Ştefănescu M., "Obţinerea de anozi cu pelicule electrocatalitic active, din complecşi metalici folosiţi în electroliza apei" ("Preparation of anodes with electrocatalytically active films from metallic complexes used in water electrolysis"), Rev. Chim.-Bucharest, 36 (1985) 832.
2. Golumbioschi F., **Bîrzescu M.**, Ştefănescu M., Nemeş M., "Elektrokatalytisch aktive anoden zur verwendung bei der wasserelektrolyse. I. Anoden mit oxydschichten aufgrund von nickel" ("Electrocatalytically active anodes for use in water electrolysis. I. Anodes with nickel oxide film"), Simpozionul de Electrochimie Aplicată, Timişoara, 1985, p. 392.
3. Vaszilcsin N., **Bîrzescu M.**, Ştefănescu M., Niculescu M., "Cathodes of copper skeleton from Cu(II)-Al(III)-glyoxylates generated in situ", Bulg. Chem. Commun., 29 (1996) 293-301.

Another important application is the use of mixed oxidic systems resulted from the decomposition of complex combinations as **catalyzers** in heterogeneous catalysis:

1. Ştefănescu M., Sasca V., **Bîrzescu M.**, Crişan D., Mracec M., "Obţinerea cromitului de cupru prin descompunerea termică a complexului heteronuclear de Cr(III)-Cu(II), conţinând ca ligand dianionul de glioxilat" ("Preparation of copper chromite through thermal decomposition of Cr(III)-Cu(II) heteronuclear complex containing the glyoxylate dianion as ligand"), Rev. Chim.-Bucharest, 40 (1989).
2. Ştefănescu M., Sasca V., **Bîrzescu M.**, "Studies on the thermal decomposition of Cr(III) and Cu(II) heteropolynuclear glyoxylates", J. Therm. Anal. Calorim., 56 (1999) 579-586.
3. Ştefănescu M., Sasca V., **Bîrzescu M.**, "Thermal behaviour of the homopolynuclear glyoxylate complex combinations with Cu(II) and Cr(III)", J. Therm. Anal. Calorim., 72 (2003) 515-524.
4. Ştefănescu M., Barbu M., Vlase T., Barvinschi P., Barbu-Tudoran L., Stoia M., "Novel low temperature synthesis method for nanocrystalline zinc and magnesium chromites", Thermochim. Acta, 526 (2011) 130-136.

Crystalline nanomaterials of **M(II)Fe_2O_4 ferrite** type obtained from homo- and heteropolynuclear complex combinations show advanced magnetic properties:

1. Caizer C., Ştefănescu M., Muntean C., Hrianca I., "Studies and magnetic properties of Ni-Zn ferrite synthesized from the glyoxylates complex combination", J. Optoelectron. Adv. M., 3 (2011) 919-924 (11 citations).
2. Caizer C., Ştefănescu M., "Magnetic characterization of nanocrystalline Ni-Zn ferrite powder prepared by the glyoxylate precursor method", J. Phys. D Appl. Phys., 35 (2002) 3035-3040 (93 citations).

3. Ştefănescu M., Stoia M., Dippong T., Ştefănescu O., Barvinschi P., "Preparation of CoxFe3-xO4 Oxydic System Starting from Metal Nitrates and Propanediol", Acta Chim. Slov., 56 (2009) 379-385 (7 citations).

4. Ştefănescu M., Stoia M., Caizer C., Dippong T., Barvinschi P., "Preparation of CoxFe3-xO4 nanoparticles by thermal decomposition of some organo-metallic precursors", J. Therm. Anal. Calorim., 97 (2009) 245-250 (3 citations).

5. Ştefănescu M., Stoia M., Ştefănescu O., Barvinschi P., "Obtaining of Ni0.65Zn0.35Fe2O4 nanoparticles at low temperature starting from metallic nitrates and polyols", J. Therm. Anal. Calorim., 99 (2010) 459-464, 2010 (10 citations).

Inside the "**Science and Engineering of Oxidic Materials**" research collective, a series of theses elaborated under the supervision of Prof.Dr.Eng. Ioan Lazău have also used the synthesis method for carboxylic complex combinations for obtaining oxidic systems with specific properties.

The same collective published a series of papers with international visibility centered around precursors obtained through the synthesis method of homo- and heteropolynuclear carboxylate coordination compounds:

1. Păcurariu C., Lazău I., Becherescu D., Bobos I., "Characterization of spinel pigments in the ZnO-CoO-Al2O3 system prepared using organometallic precursors", Rev. Roum. Chim., 42 (1997) 447-454.

2. Lazău I., Păcurariu C., Lazău R.I., "Study of the specific features regarding the formation of the spinel phases in the CoO-Co2O3-Al2O3 system", Interceram, 51 (2002) 266-271.

3. Sim A., Lazău I., Păcurariu C., Lita M., Becherescu D., "The hydration of some calcium aluminates obtained from organic precursors", Rev Chim.-Bucharest, 54 (2003) 38-42.

4. Păcurariu C., Lazău I., Ecsedi Z., Lazău R., Barvinschi P., Marginean G., "New synthesis methods of MgAl2O4 spinel", J. Eur. Ceram. Soc., 27 (2007) 707-710.

5. Lazău I., Păcurariu C., Ianoş R., Ecsedi Z., Ianoşev S., "Particular aspects of oxide powders synthesis using unconventional methods", Rev. Rom. Mat., 37 (2007) 185-197.

6. Ianoşev S., Lazău R., Suba M., Păcurariu C., Lazău I., "Synthesis and characterization of some thermoresistant pigments based on the Al3+ □ Cr3+ substitution", Stud. Univ. Babes-Bol., 54 (2009) 189-201.

Through a new synthesis method (**modified sol-gel method**), the carboxylic complex combinations were included in the pores of silica hybrid gels, which through decomposition and adequate thermal treatments lead to oxidic nanocomposites inside the SiO2 matrix.

Prof. Mircea Ştefănescu's research group was especially successful through the publication of scientific papers in specialized (ISI) journals, the elaboration of projects and Ph.D. theses:

1. Ştefănescu M., Caizer C., Stoia M., Ştefănescu O., "Ni,Zn/SiO2 ferrite nanocomposites prepared by an improved sol-gel method and their characterization", J. Optoelectron. Adv. M., 7 (2005) 607-614 (13 citations).

2. Stoia M., Caizer C., Ștefănescu M., Barvinschi P., Julean I., "Obtaining of Ni0.65Zn0.35Fe2O4/SiO2 nanocomposites by thermal decomposition of complex compounds embedded in silica matrix", J. Therm. Anal. Calorim., 88 (2007) 193-200 (11 citations).

3. Ștefănescu O., Davidescu C., Ștefănescu M., Stoia M., "Preparation of FexOy/SiO2 nanocomposites by thermal decomposition of some carboxylate precursors formed inside the silica matrix", J. Therm. Anal. Calorim., 97 (2009) 203-208 (10 citations).

4. Barbu M., Ștefănescu M., Stoia M., Vlase G., Barvinschi P., "New synthesis method for M(II) chromites/silica nanocomposites by thermal decomposition of some precursors formed inside the silica gels", J. Therm. Anal. Calorim., 108 (2012) 1059-1066.

5. Ștefănescu O., Vlase G., Barbu M., Barvinschi P., Ștefănescu M., "Preparation of CuFe2O4/SiO2 nanocomposite starting from Cu(II)-Fe(III) carboxylates embedded in hybrid silica gels", J. Therm. Anal. Calorim., 113 (2013) 1245-1253.

Projects

1. Nanocompozite de tip NixZn(1-x)Fe2O4 cu proprietăți magnetice dirijate, obținute prin două metode neconvenționale de sinteză, originale (Ni¬xZn(1-x)Fe2O4 type nanocomposites with directed magnetic properties, obtained through two original, unconventional synthesis methods), theme grant nr. 29 Cod CNCSIS 648 from 2005;

2. Study of the magnetic properties of nanocomposites of Ni(x)Zn(1-x)Fe(2)O(4) SiO2 type, contract of scientific research, No. 6891/2005;

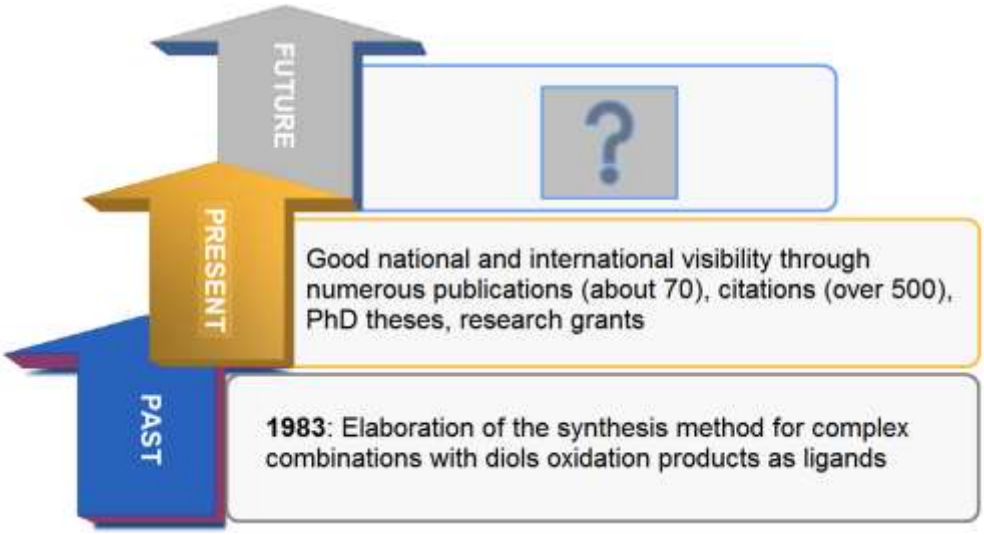
3. PN II 71 – 026/2010 with title: Cercetări complexe privind obținerea și proprietățile magnetice ale sistemelor de nanoparticule ferimagnetice de CoδFe3-δO4 surfactate/nesurfactate și biocompatibile cu potențiale aplicații în terapia cancerului (Complex research regarding the preparation and magnetic properties of surfactated/unsurfactated biocompatible CoδFe3-δO4 ferimagnetic nanoparticle systems with potential applications in cancer therapy).

CONCLUSIONS

Now that I prepared this material I realized what a great opportunity I had in my professional (scientific) carrier, to work besides Prof. Mihail Bîrzescu.

It is unfortunate that we did not succeed to be close all the time!? Still we respected each other and appreciated one another until the end when we were also ready to apply for a research grant related to the discussed research field.

More than 25 years and until the present day we have worked and elaborated this field through projects, Ph.D. theses and over 50 scientific papers with international visibility.



Prof. Mihail Bîrzescu left a valuable research field to his younger colleagues, who will maybe someday be grateful to him!

Îți mulțumesc, Mișule!