NEW FRONTIERS IN CHEMISTRY
New Front. Chem.

(*former Annals of West University of Timişoara – Series of Chemistry*)

(2016) Volume 25, Number (Issue) 1, pp. 1-81

Special Issue

– Dedicated to Prof. Dr. Mihail Bîrzescu & Prof. Dr. Carol Csunderlik, in memoriam –

Guest Editors

ADRIAN CHIRIAC
West University of Timişoara
Faculty of Chemistry, Biology, Geography
16 Pestalozzi Bd., RO-300115, Timişoara, ROMANIA
E-mail: adrian.chiriac@e-uvt.ro

MIHAI-COSMIN PASCARIU
“Vasile Goldiş” Western University of Arad
Faculty of Pharmacy
86 Liviu Rebreanu, RO-310045, Arad, ROMANIA
E-mail: mihai.cosmin.pascariu@gmail.com

TABLE OF CONTENTS

continuing…

…continued

This issue of NEW FRONTIERS IN CHEMISTRY appeared with the financial support of "CHEMEIA SEMPER" ASSOCIATION, TIMIŞOARA.

PUBLISHER:
Universitatea de Vest
din Timişoara

NEW FRONTIERS IN CHEMISTRY: METADATA

New Frontiers in Chemistry (New Front. Chem.) is an open-access fee-free peer-review international academic journal addressing the modern trends and frontiers in fundamental, applicative and multidisciplinary chemistry, paralleling the ever-expanding chemical data, methods, and compounds available and continuously produced, towards cross fertilizing the multidisciplinary ideas as coming from Chemistry combined with Mathematics, the Natural and Applied sciences (Physics, Biology, Medicine, Agriculture, Environmental, Engineering), and beyond.

NEW FRONTIERS IN CHEMISTRY
(NEW FRONT. CHEM.)
is published biannually by

West University of Timișoara
Blvd. V. Parvan 4
Timisoara 300223, ROMANIA
E-mail: newfrontchem@iqstorm.ro
Web: www.newfrontchem.iqstorm.ro

ISSN 2393 – 2171
ISSN-L 2393 – 2171

Subscription Price per Volume
Electronic: open access   Print: on demand by above email address

Additional color graphics is available in the e-version of this Journal

NEW FRONTIERS IN CHEMISTRY: EDITORS

Editorial Board:

Advisory Editors
(from members of Biology-Chemistry Department of West University of Timișoara):

VASILE OSTAFE (Biochemistry, Chromatography, Environmental Chemistry)
IONEL CIUCANU (Instrumental Techniques for Analytical Chemistry)
ADRIANA ISVORAN (Biophysics, Bioinformatics)
MIHAI V. PUTZ (Nanochemistry, Quantum Chemistry)
TITUS VLASE (Thermal Analysis, Chemical Kinetics, Chemistry of Solid State)
GABRIELA VLASE (Inorganic Chemistry, Thermal Analysis)
OTILIA BIZEREA (Inorganic Chemistry)
GABRIELA PREDA (Organic Chemistry, Catalysis)
CONSTANTIN BOLCU (Organic Chemistry, Polymers)
VLAD CHIRIAC (General and Analytical Chemistry, Electrochemistry)
DANA VLASCICI (Analytical Chemistry)
DANIELA DASCALU (Thermodynamics and Chemical Statistics)
CORINA DUDA-SEIMAN (QSAR, Organic Chemistry, Medicinal Chemistry)
LAURA PITULICE (Environmental Chemistry)
HORIA POPOVICI (Colloidal Chemistry, Analytical Chemistry)
BEATRICE VLAD-OROS (Chemical and Enzyme Kinetics)
MARIANA ALBULESCU (Organic Chemistry, Natural Compounds)
DORINA MODRA (Organic Chemistry)
MIRCEA SELEGEAN (Biotechnologies)
NICOLETA IANOVIC (Aerobiology, Plant Physiology)

Honorary Editors
(as Doctor Honoris Causa of WUT/CBG & Formers Editors and Developers of Annals of West University of Timișoara – Series Chem.):

ALEXANDRU BALABAN (Texas A&M University at Galveston, USA, & Romanian Academy, Romania)
HAGEN KLEINERT (Berlin Free University, Germany)
KATLEEN SWALLOW (Merrimack College, USA)
GABOR NÁRÁY-SZABÓ ("Lorand Eőtvős" University Budapest, Hungary)
EUGEN SEGAL (University of Bucharest, Romanian Academy, Romania)
VICTOR EMANUEL SAHINI (Polytechnic Bucharest, Romanian Academy, Romania)
MARIUS ANDRUH (Romanian Academy, Bucharest)
ZENO SIMON (Romanian Academy, Romania)
ADRIAN CHIRIAC (West University of Timisoara, Romania)
MIRCEA MRACEC (West University of Timisoara, Romania)
VASILE OSTAFE (West University of Timisoara, Romania)
NICOLAE BONCIOCAT (†, Babes-Bolyai University, Cluj-Napoca, Romania)
ALAN R. KATRITZKY (†, University of Florida, Gainesville, USA)

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 1-2
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Comment

FOREWORD

Adrian Chiriac ♣
West University of Timişoara, Faculty of Chemistry, Biology, Geography, 16 Pestalozzi Bd., RO-300115, Timişoara, Romania

The development and affirmation of the Faculty of Industrial Chemistry from Timişoara shortly after its creation in 1948, despite great difficulties in ensuring the material resources necessary for the learning system and the laboratories, was the result of the effort and the endeavor of its founders, professors Coriolan Drăgulescu and Ilie Murgulescu, and also of the decisive contribution of the first generation of teachers who made it possible for a high quality university education, successfully represented by Timişoara's chemical engineers.

During the years 1962 and 1963, the Faculty of Industrial Chemistry from Timişoara has solidified in value its teaching and researching staff, by "refreshing" itself with a new generation of young honorable graduates from the Romanian higher education facilities: Barbu Demian, Ecaterina Merca, Delia Perju, Adalbert Deaky, Maria Nemeş, Adrian Chiriac, Karlhunz Kohut, Romulus Minea (Faculty of Industrial Chemistry – Timişoara), Carol Csunderlik, Maria Nuţiu (Faculty of Chemistry – Cluj-Napoca), Mihail Bîrzescu, Ilona Bîrzescu (University of Bucharest) and Francisc Klepp (Faculty of Mathematics – Timişoara). Under specific circumstances, B. Demian ("Philip Morris", USA), F. Kerek ("Max Planck" Institute, Germany) and K. Kohut (in production) have successfully continued their professional and research activity in other workplaces.

All the others remained loyal to the Faculty where they were formed and where they ascended in their academic career, both scientifically and didactically, for over four decades, in a very beneficial collaboration for preparing Politehnica Timişoara "brand" chemical engineers. Therefore, we were deeply saddened when, in 2012, two good colleagues, Mihail Bîrzescu and Carol Csunderlik, left us by passing into eternity, especially since their close friendship was well known. In these sad circumstances, of final departure, we were struck by some "coincidences" concerning the similarities of their two destinies.

Mihail Bîrzescu (b. October 6, 1941) and Carol Csunderlik (b. October 9, 1941) were born at very close dates in the same year. Although they had degrees in chemistry at different faculties from the centers University of Bucharest and of Cluj-Napoca, respectively, they professed together as teachers at the Faculty of Industrial Chemistry from Timişoara, carrying uninterrupted a meritorious activity through which they contributed to the modernization of

---

♣ Correspondent author e-mail: adrian.chiriac@e-uvt.ro

both education and research in the Faculty, to the training of 36 generations of chemical engineers, and to their improvement through master and doctoral studies. Fortunately, it remained in the Faculty's memory book an entertaining story in which Mihail Bîrzescu and Carol Csunderlik made a chemical synthesis that used nitric acid and during which they both got "xanthoproteic freckles" on their faces. They died the same year, in 2012, with only days in between.

Wishing to better preserve and honor their memories and to pay tribute to the life and to the teaching activity of these two dear colleagues, "Chemeia Semper" Association organized three symposia under the name "Stability and Reactivity in Coordination Chemistry - in memoriam Mihail Bîrzescu", which took place on October 25, 2013, November 7, 2014, and September 18, 2015.

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 3-6
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Comment

CURRICULUM VITAE
BÎRZESCU MIHAIL (1941 – 2012)

- Date of birth: October 6, 1941.
- Place of birth: Drăgănești (Republic of Moldova).
- Education:
    - Secondary School No. 1 and "Nicolae Bălcescu" High School from Râmnicu Vâlcea (1959);
    - Faculty of Chemistry, University of Bucharest (1959-1964);
    - PhD thesis (1999): "Combinații complexe cu etilen glicol și produșii săi de oxidare (Complex combinations with ethylene glycol and its oxidation products)", Faculty of Chemistry, University of Bucharest, supervisor acad. prof. Maria Brezeanu; he developed an unconventional synthetic method based on the redox reaction between diols and metal nitrates with the formation of homo- and polynuclear coordination compounds; through their thermal degradation he obtained oxidic systems with magnetic, catalytic and electrocatalytic properties.

- Professional positions:
    - 1964-2004: Department of General, Inorganic and Analytical Chemistry, Faculty of Industrial Chemistry and Environmental Engineering, University Politehnica Timișoara.

- Teaching activity: General and Inorganic Chemistry, Analytical Chemistry.

- Research interest: the chemistry of complex compounds.

- Collaborations with West University of Timişoara, “Victor Babeş” University of Medicine and Pharmacy of Timişoara, “Babeş-Bolyai” University of Cluj-Napoca, University Politehnica of Bucharest and University of Bucharest.

- Scientific publications:
  - Books: 8;
  - Primary publications: > 80;
  - Patents: 2;
  - Research contracts: 9;
  - Communications: 37.

- Research articles:
  - Published in dedicated journals: 13 (papers published abroad: 9);
  - Published in volumes of national and international scientific events: 5;
  - Unpublished communications: 15;
  - Communicated works (as PhD student): 35.

List of scientific papers (selective)

A. Treaties, courses, laboratory guides, exercise books:

1. M. Bîrzescu, A. Ferencz, R. Pomoje-Marcu, “Îndrumător pentru lucrări practice de chimie anorganică”, Ed. IPT, 1976.
2. A. Kuzman, V. Chiriac, M. Bîrzescu, D. Lazăr, M. Mitrănescu, D. Oprescu, M. Pârlea, “Îndrumător pentru lucrări practice de chimie analitică instrumentală”, Ed. IPT, 1976.
3. R. Pomoje-Marcu, A. Ferencz, M. Bîrzescu, “Curs de chimie anorganică. Elemente reprezentative și combinațiile lor”, Ed. IPT, 1979.
4. R. Pomoje, A. Ferencz, M. Bîrzescu, “Curs de chimie anorganică. Elemente tranziționale și combinațiile lor”, Ed. IPT, 1979.
5. M. Bîrzescu, V. Chiriac, A. Ferecz, L. Magyar, D. Oprescu, R. Pomoje-Marcu, “Îndrumător pentru lucrări practice de chimie anorganică”, Ed. IPT, 1980.
6. R. Pomoje-Marcu, A. Ferencz, M. Bîrzescu, “Curs de chimie anorganică. Atomul, legătura chimică”, Ed. IPT, 1982.
7. M. Bîrzescu, V. Chiriac, R. Kuzman, Gh. Mara, M. Ştefănescu, D. Tița, “Îndrumător pentru lucrări practice de chimie analitică instrumentală”, Ed. IPT, 1982.
8. R. Pomoje-Marcu, L. Magyar, M. Bîrzescu, “Exerciții și probleme de chimie anorganică”, Ed. IPT, 1985.

B. Scientific articles (indexed in the *ISI Web of Science* and *Scopus* databases):

1. Title: New methods to obtain carboxylic acids by oxidation reactions of 1,2-ethanediol with metallic nitrates.

Authors: Niculescu, Mircea; Ledeti, Ionut; Birzescu, Mihail.

Source: JOURNAL OF ORGANOMETALLIC CHEMISTRY Volume: 767 Pages: 108-111 DOI: 10.1016/j.jorganchem.2014.05.041 Published: SEP 15 2014.

2. Title: SYNTHESIS-STRUCTURE RELATIONSHIP IN THE AQUEOUS ETHYLENE GLYCOL-IRON(III) NITRATE SYSTEM.

Authors: Rosu, Dan; Birzescu, Mihail; Milea, Marius-Silviu; Pascariu, Mihai-Cosmin; Sasca, Viorel; Niculescu, Mircea.

Source: REVUE ROUMAINE DE CHIMIE Volume: 59 Issue: 9 Pages: 789-796 Published: SEP 2014.

3. Title: SYNTHESIS AND THERMAL ANALYSIS OF THE NICKEL(II) OXALATE OBTAINED THROUGH THE REACTION OF ETHYLENE GLYCOL WITH $Ni(NO_3)_2 \cdot 6H_2O$.

Authors: Birzescu, Mihail; Milea, Marius; Rosu, Dan; Ledeti, Ionut; Rafaila, Madian; Sasca, Viorel; Niculescu, Mircea.

Source: REVUE ROUMAINE DE CHIMIE Volume: 59 Issue: 6-7 Pages: 555-563 Published: JUN-JUL 2014.

4. Title: SYNTHESIS AND CHARACTERIZATION OF THE POLYNUCLEAR COORDINATION COMPOUND OBTAINED THROUGH THE REACTION OF 1,3-PROPANEDIOL WITH $Cu(NO_3)_2 \cdot 3H_2O$.

Authors: Niculescu, Mircea; Budrugeac, Petru; Ledeti, Ionut; Pode, Vasile; Birzescu, Mihail.

Source: REVUE ROUMAINE DE CHIMIE Volume: 58 Issue: 4-5 Pages: 387-392 Published: APR-MAY 2013

5. Title: 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 $NiCo_2O_4$.

Authors: Niculescu, M.; Birzescu, M.; Dumitru, Raluca; Sisu, E.; Budrugeac, P.

Source: THERMOCHIMICA ACTA Volume: 493 Issue: 1-2 Pages: 1-5 DOI: 10.1016/j.tca.2008.03.011 Published: SEP 10 2009.

6. Title: Synthesis, structural characterization and thermal analysis of the cobalt(II) oxalate obtained through the reaction of 1,2-ethanediol with $Co(NO_3)_2 \cdot 6H_2O$.

Authors: Birzescu, M.; Niculescu, M.; Dumitru, Raluca; Carp, Oana; Segal, E.

Source: JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY Volume: 96 Issue: 3 Pages: 979-986 DOI: 10.1007/s10973-009-0054-z Published: JUN 2009.

7. Title: COPPER(II) OXALATE OBTAINED THROUGH THE REACTION OF 1,2-ETHANEDIOL WITH $Cu(NO_3)_2 \cdot 3H_2O$ Structural investigations and thermal analysis.

Authors: Birzescu, M.; Niculescu, M.; Dumitru, Raluca; Budrugeac, P.; Segal, E.

Source: JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY Volume: 94 Issue: 1 Pages: 297-303 DOI: 10.1007/s10973-007-8599-1 Published: OCT 2008.

8. Title: Structural investigations and thermal analysis of the coordination compound obtained through the reaction of 1,3-propanediol with $Co(NO_3)_2 \cdot 6H_2O$.

Authors: Niculescu, M.; Vaszilcsin, N.; Davidescu, C.M.; Negrea, P.; Birzescu, M.; Budrugeac, P.

Source: REVUE ROUMAINE DE CHIMIE Volume: 48 Issue: 12 Pages: 997-1006 Published: DEC 2003.

9. Title: Thermal behaviour of the homopolynuclear glyoxylate complex combinations with Cu(II) and Cr(III).

Authors: Stefanescu, M.; Sasca, V.; Birzescu, M.

Source: JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY Volume: 72 Issue: 2 Pages: 515-524 DOI: 10.1023/A:1024565313792 Published: 2003.

10. Title: Thermal and structural investigation of the reaction between 1,2-propanediol and $Co(NO_3)_2 \cdot 6H_2O$.

Authors: Niculescu, M.; Vaszilcsin, N.; Birzescu, M.; .Budrugeac, P.; Segal, E.

Source: JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY Volume: 65 Issue: 3 Pages: 881-889 DOI: 10.1023/A:1011944603225 Published: 2001.

11. Title: Thermal and structural investigation of the reaction between 1,2-propanediol and $Ni(NO_3)_2 \cdot 6H_2O$.

Authors: Niculescu, M.; Vaszilcsin, N.; Birzescu, M.; Budrugeac, P.; Segal, E.

Source: JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY Volume: 63 Issue: 1 Pages: 181-189 DOI: 10.1023/A:1010100823234 Published: 2001.

12. Title: Studies on the thermal decompositions of heteropolynuclear glyoxylates of Cr(III) and Cu(II).

Authors: Stefanescu, M.; Sasca, V.; Birzescu, M.

Source: JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY Volume: 56 Issue: 2 Pages: 579-586 DOI: 10.1023/A:1010165030191 Published: 1999.

13. Title: Spinel pigments in the ZnO-CoO-Al_2O_3-Cr_2O_3 system prepared from organometallic precursors.

Authors: Păcurariu, C., Ştefãnescu, M., Lazău, I., Bîrzescu, M.

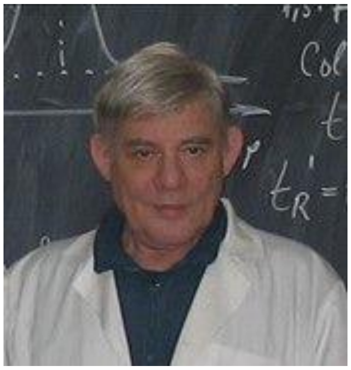
Source: KEY ENGINEERING MATERIALS Volumes: 132-136 Pages 113-116 DOI: 10.4028/www.scientific.net/KEM.132-136.113 Published: 1997.

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 7-11
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Comment

CURRICULUM VITAE
CSUNDERLIK CAROL (1941 – 2012)



- Date of birth: October 9, 1941.

- Place of birth: Reșița (Romania).

- Education:
  - Mixed High School No. 1, Reșița (1959);
  - Faculty of Chemistry, "Babeș-Bolyai" University of Cluj-Napoca (1959-1964), specialization: Organic Chemistry;
  - PhD in Chemistry (1970-1977), Faculty of Chemistry, "Babeș-Bolyai" University of Cluj-Napoca.

- Teaching career: University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering (1964-2011);
  - Teaching subjects (courses and laboratory applications): Organic Chemistry, Biochemistry, Natural Compounds Chemistry, Spectroscopic Methods for Structure Determination;
  - Full professor from 1992, PhD supervisor (over 20 theses) at Department of Organic Chemistry (head of department at Department of Applied Chemistry and Natural and Organic Compounds Engineering during 1990-2000).

- 1996-2005: scientific researcher (CS I) at Institute of Chemistry Timișoara of Romanian Academy.

- Co-author:
  - “Curs de chimie organică” (5 volumes);
  - “Structura și proprietățile compușilor organici”.

- Mentor for pupils who participated at chemistry national contests (“olimpiade”) for 15 years, also a member in the contests’ commissions.

- Research fields: the chemistry of carbonic acid’s organic derivatives, various organic syntheses, spectroscopic methods for determination of organic compounds structure (NMR, IR, MS, RX); head of national research projects (both CNCSIS and ANCSIS).

- Scientific collaborations with universities from Romania (West University of Timișoara, “Victor Babeș” University of Medicine and Pharmacy of Timișoara, “Babeș-Bolyai” University of Cluj-Napoca, University Politehnica of Bucharest, “Gheorghe Asachi” Technical University of Iași and “Alexandru Ioan Cuza” University of Iași) and other countries (Institute of Organic Chemistry – Technical University Braunschweig from Germany, INSA Lyon from France, Montpellier 2 University from France, University of Seville from Spain, University of Alabama from USA).

- Scientific career: over 100 scientific works published locally and abroad.

- Patents: 7.

- The “Nicolae Teclu” prize of the Romanian Academy (1989), member in the scientific committee of the Conference of Chemical Societies from Southeastern Europe (2002), editor for Revista de Chimie – Bucharest and editor-in-chief for Chemical Bulletin of “Politehnica” University of Timisoara, member of the American Chemical Society and leading member in the Romanian Chemical Society.

List of scientific papers (selective):

A. Books:

- Radu Bacaloglu, Carol Csunderlik, Liviu Cotarcă, “Structura și proprietățile compușilor organici”, vol. I, Ed. Tehnică. București, 1985;
- Carol Csunderlik, Liviu Cotarcă, Hans Horst Glett, “Structura și proprietățile compușilor organici”, vol II – “Hidrocarburi”, Ed. Tehnică, București, 1987.

B. Typed courses:

- Radu Bacaloglu, Carol Csunderlik, “Chimie organică”, Ed. Politehnica, Timișoara, 1985:
    - Vol. I: “Introducere. Hidrocarburi”;
    - Vol. II: “Combinații organice”;
    - Vol. III: “Combinații organice cu funcțiuni simple”;
    - Vol. IV: “Combinații organice cu funcțiuni compuse”.

C. Scientific articles (indexed in the *ISI Web of Science* and *Scopus* databases):

1. Title: Theoretical Considerations on the Hydrolysis of 2-Dichloromethylbenzimidazole
Authors: Pop, Raluca; Medeleanu, Mihai; Csunderlik, Carol
Source: INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY Volume: 111 Issue: 12 Pages: 2868-2873 DOI: 10.1002/qua.22776 Published: OCT 2011

2. Title: Bis(O-nitrophenyl) Carbonate as a New Reagent for the Synthesis of Chiral Oxazolidin-2-ones
Authors: Simon, Monika; Micle, Andreea; Badea, Valentin; Csunderlik, Carol
Source: SYNTHETIC COMMUNICATIONS Volume: 39 Issue: 15 Pages: 2633-2639 Article Number: DOI: 10.1080/00397910802663360 Published: 2009

3. Title: Synthesis of Bis-ureas from Bis(o-nitrophenyl) Carbonate
Authors: Turoczi, Maria-Cristina; Simon, Monika; Badea, Valentin; Csunderlik, Carol
Source: MOLECULES Volume: 13 Issue: 12 Pages: 3192-3197 DOI: 10.3390/molecules13123192 Published: DEC 2008

4. Title: Structural Studies of Some o- and p-Nitrophenylcarbamates by IR Spectroscopy and X-Ray Diffraction
Authors: Simon, Monika; Csunderlik, Carol; Jones, Peter G.
Source: ZEITSCHRIFT FUR NATURFORSCHUNG SECTION B-A JOURNAL OF CHEMICAL SCIENCES Volume: 63 Issue: 12 Pages: 1402-1406 Published: DEC 2008

5. Title: Solid-phase lipase biocatalysts for kinetic resolutions
Authors: Peter, Francisc; Zarcula, Cristina; Kakasi-Zsurka, Sandor; Croitoru, Ramona; Davidescu, Corneliu; Csunderlik, Carol
Source: JOURNAL OF BIOTECHNOLOGY Meeting Abstract: V3-P-049 Volume: 136 Pages: S374-S374 DOI: 10.1016/j.jbiotec.2008.07.860 Supplement: S Published: OCT 2008

6. Title: Enhancement of lipases enantioselectivity by entrapment in hydrophobic sol-gel materials: Influence of silane precursors and immobilization parameters
Authors: Peter, Francisc; Zarcula, Cristina; Kiss, Claudia; Csunderlik, Carol; Poppe, Laszlo
Source: JOURNAL OF BIOTECHNOLOGY Volume: 131 Issue: 2 Pages: S109-S109 DOI: 10.1016/j.jbiotec.2007.07.187 Supplement: S Published: SEP 2007

7. Title: Synthesis of new active o-nitrophenyl carbamates
Authors: Simon, M.; Csunderlik, C.; Cotarca, L.; Caproiu, M.T.; Neda, I.; Turoczi, M.C.; Volpicelli, R.
Source: SYNTHETIC COMMUNICATIONS Volume: 35 Issue: 11 Pages: 1471-1479 DOI: 10.1081/SCC-200057986 Published: 2005

8. Title: Synthesis, crystal structure, and spectral properties of a cobalt(II) complex with N-salicylidene-p-toluidine
Authors: Cseh, L.; Csunderlik, C.; Pantenburg, I.; Meyer, G.; Costisor, O.
Source: ZEITSCHRIFT FUR ANORGANISCHE UND ALLGEMEINE CHEMIE Volume: 629 Issue: 6 Pages: 985-988 DOI: 10.1002/zaac.200200438 Published: JUN 2003

9. Title: A second polymorph of bis(o-nitrophenyl) carbonate
Authors: Simon, M.; Csunderlik, C.; Jones, P.G.; Neda, I.; Fischer, A.K.
Source: ACTA CRYSTALLOGRAPHICA SECTION E-STRUCTURE REPORTS ONLINE Volume: 59 Pages: O688-O690 DOI: 10.1107/S1600536803007487 Part: 5 Published: MAY 2003

10. Title: N,N '-Carbonyldisuccinimide
Authors: Simon, M.; Csunderlik, C.; Jones, PG.; Neda, I.; Tarta-Micle, A.
Source: ACTA CRYSTALLOGRAPHICA SECTION E-STRUCTURE REPORTS ONLINE Volume: 59 Pages: O686-O687 DOI: 10.1107/S1600536803007815 Part: 5 Published: MAY 2003

11. Title: Bis(p-nitrophenyl) carbonate-benzene (3/1)
Authors: Simon, M.; Csunderlik, C.; Jones, P.G.; Neda, I.; Fischer, A.K.
Source: ACTA CRYSTALLOGRAPHICA SECTION E-STRUCTURE REPORTS ONLINE Volume: 59 Pages: O691-O692 DOI: 10.1107/S1600536803007499 Part: 5 Published: MAY 2003

12. Title: N,N '-Disuccinimidyl carbonate
Authors: Simon, M.; Csunderlik, C.; Jones, P.G.; Neda, I.; Tarta-Micle, A.
Source: ACTA CRYSTALLOGRAPHICA SECTION E-STRUCTURE REPORTS ONLINE Volume: 59 Pages: O683-O685 DOI: 10.1107/S1600536803007803 Part: 5 Published: MAY 2003

13. Title: Facile bromination of the benzene ring during the cyclisation of the 1H-3-methyl-4-ethoxycarbonyl-5-arylidenehydrazonopyrazoles to the 3-substituted-aryl-1H-6-methyl-7-ethoxycarbonyl-pyrazolo[3,2-c]-s-triazoles
Authors: Csunderlik, C.; Bercean, V.; Peter, F.; Badea, V.
Source: ARKIVOC Pages: 133-141 Part: 2 Published: 2002

14. Title: Synthesis and characterization of some 3D metal ions complexes with N-salicyliden-p-toluidine
Authors: Cseh, L.; Pantenburg, I.; Csunderlik, C.; Mracec, M.; Costisor, O.
Source: JOURNAL OF INORGANIC BIOCHEMISTRY Volume: 86 Issue: 1 Pages: 193-193 Published: AUG 2001

15. Title: Some aromatic amine transport through emulsion liquid membranes
Authors: Stefanut, M.; Novac, A.; Amanatidou, E.; Csunderlik, C.
Source: SEPARATION SCIENCE AND TECHNOLOGY Volume: 31 Issue: 16 Pages: 2219-2229 DOI: 10.1080/01496399608001042 Published: 1996

16. Title: SYNTHESIS OF THE MONOMERIC ANTIOXIDANT - 3,5-DI-TERT-BUTYL-4-HYDROXY-STYRENE BY THE THERMAL-DECOMPOSITION OF TRANS-3,5-DI-TERT-BUTYL-4-HYDROXYCINNAMIC ACID
Authors: MUNTEANU, D.; CSUNDERLIK, C.; TINCUL, I.
Source: JOURNAL OF THERMAL ANALYSIS Volume: 37 Issue: 2 Pages: 411-426 DOI: 10.1007/BF02055942 Published: FEB 1991

17. Title: POLYETHYLENE-BOUND ANTIOXIDANTS
Authors: MUNTEANU, D.; CSUNDERLIK, C.
Source: POLYMER DEGRADATION AND STABILITY Volume: 34 Issue: 1-3 Pages: 295-307 DOI: 10.1016/0141-3910(91)90124-A Published: 1991

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 12-14
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Perspective

MIȘU BÎRZESCU – ATYPICAL PERSONALITY

Ilona Bîrzescu ♣
West University of Timișoara, Faculty of Chemistry, Biology, Geography, 16 Pestalozzi Bd., RO-300115, Timișoara, Romania

Praised as a teacher and dedicated researcher, Mihail Bîrzescu did not have what is conventionally called "an academic career", the term "career" being associated especially with its negative connotations.

He was a graduate of "Nicolae Bălcescu" High School from Râmnicu Vâlcea. Being a passionate researcher, he affirms himself right from the first faculty year. As a student he communicated and published his first paper "Depunerea electrolitică a cuprului folosind ca electrolit fenol – sulfat de cupru (Electrolytic deposition of copper using phenol – copper sulfate as electrolyte)" in 1963. During his professional development he took advantage of exceptional scholars, like Ilie Murgulescu, Gheorghe Spacu and Maria Brezeanu, from whom he inherited an ongoing need for self-training and high standards, according to the belief that *it is always the teacher who learns the most*.

After graduation, in 1964 he became a teacher at the Department of Inorganic Chemistry from the Faculty of Industrial Chemistry, Polytechnic Institute of Timisoara. He contributed to the professional training as chemical engineers of 40 generations of students.

For all forms of teaching activity - lectures, seminars and laboratory applications - he was concerned about the modernization of the educational process, or the content and the means aspect, in agreement with the contemporary knowledge and methodologies advancement. The proofs: initiation of a seminars program, development and installation of Inorganic Chemistry practical applications, organization of the Analytical Chemistry laboratory and eight didactical works.

It is also remarkable its essential contribution to the book "*Chimie anorganică: aplicații practice și numerice* (*Inorganic chemistry: practical and numerical applications*)". This work, developed with his steady colleague and collaborator Mircea Niculescu and published posthumously in 2014, is a culmination of the authors' concern to provide students with a study material at the level of the scientific progress and of current teaching means and procedures. The basic idea of the course is the systematic, coherent exposure of the content, with interdisciplinary character, where the emphasis is put less on the information storage but which implies instead a participatory understanding.

♣ Correspondent author e-mail: adrian.chiriac@e-uvt.ro

In this book the authors also proceeded to a rational selection from a vast material presented in the developed lectures and in agreement with the extra teaching experience related to changes in the educational plans and programs and with the availability for the study of an audience consisting of fresh high school graduates with shaky training and questionable fundamental knowledge in chemistry. Compared to the original manuscript, they have reduced many notes, comments and corrections to avoid a thick text which would have invited to its memorizing as a whole.

One statement arises during the conversations Mihail Bîrzescu had with C. Noica at Păltiniș: "Everyone dreams, craves an idea, no matter how small it may be, it is important to be yours." Referring to the chemical research, he invoked the need for a responsible commitment, the investigator dealing with visible things using his mind or through imagination, being exposed to corrections, confirmations or denials by practical experiments. Mișu's "small" but original idea consisted in the discovery of a nickel - silica gel catalyst obtained by a new method and a new reaction type and with various technical applications.

In the '90s, the achievement of concurrent results has forced the postponement of his doctoral thesis defense by seven years, seeking new developments and confirmation of his own idea. He extended and intensified his interdisciplinary collaborations (inorganic and organic chemistry, physical chemistry, electrochemistry, and physics), participation in projects, contracts, patents, communications and publications.

He considered students as privileged subjects in his teaching and research work, while showing full availability for his colleagues: "wasteful" of knowledge and ideas, he generously offered his own results. In the post-revolutionary period many of them would know spectacular ascensions in the academic career, both deserved and formally based (scores, good-looking CV), masking their professional and scientific inconsistency.

The self-demanding, scientific rigor and strong ethics led him to make from his doctoral work the opera of a long consecration to provide value and confirmation.

Mihail Bîrzescu:

- graduates from "Nicolae Bălcescu" High School in Râmnicu Vâlcea (1959);
- conducts activities in the students' scientific group and publishes his first paper: "*Electrolytic deposition of copper using phenol – copper sulfate as electrolyte*" (1963);
- takes advantage of eminent professors: Ilie Murgulescu, Gheorghe Spacu, and Maria Brezeanu; assumes the belief that "*the teacher is the one who learns the most*";
- since 1964, he prepares forty generations of students at the Faculty of Industrial Chemistry in Timișoara; among his didactic contributions: upgrades all educational process activities (courses, seminars, practical applications) by content and means, in accordance with the progress of knowledge and methodologies, initiates a seminars program, modernizes applications, organizes the Analytical Chemistry laboratory, co-authors eight didactic works.
- the 2014 course book is a selective and coherent compression of the continuously developed lectures, which does not strictly reproduce the manuscript, giving up of notes, cards, notebooks; it makes possible for the development of a modern chemistry of complex combinations course; it shows high demand for content, text, chemical language, bibliography annotated with critical remarks; it regards the conditions imposed by the correlations between the theory and the specific practices which arise from the experiments conducted through laboratory applications.

Overview of original contributions:

In 1970, after successfully passes the paper presentations and exams in the doctoral program, he doesn't have the chance to benefit from a scholarship in France awarded to him.

The initial theme of his PhD thesis was "*Separation of heavy metal halides by fractional distillation*". Because of some interferences with the results published by a Dutch researcher, reluctant to dispute the priority, given that he never rushed towards publication of his own partial data, he turned to changing his original theme.

In 1977, after the death of his scientific mentor Coriolan Drăgulescu and the transfer for guidance to acad. Maria Brezeanu, his new PhD subject became "*Complex combinations with ethylene glycol and its oxidation products as ligands*" (approved only in 1985).

Between 1985 and 1990 he is the most active in terms of scientific research. He produces original results, shows originality through the synthetic method and its applications.

In his statement of activity for his promotion to lecturer he wrote:

"*In what concerns the original research for the development of my doctoral thesis, I addressed an area of perspective and current interest: the use of complex combinations as precursors in the production of metals and simple or mixed oxides with catalytic properties, or for production of ferrites. Through original research I have obtained homo- and heteropolynuclear glyoxylates directly in the reaction system, through a method not mentioned in the dedicated literature: the oxidation of ethylene glycol to glyoxylate dianion by metal nitrates with the isolation of complex combinations. In this context, I have developed a new method for preparing a nickel - silica gel catalyst used in the hydrogenation process of vegetable oils. The obtained results compare favorably with import catalysts. At the same time, through an original method - the formation and decomposition directly on the metal support of Cu(II)-Ni(II) polynuclear glyoxylates I have obtained anodes with active electrolytic films based on* Cu_3O_4*, NiO and, respectively,* $NiCu_2O_4$*, used in the oxygen discharge process during the electrolysis of alkaline solutions. The obtained anodes made it possible to reduce the energy consumption by about 10%. At the same time, they were harnessed with good results, subjected to contracts or patents, as in the preparation of ferrites with good performances, through thermal conversion of heteropolynuclear glyoxylates of Fe(III)-Me(II).*"

He defends his thesis in 1997 under the guidance of acad. Maria Brezeanu who shows competence, patience, understanding and streamlining.

In the scientific research, Mihail Bîrzescu remained a visionary, showing perseverance to complete the idea and the objectives in his own way, without "copying" others, even during the moments of setback (e.g., the poor equipment from the '80s). He benefited from the support of research colleagues from Cluj, Timișoara, and Bucharest. During his lifetime he acquired many collaborations, although there were also renouncements due to overwork and other interests.

Even more than the collaborators who abandoned him, he was strongly marked by the breaking of contact with the students. In 2004 he was "administratively executed" by retirement from work because of age.

Eight years followed in which he was deprived of communication and collaboration in academia. Many projects have remained unfulfilled. The chemistry books, however, stayed with him. He never betrayed his principles and his independence of thought.

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 15-18
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Comment

THE ANNUAL SYMPOSIUM OF SCIENTIFIC COMMUNICATIONS "STABILITY AND REACTIVITY IN COORDINATION CHEMISTRY – IN MEMORIAM MIHAIL BÎRZESCU"

The SRCC symposium is an annual scientific event organized by "Chemeia Semper" Association to honor the memory of Prof.Dr. Mihail Bîrzescu. The first three editions were held in Timişoara and welcomed researchers from Bucharest, Timişoara and Arad.

1. The first symposium "Stability and Reactivity in Coordination Chemistry – in memoriam Mihail Bîrzescu"
Timişoara, October 25, 2013

ADRIAN CHIRIAC (CHAIRMAN)
West University of Timişoara
Tradition and innovation in the chemistry of Timişoara

MARIUS ANDRUH
President of the Section of Chemistry Sciences of Romanian Academy
The interplay of non-covalent interactions in designing molecular crystals

MIRCEA MRACEC
West University of Timişoara
The electronegativity today

PETRU BUDRUGEAC
ICPE-CA, Bucharest
Applications of the thermal analysis in the study of the coordination compounds and the materials

V.Z. SASCA, ORSINA VERDES, MARINELA FURCA, A. POPA
Institute of Chemistry Timișoara of Romanian Academy, Timișoara
Determinarea parametrilor cinetici ai descompunerii termice și a duratei de viață a unor catalizatori din clasa heteropolicompușilor cu structura Keggin prin metode termogravimetrice standardizate

MIHAI-COSMIN PASCARIU[1], CARMEN-MANUELA MITAR[1], IOANA-RAMONA CIOPĂNOIU[1], ALEXANDRA GRUIA[2], EUGEN NICOLAE VINTILĂ ȘIȘU[3]
[1]"Vasile Goldiş" Western University of Arad, Faculty of Medicine, Pharmacy and Dental Medicine, Arad; [2]Clinical County Hospital of Timișoara, Immunology of Transplant Department, Timișoara; [3]"Victor Babeș" University of Medicine and Pharmacy of Timișoara, Faculty of Medicine, Timișoara
Anchimeric assistance in EI-MS carbocations - a computational investigation

MIHAIL BÎRZESCU[1], MIRCEA NICULESCU[2]
[1]University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, Timișoara; [2]"Chemeia Semper" Cultural Foundation, Timișoara
Compuși coordinativi obținuți prin reacția de oxidare a diolilor cu azotați metalici

MIRCEA ŞTEFĂNESCU, MIHAIL BÎRZESCU
University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, Timișoara
Compuși coordinativi homopolinucleari cu liganzi organici de tip carboxilat

DANIEL BARBUL[1], ZENO SIMON[1], JIVA BARBUL[2]
[1]"Victor Babeș" University of Medicine and Pharmacy of Timișoara; [2]Colegiul Național Bănățean, Timișoara
Autoimunitate și toleranță imunologică

UDREA ADRIAN
"Miracolul Plantelor" Pharmacy, Timișoara
Siliciul organic

MIHAIL BÎRZESCU[1], MARIUS JURCA[1], MARIUS MILEA[1], MIRCEA NICULESCU[2]
[1]University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, Timișoara; [2]"Chemeia Semper" Cultural Foundation, Timișoara
New methods to obtain carboxylic acids by oxidation reactions of 1,2-ethanediol with metallic nitrates

MIRCEA NICULESCU
"Chemeia Semper" Cultural Foundation, Timișoara
About stability and reactivity to the coordination compounds obtained by the reaction Bîrzescu

2. The second symposium “Stability and Reactivity in Coordination Chemistry – in memoriam Mihail Bîrzescu” Timişoara, November 7, 2014

ADRIAN CHIRIAC (CHAIRMAN)
West University of Timişoara
Theoretical and computational chemistry in Timişoara

ILONA BÎRZESCU
West University of Timişoara
A PhD as a life

PETRU BUDRUGEAC
ICPE-CA, Bucharest
Thermal analysis. Concepts and applications

V.Z. SASCA, A. POPA, ORSINA VERDES
Institute of Chemistry Timișoara of Romanian Academy, Timișoara
Quantitative measurement of Brönsted acidity from $H_3[PMo_{12}O_{40}]$ *and its Cs1 salt, in bulk and supported on SBA15, by TPD of ammonia*

MIHAI-COSMIN PASCARIU[1], MADIAN RAFAILĂ[2], ALEXANDRA GRUIA[3], MIRCEA NICULESCU[4], EUGEN ȘIȘU[5]
[1]“Vasile Goldiş” Western University of Arad; [2]University Politehnica Timișoara; [3]Clinical County Hospital of Timișoara; [4]“Chemeia Semper” Association, Timișoara; [5]“Victor Babeş” University of Medicine and Pharmacy of Timișoara
Sugar carbocation rearrangements as predicted by computational chemistry

MIHAIL BÎRZESCU[1], MARIUS MILEA[1], DAN ROŞU[1,2], IONUȚ LEDEȚI[3], MADIAN RAFAILĂ[1], VIOREL SASCA[4], MIRCEA NICULESCU[5]
[1]University Politehnica Timişoara; [2]INCEMC Timisoara; [3]“Victor Babeş” University of Medicine and Pharmacy; [4]Institute of Chemistry Timișoara of Romanian Academy, Timișoara; [5]“Chemeia Semper” Association, Timișoara
Synthesis - structure relationship in the aqueous ethylene glycol - M(III) nitrate system (Dedicated to Prof. Carol Csunderlik, in memoriam)

MIRCEA ŞTEFĂNESCU
University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, Timișoara
Combinații complexe carboxilice ale metalelor tranziționale înglobate în geluri hibride de silice. Obținerea de nanocompozite

MIRCEA NICULESCU
“Chemeia Semper” Association, Timișoara
About the reaction Bîrzescu

3. The third symposium “Stability and Reactivity in Coordination Chemistry – in memoriam Mihail Bîrzescu”
Timişoara, September 18, 2015

ADRIAN CHIRIAC (CHAIRMAN)
West University of Timişoara
45 years of scientific research performed by the Quantum Chemistry and QSAR Group from Timișoara

PETRU BUDRUGEAC
INCDIE ICPE-CA, Bucharest
Aplicarea analizei termice pentru determinarea mecanismului proceselor complexe. Aplicație: descompunerea termică a carbonatului de calciu (Applying thermal analysis for determination of the mechanism of complex processes. Application: thermal decomposition of calcium carbonate)

MIHAI-COSMIN PASCARIU[1,2,3], LORETA-ANDREA BOZIN[1], ALINA ŞERB[1], NICOLAE DINCĂ[4], MIRCEA NICULESCU[3,5], EUGEN ŞIŞU[1]
[1]“Victor Babeş” University of Medicine and Pharmacy of Timișoara, Faculty of Medicine, Timișoara; [2]“Vasile Goldiş” Western University of Arad, Faculty of Medicine, Pharmacy and Dental Medicine, Arad; [3]“Chemeia Semper” Association, Timișoara; [4]“Aurel Vlaicu” University of Arad, Faculty of Food Engineering, Tourism and Environmental Protection, Arad; [5]University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, Timişoara
Mass spectrometry fragmentation involving long bonds in some hexoses derivatives

MIRCEA ŞTEFĂNESCU
University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, Timişoara
Spinel nanocomposites obtained from carboxylate precursors embedded in SiO_2 *matrices*

MIHAIL BÎRZESCU[1], VIOREL SASCA[2], DAN ROŞU[1,3], MARIUS-SILVIU MILEA[1], MIHAI-COSMIN PASCARIU[4,5], MIRCEA NICULESCU[1,5]
[1]University Politehnica Timișoara, Faculty of Industrial Chemistry and Environmental Engineering, Timișoara; [2]Institute of Chemistry Timișoara of Romanian Academy, Timișoara; [3]INCEMC Timișoara; [4]“Vasile Goldiş” Western University of Arad, Faculty of Medicine, Pharmacy and Dental Medicine, Arad; [5]“Chemeia Semper” Association, Timișoara
Synthesis-structure relationship in the aqueous ethylene glycol – iron(III) nitrate – cobalt(II) nitrate system

NEW FRONT. CHEM. (2016)
Volume 25, Number 1, pp. 19-21
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Review

INORGANIC CHEMISTRY - PRACTICAL AND NUMERICAL APPLICATIONS I, AUTHORS: MIHAIL BÎRZESCU, MIRCEA NICULESCU – EDITURA DE VEST, TIMIŞOARA, 2014, ISBN 978-973-36-0610-9

Adrian Chiriac ♣
West University of Timişoara, Faculty of Chemistry, Biology, Geography, 16 Pestalozzi Bd., RO-300115, Timişoara, Romania

“**Chimie anorganică**” (“**Inorganic Chemistry**”), a book by Mihail Bîrzescu and Mircea Niculescu, is a much awaited and valuable contribution to the reinforcement of the prestigious tradition of Timișoara’s school of Inorganic Chemistry, founded and strengthened by Acad. Prof. Coriolan Drăgulescu and continued by Prof. Emil Petrovici and their collaborators. The treaties “*Introducere in chimia anorganică modernă*” (“*Introduction to modern inorganic chemistry*”) and “*Chimie structurală modernă. Chimia coordinanței 8*” (“*Modern structural chemistry. Eight-coordination chemistry*”) (C. Drăgulescu, E. Petrovici: 1973-1978) enjoyed a remarkable success, being seen as reference works in the current scientific community and being consulted with interest by students and researchers in the field.

After four decades, the authors of the current work, having a long teaching and scientific activity carried out at the Faculty of Chemical Engineering and Environmental Protection from Timişoara, with a rich and representative list of papers, capitalize through this book their gathered experience concerning the innovation in the educational process, being in fact one of its reorientations in which the transmission of knowledge involves the participation of the subjects concerned with their professional training.

The book “**Chimie anorganică**” is conceived by Mihail Bîrzescu and Mircea Niculescu in line with the demands of modern methodology, the immense material of scientific information in the field being selected by criteria that integrates and harmonizes the fundamental knowledge with the new progress in theoretical and applied specialty research. The paper is the result of a laborious work, having as outstanding performance the editing in coherent, essential and systematic form of the principles, of the concepts that enable a rational characterization, a judicious selection of a vast amount of descriptive data about the elements and their compounds, based on their physical and chemical properties.

♣ Correspondent author e-mail: adrian.chiriac@e-uvt.ro

The authors' effort is considerable, given that in the last two decades the evolution of inorganic chemistry faced the "pessimism" of the ones announcing the decline of this field, with the appearance of a huge number of organic substances which have a very broad spectrum of applications, synthesized in the second half of the past century. These skeptical projections were canceled by the performant research, with theoretical and applied consequences of particularly importance, through which inorganic chemistry has changed dramatically due to the deep, interactive intersection with physical chemistry, solid state physics, organic chemistry, biochemistry, and also due to the application of physical–chemical methods of modern instrumental analysis. The highlighted interdependencies motivate the fact that interdisciplinarity is not simply a methodological and epistemological option any longer, but an essential need for the advancement of knowledge and contemporary research.

In the work they developed, the authors consider the fact that the thematic portfolio that interests today's inorganic chemistry enriched unexpectedly, requiring an update of both the knowledge and of the learning process, according to the new research and application directions of inorganic chemistry. The products created by the nowadays "amazing chemistry" include not only compounds, but also materials that contain, in addition to inorganic components, organic, polymeric and biopolymeric structures (fragments). This requires the study of inorganic chemistry at different levels of depth, of relationshipness and specification in a multiform and dynamic context. Thus, in addition to knowing the molecular and crystalline structure of substances, these must also be studied from electronic and magnetic points of view, and the microimpurities distribution must be also determined, together with the study of the structure of interfaces in polycrystalline materials, of the nanostructure, of the micro- and mesopore structure, as well as of all the various influences over the substances' properties.

Based on their wide teaching and methodological experience, the authors manage a logical and efficient "assembly" of the study of theoretical principles with the practical applications, laboratory experiments, exercises and problems designed for each chapter.

Through a modern approach, the nature and the formation mechanism of chemical bonds resulting from interatomic interactions are exposed, as energetic expression of the natural tendency of elements and of chemical compounds to gain stability in a reactive field.

The first chapters are devoted to the principles and laws that govern the quality and quantity of reactions of chemical elements and their compounds. In an original manner, the exposure of chemical reactions classification principles is based on the relationship between the acid-base, redox, solubility and complexation properties, and the behavior of the reactive chemical system as a whole.

A special chapter is devoted to the ample presentation of hydrogen and its compounds, the former being considered as the reference element for interpreting the properties and the reactivity, starting from the structure of the atom. The laboratory experiments and the related numerical applications consolidate and test the accumulation of knowledge.

The bibliography includes references to the most recognized inorganic chemistry treaties and books, both classic and modern, enshrined through their scientific and methodological value.

Finally, for those who do not know, Mihail Bîrzescu and Mircea Niculescu's book is a part of the students' first year chemistry course in a compressed and somewhat standardized form of university lectures. Oral exposition accents and the unique ad-hoc correlations made through the direct dialogue with the students are thus absent, aiming not simply the transmission of knowledge about chemical processes, but stimulating a proper and independent thinking and action. Yet the book has as target a much wider audience, being a welcomed (and hopefully well received) guide for those who want to get into this "*Periodic Kingdom*" of elements, because, as Professor P.W. Atkins says: "*We stand on the elements, we eat the elements, we are the elements*.".

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 22-23
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Review

THERMAL ANALYSIS. FUNDAMENTALS AND APPLICATIONS. KINETIC ANALYSIS OF HETEROGENEOUS TRANSFORMATIONS, AUTHORS: EUGEN SEGAL, PETRU BUDRUGEAC, OANA CARP, NICOLAE DOCA, CRIȘAN POPESCU, TITUS VLASE, PUBLISHING HOUSE OF THE ROMANIAN ACADEMY, BUCHAREST, 2013, ISBN 987-973-27-2281-7

Adrian Chiriac ♣
West University of Timişoara, Faculty of Chemistry, Biology, Geography, 16 Pestalozzi Bd., RO-300115, Timişoara, Romania

The goal of this book published in Romanian language is to present an outline of the basic principles of non-isothermal kinetics, and to give a detailed grounding in the major methods of evaluation of non-isothermal kinetic parameters characteristic for a heterogeneous process. The authors keep into account the main conclusion of some recent papers, especially of ICTAC (*International Confederation for Thermal Analysis and Calorimetry*) 2000 Project (*Thermochimica Acta* 355 (2000) 125), the Workshop at ICTAC 13 (*Journal of Thermal Analysis and Calorimetry* 80 (2005) 795) and the recent ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data (*Thermochimica Acta* 520 (2011) 1) , according to which the correct kinetic analysis of non-isothermal data corresponding to a heterogeneous process can be performed only by using the experimental data recorded at several heating rates.

Non-isothermal kinetic methods have been applied, critically discussed and investigated by authors for long period, and they summarized the experiences in this field completing them with their own results.

The book is divided into 11 chapters each followed by bibliographic references.

After a very brief overview of thermo-analytical methods, including multiple techniques (thermogravimetry (TG or TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermo-magnetic analysis, thermo-optical analysis, thermo-dilatometric

---

♣ Correspondent author e-mail: adrian.chiriac@e-uvt.ro

analysis (DIL), thermo-mechanical analysis (TMA), dynamic mechanical analysis (DMA), thermo-electrical analysis (TEA) , thermally stimulated exchanged gas analysis (EGA), simultaneous thermal analyses (STA)), there are presented and critical discussed the differential and integral methods of assessment of non-isothermal kinetic parameters by using a single conversion vs. temperature curve recorded at a heating rate. It is mentioned that a single conversion vs. temperature curve recorded at a certain heating rate can be satisfactory described by some different kinetic triplets (activation energy, pre-exponential factor and conversion function), and the inherent experimental errors determine the impossibility to discriminate the correct kinetic triplet by applying a statistical criterion. The overcoming of this problem could be performed by applying the isoconversional (model-free) methods in assessing the activation energy dependence on the conversion degree, which can be correlated with the investigated process mechanism. These methods (linear and non-linear) are exhaustively presented in two chapters.

The following special techniques and procedures used for evaluation of the kinetic parameters of heterogeneous processes are also presented and discussed: controlled rate thermal analysis (CRTA) techniques (quasi-isothermal analysis, quasi-isobaric analysis, thermal analysis at low pressure and controlled rate stepwise isothermal analysis) and modulated thermal analysis techniques (modulated DSC (MDSC) and modulated thermogravimetry (MTGA)), non-parametric kinetic method (NPK), and procedures for determination of kinetic model (conversion function) corresponding to a single step heterogeneous process. Finally, a general algorithm for evaluation of kinetic parameters using non-isothermal data is suggested.

Last chapter contains a general overview concerning the methods of kinetic parameters evaluation by using non-isothermal data. By surveying the most used methods for evaluating the kinetic parameters from non-isothermal experiments, a classification scheme of the methods is suggested. This classification is based on the number of principles and theoretical approximations required to derive the equation which grounds it.

***

For a better understanding of the book content, the authors give a great number of drawings, diagrams, graphs and tables. The style of the text and the outlay are perfectly adequate to its goal. The book provides an up-to-date and comprehensive content to whole field of application of thermal analysis methods for kinetic analysis of non-isothermal data.

The book meets to requirements of specialists in chemical kinetics and chemical engineering, as well as those of students in chemistry, physics and chemical technology.

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 24-29
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Perspective

THEORETICAL AND COMPUTATIONAL CHEMISTRY IN TIMIŞOARA – PAST, PRESENT, FUTURE

Adrian Chiriac, Zeno Simon [♣]
Chemical Research Institute, Timişoara branch of the Romanian Academy,
24 Mihai Viteazul Bd., RO-300223, Timişoara, Romania

ABSTRACT

Research in theoretical and computational chemistry is performed in Timişoara mainly at the Chemical Research Institute and at the Chemistry Department of the West University. The main research directions are quantum chemistry-molecular orbital theory applied to organic molecules and transition metal complexes and quantitative chemical structure-biologic activity relations. The main achievement is the minimal steric difference method for QSAR type relations. Results obtained within these directions are described as well as achievements of a more theoretical physics oriented group of quantum chemists. Perspectives for future developments are also discussed.

1. INTRODUCTION

Timişoara, a city with beautiful civil engineering achievements since the time of the Austro-Hungarian rule, became a university center just after 1920 along with the establishment of the Polytechnic School, with Traian Lalescu being the first rector [1]. The Royal Decree no. 4822 of November 15, 1920 approved the establishment of the Polytechnic School of Timişoara. The city receives a strong influx of scholars during 1940-1945, with the refuge in these parts of the University of Cluj. This caused a strong stimulus for further development of the university and the academic life in western Romania, in the town located on the Bega River. July 29, 1948, marks the establishment of the Faculty of Industrial Chemistry, while the year 1951 - the establishment of the Timişoara branch of Romanian Academy and its Institute (Center) of Chemistry.

[♣] Correspondent author e-mail: adrian.chiriac@e-uvt.ro

Remarkable efforts were made by academics Ilie Murgulescu and Coriolan Drăgulescu, who have continuously and efficiently supported the development of a university learning establishment and of a modern chemical research. These two prestigious personalities of Romanian chemistry and science are recognized founders and leaders of the higher education in chemistry and of the chemical research in this part of the country. Theirs is the main merit, the decisive contribution to the establishment in 1960, inside the 3-years Pedagogic Institute, of the Department of Physics-Chemistry and later, in 1967, of the Departments of Inorganic Chemistry and Organic Chemistry at the Faculty of Physics of the University of Timișoara. The university specialization of Physics-Chemistry was abolished a few years later, following obtuse politics, abusively applied to the chemical university education from Timișoara. The specialization was re-established in 1990 at the West University of Timișoara, Faculty of Chemistry, Biology, Geography. In this new faculty, a center of excellence and a "Chemistry of Biologically Active Compounds" master studies specialization were created, a second QSAR research pole of Timișoara, along with that from the Institute of Chemistry of Romanian Academy.

With his vast professional experience, prof. I.G. Murgulescu was directly involved in developing and modernizing the course, the laboratory and the research topics in the field of physical chemistry. It can be said that during the years he taught the physical chemistry course at the Faculty of Chemistry of Polytechnic Institute Timişoara (1948-1949), prof. I.G. Murgulescu introduced the fundamentals of modern physical chemistry in Romania, which he has developed and strengthened in the coming years, with the help of brilliant collaborators whom he trained and promoted with utmost stringency.

A first line of research promoted by I.G. Murgulescu in Timișoara's group, in the field of theoretical chemistry, was the study of the influence of solvent on the kinetics of some chemical reactions. We mention here the study of the influence of solvent on the Menshutkin reaction kinetics (Ştefan Popovici and Mariana Pop [2]). It is worth mentioning the research in the field of chemistry nomenclature done by Professor Giorgio Ostrogovich (unfortunately unpublished) and those of D. Purdela concerning the theory of chemical shifts of the ^{31}P in the nuclear magnetic resonance spectrum [3]. We also note the research done by the Inorganic Chemistry team, led by acad. C. Drăgulescu and then by Dr. Septimia Policec, crowned with the publication of two reference treaties, written in collaboration with Emil Petrovici. The first, entitled "*Introducere în chimia anorganică modernă*" ("*Introduction to modern inorganic chemistry*") brings a systematic exposition of the atomic structure based on quantum mechanics and an explicit qualitative presentation of the chemical bond within the molecular orbital and the ligand field theories. The second treaty, "*Chimie structurală modernă. Chimia coordinanței 8*" ("*Modern structural chemistry. Eight-coordination chemistry*") is a work that systematizes, by its own concept, a bibliographic material of high theoretical and applied interest regarding the ligands of coordination 8. Both treaties currently maintain their timeliness.

Currently, the main centers where research in the field of theoretical chemistry is done are the Institute of Chemistry Timișoara of Romanian Academy, called here ICT, and the chemistry departments of the West University and of the Faculty of Industrial Chemistry and Environmental Engineering. In what follows, we describe the main achievements in this area.

In this time of beginnings, we mention the late Dr. Radu Vâlceanu (1923-1996), who was incorporated in 1954 at the Scientific Research Base from Timişoara. Promoted to university professor, he has emerged as one of the main animators, with major organizational and scientific contributions in the field of organophosphorus compounds. The book he designed, together with D. Purdela, "*Chimia compuşilor organici ai fosforului şi a acizilor lor*" ("*The chemistry of organic compounds of phosphorus and their acids*"), also translated into Russian, became and remains a valuable source of documentation for training dedicated specialists. At the suggestion of R. Vâlceanu, from 1972, the research undertaken by the QSAR Group was initiated and developed, targeting theoretical and practical contributions regarding the toxicity of organophosphorus compounds and, in particular, of the organophosphorus pesticides.

2. PROBLEMS AND ORGANIZATIONAL STRUCTURES

Systematic works of quantum chemistry (and, in general, theoretical chemistry) occurred in Timişoara in 1966, with the hiring of one of the authors of this paper at the Centre for Chemistry of the Scientific Research Base of Romanian Academy (see also the interesting article by Septimia Policec [4]). The main researchers involved were Zeno Simon, Radu Vâlceanu and Aurel Balint, followed, in 1968, by Mircea Mracec, and several years later, by Ion Moţoc and, especially after 1990, by Ludovic Kurunczi. After many organizational changes in the Ceauşescu era, this center was transformed into the Institute of Chemistry Timişoara of Romanian Academy since 2001, as it is known today. It is worth recalling the directors: Acad. Coriolan Drăgulescu (until 1977), Dr. Radu Vâlceanu (1977-1990), Dr. Walter Schmidt, Dr. Mircea Mracec and, currently, Dr. Otilia Costişor.

Among the participants from the West University, Department of Chemistry, we mention Adrian Chiriac and, from 2005, M.V. Putz from the Faculty of Industrial Chemistry (Polytechnic Institute Timişoara), F. Kerek and D. Ciubotariu, from the Institute of Medicine Timişoara (today "Victor Babeş" University of Medicine and Pharmacy), G.I. Mihalaş and T.I. Oprea. Access to computers, even relatively primitive, found in Timişoara during 1970-1990 (not exactly on legal basis, but more based on "begging",) is in particular due to the collaboration with S. Holban and, not the least, the continuing collaboration with A.T. Balaban (Institute of Atomic Physics (IFA) Bucharest), to which it was later added the one with Ion Niculescu-Duvăz (Institute of Oncology Bucharest), these being of inestimable value through competent criticism and through the facilitation of access to foreign publications.

Obtaining the approvals for publication in foreign journals was a difficult issue in the Ceauşescu era. We were lucky with the understanding of open minded rectors - N. Stanciu and C. Popa from University of Timişoara, and G. Băcanu from the Institute of Medicine from Timişoara. This made possible the emergence of a book [5] written in collaboration with A.T. Balaban, published at the Springer Verlag publishing house, and of a book published in the UK.

Especially in the early years, there was a fairly marked interest for quantum chemistry. A series of informal lectures was also held, for those interested. We self-proclaimed ourselves the QSAR and Quantum Chemistry Group, but without being formalized, and the Annals of West University, Series of Chemistry became a sort of unofficial press of the group. There were no difficulties, probably also due to links with the bodies concerned, held by some members of the group - links which were by then mandatory for those who occupied a higher hierarchy.

The continuing emergence of Preprints in the Series of Chemistry at the University of Timișoara (reviewed in Chemical Abstracts) allowed the QSAR Group to be known worldwide, to be given priority for the MTD method and, as a result, to be often quoted in the dedicated literature.

After 1990, at the Department of Chemistry, Faculty of Chemistry, Biology, Geography of the West University, there is a quantum chemistry course held many years by our colleague Mircea Mracec, while for master studies – a QSAR course, held many years by Z. Simon, also with some lessons taught by T.I. Oprea (then working at AstraZeneca, Sweden), and by other colleagues with expertise in specific areas.

3. THE MAIN RESEARCH DIRECTIONS

The first issue of theoretical chemistry systematically addressed was applying the molecular orbital theory in the simplistic Hückel (HMO) variant to issues of electronic spectra and reactivity of organic molecules. Among the areas covered we mention:

- conjugated systems with tetracoordinated pentavalent phosphorus atom: A. Balint, Z. Simon, R. Vâlceanu and other collaborators;
- electronic spectra of dyes derived from 2,5-bis-phenylamino-1,4-benzoquinone, with A. Balint as the main protagonist.

More advanced quantum chemical methods could be addressed with the arrival of M. Mracec (a product of V.E. Sahini's quantum chemistry school of Bucharest) in this group. The problem was the access to modern computers. Ceaușescu era was less encouraging for this type of research.

With the reorganization of the Centre of Chemistry (which becomes ICT) after 1989 and through the energetic interventions of the directors M. Mracec and, especially, Otilia Costișor, the computing power has increased greatly. This allowed the quantum chemistry group consisting of M. Mracec, Mioara Mracec, Liliana Păcureanu and others to address more efficient methods, such as MNDO, PM3, SCF/3-21G* and even methods for molecules and ions in aqueous solution such as DFT+PCM [6].

Another line of research, probably with the highest success, was the study of chemical structure-biological activity relationships (QSAR), addressed through the initiative of R. Vâlceanu shortly after 1970. At that time it was a big problem for QSAR to include the spatial structure of the molecules in the respective relationships. This was a success of the QSAR group represented by Z. Simon, A. Chiriac, I. Moțoc, S. Holban and others, by creating the minimum steric differences method, or MSD, and then the perfected version, MTD (see [5], chapters 4 and 5, and [7]).

The last development of MTD is the MTD-PLS method [7]. Here, besides the spatial structure of the molecules, described by occupation or non-occupation of the hypermolecule nodes, six parameters also intervene that characterize intermolecular forces (fragment volume, polarizability, partial electrical charge etc.). The number of variables involved in this type of QSAR, higher than the number of molecules considered for QSAR, required the switch from using the multiple linear correlation method to the "Partial Least Squares" (PLS) method.

From the group of theorists, Simona Funar-Timofei addressed a systematic application of the techniques used in QSAR to the study of substantivity of a large number of dyes on cellulose fibers [8]. Here, the dye is analogous to the ligand, while the textile fiber resembles the receptor. This type of application of QSAR techniques is practically a world premiere, receiving a huge number of citations in the dedicated literature. The paper [9], which has 46 non-self-citations, is the most cited work of our group.

A last major issue addressed by the group of theorists from ICT is the application of quantum chemistry to aspects of ligand-receptor interaction. We mention here the calculation of conformations energy for molecules with ligand character (Mircea Mracec and Mioara Mracec); calculating the energy of dissociation (more specifically, ΔG_d) in an aqueous solution of some complexes of ML_2 type (M: Ca^{2+}, Mg^{2+}; L: ethanediol, dioxane, acetate etc.) related to a study of the peptidoglycan interaction specificity (L. Sayti, V. Careja, Simona Muntean); also, the pairing energy calculations for aqueous bases of Watson-Crick type (Lily Păcureanu, L. Kurunczi) [6, 10].

It is worth mentioning that, in the work done, semi-empirical calculations involving intermolecular potentials gave results more consistent with the experimental data (where they do exist) than ab initio calculations, in which the end result is a small difference between two large numbers [6, 11].

A separate group of theoretical chemists is led by M.V. Putz. Its approach is closer to the theoretical physics than that of the group at ICT. Among the many researched topics prevail those related to the definition of electronegativity by density functionals (e.g., see [12]), although QSAR related topics are also present. Putz and his collaborators have published more than 80 primary papers and reviews, with over 120 citations in the dedicated literature.

4. CONCLUSIONS AND PERSPECTIVES

The main groups concerned with theoretical and computational chemistry from Timișoara are those from ICT and from the West University (M.V. Putz). The ICT group elaborated hundreds of papers in the field of computational chemistry and, in particular, related to its application in spectra, reactivity and biological activity, and dye-fiber substantivity. There are many hundreds of citations of its publications in the dedicated literature. The main achievement is related to the steric factor in the biological activity, the MTD method of structure-property relationships and the biological activity. Quantum chemistry methods were also used in these studies.

The group from the West University (led by M.V. Putz) operates from less than 10 years and will probably bring many contributions to theoretical chemistry.

Over time there have been numerous collaborations of the ICT group with research groups with similar interests at home and abroad, the most important being that with T.I. Oprea’s group from New Mexico. There have also been important exchanges of researchers with groups from abroad; unfortunately, together with departures and expatriations, as is the case with many other research groups in Romania. The causes of this “brains loss” were much discussed in this journal. It is worth mentioning, related to the Timişoara university center, a collaboration - bound to grow stronger, between the Medicine in Timișoara and its counterpart from Szeged. This collaboration also has implications in the drug design and the QSAR fields.

A larger infusion of funds into research would be required for the “brains” exchange to take place in both directions. The problem is ultimately linked to the overall economic development of Romania and this paper is not the place for a broader discussion on this topic.

REFERENCES

1. Pascu, S; Zahiu, I.; Țintă, A. (Eds.). *Timişoara: pagini din trecut şi de azi*, Consiliul Popular al Municipiului Timişoara, Romania, 1969; Haţegan, I.; Pîrşe, M.C. *Premiere și Priorități Timișorene*, Volume I, Banatul Publisher: Timişoara, Romania, 2009.
2. Popovici, S.; Pop, M. Sur la dépendance entre la constante de vitesse et caractéristiques physiques du solvant. *C. R. Chim.* **1957**, *245*, 846.
3. Purdela, D. Theory of ^{31}P n. m. r. chemical shifts. Expression of nuclear magnetic shielding constant in a steady magnetic field. *J. Magn. Reson.* **1971**, *5*, 23.
4. Policec, S. In *Academia Română - Filiala Timişoara. Istoric 1951-1999*; Anton, I, Silaş, G., Eds.; Orizonturi Universitare Publisher, Timişoara, Romania, 1999; pp. 322.
5. Balaban, A.T.; Chiriac, A.; Motoc, I.; Simon, Z. *Steric Fit in Quantitative Structure-Activity Relations*; Springer-Verlag Publisher, Lecture Notes in Chemistry Series, Heidelberg, 1980, DOI: 10.1007/978-3-642-48316-5.
6. Păcureanu, L.M.; Kurunczi, L.; Simon, Z. Quantum chemistry approaches to ligand-receptor interactions in Timişoara. *Rev. Roum. Chim.* **2011**, *56*, 289-298.
7. Chiriac, A.; Ciubotariu, D.; Funar-Timofei, S.; Kurunczi, L.; Mracec, M.; Mracec, M.; Szabadai, Z.; Șeclăman, E.; Simon, Z. QSAR and 3D-QSAR in Timişoara. 1972-2005. *Rev. Roum. Chim.* **2006**, *51*, 79-99.
8. Timofei, S.; Schmidt, W.; Kurunczi, L.; Simon, Z. A review of QSAR for dye affinity for cellulose fibres, *Dyes Pigm.* **2000**, *47*, 5-16, DOI: 10.1016/S0143-7208(00)00058-9.
9. Suzuki, T.; Timofei, S.; Iuoras, B.E.; Uray, G.; Verdino. P.; Fabian, W.M.F. Quantitative structure-enantioselective retention relationships for chromatographic separation of arylalkylcarbinols on Pirkle type chiral stationary phases, *J. Chromatogr. A* **2001**, *922*, 13-23, DOI: 10.1016/S0021-9673(01)00921-9.
10. Careja, V.; Muntean, S.; Mracec, M.; Sayti, L.; Simon, Z. Molecular modeling of some calcium and magnesium ionic bridges, *Int. J. Quantum Chem.* **2007**, *107*, 1714-1718, DOI: 10.1002/qua.21272.
11. Şeclăman, E.; Kurunczi, L.; Simon, Z. “False” Thymine–1H-Enol Guanine Base Pair. Low Misinsertion Rate by DNA Polymerase Explained by Computational Chemistry Considerations. *Biochemistry (Moscow)* **2007**, *72*, 328-331, DOI: 10.1134/S000629790703011X.
12. Matito, E.; Putz, M.V. New Link between Conceptual Density Functional Theory and Electron Delocalization, *J. Phys. Chem. A* **2011**, *115*, 12459-12462, DOI: 10.1021/jp200731d.

* Simon, Z.; Chiriac, A. Chimie teoretică şi computaţională la Timişoara – Trecut, Prezent, Viitor. *Revista de Politica Științei si Scientometrie* **2012**, *1*, 338-341.

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 30-38
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Comment

PROFESSOR DOCTOR MARIUS ANDRUH, MEMBER OF ROMANIAN ACADEMY, DOCTOR HONORIS CAUSA SCIENTIARUM OF WEST UNIVERSITY OF TIMIŞOARA

Adrian Chiriac ♣
West University of Timişoara, Faculty of Chemistry, Biology, Geography, 16 Pestalozzi Bd., RO-300115, Timişoara, Romania

1. INTRODUCTION

On May 10, 2013, the West University of Timişoara's Senate decided to award the *Doctor Honoris Causa Scientiarum* title to **Acad. Marius Andruh**, illustrious scientist and creator of school in the field of polynuclear coordination compounds' chemistry. The decision was supported through the *Laudatio* presented by the Analysis Commission which was convened for awarding the *Doctor Honoris Causa Scientiarum* title by the West University of Timişoara.

Profesorul Marius Andruh s-a născut la 15 iunie 1954, la Smeeni - Buzău. În timpul studiilor ca elev al liceului B.P. Haşdeu din Buzău s-a remarcat prin excelente performanţe şcolare la învăţătură, îndeosebi printr-o statornică pasiune pentru chimie, pentru experimentul de laborator. A participat cu succes la olimpiadele şcolare de nivel naţional si la olimpiadele internaţionale de chimie ale elevilor, obţinând numeroase premii şi medalii şi mai ales recunoaşterea ca lider al unei valoroase generaţii de tineri pasionaţi de studiul chimiei.

Urmează studiile universitare la Facultatea de Chimie a Universităţii din Bucureşti, specialitatea Chimie Anorganică si Chimie Fizică, pe care le absolvă in anul 1979. Ca student eminent s-a bucurat de aprecierea profesională, de iniţierea şi îndrumarea în cercetarea ştiinţifică a emeriţilor Profesori Academicieni Petre Spacu si Maria Brezeanu.

După absolvirea facultăţii, a efectuat perioada de stagiu in industrie (1579-1982) iar din anul 1982 a lucrat la Centrul de Chimie Fizică, în grupul de chimie coordinativă. Din anul 1984 domnul Marius Andruh a fost angajat prin concurs asistent de cercetare si apoi cadru

---

♣ Correspondent author E-mail: adrian.chiriac@e-uvt.ro

didactic la Catedra de Chimie Anorganică a Universității din București, în cadrul căreia s-a afirmat prin activitatea științifică și prin excelenta prestație didactică. Cariera sa academică se recomandă prin conținutul științific modern al cursurilor, prin metodica si eficiența activităților de seminar, prin aparatura si tehnicile moderne integrate in lucrările și experimentele de laborator.

În 1988 a susținut teza de doctorat care a avut ca temă compuși coordinativi ai Fe(II), Ni(II) și Co(II) cu derivați piridinici, structură electronică si comportare termică sub conducerea științifică a regretatei Academician Maria Brezeanu.

În perioada anilor 1991-1993 a beneficiat de burse pentru studii postdoctorale la Laboratorul de Chimie Anorganică de la Universitatea Paris-Sud (Profesor Olivier Kahn) și la Institutul de Chimie Anorganică al Universității din Göttingen (Profesor Herbert W. Roesky).

După finalizarea studiilor doctorale și postdoctorale, ca urmare a unei consistente și valoroase activități academice și științifice, domnul Marius Andruh a parcurs toate treptele carierei didactice: asistent (1982-1990), lector (1990-1994), conferențiar (1994-1996). Din anul 1996 devine Profesor Universitar titular la Catedra de Chimie Anorganică din Facultatea de Chimie a Universității din București.

Reputația științifică și excelenta prestație de cadru didactic universitar l-au recomandat pentru un număr însemnat de stagii de visiting professor *pe care le-a efectuat la prestigioase universități din Bordeaux, Göttingen, Brno, Paris, Jena, Manchester, Strasbourg, Toulouse, Valencia si Rio de Janeiro. La acestea se adaugă aproape 100 de conferințe susținute la manifestări științifice din străinătate și din țară.*

În calitate de Profesor, a susținut activități didactice la disciplinele Chimie Anorganică, Chimie Bioanorganică și Stereochimie anorganică – pentru licență și la disciplinele Chimie Supramoleculară și Complecși Polinucleari – pentru studii de master precum si cea de conducător științific de doctorat. În prezent predă cursul de Chimie coordinativă. Este șeful Departamentului de Chimie Anorganică de la Universitatea din București.

Remarcabila este și participarea sa nemijlocită, de consultanță și de management a pregătirii și participării elevilor români la Olimpiadele Internaționale de chimie timp de peste 3 decenii. În această preocupare statornică pentru învățământul de excelență în domeniul chimiei Profesorul Marius Andruh a manifestat și menținut o colaborare benefică cu colegii de la Universitatea de Vest din Timişoara în pregătirea de performanță a elevilor pentru olimpiadele naționale și internaționale ale elevilor.

Opera științifica a Domnului Academician Marius Andruh a cărei valoare a fost validată la nivelul celor mai exigente criterii de performanță în domeniul chimiei l-a recomandat pentru alegerea Domniei Sale ca membru corespondent al Academiei (2000) și ca membru titular al Academiei Române (2009). Tot din anul 2009 a fost desemnat Președinte al Secției de Chimie al Academiei.

Valorificând o bogată experiență privind actuala problematică din spațiul academic al marilor universități și Institutele de cercetare științifică cu prestigiu mondial, Domnul Academician Marius Andruh este o prezență activă în elaborarea politicilor și strategiei de dezvoltare a învățământului și cercetării științifice de chimie din România.

Rezultatele cercetării științifice ale Domnului Academician Marius Andruh sunt bine-cunoscute și unanim apreciate de chimiști cu mare prestigiu din Universități și Centre de cercetare din țară și străinătate. Contribuțiile sale originale, cu tematică modernă din domeniul combinațiilor coordinative polinucleare privind complecșii homo și heteronucleari, *chimia supramoleculară, ingineria cristalelor, proprietăți magnetice ale complecșilor polimetalici au fost valorificate prin cele 209 lucrări științifice publicate in revistele cele mai cotate în domeniile congruente cu domeniul de cercetare. Activitatea didactică și științifică cuprinde de asemenea 3 cărți și 4 patente.*

Contribuțiile originale rezultate din cercetările științifice întreprinse de domnul Academician Marius Andruh se referă la domeniile următoare:

1. Inginerie cristalină.

Au fost dezvoltate noi abordări în sinteze care au condus la polimeri de coordinare mono-, bi- și tridimensionali cu topologii deosebit de interesante, prin implicarea ca noduri ale unor complecși homo și heteronucleari. Aceste noi structuri au permis elaborarea unei strategii proprii pentru obținerea de materiale magnetice și luminescente.

2. Chimia metalo-supramoleculară.

Domnul Academician Marius Andruh și colaboratorii au valorificat creativ principiile chimiei supramoleculare în sinteza de structuri în care ionul metalic determină procesele de autoasamblare dar și de formare de supercomplecși prin folosirea complecșilor metalici ca liganzi în a doua sferă de coordinare. O deosebită importanță o are contribuția sa la raționalizarea sintezelor de ansamble supramoleculare ceea ce a oferit un foarte bun instrument de lucru pentru chimiștii interesați în obținerea de noi structuri supramoleculare. O preocupare prioritară a fost orientată spre caracterizarea proprietăților polimerilor obținuți – magneți moleculari, materiale luminiscente și altele – din perspective aplicative.

3. Magnetism molecular.

Grupul de cercetare coordonat de Profesorul Marius Andruh a sintetizat un număr mare de noi complecși polinucleari cu proprietăți magnetice urmare a dezvoltărilor teoretice a principiilor care corelează structura și proprietățile fizico-chimice ale acestor compuși. Au fost obținute și caracterizate:

- *Structuri de spin iregulare, fiind descrise primele cazuri de complecși trinucleari cu purtători de spin 3/2 – 1/2 – 3/2 și 5/2 – 3/2 – 5/2;*
- *Interacțiuni feromagnetice prin mecanism de polarizare de spin;*
- *Nanomagneți moleculari. Academicianul Marius Andruh și grupul de cercetare pe care îl conduce au sintetizat prin utilizarea unor sintoni aleși cu o ingeniozitate creativă remarcabilă un număr semnificativ de structuri descrise în premieră și a căror prioritate a fost consemnată în literatura de specialitate:*
  - *primele sisteme heterospin 2p – 3d – 4f; 3p – 3d – 4f și 3d – 4d – 4(5)d;*
  - *primele sisteme sintetizate 3d – 3d' – 4f și primele sisteme trimetalice de tip single-chain-magnets (3d – 4f – 4d; 3d – 4f – 5d).*

Ca urmare a acestor remarcabile realizări originale și prioritare laboratorul de cercetare al Profesorului Marius Andruh a fost acreditat ca membru al rețelei de excelență MAGMANet (F.P. 6).

Activitatea științifică a Domnului Academician Marius Andruh concretizată în cele 209 lucrări publicate în reviste de mare prestigiu internațional (lista lucrărilor publicate constituie Anexa 1) este validată la cele mai înalte cote valorice prin peste 4000 de citări bibliografice ale articolelor științifice elaborate și printr-un indice Hirsch foarte înalt, h = 32.

Un număr de 16 lucrări s-au situat pe lista celor mai citite si citate lucrări ale revistelor în care au fost publicate (Anexa 2) fiind clasificate si incluse in Top 10, Top 20 sau Top 25. Studiile realizate prin colaborări între grupe de cercetare din țări diferite, coordonate multe dintre ele de Profesorul Marius Andruh demonstrează talentul Domniei Sale de a organiza colaborări pe teme științifice. Aceste colaborări i-au prilejuit onoranta reprezentare a învățământului universitar și a cercetării științifice la nivel de excelență, prin calitatea de visiting professor *la mari Universități, prin 74 de conferințe internaționale (invited lectures) și 21 conferințe naționale (Anexa 3).*

Opera științifică a domnului academician M. Andruh a fost apreciată și recompensată prin acordarea unor premii și distincții atât in țară cât și în străinătate:

- *Premiul Academiei „Gheorghe Spacu” (1990);*
- *Ordinul Național pentru Merit în grad de Cavaler (2006);*
- *Profesor Gauss, la invitația Academiei de Științe din Göttingen;*
- *Medalia „Gheorghe Spacu” a Societății de Chimie din România (2009);*
- *Membru de onoare al Societății Române de Știința Materialelor – Creșterea Cristalelor (2009);*
- *Premiul Nenițescu – Criegee acordat Gesellschaft Deutscher Chemiker (2009).*

Este membru al unor Academii din străinătate:

- *Academia Europaea (Londra 2004);*
- *Academia Europeană de Știință, Artă și Litere (Paris 2004);*
- *Academia Europeana de Științe (2010).*

Domnul Academician Marius Andruh este, de asemenea, membru în comitetele editoriale ale unor reviste importante precum:

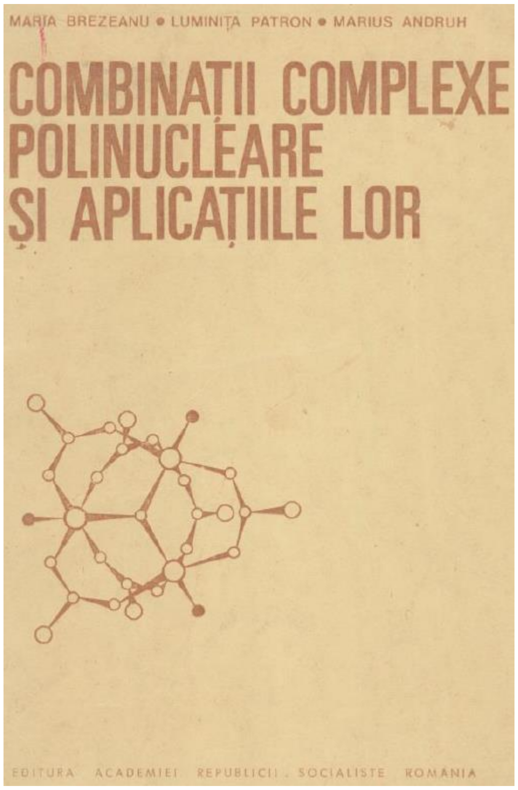
- *Revue Roumaine de Chimie – Editor Șef;*
- *Journal of Coordination Chemistry (2010);*
- *The Open Journal of Inorganic Chemistry (2010);*
- *The Open Material Science Journal (2007).*

A fost desemnat membru în comitetul director al Institutului European de Magnetism Molecular.

Prin valoarea operei științifice și prestanța academică Domnul Profesor Marius Andruh este printre primii chimiști din România in ceea ce privește recunoașterea pe plan internațional și național a contribuției sale la dezvoltarea domeniului de cercetare abordat, a științei de chimie in general.

Realizările Academicianului Marius Andruh in domeniul chimiei combinațiilor complexe sunt în prezent incluse in „Chimia Mare” la nivel mondial și au creat un capitol nou și original in aceasta știință. Ele sunt rezultatul unei munci experimentale de mare anvergură, extrem de judicios coordonata cuplata cu o interpretare la nivelul cunoașterii de ultimă oră a chimiei moderne.

Este o onoare deosebită pentru Universitatea de Vest din Timişoara, în special pentru chimiști, la care participă toți colegii din centrul nostru universitar, de a conferi Domnului Academician Marius Andruh titlul de doctor Honoris Causa Scientiarum și sperăm sa ne fie alături la bine și la greu, in reconstrucția învățământului și cercetării științifice românești.



MARIA BREZEANU • LUMINIȚA PATRON • MARIUS ANDRUH

COMBINAȚII COMPLEXE
POLINUCLEARE
ȘI APLICAȚIILE LOR

EDITURA ACADEMIEI REPUBLICII SOCIALISTE ROMANIA

COMISIA DE ANALIZĂ:

***Președinte**: Conf.univ.dr.ing.* **Constantin Bolcu** *– Decanul Facultății de Chimie Biologie, Geografie – Universitatea de Vest Timişoara;*

***Membrii**:*

Prof.univ.dr. **Gábor Náray-Szabó -** *Eötvös Loránd University, Budapest, DHC al Universității de Vest din Timişoara;*

Prof.univ.dr. **Ionel Mangalagiu** *– Decanul Facultății de Chimie – Universitatea „A.I. Cuza" Iași;*

Prof.univ.dr. **Luminița Silaghi-Dumitrescu** *– Facultatea de Chimie şi Inginerie Chimică, Prorector al Universității Babeș-Bolyai Cluj-Napoca;*

Prof.univ.dr.ing. **Nicolae Vaszilcsin** *– Decan al Facultății de Chimie Industrială și Ingineria Mediului, Universitatea Politehnica din Timişoara;*

Dr. **Maria Zaharescu**, *Membru Corespondent al Academiei Române, Institutul de Chimie Fizică „Ilie. G. Murgulescu" – Academia Română;*

Dr. **Zeno Simon -** *Membru Corespondent al Academiei Române, Institutului de Chimie Timişoara al Academiei Române;*

Dr. **Otilia Costișor** *– Director al Institutului de Chimie Timişoara al Academiei Române;*

Conf.univ.dr. **Vlad Chiriac -** *Facultatea de Chimie, Biologie, Geografie – Universitatea de Vest Timişoara.*

In the speech presented with the occasion of receiving the *Doctor Honoris Causa Scientiarum* of the West University of Timişoara title, named "***Se poate face ştiinţă în România?***" ("*Can science be done in Romania?*"), Acad. Marius Andruh, professor at the University of Bucharest, did a very analytical exposition of the way in which the Romanian university education accomplishes its mission and its assumed objectives for the high professional training of graduates capable of facing today's imposed requirements for a performant scientific research.

Lumea științifică românească se confruntă, de multă vreme, cu fenomenul migrării cercetătorilor săi în alte țări. Principalele motive, în perioada comunismului, erau de ordin economic și politic. După douăzeci și trei de ani motivul economic încă persistă, dar capătă o importanță o alta cauză, cu semnificații mult mai ample, în special pentru tânăra generație: ea privește posibilitățile de realizare profesionala a cercetătorilor cu aspirații înalte. Desigur, condițiile favorabile pentru construirea unei cariere științifice au atras întotdeauna, cu precizarea că majoritatea celor care plecau înainte de 1989 erau cercetători formați și nu studenți sau doctoranzi. Aceștia din urmă ne interesează în mod deosebit acum.

Migrarea cercetătorilor nu a apărut numai în țările comuniste imediat după al doilea Război Mondial. În anii '30 și imediat după război, mulți cercetători au părăsit țări din Europa de Vest pentru a se instala in Statele Unite.

Ce le oferă universitățile (și societățile) occidentale tinerilor talentați? Într-o primă etapă, o instruire flexibilă, modernă, cu un puternic și real caracter formativ (ceea ce pot găsi, câteodată, și în unele universități românești). Trebuie spus ca sesizarea relației dintre componentele formativă și informativă ale învățământului nu este nouă și a fost, cel puțin la nivel declarativ, o preocupare veche în școala românească. Dan Barbilian spunea despre profesorul lui din liceu, Ion Banciu: „A fost omul care m-a format, de la care am învățat esențialul. Ceilalți profesori de matematică, inclusiv cei de la Universitate, m-au informat". Din păcate, nivelul declarativ a fost rareori depășit. Cu toate acestea, liceele și universitățile românești au dat, și dau încă, buni candidați pentru studii la toate nivelurile (licență, master, doctorat) în universitățile occidentale, fapt care a creat, la un moment dat, mitul caracterului excepțional al învățământului romanesc. Un mit periculos, de altfel, pentru că, la adăpostul lui, școala românească a fost extrem de inertă la modificările cerute de societatea în continuă transformare. Un alt mit care poate fi periculos este cel al „olimpicilor": succesele câtorva zeci de adolescenți la Olimpiadele Internaționale nu trebuie privite ca o dovadă a calității învățământului românesc. Aceste succese sunt datorate mai degrabă pasiunii unui tânăr pentru o anumită disciplină, inteligenței și ambiției lui și, de cele mai multe ori, unui profesor care știe să descopere și să modeleze talente. O analiză statistică a distribuției medaliilor pe națiuni la Olimpiadele Internaționale este foarte utilă, dar nu este locul aici să o discutăm.

O parte din tinerii plecați la studii in străinătate se opresc după obținerea masterului și, în funcție de competențele dobândite, aureolate de multe ori și de prestigiul universității absolvite, își găsesc ușor un loc de muncă. Deși și aceștia sunt o pierdere importantă pentru societatea românească, nu mă voi referi la ei și voi restrânge discuția numai asupra celor care vor să urmeze o carieră academică.

Terminând studiile de licență și masterat, cei atrași de cercetarea științifică se înscriu la doctorat și, din acel moment, aproape toți sunt definitiv pierduți de cercetarea românească. Ei vor alege pentru un stagiu post-doctoral o universitate la fel de prestigioasă. Acestora li se *adaugă cei care absolvă studiile de licență și master în România și care aleg să continue doctoratul în străinătate. Să fim bineînțeleși: a le reproșa acestor tineri că pleacă din țară ne face pe noi, acum, la fel de vinovați ca pe aceia care îi declarau trădători de țară pe emigranții din perioada comunistă. Tinerii au căpătat în urmă cu douăzeci și trei de ani libertatea de a circula și de a se instrui acolo unde cred că este bine pentru cariera lor viitoare. Societatea contemporană trebuie să se întrebe de ce tinerii pleacă și, mai ales, de ce nu se mai întorc. Ea, societatea românească, trebuie să ofere condiții tinerilor români (și nu numai români!) de a face cercetare în aceleași condiții ca în țările dezvoltate. Şi tot societatea românească ar trebui să se întrebe, obsesiv, de ce, după studii strălucite în străinătate, Spiru Haret, Constantin I. Istrati, Petru Poni, Nicolae Iorga, Victor Babeș, Ştefan Procopiu, Costin D. Nenițescu, Horia Hulubei, Simion Stoilow și mulți alții s-au întors în țară. Unul dintre răspunsuri este că își iubeau țara.*

În anii comunismului, marile școli de cercetare din perioada interbelică s-au pierdut treptat. Ingerința politicului în viața academică, izolarea treptată, devenită totală în anii ’80 ai secolului trecut, au fost fatale. Cercetarea românească de bună calitate a supraviețuit doar în câteva insule.

Anul 1990 ne-a găsit, pe mulți dintre noi, săraci din punct de vedere științific, dezorientați și rupți de adevărata cercetare. Consecințele se văd și azi. În multe domenii a trebuit să o luăm de la capăt. Din fericire, numeroși cercetători români, care aveau atunci 30-40 de ani, au fost acceptați pentru stagii de lungă durată în prestigioase laboratoare din Europa, Statele Unite sau Japonia, care le-au facilitat racordarea la marea știință. Mulți dintre ei s-au întors și lor le datorăm, în bună parte, renașterea științei românești. Aici este locul să mai spunem ceva: succesul demersului celor care se întorc este deplin numai dacă reușesc să se desprindă de proiectele laboratoarelor în care au petrecut o perioadă de timp. Altfel, rămân o simplă anexă, utilă uneori, dar totuși anexă, a unei tematici care nu le aparține și la care pot aduce cel mult contribuții de rutină. Este ca un ucenic al unui mare pictor care nu și-a găsit drumul și continuă să picteze detalii minore din opera maestrului.

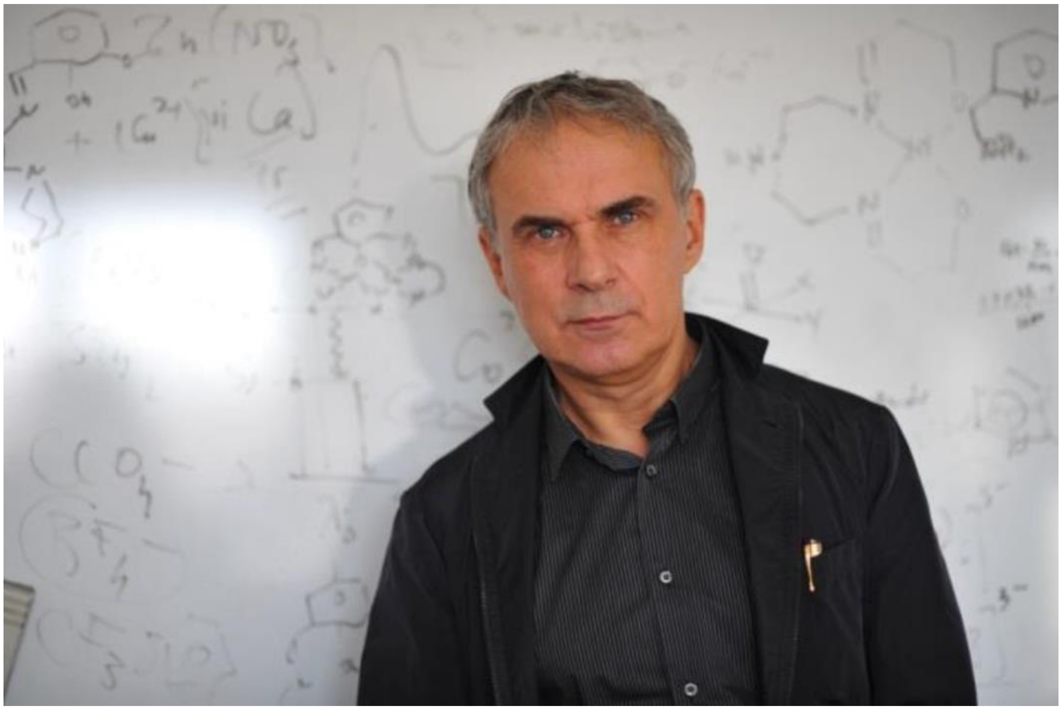
Cercetarea românească a pierdut enorm până a înțeles, într-un târziu, că doctoratul este un ciclu, superior, al învățământului, că activitatea în cadrul doctoratului nu se face „la fără frecvență”, că doctorandul trebuie sa fie zilnic și complet implicat în tema de cercetare și în permanență atent la ce se publică în domeniul în care activează. Doctoratul în științe se face la școala unui maestru iar tezele de doctorat elaborate sub îndrumarea acestuia trebuie să ilustreze direcții de cercetare originale și, în cazul ideal, de anvergura. Doctoratul este, în orice universitate, o ucenicie. Bine instruit și format, un tânăr doctor trebuie să știe că va avea succes în cariera științifică doar dacă va ști să își găsească apoi drumul propriu, diferit de al maestrului. Conducătorul de doctorat trebuie să stimuleze creativitatea doctorandului, pregătindu-l pentru o carieră independentă. Doctorandul și conducătorul său vor contribui la prestigiul științei românești numai atunci când ceea ce lucrează interesează pe alți mari cercetători. Citarea de către autori minori în jurnale mediocre poate să fie periculoasa, creând cercetătorului falsa imagine a reușitei în știință.

O Universitate care dorește a fi prestigioasă trebuie să atragă studenți talentați în programele sale de master si doctorat și să le ofere acestora posibilitatea de a efectua stagii de cercetare în Universități din străinătate. Traseul tânărului cercetător format într-o Universitate românească trebuie continuat cu un stagiu post-doctoral într-o altă Universitate, de preferință în străinătate. Totodată, prestigiul universităților noastre va crește și atunci când tineri doctori din alte țări vor fi atrași pentru stagii post-doctorale.

Spuneam într-un text publicat în urmă cu câțiva ani că sunt optimist în privința destinului cercetării românești. Sunt în continuare optimist și, în plus față de atunci, am certitudinea că suntem pe un drum bun, chiar dacă mai sunt multe de făcut. Avem câteva laboratoare, în Universități si Institute de cercetare din țară, echipate la nivelul secolului XXI. Avem deja cercetători cu o bună recunoaștere internațională. Mai trebuie însă ceva: cercetarea românească va fi așezată deplin pe drum ascendent numai atunci când cercetătorii vor înțelege că finanțarea, oricât de generoasă ar fi, nu este suficientă pentru succesul în știință. ***Originalitatea ideilor, semnificația lor pentru avansarea științei sunt esențiale.***

În epoca contemporană, marea cercetare se face prin colaborări internaționale implicând grupuri cu expertize complementare. Aceste colaborări sunt încurajate puternic sau chiar devin o condiție de eligibilitate a proiectelor, impusă de către instituțiile organizatoare de competiții pentru granturi de cercetare. Participarea cercetătorilor români la astfel de rețele este necesară și obligatorie. Și aici s-au făcut pași importanți. Laboratoarele însele au devenit tot mai internaționale, atât prin doctoranzi cât și prin cercetătorii cu poziții permanente proveniți din alte țări. Cercetarea europeană are un caracter național doar prin localizarea, într-o anumită țară, a laboratorului. Aspectul național al cercetării se referă tot mai mult la capacitatea unei țări sau alteia de a selecta și finanța proiecte cu adevărat valoroase și de a atrage pe cei mai talentați cercetători, indiferent de țara din care provin.

Dincolo de considerațiile de mai sus, întrebarea din titlu cere un răspuns răspicat: ***DA,*** *se poate face cercetare de bună calitate și în România, în ciuda multor greutăți. Cu suișuri și coborâșuri, cercetarea românească a adus de-a lungul anilor contribuții importante la dezvoltarea științei. Trebuie să credem în destinul ei și să facem, ca actori și organizatori ai cercetării românești, tot ce este posibil pentru a-i asigura succesul. (Marius Andruh)*



The scientific opera of Acad. Marius Andruh contains a list of over 200 scientific articles published in prestigious journals (Angew. Chem., J. Am. Chem. Soc., Chem. - Eur. J.; Chem. Commun.; Inorg. Chem.; Dalton Trans.; Eur. J. Inorg. Chem.; Cryst. Growth Des., CrystEngComm; Adv. Mater., Chem. Soc. Rev., J. Phys. Chem., New J. Chem., Inorg. Chim. Acta; Inorg. Chem. Commun.; Polyhedron; Coord. Chem. Rev.; J. Mol. Struct.; J. Inclusion Phenom.; J. Solid State Chem., Z. Anorg. Allg. Chem.), which have gathered around 4000 citations and produced an *h-index* of 39 (according to *Scopus* and *Web of Science*).

In his scientific activity memo, Acad. Marius Andruh synthetically presents "*Main Accomplishments*": 16 of his papers were included in the Top 10, Top 20, or Top 25 of the most accessed/cited papers.

REFERENCES

∗ Universitatea de Vest din Timișoara, Facultatea de Chimie, Biologie, Geografie, "*Doctor Honoris Causa Scientiarum al UVT, Profesor Dr. Marius Andruh, membru al Academiei Române*", Timișoara, 22 mai 2013, Editura Universității de Vest, Timișoara, 2013.

NEW FRONT. CHEM. (2016)
Volume 25, Number 1, pp. 39-52
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Article

COORDINATION COMPOUNDS OBTAINED THROUGH OXIDATION OF DIOLS WITH METAL NITRATES PART I. SYNTHESIS - STRUCTURE RELATIONSHIP FOR AQUEOUS ETHYLENE GLYCOL - METAL NITRATE SYSTEMS*

Mihail Bîrzescu[1†], Dan Roşu[1,2], Marius-Silviu Milea[1], Mihai-Cosmin Pascariu[3,4♣], Madian Rafailă[1], Viorel Sasca[5], Mircea Niculescu[1,4]

[1] University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Pârvan Blvd., 300223, Timişoara, Romania
[2] INCEMC Timişoara, 144 Dr. Aurel Păunescu Podeanu, 300569, Timişoara, Romania
[3] "Vasile Goldiş" Western University of Arad, Faculty of Medicine, Pharmacy and Dental Medicine, 86 Liviu Rebreanu, 310045, Arad, Romania
[4] "Chemeia Semper" Association, 6 Giuseppe Verdi, 300493, Timişoara, Romania
[5] Institute of Chemistry Timişoara of Romanian Academy, 24 Mihai Viteazul Blvd., 300223, Timişoara, Romania
[†] Deceased in 2012

ABSTRACT

The oxidation of ethylene glycol with Ni(II) and Fe(III) nitrates was investigated. The Ni(II)/Fe(III) heteropolynuclear coordination compound, which contains the oxidation product of ethylene glycol as ligand, was prepared, and its thermal and spectroscopic properties were established. The synthesis reaction occurs, under strict working conditions, with the oxidation of ethylene glycol to glyoxylic acid, coordinated to nickel and iron cations as glyoxylate dianion, with simultaneous isolation of the corresponding complex compound. After its treatment with R-H cationite and the retention of the metal cations, the ligand was isolated and identified. The resulting acid compound (glyoxylic acid) was characterized by measuring its physical constants, by specific reactions and by

---

[*] Dedicated to Prof.Dr. Carol Csunderlik, in memoriam

[♣] Correspondent author E-mail: mihai.cosmin.pascariu@gmail.com

using spectroscopic methods. The structural and thermal analysis (TG, DTG and DSC) of the heteropolynuclear coordination compound, which is a precursor of a mixed oxide, are presented. This mixed oxide (spinel) obtained through thermolysis was characterized by FTIR, X-ray spectroscopy and elemental analysis.

Keywords: heteropolynuclear coordination compounds, glyoxylate, metal nitrates, thermal analysis, FTIR, X-ray spectroscopy.

1. INTRODUCTION

The usage of diols and their oxidation products as ligands is a well-established field in the coordination compounds chemistry. Knetsch and Groeneveld, for example, have synthesized and studied a number of coordination compounds with diols as ligands [1]. Also, the oxidation of 1,2-ethanediol, 1,2-propanediol and 1,3-propanediol with metal nitrates have been described [2-10]. The coordination compounds synthesized in this manner contain glyoxylate, oxalate, lactate and 3-hydroxypropionate anions as ligands.

The thermal conversion of homo- and heteropolynuclear complexes with carboxylic acid anions as ligands has been carried out, producing metal oxide systems with irreducible structure and properties, which are required by the modern technologies implemented in diverse industrial areas, such as heterogeneous catalysis, electrocatalysis, electronic engineering, physical supports (carriers, brackets) for information storage and processing, ceramic pigments, and drug industry [11-13]. These complexes decompose at relatively low temperatures with the formation of simple or mixed oxides, and of various volatile products (CO, CO_2, H_2, H_2O).

Depending on the working conditions, the reaction of ethylene glycol (EG) with copper(II) nitrate occurs with the oxidation of the former, with the possibility of forming the glyoxylate [11] or the oxalate anion [2,11b].

The colloidal crystal templating process is used to generate three-dimensionally ordered MFe_2O_4 (in which M = Co, Mn, Ni, Zn) macroporous structures [14]. Gao et al. [15] synthesized the $NiFe_2O_4$ mesoporous spinel with well-defined pore sizes (2.5-16.2 nm) by oxalate decomposition, which is useful for adsorption of acid orange 7. The preparation process for three-dimensional porous materials always uses the template method, which includes two steps: infiltration and template removal [16]. A simple way of producing 3D porous materials is required in the field of adsorbents.

Magnetic separation is considered an effective technique for separating adsorbents from wastewater, and magnetic adsorbents have been widely investigated in recent times [17-19]. At room temperature, the spinel ferrite (MFe_2O_4, where M is a d-block metal) shows a typical ferromagnetic property and is widely used as magnetic carrier in adsorbents to accomplish the magnetic separation [20,21]. For example, the magnetic microsphere containing ferrite is used for the adsorption of organic dye [17], bromide-coated ferrites are used for the preconcentration of phenolic compounds [18], while a magnetic polymer nanosphere adsorbent is used for dye molecules removal [19]. The composite adsorbents generally lose some adsorption capacity or ferromagnetism, but applying the spinel ferrite as adsorbent directly solves this problem, because of the intrinsic good adsorption and magnetic separation properties. Another application of $NiFe_2O_4$ as adsorbent was to treat wastewater [22].

In the last decades the thermal decomposition of heteropolynuclear coordination compounds, used as precursors, was frequently used for the generation of nanoferrites. This process represents a predictable and versatile unconventional method, having the advantage of controlling the quality (both the composition and the microstructure) of the final products' features by selecting suitable ligands.

The determination of the forming conditions for non-stoichiometric oxides of cobalt and nickel led to an original method of producing anodes covered with active electrocatalytic films for evolving oxygen during alkaline solutions electrolysis [23].

The spinel ferrites and the mixed oxides of spinel type in general show great promise in modern electronic technologies, as microwave absorbers, chemical sensors and catalysts, and also in biomedical applications. The ferrites' fine particle nature is essential for all these applications, being generally achieved by soft chemistry synthesis methods, like low temperature range decomposition of suitable precursors [24-32].

This paper, which is the first part of a series of papers, shows the results obtained during investigation of EG's oxidation with iron(III) and nickel(II) nitrates, in weak acidic media (pH around 2.5). The obtained coordination compound was studied regarding its composition and physical-chemical properties. It was shown that it can also be a precursor for nickel ferrite ($NiFe_2O_4$), which can thus be obtained at relatively low temperatures.

2. METHODS

2.1. Chemicals and analysis methods

EG, nickel(II) nitrate hexahydrate $Ni(NO_3)_2{\cdot}6H_2O$ and ferric nitrate nonahydrate $Fe(NO_3)_3{\cdot}9H_2O$, all reagent grade, were employed as starting materials. The subsequent purification step assured the removal of reagent impurities.

The metal content was determined by atomic absorption spectrometry, while carbon and hydrogen were quantified with the help of a Carlo Erba 1108 elemental analyzer.

The TG, DTG and DSC curves (25-1000°C temperature range), corresponding to the decomposition of the heteropolynuclear coordination compound, were registered in a static air atmosphere using a 10 $K{\cdot}min^{-1}$ heating rate, on a Simultaneous TG-DTA/DSC 409 PC apparatus produced by Netzsch-Gerätebau GmbH (Germany).

The coordination compound was also characterized by chemical analysis, Fourier transform infrared spectroscopy (FTIR) and electronic spectroscopy (using diffuse reflectance technique).

The FTIR spectra (KBr pellets) were registered on a Jasco FT/IR-410 spectrometer in the 400-4000 cm^{-1} domain.

The electronic spectrum was registered through the diffuse reflectance technique with a Spekol 10 spectrophotometer from Carl Zeiss Jena (reference material: MgO).

The characterization of the nickel ferrite obtained by thermal decomposition of the coordination compound was performed by elemental analysis, FTIR and X-ray diffraction (XRD).

A Bruker D8 Advance diffractometer, equipped with a graphite monochromator, was used to register the XRD patterns on the diffracted beam with Mo K_α radiation ($\lambda = 0.70930$ Å). The X-ray power was set at 40 KV and 30 mA. The powder samples were grounded, if required, to reduce the granulation, after which they were pressed in the specimen holder. The XRD patterns were registered over a range of 2θ angles beginning from 5° to 50°. The crystalline phases were identified using the JCPDS-ICDD files. The diffraction data were acquired and processed using the "Diffrac Plus" software.

2.2. Synthesis of the heteropolynuclear coordination compound

The method developed for the synthesis of the coordination compound is based on the oxidation of EG in a diol-water system by using the nickel(II) and ferric nitrates, with simultaneous isolation of the coordination compound from the reaction system.

An aqueous solution of nickel(II) nitrate, ferric nitrate and EG (1:2:2 molar ratio) was gradually heated in a thermostat until 90°C. When the gas evolution ceased the reaction was considered complete. The obtained powdery solid was purified by refluxing in an acetone-water mixture. The solution was filtered and the obtained beige solid was washed with acetone and exposed to air until constant mass (yield 85% based on EG).

The metal nitrates are completely consumed during the preparation of the coordination compound. This is easily verified by treating a sample with concentrated sulfuric acid, when no brown vapors release was noticed. Also, a negative ring reaction was observed, i.e. no intensely brown colored $[Fe(OH_2)_5NO]SO_4$ was produced in the reaction with $FeSO_4$ and sulfuric acid. The Braccio reaction was negative as well (no NO_3^- or NO_2^- anions were detected using the antipyrine test, which means that the oxidizing action of the nitrate did not lead to its reduction to nitrite).

In order to isolate and identify the ligand present in the coordination compound, its aqueous suspension thus obtained through the reaction of EG with metal nitrates (in the absence of other reagents), was treated with R-H cationite. The resulting acidic solution obtained after the retention of the metal cations was lyophilized and a white crystalline solid, with a 98°C melting point, highly soluble in water but with a poor solubility in alcohols or ethylic ether, was produced.

3. RESULTS AND DISCUSSIONS

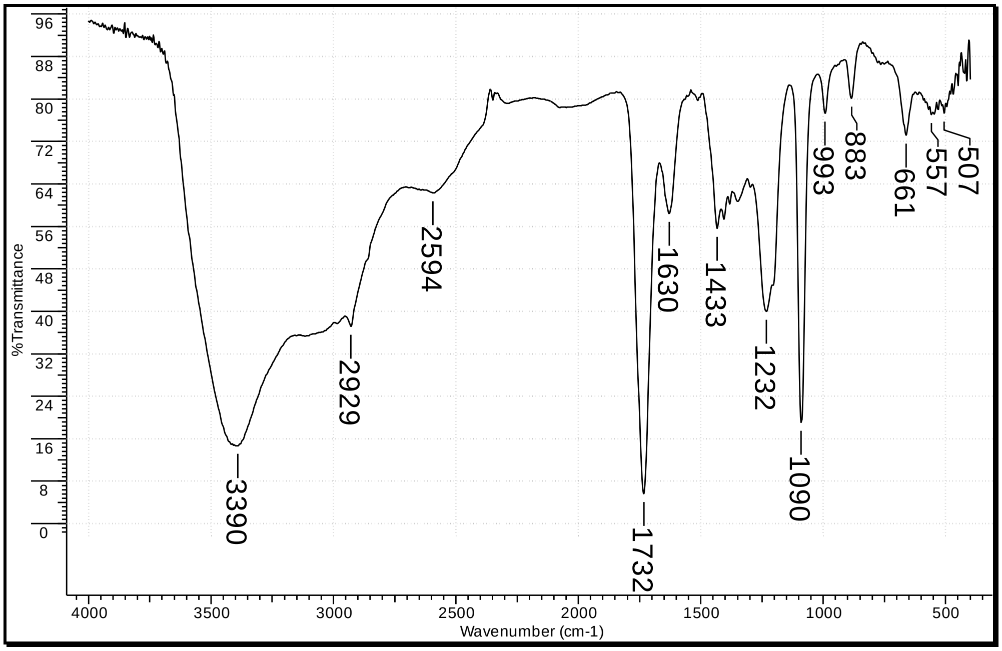
The progress of the reaction between nickel(II) nitrate, ferric nitrate and EG was first investigated by FTIR spectroscopy. As the reaction advances, the intensity of the nitrate bands decreases, proving that this ion is consumed.

Simultaneously, the appearance and the increase in intensity of one band in the range of 1580-1680 cm^{-1} ($\nu_{asym}(COO^-)$) is observed. This band appears for ligands that contain two oxygen atoms as donors, like carboxylic acid anions [33].

After the cations retention on R-H cationite (Purolite C-100 resin), the ligand was identified in its protonated form as glyoxylic acid by using specific reactions and by studying the physical properties of the lyophilization product.

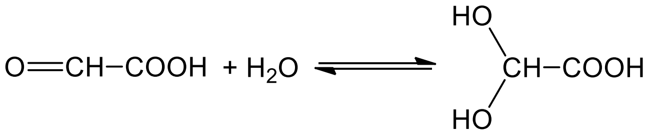
The FTIR spectrum of the glyoxylic acid is given in Figure 1.

Figure 1: FTIR spectrum of glyoxylic acid



In the FTIR spectrum from Figure 1, the characteristic bands for both forms of glyoxylic acid, which coexist in equilibrium in the presence of water (Figure 2), can be spotted.

Figure 2: Glyoxylic acid (left) and hydrated glyoxylic acid (right)



$$O{=}CH{-}COOH + H_2O \rightleftharpoons (HO)_2CH{-}COOH$$

Chemical Formula: $C_2H_2O_3$
Molecular Weight: 74.0

Chemical Formula: $C_2H_4O_4$
Molecular Weight: 92.1

The broad band in the 3200 - 3600 cm^{-1} domain, with the maximum at 3390 cm^{-1}, is assigned to the stretching of the two different types of O-H bonds: the one in the carboxyl group and the alcohol type which comes from the hydrated aldehyde group (structure at right in Figure 2). The 1732 cm^{-1} sharp band is attributed to the $\nu(C{=}O)$ vibration. The 1630 cm^{-1}

band is assigned to the carboxylate asymmetric vibration. The 1381 cm^{-1} band is assigned to the ν_{sym}(OCO) vibration. The 1232 cm^{-1} band could arise from the coupling between a ν(CO) vibration and a δ(OH) vibration. The 1090 cm^{-1} and 993 cm^{-1} bands are attributed to the $CH(OH)_2$ geminal diol (hydrated aldehyde). The 661 cm^{-1} band is attributed to the γ(OCO) bending vibration [33].

The chemical analysis of the lyophilization product was done through specific redox, color and precipitation reactions: with metallic zinc (glycolic acid is obtained), with Ag_2O (metallic silver was obtained), with indole or pyrogallol in concentrated H_2SO_4 (a red or, respectively, blue color occurred), with resorcinol (the lactone of 2,4,2',4'-tetrahydroxydiphenylacetic acid is formed in the presence of sulfuric acid; the oxygen then oxidizes the lactone in alkaline conditions and a blue-violet color appeared); also, precipitates are obtained in the reactions with both 4-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine.

The physical properties (white, crystalline, water-soluble solid, with poor solubility in alcohol or ether, and with a melting point of 98°C) correspond to those found in literature [11,34].

The elemental analysis results (Table 1), as well as the FTIR studies, have indicated that the synthesized coordination compound should have the empirical chemical formula: $NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2\cdot1.5H_2O$.

Table 1: Elemental analysis data for the coordination compound

Empirical formula	%C		%H		%Fe		%Ni	
$NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2\cdot1.5H_2O$	found	calcd.	found	calcd.	found	calcd.	found	calcd.
	9.05	9.28	3.49	3.70	21.62	21.58	10.71	11.34

These results, as well as those previously reported [6-8,11] concerning the oxidation of diols with ferric nitrate, respectively nickel(II) nitrate, suggest that the simultaneous oxidation of EG with these nitrates gives, in the specified working conditions, the glyoxylate anion, coordinated to both Ni(II) and Fe(III) cations.

In consequence, we propose the following mechanism for the reaction between EG and these metal nitrates, in the absence of other reagents:

$$C_2H_3O_4^- + 6e^- + 7H^+ \rightleftharpoons C_2H_4(OH)_2 + 2H_2O \qquad (1)$$

$$NO_3^- + 3e^- + 4H^+ \longrightarrow NO + 2H_2O \qquad (2)$$

$$C_2H_4(OH)_2 + 2NO_3^- + H^+ \rightleftharpoons C_2H_3O_4^- + 2NO + 2H_2O \qquad (3)$$

$$[Fe(OH_2)_6]_3^+ + 2H_2O \rightleftharpoons [Fe(OH)_2(OH_2)_4]^+ + 2H_3O^+ \qquad (4)$$

$[Ni(OH_2)_6]^{2+} \rightleftharpoons [Ni(OH_2)_6]^{2+}$ (hydrolysis does not occur in the specified conditions)

By summing Eqs. (3) and (4) and considering the interaction between the ligand and the metal cations, one obtains:

$$2C_2H_4(OH)_2 + (4NO_3^- + [Ni(OH_2)_6]^{2+} + 2[Fe(OH)_2(OH_2)_4]^+) + xH_2O \longrightarrow$$
$$NiFe_2(C_2H_2O_4)_2(OH)_4\cdot xH_2O + 18H_2O + 4NO \qquad (5)$$

Ni(II)/Fe(III) glyoxylate
(composition formula)

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad (6)$$

It can be noticed that the presence of protons, involved in equilibrium 3, is necessary to potentiate the oxidation activity of NO_3^- ions.

The proposed formula for the complex compound and the information regarding its structure are going to be further confirmed by the following results.

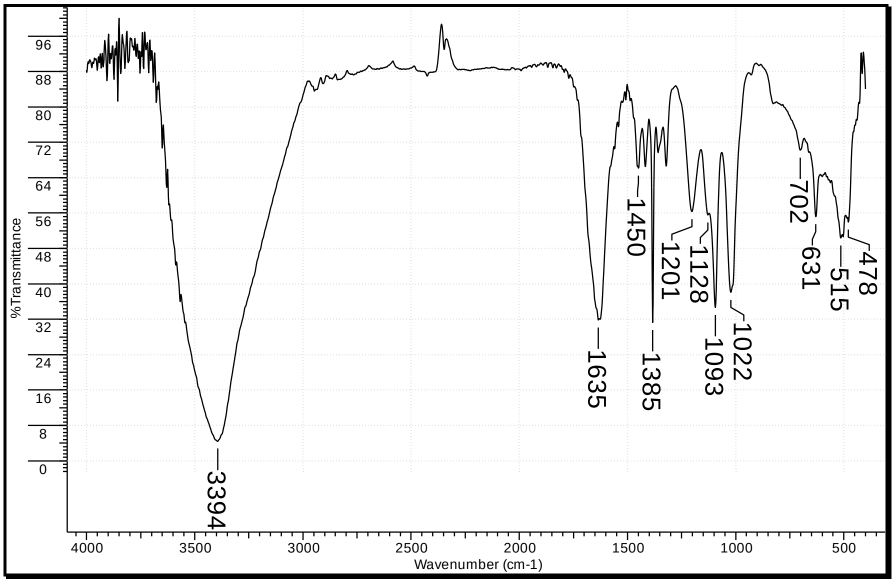
The diffuse reflectance spectrum of the coordination compound illustrates the characteristic bands for the hexacoordinated nickel(II) and ferric ions in a (pseudo)octahedral environment.

The absorption band at 26,316 cm^{-1} (with $\lambda = 380$ nm) can be attributed to the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (ν_3) transition, which is characteristic to the nickel(II) ion in a high spin octahedral configuration. The band at 13,158 cm^{-1} (with $\lambda = 760$ nm) can be assigned to the $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (ν_2) transition. The obtained results agree with the literature [6-10].

Accordingly, the nickel(II) ion is in fundamental state $t_{2g}^{6}e_{g}^{2}$, high spin, the ligands being of low field and of similar strength. At 920 nm, the reflectance spectrum reveals the characteristic band of iron(III) in a high spin octahedral configuration and also the forbidden spin transition bands in the same configuration for iron(III) (t_{2g}^{3} e_{g}^{2}) ions (ν3) [11].

In order to obtain more data regarding the structure of the synthesized complex compound and the ligand coordination, the FTIR spectrum was recorded (Figure 3).

Figure 3: FTIR spectrum of the heteropolynuclear coordination compound



The characteristic FTIR bands (in cm^{-1}) for the complex and the corresponding assignments are shown in Table 2.

Table 2: Characteristic FTIR absorption bands for $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]n\cdot 1.5nH_2O$

Wavenumber [cm^{-1}]	Assignment
3394 vs,b	ν(OH), hydrogen bonding
1635 s	ν_{asym}(C=O), δ(H_2O*)
1560 m,sh	lattice water
1385 s	ν_{sym}(CO)+ν(CC)
1321 m	ν_{sym}(CO)+δ(O-C=O)
1093 s	ν(CO)
827 w	δ(O-C=O)+ν(FeO,NiO)
702 w	ρ(H_2O*)
631 m	lattice water
563 m	ρ(H_2O*)
515 m	ν(FeO,NiO)+ν(CC)

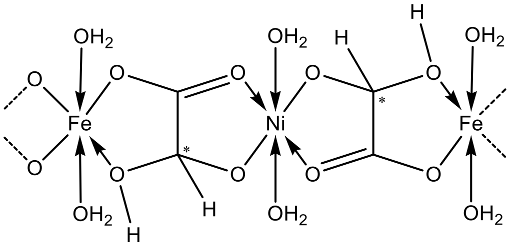
s-strong; b-broad; m-medium; w-weak; sh-shoulder; *coordinated water

The broad band from the 3200-3600 cm^{-1} range, with the maximum at 3394 cm^{-1}, is assigned to the hydrogen bonds formed between the water molecules and the hydroxyl groups [9-11]. The 1635 cm^{-1} intense band is assigned to the carboxylate asymmetric vibration, the value also showing that the carboxylate group resonance is maintained during complex formation and that the metal-carboxylate bond has a predominantly ionic character [33].

The band with maximum at 1385 cm^{-1} is attributed to the ν_{sym}(CO) vibration. Because the ν_{asym}-ν_{sym} value is higher than 170 cm^{-1}, the metal-carboxylate bond seems to be mainly ionic, and the carboxylate group must act as a bidentate ligand [33]. Moreover, the existence of the two bands for ν_{sym}(CO) can be explained through the octahedral deformation. The 1321 cm^{-1} band confirms that the carboxylate group is behaving as a bidentate ligand [23,33]. The band at 1093 cm^{-1} is assigned to the C-OH vibration. The 1022 cm^{-1} strong intensity band is assigned to the hydroxyl bridge group vibration, while the band at 827 cm^{-1} is assigned to the δ(OCO) vibration.

The complex combination is insoluble in water, ethanol or ether, although concentrated HCl or H_2SO_4 are able to destroy its structure. These properties, as well as the previous discussed data, confirm a polynuclear structure corresponding to the formula: $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]n\cdot 1.5nH_2O$.

In accordance with the empirical formula, the (pseudo)octahedral stereochemistry of Ni(II) and Fe(III) and the structure of the bridging glyoxylate dianion, the heteropolynuclear coordination compound must have the following structure:



The thermal analysis methods were invoked to establish the conditions in which the $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]n\cdot1.5nH_2O$ coordination compound is decomposed to $NiFe_2O_4$. The recorded TG, DTG and DSC curves suggest six steps:

I (*20-160°C*): $NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2\cdot1.5H_2O_{(s)} \xrightarrow{-1.5H_2O} NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2$
II, **III** (*160-310°C*): $NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2 \xrightarrow{-6H_2O} NiFe_2(C_2H_2O_4)_2O_2$
IV (*310-450°C*): $NiFe_2(C_2H_2O_4)_2O_2 \xrightarrow{-CO_2;-H_2O} NiFe_2(C_2H_2O_4)CO_3$
V (*450-700°C*): $NiFe_2(C_2H_2O_4)CO_3 \xrightarrow{-H_2;-CO} NiFe_2(CO_3)_2$
VI (*700-765°C*): $NiFe_2(CO_3)_2 \xrightarrow{-2CO} NiFe_2O_{4(s)}$

In the 20-310°C temperature range, $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]_n\cdot1.5nH_2O$ displays two dehydration DSC peaks, one endothermic (broad) and one exothermic (maximum at 263°C), for the two stages of water loss. The TG mass losses correspond to $1.5H_2O$ (process I) and, respectively, $6H_2O$ (process II-III).

The exothermic effects found in steps IV and V (maxima at 360°C and 516°C) are due to ligand combustion which leads to the spinel formation.

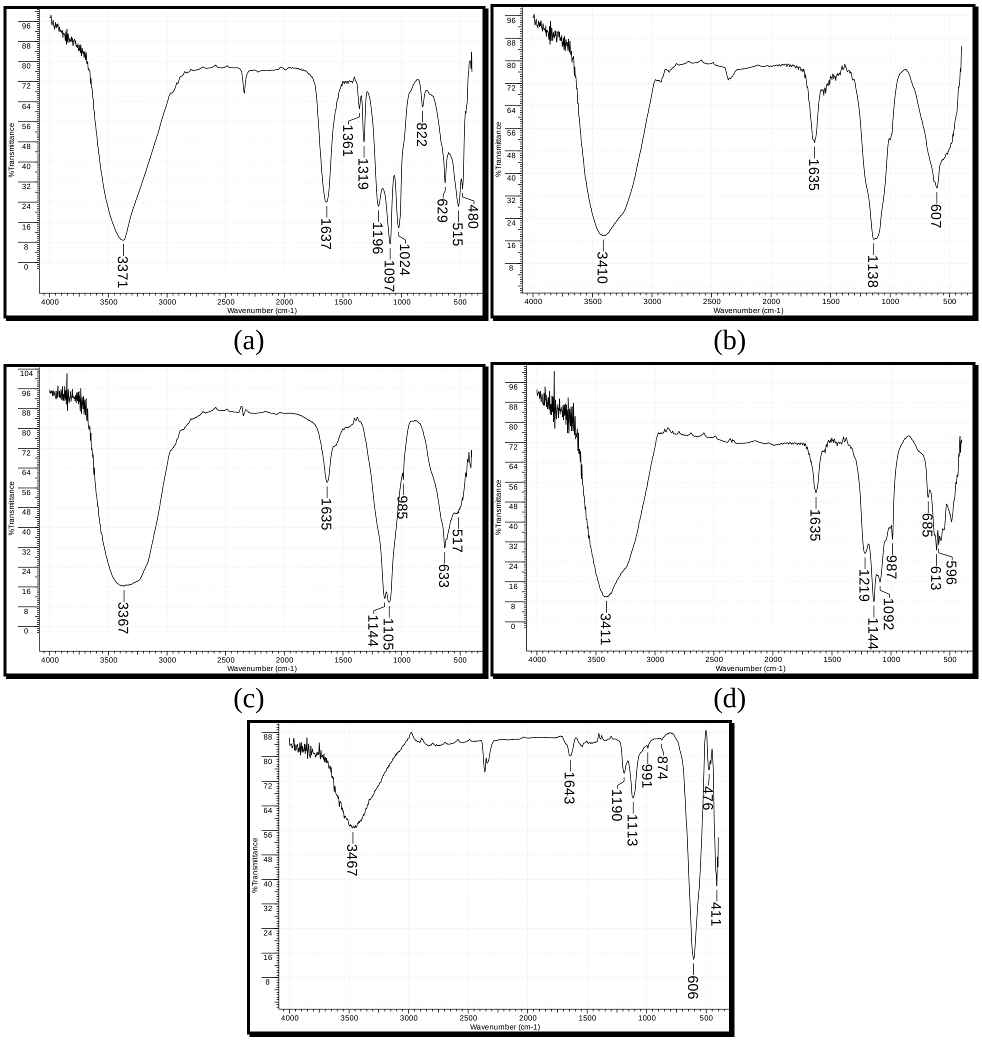
The spinel $NiFe_2O_4$ [14-19], obtained at the temperature of 765°C, is the main decomposition component.

In order to support the proposed conversion mechanism, the thermal decomposition of the synthesized heteropolynuclear coordination compound was followed by the analysis of the residues by FTIR and XRD spectroscopy. In Figure 4, the FTIR spectra are shown for different decomposition temperatures.

By analyzing the FTIR spectrum recorded for the residue obtained after decomposition of the coordination compound in air at 300°C (Figure 4a), the band at 1637 cm^{-1} can be noticed. This band is assigned to the ν(C=O) asymmetric vibration in the carboxylate, while the bands with maxima at 1361 and 1319 cm^{-1} are attributed to the ν_{sym}(O–C=O) vibration. The 1196, 1097 and 1024 cm^{-1} sharp bands are attributed to the ν(C–O) vibration from the former hydrated aldehyde. The band with maximum at 629 cm^{-1} is assigned to the δ(OCO) vibration. The 1732 cm^{-1} band, which corresponds to the ν(C=O) vibration from the aldehyde group, was not detected. The broad band at 3371 cm^{-1} is assigned to the ν(O–H) stretching vibration.

The decrease in intensity of the band at 1635 cm^{-1} (Figure 4b) was observed along with the emergence of the 607 cm^{-1} band, assigned to the ν(Fe–O) vibration, typical to iron oxides. The FTIR spectra recorded after calcination at 450°C (Figure 4c) is very similar to the one registered at 400°C.

Figure 4: FTIR spectra of residues obtained after decomposition of the coordination compound in air at: **(a)** 300°C; **(b)** 400°C; **(c)** 450°C; **(d)** 600°C and **(e)** 800°C



(a) (b)

(c) (d)

(e)

The FTIR spectrum of the residue obtained at 600°C (Figure 4d) reveals a significant decrease in the intensity of the band at 1635 cm^{-1}, indicating an advanced decomposition of the metal-glyoxylate complex. The bands at 613 and 577 cm^{-1} are typical to hematite [35]. The bands at 553 and 596 cm^{-1} are assigned to the stretching vibration of tetrahedrally coordinated Fe^{3+}–O^{2-} bond [36] and tetrahedrally Fe^{3+}–O^{2-} groups from the inverse spinel [37]. The 488 cm^{-1} band is assigned to the Ni–O octahedral metal stretching [38].

By analyzing the FTIR spectrum for the final conversion product (Figure 4e), the characteristic bands for the $NiFe_2O_4$ spinel, as found in the literature data [33,34,39], are revealed. The significant decrease of the 1643, 1190 and 1113 cm^{-1} bands proves that the decomposition of the complex compound and the carbonates led to their almost complete disappearance. Also, the most intense band centered at 606 cm^{-1} was attributes to the tetrahedral metal-oxygen bond stretching vibration from the inverse spinel ferrites [37].

As a final argument for the formation of the desired compound, the XRD patterns of the decomposition products, taken at different temperatures, show the appearance and increase in intensity of the characteristic peaks for the $NiFe_2O_4$ spinel, as found in the literature [40,41]. The studied samples seem to be relatively well crystallized.

4. CONCLUSIONS

An original method for synthesizing the coordination compound having the glyoxylate dianion as ligand, based on the oxidation reaction of EG in a diol-water system by nickel(II) and ferric nitrates, with the simultaneous isolation of the coordination compound, was developed.

The complex compound synthesized by this new synthetic method is a heteropolynuclear combination with the formula $[NiFe_2(C_2H_2O_4)_2(OH_2)_6O_2]_n \cdot 1.5nH_2O$. It was investigated by elemental and thermal analysis, electronic and FTIR spectroscopy. All the experimental studies lead to the conclusion that the coordination compound is characterized by a (pseudo)octahedral configuration of the cations.

The $NiFe_2O_4$ spinel, obtained by thermal conversion of the heteropolynuclear coordination compound, is the main degradation product.

REFERENCES

1. a) Knetsch D., Groeneveld W.L., “Alcohols as ligands: Part IV. Complexes of ethylene glycol with some metal(II) sulfates and nitrates”, Recl. Trav. Chim. Pay-B., 92 (1973) 855-864; b) Knetsch D., Groeneveld W.L., “Far-infrared spectra and magnetic measurements of complexes of ethylene glycol”, Inorg. Nucl. Chem. Lett., 12 (1976) 27-32.
2. 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.
3. Niculescu M., Vaszilcsin N., Muntean C., Davidescu C.M., Bîrzescu M., “Oxidation Reaction of Some Diols with M(NO3)2·6H2O (M: Ni(II), Co(II)). Thermal Behaviour of the Obtained Complex Intermediates (I)”, Chem. Bull. “Politehnica” Univ. Timișoara, 43 (1998) 259-274.
4. Niculescu M., Vaszilcsin N., Magda A., Medeleanu M., “Oxidation reaction of 1,3-propanediol with M(NO3)2 (M=Co,Ni). Characterization of the obtained complex intermediates”, Chem. Bull. ”Politehnica” Univ. Timișoara, 43 (1998) 145-153.

5. Niculescu M., Vaszilcsin N., Budrugeac P., “Structural investigations and thermal analysis of the complex compound obtained through the reaction of 1,3-propanediol with Ni(NO3)2·6H2O”, Studia UBB Chemia, XLIV (1999) 275-286.
6. 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.
7. 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.
8. 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.
9. Niculescu M., Dumitru R., Magda A., Bandur G., Sisu E., “Noi metode de obținere a unor acizi carboxilici prin reacții de oxidare a poliolilor cu azotați de metal(II). I. Reacții de oxidare a 1,2-propandiolului cu azotați de metal(II)”, Rev. Chim.-Bucharest, 58 (2007) 932-936.
10. Niculescu M., Vaszilcsin N., Davidescu C.M., Negrea P., Bîrzescu M., Budrugeac P., “Structural investigations and thermal analysis of the coordination compound obtained through the reaction of 1,3-propanediol with Co(NO3)2·6H2O”, Rev. Roum. Chim., 48 (2003) 997-1006.
11. a) Ștefănescu 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; b) Bîrzescu M., “Complexes combinations with ethylene glycol and their oxidation products. Ph.D. Thesis”, University of Bucharest, 1998.
12. Brezeanu M., Safarica E., Segal E., Patron L., Robu T., “An analysis of thermal decomposition of coordination polynuclear compounds in Fe(III), Mn(II), Ni(II) system”, Rev. Roum. Chim., 27 (1982) 137-140.
13. Brezeanu M., Tatu E., Bocai S., Brezeanu O., Segal E., Patron L., “Non-isothermal decomposition kinetics of polynuclear coordination compounds”, Thermochim. Acta, 78 (1984) 351-355.
14. Sadakane M., Takahashi C., Kato N., Ogihara H., Nodasaka Y., Doi Y., Hinatsu Y., Ueda W., “Three-Dimensionally Ordered Macroporous (3DOM) Materials of Spinel-Type Mixed Iron Oxides. Synthesis, Structural Characterization, and Formation Mechanism of Inverse Opals with a Skeleton Structure”, B. Chem. Soc. Jpn., 80 (2007) 677-685.
15. Gao Z., Cui F., Zeng S., Guo L., Shi J., “A high surface area superparamagnetic mesoporous spinel ferrite synthesized by a template-free approach and its adsorptive property”, Micropor. Mesopor. Mat., 132 (2010) 188-195.
16. Imhof A., Pine D.J., “Ordered macroporous materials by emulsion templating”, Nature, 389 (1997) 948-951.
17. Rocher V., Siaugue J.M., Cabuil V., Bee A., “Removal of organic dyes by magnetic alginate beads”, Water Res., 42 (2008) 1290-1298.

18. Zhao X., Shi Y., Cai Y., Mou S., “Cetyltrimethylammonium Bromide-Coated Magnetic Nanoparticles for the Preconcentration of Phenolic Compounds from Environmental Water Samples”, Environ. Sci. Technol., 42 (2008) 1201-1206.
19. Liu X., Guan Y., Ma Z., Liu H., “Surface Modification and Characterization of Magnetic Polymer Nanospheres Prepared by Miniemulsion Polymerization”, Langmuir, 20 (2004) 10278-10282.
20. Lv S., Chen X., Ye Y., Yin S., Cheng J., Xia M., “Rice hull/MnFe2O4 composite: Preparation, characterization and its rapid microwave-assisted COD removal for organic wastewater”, J. Hazard. Mater., 171 (2009) 634-639.
21. Hencl V., Mucha P., Orlikova A., Leskova D., “Utilization of ferrites for water treatment”, Water Res., 29 (1995) 383-385.
22. Zhu Z., Li X., Zhao Q., Li H., Shen Y., Chen G., “Porous “brick-like” NiFe2O4 nanocrystals loaded with Ag species towards effective degradation of toluene”, Chem. Eng. J., 165 (2010) 64-70.
23. Rădoi I., Bîrzescu M., Ştefănescu M., Golumbioschi F., Ferencz A., “Obţinerea de anozi cu pelicule electrocatalitice active din complecşi metalici, folosiţi în electroliza apei”, Rev. Chim.-Bucharest, 36 (1984) 832-835.
24. Haenen J., Visscher W., Barendrecht E., “Characterization of NiCo2O4 electrodes for O2 evolution: Part I. Electrochemical characterization of freshly prepared NiCo2O4 electrodes”, J. Electroanal. Chem., 208 (1986) 273-296.
25. Lapham D.P., Colbeck I., Schoonman J., Kamlag Y., “The preparation of NiCo2O4 films by electrostatic spray deposition”, Thin Solid Films, 391 (2001) 17-20.
26. Yang J., Li J., Lin H., Yang X., Tong X., Guo G., “A novel preparation method for NiCo2O4 electrodes stacked with hexagonal nanosheets for water electrolysis”, J. Appl. Electrochem., 36 (2006) 945-950.
27. Lefez B., Nkeng P., Lopitaux J., Poillerat G., “Characterization of cobaltite spinels by reflectance spectroscopy”, Mater. Res. Bull., 31 (1996) 1263-1267.
28. Windisch C.F., Exarhos G.J., Sharma S.K., US Patent CA 2424919, 14 Mar. 2006.
29. Marco J.F., Gancedo J.R., Gracia M., Gautier J.L., Ríos E., Berry F.J., “Characterization of the Nickel Cobaltite, NiCo2O4, Prepared by Several Methods: An XRD, XANES, EXAFS, and XPS Study”, J. Solid State Chem., 153 (2000) 74-81.
30. Kim J.G., Pugmire D.L., Battaglia D., Langell M.A., “Analysis of the NiCo2O4 spinel surface with Auger and X-ray photoelectron spectroscopy”, Appl. Surf. Sci., 165 (2000) 70-84.
31. Guan H., Shao C., Liu Y., Yu N., Yang X., “Fabrication of NiCo2O4 nanofibers by electrospinning”, Solid State Commun., 131 (2004) 107-109.
32. Nkeng P., Poillerat G., Koenig J.F., Chartier P., Lefez B., Lopitaux J., Lenglet M., “Characterization of Spinel-Type Cobalt and Nickel Oxide Thin Films by X-Ray Near Grazing Diffraction, Transmission and Reflectance Spectroscopies, and Cyclic Voltammetry”, J. Electrochem. Soc., 142 (1995) 1777-1783.
33. a) Nakamoto K., Morimoto Y., Martell A.E., “Infrared Spectra of Aqueous Solutions. I. Metal Chelate Compounds of Amino Acids”, J. Am. Chem. Soc., 83 (1961) 4528-4532; b) Ekström G.N., McQuillan A.J., “In Situ Infrared Spectroscopy of Glyoxylic Acid Adsorption and Photocatalysis on TiO2 in Aqueous Solution”, J. Phys. Chem. B, 103 (1999) 10562-10565.

34. Sandulescu D. (coordinator), “The Book of the Chemical Engineer”, vol. II, Ed. Tehnică, Bucharest, 1973, p. 820.
35. Cornell R.M., Schwertmann U., “The Iron Oxides. Structure, Properties, Reactions, Occurences and Uses”, 2nd Edition, Wiley-VCH, Weinheim, 2003.
36. Senthilkumar B., Selvan R.K., Vinothbabu P., Perelshtein I., Gedanken A., “Structural, magnetic, electrical and electrochemical properties of NiFe2O4 synthesized by the molten salt technique”, Mater. Chem. Phys., 130 (2011) 285-292.
37. Gunjakar J.L., More A.M., Gurav K.V., Lokhande C.D., “Chemical synthesis of spinel nickel ferrite (NiFe2O4) nano-sheets”, Appl. Surf. Sci., 254 (2008) 5844-5848.
38. Niasari M.S., Davar F., Mahmoudi T., “A simple route to synthesize nanocrystalline nickel ferrite (NiFe2O4) in the presence of octanoic acid as a surfactant”, Polyhedron, 28 (2009) 1455-1458.
39. Bentley F.F., Smithson L.D., Rozek A.L., “Infrared Spectra and Characteristic Frequencies ~ 700 - 300 cm-1”, Interscience Publishers John Wiley & Sons, New York – London – Sydney, 1968.
40. Cheetham A.K., Day P., “Solid-State Chemistry: Techniques”, Clarendon Press, Oxford, 1988.
41. Klug H.P., Alexander L.E., “X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials”, Wiley, New York, 1974.

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 53-63
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Article

ANCHIMERIC ASSISTANCE IN EI-MS CARBOCATIONS – A COMPUTATIONAL INVESTIGATION*

Mihai-Cosmin Pascariu[1,2], Carmen-Manuela Mitar[1], Ioana-Ramona Ciopănoiu[1], Alexandra Gruia[3], Mircea Niculescu[2,4], Eugen Sisu[5♣]

[1] "Vasile Goldiş" Western University of Arad, Faculty of Medicine, Pharmacy and Dental Medicine, Department of Pharmaceutical Sciences, 86 Liviu Rebreanu, 310045, Arad, Romania
[2] "Chemeia Semper" Association, 6 Giuseppe Verdi, 300493, Timişoara, Romania
[3] Clinical County Hospital of Timişoara, Immunology of Transplant Department, 10 Iosif Bulbuca Blvd., 300736, Timişoara, Romania
[4] University Politehnica Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Vasile Pârvan Blvd., 300223, Timişoara, Romania
[5] "Victor Babeş" University of Medicine and Pharmacy of Timişoara, Faculty of Medicine, Department of Biochemistry, 2 Eftimie Murgu Sq., 300041, Timişoara, Romania

ABSTRACT

A set of heptyl di-*O*-isopropylidene-D-mannofuranoside structures, which could find applications as biocompatible surfactant precursors in fields like pharmaceuticals and biotechnology, were analyzed using semi-empirical quantum chemical methods. Cations derived from them by removing one methyl group from the heptyl residue were constructed and conformationally optimized. Strong interactions between the sugar moiety oxygen atoms and the alkyl positively charged centers were detected in some cases, providing new cyclic enclosures which offer enhanced stability. The results obtained in this paper concern mainly the mass spectrometry analysis of side-chain glycoderivatives, but similarities can also be found for other oxygenated classes of compounds.

---

[*] Dedicated to Prof.Dr. Mihail Bîrzescu, in memoriam
♣ Correspondent author E-mail: sisueugen@umft.ro

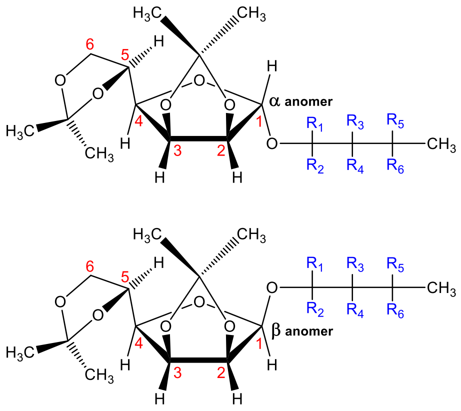
Keywords: glycoderivative, computational chemistry, RM1 semi-empirical method, heat of formation, carbocation, anchimeric assistance, dative bond, mass spectrometry.

1. INTRODUCTION

Sixty glycoderivatives possessing the 2,3:5,6-di-*O*-isopropylidene-D-mannofuranoside base structure, connected at the anomeric position to different alkyl side chains, were investigated using quantum chemical calculations [1,2]. These compounds, after simple hydrolysis of the isopropylidene acetal units [3], can function as biocompatible and biodegradable surfactants in many fields, particularly in pharmaceuticals, veterinary medicine and biotechnologies, but also as household nontoxic detergents [4].

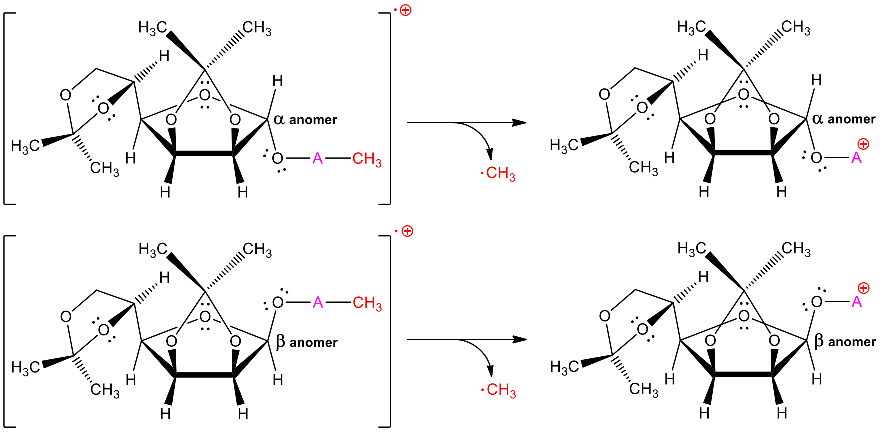
The side chains include the following branched heptyl isomers: 1,1,2-trimethylbutyl (*R*/*S*), 1,1,3-trimethylbutyl, 1,2,2-trimethylbutyl (*R*/*S*), 1,2,3-trimethylbutyl (*R*,*R*/*R*,*S*/*S*,*R*/*S*,*S*), 2,2,3-trimethylbutyl, 1,3,3-trimethylbutyl (*R*/*S*), 2,3,3-trimethylbutyl (*R*/*S*), 1-ethyl-1-methylbutyl (*R*/*S*), 1-ethyl-2-methylbutyl (*R*,*R*/*R*,*S*/*S*,*R*/*S*,*S*), 1-ethyl-3-methylbutyl (*R*/*S*), 2-ethyl-1-methylbutyl (*R*/*S*), 2-ethyl-2-methylbutyl, 2-ethyl-3-methylbutyl (*R*/*S*), 1-propylbutyl and 1-isopropylbutyl (*R*/*S*). The general structures for the studied glycoderivatives are given in Figure 1. As can be seen, all the lateral chains are composed of a butyl main chain on which three other carbon atoms are linked as smaller chains (methyl, ethyl, propyl or isopropyl). The four carbon atoms linear core chain was specifically chosen to test for the possible formation of an anchimerically stabilized nine member ring, as explained further in this paper (in "Results and discussion" section). The study consists of removing one methyl radical from the side chain in all possible variants and calculating the heat of formation of the carbocation thus obtained with the help of the RM1 semi-empirical method [5].

Figure 1: General structures of the studied mannofuranoside anomers; R_1-R_6 = H or short alkyl chains (methyl, ethyl, propyl or isopropyl)



Such carbocations [6-9] could be obtained in molecular fragmentation processes involved in the electron ionization mass spectrometric (EI-MS) analysis of this type of compounds, as seen in Figure 2 [4,10]. When some peaks found in the mass spectrum have an unexpected high-intensity, one can propose the hypothesis of an anchimeric effect as a plausible explanation. Indeed, anchimeric-type stabilizations [11-14] spontaneously occurred after geometry optimization in some of the studied cations, with the formation of new three (oxirane), four (oxetane), five (1,3-dioxolane), six (1,3-dioxane) or nine (1,3,6-trioxonane) member cyclic structures [15-17]. This phenomenon could therefore have implications in peak patterns observed in EI-MS spectra of side chain glycoderivatives [4,18-21].

Figure 2: One possible way of producing $[M-15]^+$ cations from the radical cations in EI-MS fragmentation; A = alkylene group



2. METHODS

All structures were drawn using the *HyperChem* molecular modeling software [22] and were optimized with the RM1 semi-empirical method [5], with and without molecular mechanics pre-optimization. RHF operators were used for “Spin Pairing” while the SCF “Convergence limit” was set at 10^{-5}, without using the “Accelerate convergence” procedure. Force fields used for cations pre-optimization include MM+, AMBER99, BIO+ (CHARMM27) and OPLS, with their default parameters as implemented in *HyperChem*. For geometry optimization and ΔH_f calculation [14], the “Polak-Ribière (conjugate gradient)” algorithm was selected with a RMS gradient of 0.01 kcal/(Å mol), the molecules being considered in vacuum (*in vacuo*). The initial neutral molecules, from which all carbocations were constructed, were pre-optimized with the OPLS force field, followed by the RM1 semi-empirical method. All calculations were done with a system comprised of an *Intel® Core™2 Quad CPU Q8400@4x2.66 GHz* with 4 GB of RAM.

3. RESULTS AND DISCUSSIONS

For some of the studied carbenium ions, the positively charged carbon atom approached O1, O4 or O5 at a distance similar to a normal C-O single bond length (~1.47 Å), while at the same time changing from sp^2 to sp^3 hybridisation and thus acting as a prochiral center (Figures 3 and 4). In Table 1 only the isomers that produced such an anchimeric-type stabilization are presented. The newly formed ring types are denoted as *3m* (three member), *4m* (four member), *5m* (five member), *6m* (six member) or *9m* (nine member). All these interactions could be classified as exo-tet, according to Baldwin's rules [23-25].

Figure 3: Closing of 3-member **(a, b)** and 4-member **(c, d)** cycles; R_A-R_D = H or short alkyl chains

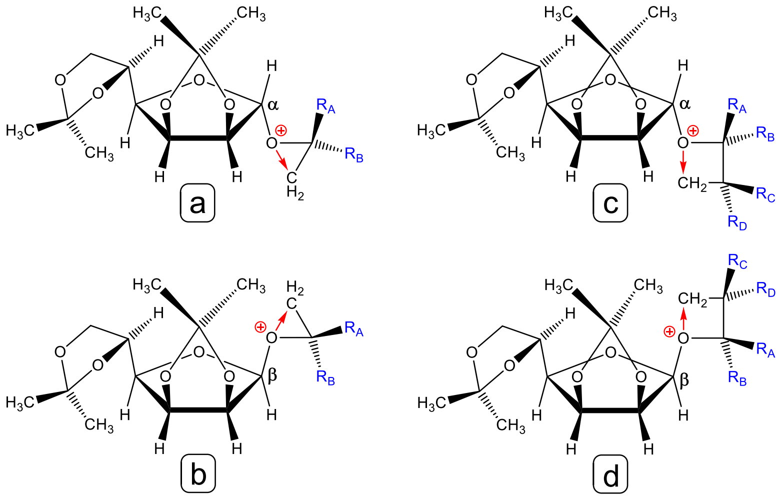


Figure 4: Closing of 5-member **(a, b)** and 6-member **(c, d)** cycles; R_A-R_D = H or short alkyl chains

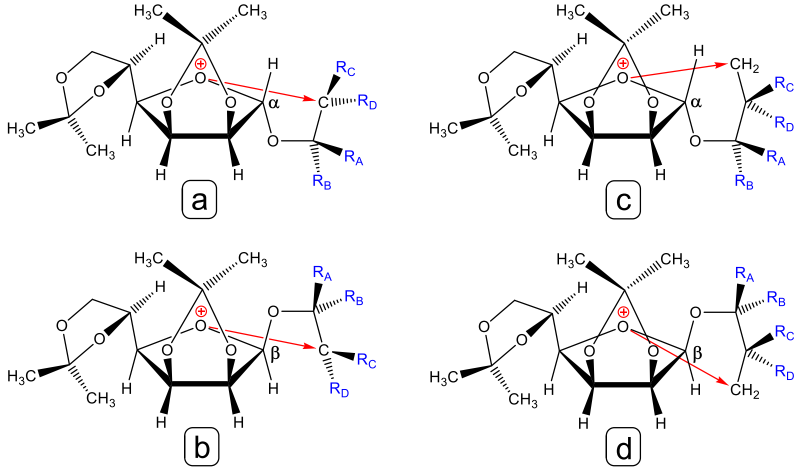


Table 1: Comparison between cation heats of formation and dative bond lengths; the type of ring formed (*3m*, *4m*, *5m*, *6m* or *9m*) is shown in parenthesis (see Figures 3 and 4), the values obtained for structures without anchimeric assistance (marked with “$” sign) being also included for reference; oxygen atoms are numbered as for mannose, while the lateral chain carbon atoms and the hydrogen atoms attached to them are referenced in the table footnotes as α, β or γ, with increasing distance from O1

No.	R_1	R_2	R_3	R_4	R_5	R_6	Conf.	RM1		RM1/MM+		RM1/AMBER99		RM1/BIO+		RM1/OPLS	
								C-O distance (Å)	$\Delta_f H$ (kcal/mol)	C-O distance (Å)	$\Delta_f H$ (kcal/mol)	C-O distance (Å)	$\Delta_f H$ (kcal/mol)	C-O distance (Å)	$\Delta_f H$ (kcal/mol)	C-O distance (Å)	$\Delta_f H$ (kcal/mol)
1	Me	H	Me	H	Me	H	α,*S*,*R*	1.477 (*5m*)	-117.606	1.479 (*5m*)	-117.430	F.O.	F.O.	1.479 (*5m*)	-117.430	1.477 (*5m*)	-115.993
2	Et	Me	H	H	H	H	α,*R*	1.462 (*5m*)	-117.606	1.462 (*5m*)	-117.961	1.463 (*5m*)	-117.757	1.462 (*5m*)	-117.757	1.462 (*5m*)	-117.757
3	Et	Me	H	H	H	H	β,*R*	1.401 ($*3m*)[a]	-114.424	2.322 ($*3m*)[b]	-133.381	1.400 ($*3m*)[a]	-113.287	1.464 (*3m*)	-91.735	1.400 ($*3m*)[a]	-113.287
4	Et	Me	H	H	H	H	α,*S*	1.399 ($*3m*)[a]	-115.943	2.333 ($*3m*)[b]	-133.502	1.401 ($*3m*)[a]	-115.327	1.462 (*3m*)	-90.632	1.401 ($*3m*)[a]	-115.327
5	Et	Me	H	H	H	H	β,*S*	1.463 (*5m*)	-112.889	1.460 (*5m*)	-110.796	1.463 (*5m*)	-112.889	1.463 (*5m*)	-112.889	1.463 (*5m*)	-112.889
6	Et	H	Me	H	H	H	α,*R*,*R*	4.142 ($*5m*) 1.463 (*5m*)	-98.024 -113.386	1.481 (*5m*) 1.463 (*5m*)	-114.275 -113.386	3.814 ($*5m*) 1.463 (*5m*)	-97.922 -113.386	4.174 ($*5m*) 1.464 (*5m*)	-98.727 -113.187	1.481 (*5m*) 1.463 (*5m*)	-114.276 -113.385
7	Et	H	Me	H	H	H	β,*R*,*R*	2.443 ($*3m*)[c]	-135.216	2.436 ($*3m*)[c]	-133.474	1.472 (*3m*)	-84.390	1.472 (*3m*)	-85.629	1.466 (*3m*)	-84.217
8	Et	H	Me	H	H	H	α,*R*,*S*	1.464 (*5m*)	-112.835	1.464 (*5m*)	-112.834	1.464 (*5m*)	-112.835	1.464 (*5m*)	-112.835	1.463 (*5m*)	-113.032
9	Et	H	Me	H	H	H	α,*S*,*R*	2.052 ($*5m*) 1.471 (*3m*)	-107.996 -84.529	3.066 ($*5m*) 2.343 ($*3m*)[d]	-103.712 -123.001	1.482 (*5m*) 2.342 ($*3m*)[d]	-116.950 -123.998	1.482 (*5m*) 2.344 ($*3m*)[d]	-116.728 -123.004	3.063 ($*5m*) 1.471 (*3m*)	-103.712 -84.528
10	Et	H	Me	H	H	H	β,*S*,*R*	1.466 (*5m*)	-107.213	2.832 ($*5m*)	-85.923	1.466 (*5m*)	-107.389	1.467 (*5m*)	-106.154	1.466 (*5m*)	-107.389
11	Et	H	Me	H	H	H	α,*S*,*S*	1.482 (*5m*) 2.342 ($*3m*)	-116.950 -81.550	3.063 ($*5m*) 1.471 (*3m*)	-103.712 -85.217	1.482 (*5m*) 1.470 (*3m*)	-116.950 -85.333	1.481 (*5m*) 1.471 (*3m*)	-116.905 -85.065	1.480 (*5m*) 1.473 (*3m*)	-117.114 -85.136
12	Et	H	Me	H	H	H	β,*S*,*S*	1.465 (*5m*)	-108.554	1.465 (*5m*)	-108.555	1.465 (*5m*)	-108.555	1.465 (*5m*)	-108.554	1.465 (*5m*)	-108.554
13	Et	H	H	H	Me	H	α,*R*	2.807 ($*5m*)[c]	-135.496	1.464 (*5m*)	-113.613	2.661 ($*5m*)	-86.563	2.722 ($*5m*)	-86.810	1.462 (*5m*)	-113.828
14	Et	H	H	H	Me	H	β,*R*	2.442 ($*3m*)[c]	-135.758	1.471 (*3m*)	-86.633	2.442 ($*3m*)[c]	-135.757	1.471 (*3m*)	-86.632	1.468 (*3m*)	-85.873
15	Et	H	H	H	Me	H	α,*S*	2.443 ($*3m*)[c]	-135.990	1.470 (*3m*)	-85.779	2.340 ($*3m*)[e]	-123.044	2.311 ($*3m*)	-83.169	1.470 (*3m*)	-85.780
16	Et	H	H	H	Me	H	β,*S*	4.453 ($*5m*)[c]	-133.606	1.465 (*5m*)	-109.084	4.100 ($*5m*)[c]	-134.621	1.465 (*5m*)	-109.085	4.129 ($*5m*)[c]	-135.126
17	Me	H	Et	H	H	H	α,*R*	2.730 (*4m*)	-87.945	1.481 (*4m*)	-105.813	1.481 (*4m*)	-105.813	1.481 (*4m*)	-105.814	1.481 (*4m*)	-105.814
18	Me	H	Et	H	H	H	β,*S*	1.488 (*4m*)	-106.979	1.488 (*4m*)	-106.979	4.554 ($*4m*)[f]	-104.642	4.548 ($*4m*)[f]	-104.875	1.488 (*4m*)	-106.980
19	H	H	Et	Me	H	H	β	2.706 ($*4m*)	-86.418	1.491 (*4m*)	-106.207	2.676 ($*4m*)	-86.416	2.679 ($*4m*)	-86.416	2.675 ($*4m*)	-86.416
20	H	H	Et	H	Me	H	α,*R*	1.478 (*6m*)	-114.539	3.303 ($*6m*)[g]	-111.466	1.477 (*6m*)	-114.539	2.957 ($*6m*)[h]	-115.985	1.476 (*6m*)	-114.861
21	H	H	Et	H	Me	H	β,*R*	1.464 (*6m*)	-107.275	1.464 (*6m*)	-109.808	3.932 ($*6m*)	-89.095	F.O.	F.O.	3.934 ($*6m*)	-89.095
22	H	H	Et	H	Me	H	α,*S*	1.464 (*6m*)	-114.738	1.464 (*6m*)	-114.738	1.464 (*6m*)	-114.739	1.464 (*6m*)	-114.738	1.464 (*6m*)	-114.739
23	H	H	Et	H	Me	H	β,*S*	2.739 ($*9m*)[h]	-114.066	1.473 (*9m*)	-107.140	2.739 ($*9m*)[h]	-114.229	2.741 ($*9m*)[h]	-113.176	2.740 ($*9m*)[h]	-114.230
24	Pr	H	H	H	H	H	α	3.755 ($*6m*)[i]	-99.545	4.367 ($*6m*)[j]	-101.126	1.459 (*6m*)	-114.989	3.900 ($*6m*)[i]	-99.956	3.560 ($*6m*)[g]	-107.886
25	Pr	H	H	H	H	H	β	1.460 (*6m*)	-110.261	2.891 ($*6m*)	-97.068	1.487 (*4m*)	-102.843	1.460 (*6m*)	-110.261	1.487 (*4m*)	-102.842

No.	R_1	R_2	R_3	R_4	R_5	R_6	Conf.	RM1		RM1/MM+		RM1/AMBER99		RM1/BIO+		RM1/OPLS	
								C-O distance (Å)	Δ_fH (kcal/mol)	C-O distance (Å)	Δ_fH (kcal/mol)	C-O distance (Å)	Δ_fH (kcal/mol)	C-O distance (Å)	Δ_fH (kcal/mol)	C-O distance (Å)	Δ_fH (kcal/mol)
26	i-Pr	H	H	H	H	H	α,*R*	3.750 ($6*m*)[i]	-100.858	3.824 ($6*m*)[g]	-108.940	4.865 ($6*m*)[i]	-99.143	1.460 (*6m*)	-115.910	1.460 (*6m*)	-115.911
27	i-Pr	H	H	H	H	H	α,*S*	1.968 ($5*m*)	-106.482	1.486 (*5m*)	-111.926	3.641 ($5*m*)	-100.118	1.971 ($5*m*)	-106.481	2.810 ($5*m*)	-103.603
								1.483 (*5m*)	-117.208	1.482 (*5m*)	-117.407	1.481 (*5m*)	-117.300	1.483 (*5m*)	-117.208	1.481 (*5m*)	-117.301

F.O. = failed optimization;

[a] rearrangement, see Figure 5;

[b] rearrangement, see Figure 6 (C_{α}=O1 bond length: 1.291-1.295 Å) [26,27];

[c] $H_{\alpha}\rightarrow H_{\beta'}$ hydride shift, C_{α}=O1 double bond formed (1.285-1.297 Å) [26,27];

[d] rearrangement, see Figure 7 (C_{α}=O1 bond length: 1.283-1.284 Å) [26,27];

[e] rearrangement, see Figure 8 (C_{α}=O1 bond length: 1.284 Å) [26,27];

[f] butene loss;

[g] $H_{\beta/\beta'}$ proton shift to O4 (furanose oxygen), $C_{\beta/\beta'}=C_{\gamma'}$ double bond formed (1.328-1.331 Å);

[h] $H_{\beta}\rightarrow H_{\gamma'}$ hydride shift;

[i] ethene loss;

[j] $H_{\gamma}\rightarrow H_{\gamma'}$ hydride shift.

As observed from the heat of formation values, when compared with similar open-structure cations (marked with “$” in Table 1), these enclosures imply increased stability (e.g., entries no. 10, 15, 17 and 21 in Table 1) [28].

Regarding the ring type abundance, the 1,3-dioxolane is the most abundant structure formed, being present in almost half of the stabilized structures, as can be seen in Table 2.

Figure 5: Rearrangement seen for entries 3 and 4 in Table 1

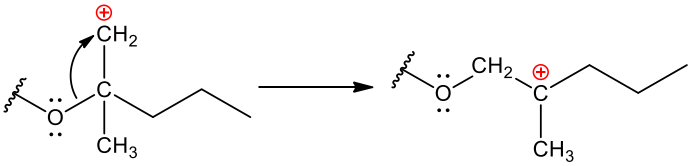


Figure 6: Rearrangement seen for entries 3 and 4 in Table 1

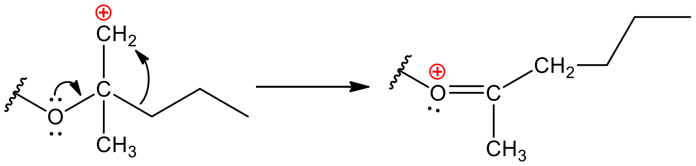


Figure 7: Rearrangement seen for entry 9 in Table 1

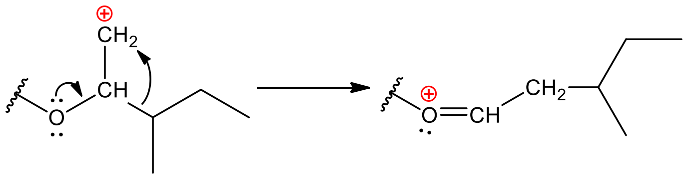


Figure 8: Rearrangement seen for entry 15 in Table 1

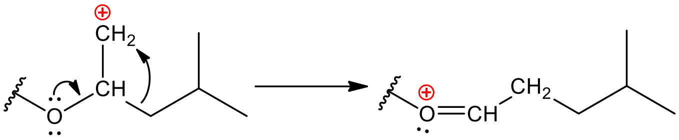


Table 2: Ring statistics

Ring type/ ring closure	***3m*** 3-exo-tet	***4m*** 4-exo-tet	***5m*** 5-exo-tet	***6m*** 6-exo-tet	***9m*** 9-exo-tet
Number of structures	7	4	12	6	1
C-O bond length (Å)	1.462 ÷ 1.473	1.481 ÷ 1.491	1.460 ÷ 1.486	1.459 ÷ 1.478	1.473
Dative C charge	-0.041 ÷ -0.015	0.022 ÷ 0.053	-0.056 ÷ 0.079	0.019 ÷ 0.055	0.047
Dative O charge	-0.177 ÷ -0.114	-0.173 ÷ -0.131	-0.162 ÷ -0.110	-0.190 ÷ -0.153	-0.167

Besides the heat of formation and the bond length values, another strong argument in favor of the anchimeric assistance is the charge distribution for the two atoms involved in the formation of the dative bond. A good example to illustrate this would be entry 25 in Table 1, corresponding to the 1-propylbutyl lateral chain in β configuration (see Figure 1, where R_1=propyl, R_2-R_6=H). As can be seen in Table 1, two new stable rings can be formed, a *4m* (see Figure 3d, where R_A=propyl, R_B-R_D=H) and a *6m* ring (see Figure 4d, where R_A=propyl, R_B-R_D=H). While the calculated charge for the carbon atom is 0.444 for the open structure (marked with "$" sign in Table 1), this drops to 0.055 when the *6m* ring is formed and to 0.053 when the *4m* ring is formed. Similarly, for the oxygen atom the charge corresponding to the open form is -0.290 (O1) / -0.336 (O4), and this rises to -0.186 (O4) for the *6m* ring and to -0.150 (O1) for the *4m* ring. Clearly a charge transfer has occurred, with the formation of the dative bond between the two atoms.

Table 3 shows the energy gain when the new rings are formed, by comparison with non-stabilized (open) structures. These values could also be interpreted as the dative bond energies: at least 2.6 kcal/mol for *3m* rings, 5.8 kcal/mol for *4m* rings, 9.0 kcal/mol for *5m* rings and 13.2 kcal/mol for *6m* rings. Also, the energy difference between a *4m* and a *6m* ring could be calculated, the *6m* ring being more stable by 7.4 kcal/mol. The obtained results generally agree with the literature concerning the stability of organic rings [15,29].

The majority of anchimerically stabilized structures are formed from primary carbocations (two hydrogens attached to the sp^2 positive carbon atom). Some secondary carbocations are also stabilized in this way but only giving five member rings, the resulting sp^3 geometry truly offering chiral properties to the dative carbon atom (entry 27 in Table 1, 5.481 kcal/mol difference between the two *5m* diastereomers formed). However, no tertiary carbocations took part in anchimeric stabilizations, probably because such species are already stabilized by the two extra alkyl radicals by donor inductive effects, and also because of the steric crowding generated by the same radicals which could inhibit a favorable approach to the oxygen electron donor [30]. Also, a lot of decompositions were registered in the studied set of compounds, with various elimination products such as ethene, propene, butene or isobutene [31], and different proton and hydride shifts [32,33] were also frequently encountered. All this phenomena may have masked other cases of anchimeric stabilization.

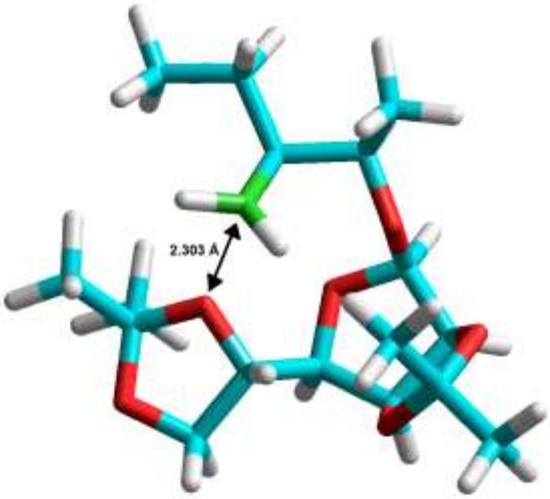
Table 3: Heat of formation differences, in kcal/mol (Table 1 entries from which these were calculated are given in parenthesis)

Open form* – ***3m***	Open form* – ***4m***	Open form* – ***5m***	Open form* – ***6m***	***4m*** – ***6m***
3.783 (11) 2.611 (15)	17.869 (17) 19.789 (19) 5.775 (25)	15.549 (6) 8.954 (9) 21.466 (10) 13.402 (11) 27.018 (13) 10.925 (27)	20.713 (21) 13.193 (25)	7.418 (25)

* structure in which, after geometry optimization, no anchimeric assistance was observed

Although we have found multiple computational evidence for anchimerically stabilized seven, eight or ten member rings in other related mannofuranose derivatives we have studied [34], only one nine member (1,3,6-trioxonane) cycle was produced to this day using this method (entry 23 in Table 1). However, we have also obtained the conformation shown in Figure 9 with one of the compounds considered in this paper ((R)-2-ethyl-1-methylbutyl initial lateral chain, β anomer), in which the sp^2 positive charged carbon atom approached O5 to a distance of 2.303 Å with a favorable atom arrangement but without becoming tetrahedral, suggesting the first step in a nine member ring closure.

Figure 9: Precursor to a nine member ring (formally charged carbon atom has sp^2 geometry)



4. CONCLUSIONS

Anchimerically stabilized rings with three to six members, along with a single nine-membered cyclic structure, were obtained in silico for different alkyl substituted glycoderivatives. The dative interaction between the formally positive carbon atom in the side chain and the oxygen atom from the mannose residue is revealed by the distance between the two atoms, similar to a normal C-O single bond, from heat of formation values, but also from the final charge repartition calculated using the RM1 semi-empirical method.

ACKNOWLEDGEMENTS

The authors would like to thank prof.dr. Mircea Mracec and prof.dr.eng. Nicolae Dincă for access to HyperChem software and also for fruitful discussions. This work was supported by the Romanian National Authority for Scientific Research (CNCS-UEFISCDI) through project PN-II-PCCA-2011-142.

REFERENCES

1. Box V.G.S., Evans-Lora T., “Exploring the relative reactivities of the hydroxyl groups of monosaccharides by molecular modeling and molecular mechanics”, J. Mol. Struct., 516(2-3) (2000) 203-214.
2. Gerbst A.G., Grachev A.A., Shashkov A.S., Nifantiev N.E., “Computation techniques in the conformational analysis of carbohydrates”, Russ. J. Bioorg. Chem+., 33(1) (2007) 24-37.
3. Kohnstam G., Williams D.L.H., “Directive and activating effects of alkoxy and aryloxy groups in aromatic and aliphatic reactions” in (Patai S., Ed.) “The chemistry of the ether linkage, PATAI'S Chemistry of Functional Groups”, Ch. 3, John Wiley & Sons Ltd., London, 1967, p. 81-166.
4. Rafailă M., Pascariu M.C., Gruia A., Penescu M., Purcarea V.L., Medeleanu M., Rusnac L.M., Davidescu C.M., (2013) “GC-MS analysis of long chain mannofuranose derivatives as biocompatible surfactant precursors. Correlation between peak intensities and stability of corresponding fragments”, Farmacia (Bucharest), 61(1) (2013) 116-126.
5. Rocha G.B., Freire R.O., Simas A.M., Stewart J.J.P., “RM1: A reparameterization of AM1 for H, C, N, O, P, S, F, Cl, Br, and I”, J. Comput. Chem., 27(10) (2006) 1101-1111.
6. Olah G.A., “100 years of carbocations and their significance in chemistry”, J. Org. Chem., 66(18) (2001) 5943-5957.

7. Carey F.A., Sundberg R.J., "Advanced organic chemistry. Part A: Structure and mechanisms", 5th edn., Springer Science+Business Media, LLC, New York, 2007.
8. Aue D.H., "Carbocations", WIREs Comput. Mol. Sci., 1(4) (2011) 487-508.
9. Abboud J.L.M., Alkorta I., Dávalos J.Z., Müller P., Quintanilla E., "Thermodynamic stabilities of carbocations" in (Richard J.P., Tidwell T.T., Eds.) "Adv. Phys. Org. Chem.", Volume 37, Elsevier Science Ltd, London, 2002, p. 57-135.
10. Pascariu M.C., Sisu E., Ordodi V.L., Rusnac L.M., (2011) "Spectral analysis of diisopropylidenated monosaccharides. Low energy EI-MS fragmentation study", Chem. Bull. "Politehnica" Univ. (Timișoara), 56(1) (2011) 6-11.
11. Fărcaşiu D., Leu R., "Theoretical studies of carbocations in ion pairs. 8. Search for anchimeric assistance in the ionization of 2-buthyl cation precursors", J. Phys. Chem. A, 112(13) (2008) 2955-2961.
12. Pale P., Vogel P., "Tricoordinate carbanions, cations and radicals" in (Katritzky A.R., Taylor R.J.K., Eds.) "Comprehensive organic functional group transformations II, Volume 1: Synthesis: Carbon with no attached heteroatoms", Ch. 1.19, Elsevier Ltd, 2004, p. 889-1017.
13. Ari J.B., Navon I., Mandelbaum A., "The effect of steric hindrance on the relative rates of anchimerically assisted alcohol eliminations from MH+ ions of 2-substituted 1,4-dialkoxybutanes upon CI and CID: Experiment and theory", Int. J. Mass Spectrom., 249-250 (2006) 433-445.
14. Kimatrai M., Cruz-López O., García-Rubiño M.E., Morales F., Gómez-Pérez V., Campos J.M., "Neighboring-group participation involving the oxygen atom of the O,O- or O,N-acetal functional groups", Curr. Org. Chem., 14(14) (2010) 1461-1477.
15. Eliel E.L., Wilen S.H., Mander L.N., "Stereochemistry of organic compounds", John Wiley & Sons, Inc., New York, 1994.
16. Bobylev V.A., Koldobskii S.G., Tereshchenko G.F., Gidaspov B.V., "Nucleophilic reactions involving opening and closing of saturated heterorings (review)", Chem. Heterocyc. Compd., 24(9) (1989) 947-959.
17. Kiprof P., Miller S.R., Achord P., "Dative stabilization of carbocations", J. Mol. Struc.-Theochem, 896(1-3) (2009) 69-72.
18. Mandelbaum A., "Stereochemistry studied using mass spectrometry" in (Lindon J.C., Tranter G.E., Holmes J.L., Eds.) "Encyclopedia of spectroscopy and spectrometry", Volume 1, Elsevier Ltd, 2000, p. 2211-2223.
19. Mutenda K.E., Matthiesen R., "Analysis of carbohydrates by mass spectrometry" in (Matthiesen R., Ed.) "Mass Spectrometry Data Analysis in Proteomics, Methods in Molecular Biology", Volume 367, Humana Press, 2007, p. 289-301.
20. De Jongh D.C., Biemann K., "Mass spectra of O-isopropylidene derivatives of pentoses and hexoses", J. Am. Chem. Soc., 86(1) (1964) 67-74.
21. Morgenlie S., "Analysis of mixtures of the common aldoses by gas chromatography – mass spectrometry of their O-isopropylidene derivatives". Carbohyd. Res., 41(1) (1975) 285-289.
22. HyperChem™ Professional, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA
23. Alabugin I.V., Gilmore K., "Finding the right path: Baldwin "Rules for Ring Closure" and stereoelectronic control of cyclization", Chem. Commun., 49(96) (2013) 11246-11250.

24. Gilmore K., Alabugin I.V., "Cyclizations of alkynes: revisiting Baldwin's rules for ring closure", Chem. Rev., 111(11) (2011) 6513-6556.
25. Baldwin J.E., (1976) "Rules for ring closure", J. Chem. Soc. Chem. Comm., 1976(18) (1976) 734-736.
26. Miller S.R., Krasutsky S., Kiprof P., "Stability of carboxonium ions". J. Mol. Struc.-Theochem, 674(1-3) (2004) 43-47.
27. Apeloig Y., Karni M., "The stabilities of α-oxy and α-thio carbenium ions: the importance of the ground-state energies of the neutral precursors", J. Chem. Soc. Perk. T. 2, 1988(5) (1988) 625-636.
28. Benassi R., Taddei F., "Cyclic and open-chain carbonium ion intermediates in nucleophilic halogen displacement: 2-chloroethanol, 2-chloroethanethiol and their 1,3-propane homologues. A theoretical ab-initio MO approach", J. Mol. Struc.-Theochem, 205 (1990) 177-190.
29. Mills J.A., "The stereochemistry of cyclic derivatives of carbohydrates" in (Wolfrom M.L., Ed.) "Advances in carbohydrate chemistry", Volume 10, Elsevier Inc., 1955, p. 1-53.
30. Capon B., McManus S.P., "Neighboring group participation", Volume 1 withdrawn, Plenum Press, 1976, New York.
31. Bowen R.D., Williams D.H., "The concept of a hierarchy of unimolecular reactions in a homologous series. Prediction of the unimolecular chemistry of some saturated carbenium ions", J. Chem. Soc. Perk. T. 2, 1976(13) (1976) 1479-1485.
32. Ahlberg P., Jonsäll G., Engdahl C., "Degenerate carbocation rearrangements" in (Gold V., Bethell D., Eds.) "Adv. Phys. Org. Chem.", Volume 19, Academic Press Inc. Ltd, London, 1983, p. 223-379.
33. Planelles J., Sánchez-Marín J., Tomás F., Corma A., "A molecular orbital approach to a comprehensive cracking mechanism for linear long chain alkanes in heterogeneous acid catalytic conditions through carbenium ion β-cleavage", J. Chem. Soc. Perk. T. 2, 1985(3) (1985) 333-340.
34. Pascariu M.C., Rafailă M., Medeleanu M., Badea V., Gruia A.T., Penescu M., Sisu E., "Computational search for long bonds in radical cations of sugars. 1. Glucofuranose, galactofuranose and mannofuranose di-*O*-isopropylidene derivatives", Farmacia (2015), in press.

NEW FRONT. CHEM. (**2016**)
Volume 25, Number 1, pp. 64-72
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Article

INVESTIGATION OF LAMINAR FLAME PROPAGATION OF THE MOST HAZARDOUS CONFINED METHANE/AIR MIXTURE USING PRESSURE-TIME RECORDS IN A SMALL VESSEL

***Dumitru Oancea*[1]♣*, *Maria Prodan*[1]*, *Domnina Razus*[2]**
[1] University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry,
4-12 Regina Elisabeta Blvd., 030018, Bucharest, Romania
[2] "Ilie Murgulescu" Institute of Physical Chemistry of the Romanian Academy,
202 Splaiul Independenţei, 060021, Bucharest, Romania

ABSTRACT

The study of flame propagation in closed vessels, a subject of increasing consequence for safety measures designed to minimize the risks of explosion hazards, requires either complex equipment or high level computational effort. Simple methods to evaluate the explosivity parameters like maximum explosion pressure, maximum rate of pressure rise, time to peak explosion pressure, burning velocity, flame speed, even for mixtures with unknown nature and composition, are profitable at least for a preliminary stage. The paper describes such a method based on an elementary analysis of the cubic law of pressure rise during early stages of flame propagation. The validity of the method, previously proved and reported for spherical vessels, is now extended for a symmetrical cylindrical vessel of small volume (0.17 L) for the 10% methane/air mixture, known as the most explosive one. The results are in agreement with literature data.

Keywords: methane/air, deflagration, pressure-time variation, burning velocity, flame speed.

1. INTRODUCTION

Methane is a widespread compound encountered in many natural, domestic and industrial processes. Its oxidation with gaseous oxygen from air, either as such or mixed with other

---

♣ Correspondent author E-mail: dumitruoancea@yahoo.com

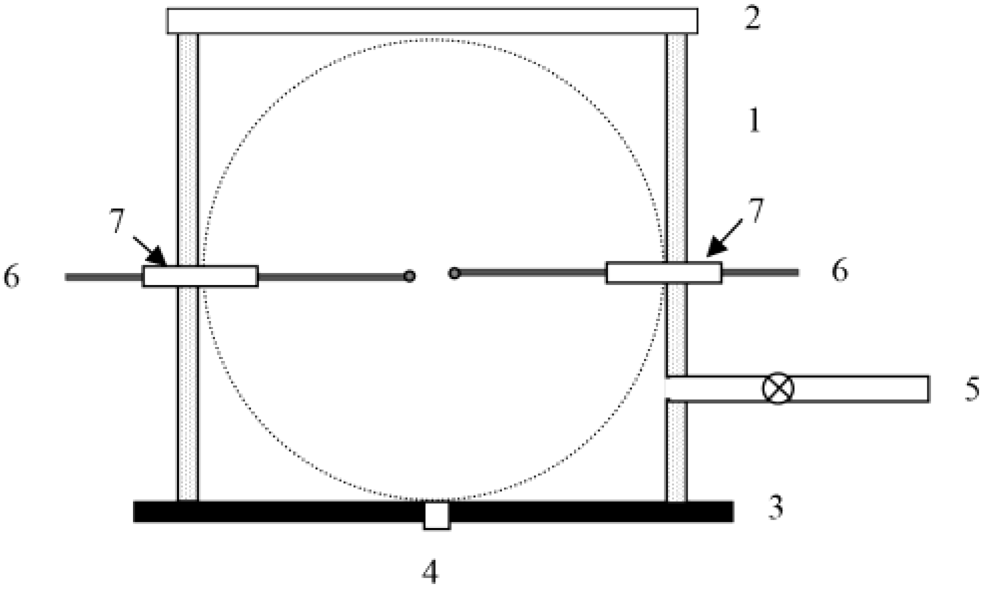
fuels, is an exothermic process frequently used as a source of heat or energy. At the same time, within some concentration limits, the methane/air mixtures are hazardous systems, being able to sustain explosions, either as deflagrations or as detonations, thus requiring severe safety norms to protect the people and the environment. The flammability limits of CH_4 in air range between 5 and 15% in normal conditions [1]. Within this range, the main deflagration properties exhibit extremes (maxima or minima) which define the most explosive mixture. Properties like the maximum explosion pressure, maximum rate of pressure rise, deflagration index, burning velocity and flame speed are situated on maxima, while the quenching distance, minimum ignition energy and time necessary to reach the peak pressure are situated on minima. For methane/air mixtures, the most explosive composition is approximately 10%, slightly higher than the stoichiometric one (9.5%). For safety reasons, the evaluation of the explosivity parameters for the most explosive mixture is of the first importance, although the whole explosivity range is of relevance for a complete characterization of this hazardous system. In this paper we present several aspects of flame propagation as laminar deflagration of this mixture in a small explosion vessel and compare the results with the available literature data. There are numerous experimental and computational methods [2,3] able to provide data on flame propagation. Among these, the analysis of pressure evolution during the flame propagation in relatively large spherical vessels with central ignition proved to be a highly informative and productive method [4-7]. The method can be extended even for easier available small vessels with lower symmetry, especially for cylindrical vessels with diameter equal to height, as will be shown subsequently. From the pressure-time curves recorded during the flame propagation with central ignition in such a vessel, the following relevant properties can be evaluated: maximum explosion pressure, maximum rate of pressure rise, time necessary to reach the peak pressure, quasi-adiabatic pressure rise, burning velocity, flame speed, as well as several derived properties.

2. EXPERIMENTAL METHOD/MODEL

The gaseous mixture containing 10% methane in air was prepared in a stainless steel cylinder at 4 bar total pressure by partial pressure method using methane 99.99% purity from SIAD and used 24 h after mixing. The ignition was initiated by high voltage inductive sparks between 1.5 mm diameter stainless steel electrodes with rounded tips within a spark gap of 2 mm. The ignition energy (0.09 J) was higher than the minimum ignition energy (0.29 mJ) ensuring a safe ignition without important induced turbulence. The pressure variation during the explosion process was monitored with a Kistler piezoelectric pressure transducer type 601A coupled with a charge amplifier type 5011B and recorded using a Tektronix TDS 210 oscilloscope. Details on the experimental procedure were given elsewhere [2,3].

The experiments were carried out in a cylindrical explosion vessel with diameter equal to height: $\Phi = h = 6$ cm ($V_0 = 1.70 \cdot 10^{-4}$ m^3 and with a radius of the equivalent spherical volume $R^* = 0.03434$ m) given in Figure 1.

Figure 1: Explosion vessel: 1-vessel body; 2-transparent top cover; 3-bottom cover; 4-pressure transducer; 5-feeding/evacuation pipe with tap; 6-high voltage electrodes; 7-electric insulation (the inscribed sphere with $r_i = 0.03$ m is outlined inside the vessel)



3. RESULTS AND DISCUSSIONS

A typical pressure-time record, “1”, and its derivative dP/dt, “2”, are given in Figure 2 for a mixture at $P_0 = 1$ bar and $T_0 = 298$ K. The maximum pressure rise, ΔP_{max}, and the time to peak pressure, θ_{max}, are measured directly on the recorded diagram. The derivative dP/dt is obtained by numerical derivation of curve ΔP-t, using a previous smoothing through polynomial interpolation followed by the Savitzky-Golay derivative algorithm with a 5% smoothing level. The early stage of pressure evolution was considered for $\Delta P \leq P_0$, when the compression of the unreacted gas was sufficiently small to approximate its temperature equal to the initial temperature. A user defined function of the cubic form was fitted on the resulted curve.

Similar measurements were carried out for different initial pressures. The results are given in Table 1.

According to several previous analyses of data for similar systems [8-10], ΔP_{max} is related to the heat released during explosion, while $(dP/dt)_{max}$ and θ_{max} depend also on the rate of this process. Within the explored pressure range both $P_{max} = P_0 + \Delta P_{max}$ and $(dP/dt)_{max}$ are linear functions on P_0:

$$P_{max} = a \cdot P_0 + b \quad (1)$$

$$(dP/dt)_{max} = \alpha \cdot P_0 + \beta \quad (2)$$

while θ_{max} slightly increases with initial pressure according to a third power law:

$$\theta_{max} = a' + b' \cdot P_0^3 \tag{3}$$

Figure 2: Illustration of the experimental pressure-time curve, ΔP-t, its calculated derivative (dP/dt)-t and resulted characteristic parameters ΔP_{max}, $(dP/dt)_{max}$, θ_{max}. The initial pressure rise for $\Delta P \leq P_0$ is shown in the lower left side

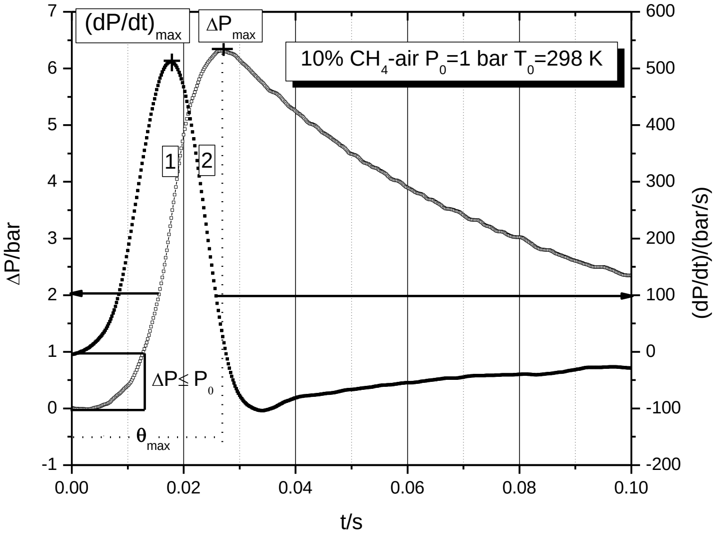


Table 1: Characteristic parameters of pressure evolution for initial pressures, P_0, of 10% CH_4/air mixture

P_0 (bar)	ΔP_{max} (bar)	$(dP/dt)_{max}$ (bar/s)	θ_{max} (s)
1.50	9.328	690.9	0.0299
1.40	8.795	665.7	0.0299
1.30	8.070	620.0	0.0287
1.20	7.518	591.7	0.0279
1.10	6.967	556.0	0.0269
1.01	6.293	510.7	0.0265
0.80	5.067	423.6	0.0261
0.60	3.716	327.1	0.0259
0.40	2.446	228.3	0.0253

The following results were obtained from the data in Table 1, with the corresponding coefficients of determination, r^2:

$$P_{\max} = (7.271 \pm 0.058) \cdot P_0 - (0.023 \pm 0.063) \qquad r^2 = 0.999$$

$$(dP/dt)_{\max} = (423 \pm 12) \cdot P_0 + (74.7 \pm 13) \qquad r^2 = 0.994$$

$$\theta_{\max} = (0.0253 \pm 0.0002) + (0.00148 \pm 0.00010) \cdot P_0^3 \qquad r^2 = 0.966$$

The slope a = dP_{max}/dP_0 = 7.271 represents a good approximation for the quasi-adiabatic pressure rise [8,9]. It can be compared with other measured data (8.3 in a 20 L vessel [1], 7.0 in a 4.2 L vessel [11]) and with the calculated adiabatic value (8.897 using codes described in [12,13]). On the other hand, the maximum rate of pressure rise and the time necessary to reach the peak pressure are significantly more dependent on vessel volume and form, as well as on the power of the ignition source.

It has been observed long ago that during initial stage of the flame propagation the pressure rise is proportional with the third power of time:

$$\Delta P = k_3 \cdot t^3 \tag{4}$$

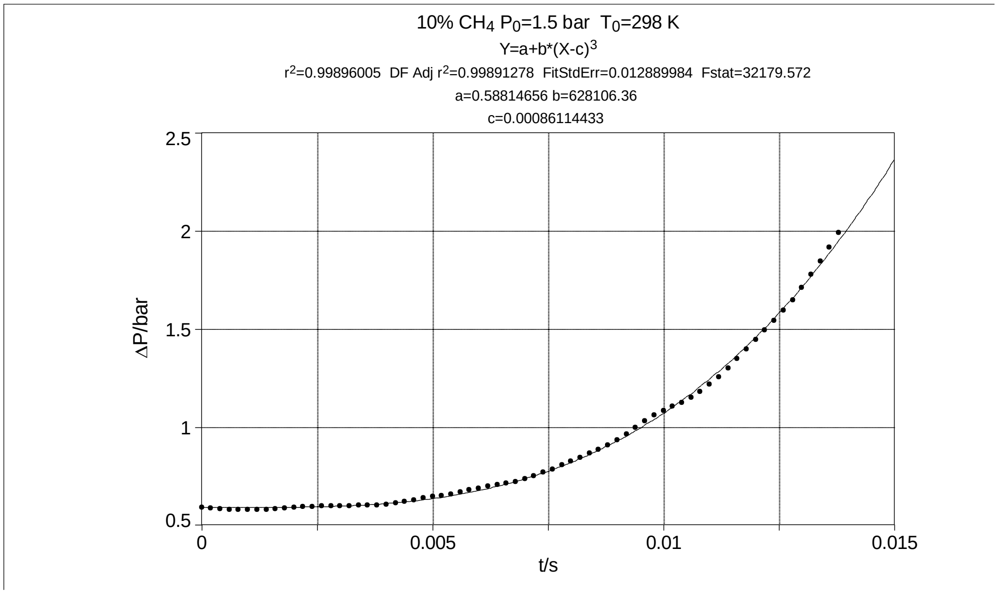
where k_3 is related to the normal burning velocity, S_u, measured with reference to the unburned gas.

Due to inherent displacements of both abscissa and ordinate during the pressure-time recording, an improved correlation equation with three adjustable parameters proved to fit better the experimental data for $\Delta P \leq P_0$ [2]:

$$\Delta P = a_0 + k_3 \cdot (t - \tau)^3 \tag{5}$$

An example is given in Figure 3:

Figure 3: Illustration of the third power law for initial pressure rise of 10% CH_4/air mixture



Two simplified models have been used to give a physical significance of constant k_3 [2]. The isothermal model, more convenient for our calculations, assumes that during this initial period the unburned gas preserves its initial temperature, T_0, leading to [2]:

$$S_u = R^* \cdot (k_3/\Delta P_{max})^{1/3} \cdot (P_0/P_{max})^{2/3} \tag{6}$$

Table 2: Normal burning velocities, S_u and flame speeds, S_s evaluated with the third power law (6)

P_0 (bar)	$k_3 \cdot 10^{-5}$ (bar/s)	τ (ms)	ΔP_{max} (bar)	S_u (m/s)	E_0	S_s (m/s)
1.50	6.74	1.00	9.328	0.383	7.490	2.86
1.40	6.94	1.09	8.795	0.377	7.487	2.82
1.30	6.70	1.17	8.070	0.402	7.483	3.04
1.20	6.16	1.35	7.518	0.398	7.479	3.01
1.10	7.48	1.41	6.967	0.432	7.740	3.23
1.01	6.69	1.50	6.293	0.435	7.470	3.25
0.80	5.36	1.83	5.067	0.430	7.455	3.21
0.60	4.61	3.03	3.716	0.460	7.440	3.42
0.40	3.28	4.40	2.446	0.475	7.403	3.52

The results are given in Table 2 together with the flame speed, S_s, evaluated as $S_s = E_0 \cdot S_u$, where E_0 is the expansion ratio at constant pressure. The flame speed represents the flame front displacement relative to the fix vessel walls. The expansion ratio, E_0, was approximated as the ratio of the flame temperature, $T_{f,P}$ at constant pressure, and initial temperature T_0 = 298 K, neglecting in this case the change in the mole number as a result of combustion. The flame temperatures were calculated using the codes described in [12,13]. The result S_u = 0.435 m/s at P_0 = 1.01 bar is in good agreement with literature data, 0.36 - 0.45 m/s compiled by [4,5] or measured for both stretched and un-stretched flames of methane/air mixtures [14]. In the above calculations, ΔP_{max} and consequently P_{max} are evaluated from experimentally recorded pressure-time curves, implying significant heat losses. An alternative approach relies on the following calculations: $P'_{max} = a \cdot P_0$ or $(P_{max})_{ad} = (\Delta P_{max})_{ad} \cdot P_0$ and $\Delta P_{max} = P_{max} - P_0$. For P_0 = 1.01 bar the results are given in Table 3:

Table 3: Propagation parameters at P_0 = 1.01 bar and T_0 = 298 K using different data sources

Source	P_{max} (bar)	ΔP_{max} (bar)	S_u (m/s)	S_s (m/s)
Experimental	7.303	6.293	0.435	3.25
$a = dP_{max}/dP_0$ (7.271)	7.344	6.334	0.433	3.24
$(\Delta P_{max})_{ad}$ (8.897)	8.986	7.976	0.350	2.62

It can be observed that the differences between experimental and quasi-adiabatic data are negligible, while for adiabatic data significantly lower values are obtained for the burning velocity (and consequently for the flame speed), but they are still in the range of the reported data in literature. There are no sound reasons to state which result is the best one but, for safety applications, the highest value of S_u is preferable.

Within the range of the experimental error, there is a systematic increase of S_u and also of S_s, when the initial pressure decreases. This is usually rationalized with a power law:

$$S_u = S_{u,0} \cdot (P/P_{ref})^{\nu} \tag{7}$$

where P_{ref} is the reference pressure, taken usually as $P_{ref} = 1$ bar, and ν is the baric coefficient of normal burning velocity. The linear regression $\ln(S_u)$ against $\ln(P/P_{ref})$ gives $\nu = -0.166 \pm 0.027$ which is in the range - 0.13 to - 0.30, reported for many hydrocarbon/air mixtures [15]. This parameter can be used to evaluate an overall reaction order n_r, assuming that the reaction rate, r_R, is given by a kinetic equation of factorized form:

$$r_R = k_0 \cdot (P / P_{ref})^{n_r} \cdot \exp(-E_a / RT) \tag{8}$$

where k_0 is a proportionality constant and E_a is the overall activation energy. In isothermal condition, the reaction order can be evaluated using the relationship [16]:

$$n_r = 2(1+\nu) \tag{9}$$

and obtaining $n_r = 1.67$, in accord with similar data for other hydrocarbon/air mixtures [15].

The adjustable parameter τ in the correlation equation (5) has the significance of an induction period meant as the time needed from ignition to the time when a significant pressure increase can be detected. The existence of an induction period for an electric spark ignition was recently substantiated through a numerical study of this process using detailed chemical kinetics [17]. The results indicate induction periods around 1.5 ms, similar with those reported in Table 2. If a kinetic equation of the form (8) is assumed, then, in isothermal conditions the induction period is given by:

$$\tau = k^* \cdot (P/P_{ref})^{-n_r} \tag{10}$$

The linear regression $\ln(\tau)$ versus $\ln(P/P_{ref})$ gives $n_r = 1.130 \pm 0.044$, a figure slightly different from that obtained with equation (9), an acceptable result taking into account the use of two different models based on different assumptions.

4. CONCLUSIONS

The analysis of pressure-time variation during laminar deflagration of the most explosive methane/air mixture in a small cylindrical laboratory vessel with diameter equal to height (V_0 = 0.17 L) provided valuable parameters necessary for safety design of equipment working in explosive atmospheres. The primary analysis gave the maximum explosion pressure, maximum rate of pressure rise and time to peak pressure. A recently proposed method for the processing of pressure variation during the initial stage of the flame propagation in large spherical vessels was successfully used even in this case to obtain reliable values for the burning velocity, flame speed and ignition period. The required necessary information is not dependent on the specific properties of the explosive mixture, rendering the method applicable to explosive systems of unknown nature and composition.

REFERENCES

1. Cashdollar K.L., Zlochower I.A., Green G.M., Thomas R.A., Hertzberg M., "Flammability of methane, propane, and hydrogen gases", *J. Loss Prevent. Proc., 13* (**2000**) 327-340.
2. Razus D., Oancea D., Movileanu C., "Burning velocity evaluation from pressure evolution during the early stage of closed-vessel explosions", *J. Loss Prevent. Proc., 19* (**2006**) 334-342.
3. Razus D., Brinzea V., Mitu M., Movileanu C., Oancea D., "Burning Velocity of Propane−Air Mixtures from Pressure−Time Records during Explosions in a Closed Spherical Vessel", *Energ. Fuel., 26* (**2012**) 901−909.
4. Dahoe A.E., de Goey L.P.H., "On the determination of the laminar burning velocity from closed vessel gas explosions", *J. Loss Prevent. Proc., 16* (**2003**) 457–478.
5. Rallis C.J., Garforth A.M., "The determination of laminar burning velocity", *Prog. Energ. Combust., 6* (**1980**) 303-329.
6. Huzayyin A.S., Moneib H.A., Shehatta M.S., Attia A.M.A., "Laminar burning velocity and explosion index of LPG–air and propane–air mixtures", *Fuel, 87* (**2008**) 39–57.
7. Mitu M., Razus D., Giurcan V., Oancea D., "Experimental and numerical study of laminar burning velocity of ethane−air mixtures of variable initial composition, temperature and pressure", *Energ. Fuel., 28* (**2014**) 2179−2188.
8. Oancea D., Gosa V., Ionescu N.I., Popescu D., "An experimental method for the measurement of the adiabatic maximum pressure during an explosive gaseous combustion", *Rev. Roum. Chim., 30* (**1985**) 767-776.
9. Razus D., Movileanu C., Brinzea V., Oancea D., "Explosion pressures of hydrocarbon-air mixtures in closed vessels", *J. Hazard. Mater., 135* (**2006**) 58-65.
10. Razus D., Movileanu C., Oancea D., "The rate of pressure rise of gaseous propylene-air explosions in spherical and cylindrical enclosures", *J. Hazard. Mater., 139* (**2007**) 1-8.

11. Shebeko Yu.N., Azatyan V.V., Bolodian I.A., Navzenya V.Y., Kopylov S.N., Shebeko D.Yu., Zamishevski E.D., "The influence of fluorinated hydrocarbons on the combustion of gaseous mixtures in a closed vessel", *Combust. Flame, 121* (**2000**) 542–547.
12. Razus D., Brinzea V., Mitu M., Movileanu C., Oancea D., „Temperature and pressure influence on maximum rates of pressure rise during explosions of propane-air mixtures in a spherical vessel", *J. Hazard. Mater.*, *190* (**2011**) 891–896.
13. Mitu M., Giurcan V., Razus D., Oancea D., "Temperature and pressure influence on ethane−air deflagration parameters in a spherical closed vessel", *Energ. Fuel.*, *26* (**2012**) 4840−4848.
14. Tseng L.-K., Ismail M.A., Faeth G.M., "Laminar burning velocities and Markstein numbers of hydrocarbon/air flames", *Combust. Flame*, *95* (**1993**) 410-426.
15. Razus D., Oancea D., Brinzea V., Mitu M., C. Movileanu, "Experimental and computed burning velocities of propane–air mixtures", *Energ. Convers. Manage.*, *51* (**2010**) 2979–2984.
16. Potter Jr. A.E., Berlad A.L., "The effect of fuel type and pressure on flame quenching", *Symposium (International) on Combustion*, *6* (**1957**) 27–36.
17. Han J., Yamashita H., Hayashi N., "Numerical study on the spark ignition characteristics of a methane – air mixture using detailed chemical kinetics. Effect of equivalence ratio, electrode gap distance, and electrode radius on MIE,quenching distance, and ignition delay", *Combust. Flame*, *157* (**2010**) 1414–1421.

NEW FRONT. CHEM. (2016)
Volume 25, Number 1, pp. 73-81
ISSN 2393-2171; ISSN-L 2393-2171

Former: Ann. West Univ. Timisoara – Series Chem.
ISSN: 1224-9513

Review

HOMOPOLYNUCLEAR COORDINATION COMPOUNDS WITH CARBOXYLATE ORGANIC LIGANDS

Mircea Ştefănescu[1]♣
[1] Politehnica University Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, 6 Vasile Pârvan, 300223, Timişoara, ROMANIA

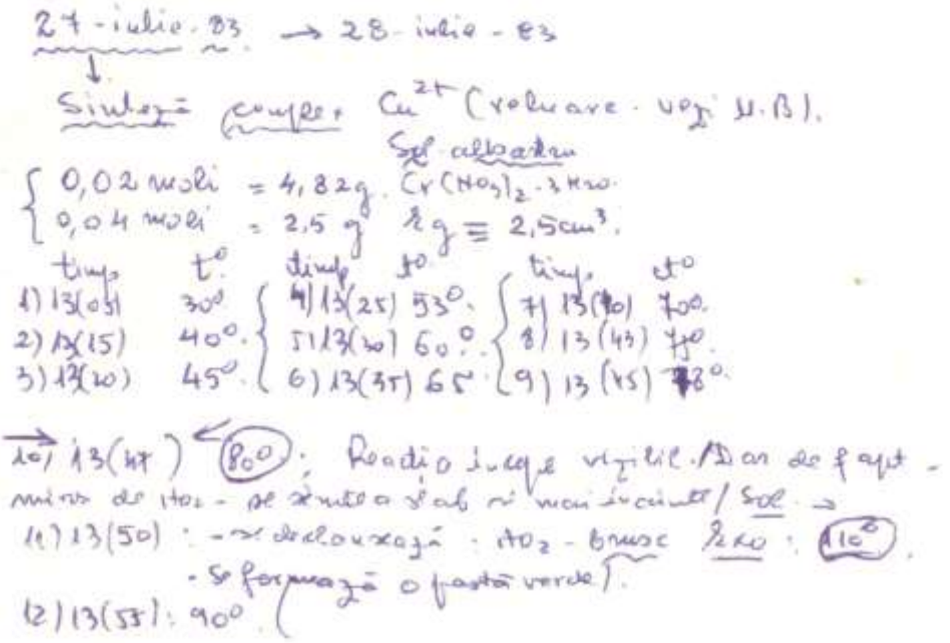
Year 1982

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.

♣ Correspondent author E-mail: mircea.stefanescu@upt.ro



27-iulie-83 → 28-iulie-83

Sinteză complex Cu^{2+} ([illegible] · vezi M.B.).

Sol albastru

0,02 moli = 4,82 g $Cu(NO_3)_2 \cdot 3H_2O$.

0,04 moli = 2,5 g EG ≡ 2,5 cm³.

timp	t°	timp	t°	timp	t°
1) 13(05)	30°	4) 13(25)	53°	7) 13(40)	70°
2) 13(15)	40°	5) 13(30)	60°	8) 13(43)	75°
3) 13(20)	45°	6) 13(35)	65°	9) 13(45)	78°

10) 13(47) (80°): Reacție intensă vizibilă. Dar de fapt - mult de NO_2 - se simte o [illegible] și mai încălzit / Sol →

11) 13(50): - se declanșează · NO_2 - brusc [illegible]: 110°.

- Se formează o pastă verde].

12) 13(55): 90° (

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

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

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.

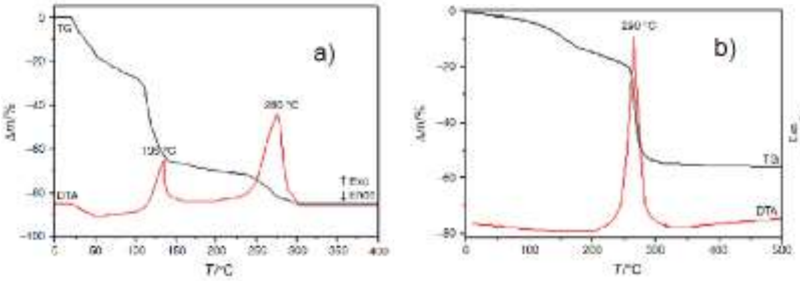
$$[Cu(H_2O)_6]^{2+} + H2O \Leftrightarrow [Cu(OH)(H_2O)_5]^+ + H_3O^+$$

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).

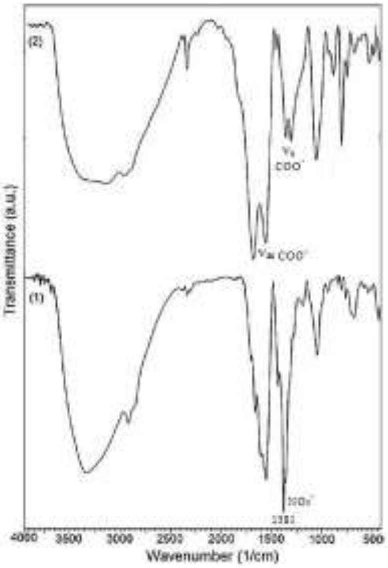
Figure 1: (a) $Ni(NO_3)_2$ – EG solution (redox reaction); **(b)** Ni(II) complex compound synthesized at 140°C (decomposition)



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 νasim(COO^-) bands in the 1580-1650 cm^{-1} region and the νsim(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., Ştefănescu 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., Ianoș R., Ecsedi Z., Ianoșev S., “Particular aspects of oxide powders synthesis using unconventional methods”, Rev. Rom. Mat., 37 (2007) 185-197.

6. Ianoșev 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., Ştefănescu 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. Ştefănescu O., Davidescu C., Ştefănescu 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., Ştefănescu 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. Ştefănescu O., Vlase G., Barbu M., Barvinschi P., Ştefănescu 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 proprietăţi magnetice dirijate, obţinute prin două metode neconvenţionale 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;

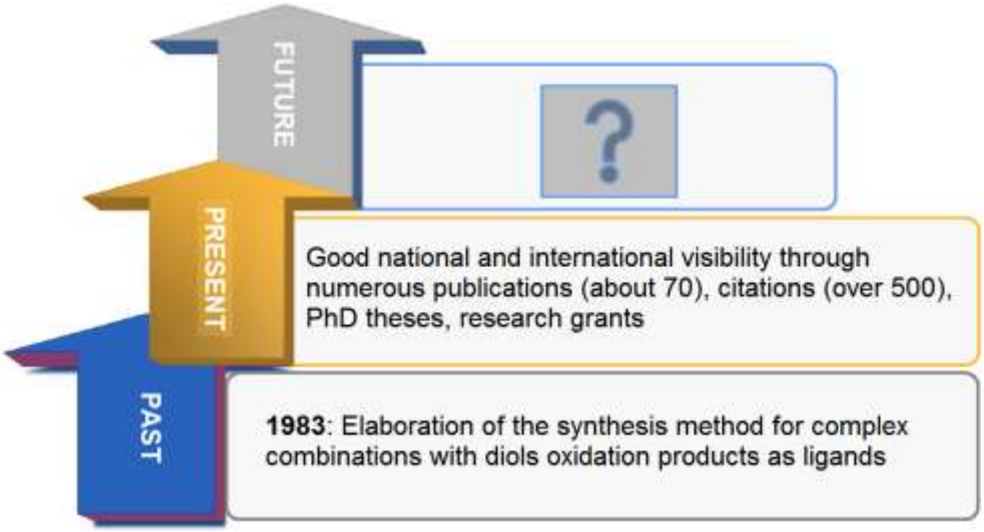
3. PN II 71 – 026/2010 with title: Cercetări complexe privind obţinerea şi proprietăţile magnetice ale sistemelor de nanoparticule ferimagnetice de CoδFe3-δO4 surfactate/nesurfactate şi biocompatibile cu potenţiale aplicaţii în terapia cancerului (Complex research regarding the preparation and magnetic 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.



Good national and international visibility through numerous publications (about 70), citations (over 500), PhD theses, research grants

1983: Elaboration of the synthesis method for complex combinations with diols oxidation products as ligands

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

Îți mulțumesc, Mișule!