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POLITEHNICA UNIVERSITY OF TIMISOARA
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CONTENTS

DESIGN OF COORDINATION POLYMERS BUILT FROM POLYOXALAMIDE LIGANDS	1
Yves JOURNAUX, M. PONCET, X. OTTENWAELDER, MC. DUL, R. LESCOUËZEC, L. LISNARD, L.M. CHAMOREAU, G. GONTARD, Y. LI, J. FERRANDO, E. PARDO, R. RUIZ-GARCÍA, F. LLORET, M. JULVE, J. CANO, C. LOPES PEREIRA	
POLYMORPHISM, MESOMORPHISM AND ENANTIOMORPHISM IN LUMINESCENT Ir(III) CYCLOMETALATED COMPLEXES	2
Alessandra CRISPINI	
LIGAND-DIRECTED SELF-ASSEMBLY OF NANOPARTICLES	3
Bertrand DONNIO	
MULTIRESPONSIVE SUPRAMOLECULAR SYSTEMS BASED ON FLAVYLIUM / 2-HYDROXYCHALCONE DERIVATIVES	4
A. Jorge PAROLA, Fernando PINA	
COLUMNAR LIQUID CRYSTALS IN CYLINDRICAL CONFINEMENT	5
Ruibin ZHANG, Xiangbing ZENG, Marko PREHM, Bongseock KIM, Richard BUSHBY, Kyusoon SHIN, Zhihao SHEN, Patrick BAKER, Martin STEINHART, Carsten TSCHIERSCHE, Virgil PERCEC, Goran UNGAR	
IONIC LIQUID CRYSTALS AS NEW ALIGNMENT MEDIA: A MULTINUCLEAR NMR INVESTIGATION	6
Giuseppina DE LUCA, Maria Enrica DI PIETRO, Giorgio CELEBRE	
TITANIUM AND ITS BIOMIMETIC REACTIVITY TOWARD METABOLIC PATHOPHYSIOLOGIES	7
Athanasios SALIFOGLU	
SPIRO-CHROMENES AND ANTHOCYANINS – TWO FAMILIES REUNITED	8
Artur J. MORO, A. Jorge PAROLA, Fernando PINA, Ana-Maria PANA, Valentin BADEA, Iulia PAUSESCU, Sergiu SHOVA, Liliana CSEH	
PORPHYRINS – IN TANDEM WITH OTHER COMPOUNDS - NOVEL OPTOELECTRONIC APPLICATIONS	9
Eugenia FAGADAR-COSMA, Iuliana SEBARCHIEVICI	
MODIFIED BITUMEN: RHEOLOGICAL PROPERTIES AND PYSICAL CHEMISTRY CHARACTERIZATION	10
Cesare OLIVIERO ROSSI, Loredana MAIUOLO, Giuseppina DE LUCA	
LITHIUM POLYPHOSPHONATES MEMBRANES-IONIC CONDUCTIVITY AND DIELECTRIC BEHAVIOUR	11
Nicoleta PLESU, Smaranda ILIESCU, Lavinia MACARIE, Adriana POPA, Gheorghe ILIA	
SELF-ASSEMBLY IN SURFACTANT MIXTURES	12
Pietro CALANDRA, Vincenzo Turco LIVERI	

- MESOPOROUS SILICA BASED DRUG DELIVERY SYSTEMS. THE LOADING CAPACITY AND THE RELEASE PROFILE OF THE KETOPROFEN FROM THE MATRIX** 13
Ana-Maria PUTZ, László ALMÁSY, Reka BARABAS, Melinda RIGO, Gennady P. KOPITSA, Tamara V. KHAMOVA, Marius MIRICA, Bogdan ȚĂRANU, Attila BÓTA, András WACHA, Qiang TIAN, Cecilia SAVII
- THE STUDY OF TRANSITION METAL SOAPS AS MODEL COMPOUNDS OF PAINTING ARTWORKS** 14
Jiří PLOCEK, Ondřej VIK, Petr BEZDIČKA, Jitka BEZDIČKOVÁ, Pavel VOJTÍŠEK
- SINGLE-STEP SYNTHESIS OF $\text{LaAl}_{0.95}\text{Cr}_{0.05}\text{O}_3$ PIGMENTS AND THEIR NIR-REFLECTIVE PROPERTIES** 15
Robert IANOȘ, Roxana BABUȚĂ, Radu LAZĂU, Eliza MUNTEAN, Cornelia PĂCURARIU, Anamaria DABICI, Alina MOACĂ
- NEW CHIRAL FERROCENYLBISPHOSPHINES AS LIGANDS FOR ASYMMETRIC CATALYSIS** 16
Iudit FILIP, Stefan TSCHIRSCHWITZ, Santi GÓMEZ-RUIZ, Luminita SILAGHI-DUMITRESCU, Evamarie HEY-HAWKINS
- SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF POLYNUCLEAR Co(II,III) ISOBUTYRATE CLUSTER** 17
Dumitru D. STATI, Victor Ch. KRAVTSOV, Svetlana G. BACA
- BIOLOGICAL PROMISCUITY MODELED USING *IN-SILICO* TOOLS** 18
Ramona CURPĂN, Sorin AVRAM, Alina BORA, Liliana HALIP, Ludovic KURUNCZI
- NEW 1-(1H-4-ETHOXYCARBONYL-3-METHYL-PYRAZOL-5-YL)-AZO-2,7-DIHYDROXY-NAPHTHALENE AND ITS CYCLIZED DERIVATIVES OF 8-HYDROXY-2-METHYL-NAPHTHO[2,1-E]PYRAZOLO[5,1-C][1,2,4]TRIAZINE SYNTHESIS AND CHARACTERIZATION BY 2D NMR AND UV-VIS SPECTROSCOPY** 19
Valentin BADEA, Alina Mihaela MUSCOI MÎNDRULEANU, Vasile Nicolae BERCEAN
- A NEW NMR SPECTROSCOPY APPROCH TO CHARACTERIZE DIFFERENT BITUMEN'S** 20
Loredana MAIUOLO, Cesare OLIVIERO ROSSI, Giuseppina DE LUCA, Bagdat TELTAYEV
- CHROMATOGRAPHIC ANALYSES OF ESSENTIAL OILS OBTAINED FROM DIFFERENT PLANT SPECIES CULTIVATED IN ROMANIA** 21
Andreea I. LUPITU, Lucian COPOLOVICI, Georgeta POP, Dana COPOLOVICI
- GRADUAL CHANGING OF THE PHYSICOCHEMICAL PROPERTIES OF HYBRID SILICA XEROGELS WITH THE VINYL SUBSTITUTION** 22
Zoltán DUDÁS, Adél LEN, László ALMÁSY, Ana-Maria PUTZ, Cătălin IANAȘI, Cecilia SAVII
- MANGANESE(III) PORPHYRIN A MULTIVALENT USEFUL MACROCYCLE FOR OPTICAL DETECTION OF H_2O_2 AND ASCORBIC ACID** 23
Anca LASCU, Ionela FRINGU, Anca PALADE, Iuliana SEBARCHIEVICI, Eugenia FAGADAR-COSMA

NANOSTRUCTURAL INVESTIGATIONS ON CARBON NANOTUBES/EPOXY POLYMER COMPOSITES	24
Adel LEN, Sofia BOUKHEIR, Janos FÜZI, Viktor KENDERESI, Mohammed E. ACHOUR, Éber NANDOR, Luiz C. COSTA, Amane OUERIAGLI, Abdelkader OUTZOURHIT	
THE USEFUL SIDE OF THE RESULTS OBTAINED BY NAA METHOD ON RAW PLANT MATERIALS FOR PHYTOPHARMACEUTICALS	25
Daniela HAIDU, Dénes PÁRKÁNYI, Diana ANTAL, Cecilia SAVII, Ludovic KURUNCZI	
NOVEL ADAPTATION OF MANNICH REACTION IN THE SYNTHESIS OF NEW COMPOUNDS	26
Nóra Zsuzsa KISS, Ramona Tudose, György KEGLEVICH, Elemér FOGASSY, Emese PÁLOVICS	
SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW SCHIFF BASE COPPER(II) COMPLEX	27
Ildiko BUTĂ, Anamaria ARDELEAN, Viorel SASCA, Peter LÖNNECKE, Evamarie HEY-HAWKINS, Otilia COSTIȘOR	
RESEARCH ON OBTAINING ENOTANNINS FROM MOLDOVAN GRAPE SEEDS	28
Tudor LUPASCU, Nina TIMBALIUC, Lucian LUPASCU, Oxana SPINU, Igor POVAR	
THE STABILITY OF CALCAREOUS SUSPENSION IN PLUVIAL WATERS	29
Petru SPATARU, Silvia BUZILA, Alexei MAFTULEAC, Igor POVAR	
FUNDAMENTAL INSIGHT ON DEVELOPMENT OF LOW DIELECTRIC CONSTANT QUATERNIZED POLYSULFONE/CELLULOSE ACETATE PHTHALATE BLENDS: ORIGIN OF DIELECTRIC RESPONSE	30
Anca FILIMON, Adriana POPA	
HYBRID ENCAPSULATED ZINC COMPLEXES TOWARD ANTIMICROBIAL NANOTECHNOLOGY APPLICATIONS	31
Christiane M. NDAY, Eleftherios HALEVAS, Graham JACKSON, Athanasios SALIFOGLOU	
BETA-CYCLODEXTRIN CONJUGATED MAGNETIC IRON OXIDE NANOPARTICLES FOR BIOMEDICAL APPLICATIONS	32
Elena-Alina MOACĂ, Roxana Marcela BABUȚĂ, Ioana Zinuca PAVEL, Cristina Adriana DEHELEAN, Codruța Marinela ȘOICA	
OCTANUCLEAR IRON(III) ISOBUTYRATE CAGE BASED ON TRIETHANOLAMINE LIGAND	33
Olga BOTEZAT	
ANTI-PROLIFERATIVE ACTIVITY OF NOVEL 2-(2-((1H-INDOL-5YL) METHYLENE)-HYDRAZINYL)-THIAZOLE DERIVATIVES	39
Luiza Ioana GĂINĂ, Adriana GROZAV, Daniela HANGANU, Luminita SILAGHI-DUMITRESCU	
HYBRID BINARY Bi(III) COMPLEXES TOWARDS ANTIBACTERIAL APPLICATIONS	40
Christiane M. NDAY, Eleftherios HALEVAS, Graham JACKSON, Athanasios SALIFOGLOU	

APPLICATION OF STYRENE-DIVINYLBENZENE COPOLYMERS FUNCTIONALIZED WITH PHOSPHONATE GROUPS AS ADSORBENTS FOR THE REMOVAL OF PHENOL FROM SYNTHETIC WASTEWATER	41
Radu Ardelean, Adriana Popa, Corneliu-Mircea Davidescu	
ANODIC OXIDATION OF 4-FLUOROBENZYLIDENEHYDRAZINO - PYRAZOLE IN ROOM TEMPERATURE IONIC LIQUIDS	42
Liviu-Virgil COSTEA, Vasile BERCEAN	
Mn(II) COORDINATION COMPLEXES BASED ON 2,4,6-TRIS(2-PYRIDYL)-S-TRIAZINE	43
Mariana DARII, Victor Ch. KRAVTSOV, Svetlana G. BACA	
STRUCTURAL AND ELECTRICAL INVESTIGATIONS OF NEW TRANSPARENT CONDUCTORS WITH BIXBYITE STRUCTURE	44
Liliana BIZO, Maria GOREA, Klara MAGYARI	
<i>IN VITRO</i> ENHANCED ANTIOXIDANT PROPERTIES OF CATECHIN NANOPARTICLES AGAINST NEURODEGENERATIVE PHENOTYPES	45
Christiane M. NDAY, Eleftherios HALEVAS, Athanasios SALIFOGLU	
AN EVALUATION REGARDING THE CANNABINOID THERAPIES IN ONCOLOGY	46
Daniela FLONDOR (IONESCU), Simona FUNAR-TIMOFEI, Raluca DUMACHE, Cristina DEHELEAN	
COOKING AND REGENERATION OF PURE AND PALLADIUM DOPED H₃PW₁₂O₄₀/SBA-15 CATALYSTS	47
Orsina VERDES, Viorel SASCA, Alexandru POPA, Mariana SUBA	
PREPARATION OF PURE ENANTIOMERS BY SEPARATION OF DIASTEREOMERS	48
Emese PÁLOVICS, Zsolt SZELECZKY, Elemér FOGASSY	
CALCIUM SILICATE BASED BIOMATERIALS FOR DENTAL CEMENTS	49
Maria GOREA, Lucia TIMIS, Nicolae HAR, Liliana BIZO, Maria TOMOAI A-COTIȘEL	
EXPERIMENTAL STUDY ON THE INTERACTION OF DICLOFENAC WITH SOME NATURAL SUPPORTS	50
Georgeta-Maria SIMU, Alexandra POPESCU, Cristina Adriana DEHELEAN	
COPOLYMERS OF VINYLPHOSPHONIC ACID WITH DIALKYLVINYL PHOSPHONATES AND THEIR PROPERTIES IN AQUEOUS SOLUTION	51
Lavinia MACARIE, Nicoleta PLESU, Smaranda ILIESCU, Gheorghe ILIA, Milica TARA-LUNGA-MIHALI, Adriana POPA	
PORPHYRINS IN MEDICAL APPLICATIONS	52
Luminita SALAGEANU, Eugenia FAGADAR-COSMA	
SOLIDE POLYMER ELECTROLYTES BASED ON POLYPHOSPHOESTERS	53
Smaranda ILIESCU, Nicoleta PLESU, Adriana POPA, Lavinia MACARIE, Gheorghe ILIA	

SUPRAMOLECULAR STRUCTURE OF DINUCLEAR Cu(II) ACETYLACETONATE COMPLEXES WITH BIDENTATE AROMATIC LIGANDS	54
Elena MELNIC, Victor KRAVTSOV	
LIQUID CRYSTALLINE COMPLEXES BASED ON CU(I) METAL CENTRES	55
Carmen CRETU, Adelina A. ANDELESCU, Viorel Z. SASCA, Liliana CSEH, Elisabeta I. SZERB, Otilia COSTISOR	
A NOVEL TOOL FOR THE CHEMICAL SPACE MAPPING OF BIOLOGICAL ACTIVE COMPOUNDS	56
Liliana HALIP, Sorin AVRAM, Alina BORA, Ramona CURPAN	
INSULIN MIMETIC ZINC-INDUCED ADIPOGENESIS IN VITRO. STRUCTURE-SPECIFIC DESIGN AND SYNTHESIS OF A FAMILY OF BINARY AND TERNARY ZN(II)-SCHIFF BASE MATERIALS	57
Olga TSAVE, Maria P. YAVROPOULOU, John G. YOIVOS, Athanasios SALIFOGLOU	
COMBINED MOLECULAR DOCKING AND MLR STUDY OF NEONICOTINOIDS DERIVATIVES WITH INSECTICIDAL ACTIVITIES AGAINST PEA APHIDS	58
Simona FUNAR-TIMOFEI, Alina BORA, Daniela FLONDOR (IONESCU), Takahiro SUZUKI	
HETEROMETALLIC TETRANUCLEAR Fe-Dy PIVALATE CLUSTER BASED ON 1,1,1-TRIS(HYDROXYMETHYL)ETHANE	59
Daniel PODGORNYI, Victor Ch. KRAVTSOV, Svetlana G. BACA	
HETEROGENOUS CATALYST APPLICATION OF PHOSPHONATE METAL ORGANIC FRAMEWORK	60
Aurelia VISA, Bianca MARANESCU	
POROUS COORDINATION POLYMERS OF Co(II) AND Zn(II) TRICARBOXYLATE WITH 1,2-BIS(4-PYRIDYL)PROPANE	61
Aliona VITIU, Eduard COROPCEANU, Polina BOUROSH	
COMPARATIVE ANALYSIS OF THE BINDING MODE AT ERα OF TWO DERIVATIVES OF 4-HYDROXY-TAMOXIFEN (4OHT)	62
Ramona CURPĂN, Liliana HALIP, Ana BOROTA, Philipp MAXIMOV, Craig V. JORDAN	
STRUCTURAL AND CONDUCTANCE STUDIES OF ETHYLETHANOLAMINE 4-NITROBENZOATE	63
Nicoleta PLESU, Manuela CRISAN, Mihaela PETRIC, Lilia CROITOR, Victor KRAVTSOV, Paulina BOUROSH	
FLAVONOID NANOPARTICLES AS POTENTIAL ALZHEIMER'S DISEASE THERAPEUTIC AGENTS	64
Christiane M. NDAY, Eleftherios HALEVAS, Graham JACKSON, Athanasios SALIFOGLOU	
QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS STUDY OF SOME FLAME-RETARDANT POLYPHOSPHONATES	65
Simona FUNAR-TIMOFEI, Luminita CRISAN, Smaranda ILIESCU	

SUPRAMOLECULAR ARCHITECTURES OF ISOMERIC METHYLETHANOL-AMINE CHLORONITROBENZOATES	66
Manuela CRISAN, Mihaela PETRIC, Lilia CROITOR, Pavlina BOUROSH	
A SURVEY OF ELECTRONIC PROPERTIES INFLUENCE ON BIOLOGICAL ACTIVITY OF FLAVONOIDS	67
Alina BORA, Liliana HALIP, Ramona CURPAN, Sorin AVRAM	
ELECTROCHEMICAL EVALUATION OF COATINGS BASED ON MEDIUM ALKYD RESINS MODIFIED WITH AROMATIC POLYURETHANES ON METALS	68
Nicoleta PLESU, Lavinia MACARIE, Simona POPA, Dorin JURCAU	
EVOLUTIONARY RELATIONSHIPS AMONG G PROTEIN-COUPLED RECEPTORS USING LIGAND INFORMATION	69
Liliana HALIP, Cristian G. BOLOGA	
GRAFTING OF SnO₂ ON PHENYL-PHOSPHONIC ACIDS	70
Eleonora Cornelia CRASMAREANU, Ramona GHEONEA, Vasile SIMULESCU, Gheorghe ILIA	
CHEMICAL AND BIOLOGICAL INVESTIGATION INTO BORON-HYDROXYCARBOXYLIC ACID BINARY SYSTEMS	71
Sevasti MATSIA, Olga TSAVE, Athanasios SALIFOGLOU	
DETERMINATION OF HEAVY METALS IN WASTE WATERS AND THEIR REMOVAL BY PHOSPHONATE METAL ORGANIC FRAMEWORKS	72
Bianca MARANESCU, Aurelia VISA, Lavinia LUPA	
IDENTIFICATION OF ORIENTATION AND INTERACTIONS OF NEW 2-(TRIMETHOXYPHENYL)-THIAZOLES WITHIN COX-1/2 BINDING SITES	73
Liliana PACUREANU, Cătălin ARANICIU, Smaranda Dafina ONIGA, Cristina Ioana STOICA, Mariana Doina PALAGE, Alexandra CRĂCIUN, Laurentiu Răzvan RUSU, Luminita CRISAN	
QUERCETIN NANOPARTICLES PROTECT CELL SYNAPTIC CONNECTIVITY AND SURVIVAL RATE UNDER Cu(II)-LINKED OXIDATIVE STRESS IN NEURODEGENERATION	74
Christiane M. NDAY, Graham JACKSON, Athanasios SALIFOGLOU	
SYNTHESIS AND STRUCTURAL STUDY 2:1 CLATHRATE INCLUSION COMPLEXES OF BIS(IMINOPHOSPHORANE)ETHANE WITH DIFFERENT SOLVENTS GUEST MOLECULES	75
Mihaela PETRIC, Manuela CRISAN, Lilia CROITOR, Paulina BOUROSH, Victor KRAVTSOV, Andreea MICLE, Gheorghe ILIA	
VANADIUM REDUCES AUTOPHAGY AND INHIBITS METASTATIC NICHE BY INDUCTION OF TRAIL-INDUCED APOPTOSIS IN CANCER CELLS	76
Savvas PETANIDIS, Efrosini KIOSEOGLOU, Doxakis ANESTAKIS, Margarita HADZOPOULOU-CLADARAS, Athanasios SALIFOGLOU	
SYNTHESIS, CHARACTERIZATION AND EVALUATION OF ADSORPTION CAPACITY OF NEW MAGNETIC NANOCOMPOSITES	77

Simona Gabriela MUNTEAN, Robert IANOȘ, Eliza MUNTEAN, Maria Andreea NISTOR,
Cornelia PĂCURARIU

STUDY ON CdSO₄ DECOMPOSITION IN THE PRESENCE OF CdO 78

Mariana SUBA, Paula SVERA, Viorel SASCA, Daniel URSU, Orsina VERDES, Alexandru POPA

PRELIMINARY THEORETICAL INVESTIGATIONS OF SOME SELECTIVE COX-1 INHIBITORS 79

Luminita CRISAN, Liliana PACUREANU, Alina BORA

3D STRUCTURE MODELING OF COMPOSITE MATERIALS USED IN 3D PRINTING BIOAPPLICATIONS 80

Konstantinos ROGOTIS, Athanasios SALIFOGLOU

INVESTIGATIONS ON PHOTOCROMIC PROPERTIES OF 2,6-BIS(2,4-DIHYDROXYBENZYLIDENE)CYCLOHEXANONE 81

Livia DEVESELEANU-CORÎCI, Valentin BADEA, Otilia COSTIȘOR, Liliana CSEH

THE COMPUTATION OF PREDICTION INTERVALS IN KINASE-INHIBITOR MODELLING 82

Sorin AVRAM, Alina BORA, Ramona CURPAN, Liliana HALIP

INVESTIGATION OF MAGNETITE/CARBON NANOCOMPOSITES AS SORBENTS FOR REMOVAL OF METALS IONS FROM AQUEOUS SOLUTIONS 83

Simona Gabriela MUNTEAN, Adelina ANDELESCU, Maria Andreea NISTOR, Maria Elena RĂDULESCU-GRAD

SYNTHETIC DIVERSITY IN AQUEOUS BINARY Ga(III)-HYDROXY)CARBOXYLIC ACID SYSTEMS. POTENTIAL BIOLOGICAL ROLES 84

Maria N. ANTONOPOULOU, Olga TSAVE, Athanasios SALIFOGLOU

3D QSAR MODEL BASED ON PHARMACOPHORE HYPOTHESIS FOR SMO RECEPTOR INHIBITORS 85

Ana BOROTA, Daniela VARGA, Ramona CURPAN, Liliana HALIP, Alina BORA, Simona FUNAR-TIMOFEI

NOVEL Zn-METALLOPORPHYRINS DERIVED FROM ASYMMETRIC A₃B PYRIDYL-*meso*-SUBSTITUTED PORPHYRINS 86

Anca PALADE, Anca LASCU, Ionela FRINGU, Mihaela BIRDEANU, Eugenia FAGADAR-COSMA

CATALYTIC ACTIVITY IN TERNARY V(V)-DIPEROXIDO-BETAINE SPECIES 87

Efrosini KIOSEOGLOU, Athanasios SALIFOGLOU

MLR AND PHARMACOPHORE STUDY OF DIBENZOYLHYDRAZINES INSECTICIDES 88

Luminita CRISAN, Ana BOROTA, Simona FUNAR-TIMOFEI

CATALYTIC OXIDATION OF BENZENE WITH OXIDO-PEROXIDO-ZWITTERION VANADATE COMPOUNDS 89

Efrosini KIOSEOGLOU, Athanasios SALIFOGLOU

COLOUR STUDY OF A DISAZO DIRECT SYMMETRICAL STILBENE DYE	90
Maria Elena RĂDULESCU-GRAD, Simona Gabriela MUNTEAN, Maria Andreea NISTOR	
SPHERICAL SILICA NANOPARTICLES OBTAINED BY STÖBER PROCESS. TETRA-ETHYL-ORTHOSILICATE CONCENTRATION INFLUENCE UPON SILICA NANOPARTICLES MORPHOLOGY	91
Mirela PICIORUS, Adelina ANDELESCU, Catalin IANASI, Paula SFIRLOAGA, Cecilia SAVII	
THEORETICAL ANALYSIS OF PAN-FGFR INHIBITORS	92
Luminita CRISAN, Daniela VARGA, Liliana PACUREANU	
TIME AND TEMPERATURE DEPENDENCE OF OLEFIN OXIDATION WITH PEROXIDO VANADATE CATALYSTS	93
Efrosini KIOSEOGLOU, Athanasios SALIFOGLU	
PYRIMIDINE ANALOGUES AS TYROSINE KINASE INHIBITORS: A PARTIAL-LEAST-SQUARE DISCRIMINANT-ANALYSIS (PLS-DA) APPROACH	94
Alina BORA, Sorin AVRAM, Ana BOROTA, Liliana PACUREANU, Luminita CRISAN	
SEC-MALLS CHARACTERIZATION OF NEW SYNTHESIZED POLYMERS OF VINYLPHOSPHONIC ACID DERIVATIVES	95
Vasile SIMULESCU, Miloslav PEKAŘ, Lavinia MACARIE, Nicoleta PLESU, Smaranda ILIESCU, Gheorghe ILIA, Milica TARA-LUNGA-MIHAI	
NEW N^N LIGAND FOR WATER SOLUBLE COORDINATION COMPLEXES BASED ON 3d METAL IONS	96
Adelina-Antonia ANDELESCU, Carmen CREȚU, Valentin BADEA, Liliana CSEH, Elisabeta I. SZERB, Otilia COSTIȘOR	
ASSESSMENT OF THE ADIPOGENIC POTENTIAL OF V(V)-SCHIFF BASE COMPLEXES IN 3T3-L1 PRE-ADIPOCYTES	97
Olga TSAVE, Catherine GABRIEL, Athanasios SALIFOGLU	
SYNTHESIS AND SPECTRAL CHARACTERIZATION OF COOPER(II) COMPLEX WITH CARBOXYLIC SCHIFF BASE AS LIGAND	98
Anamaria ARDELEAN, Ildiko BUTĂ, Viorel SASCA, Otilia COSTIȘOR	
BETACAROTENE DETECTION WITH Mn(III)-PORPHYRIN-nanoAu PLASMONIC COMPLEX	99
Ionela FRINGU, Mihaela BIRDEANU, Anca LASCU, Anca PALADE, Eugenia FAGADAR-COSMA	
REMOVAL OF METAL IONS FROM AQUEOUS SOLUTIONS USING VARIOUS TYPES OF ADSORBENTS	100
Adelina ANDELESCU, Maria Andreea NISTOR, Simona Gabriela MUNTEAN, Raisa NASTAS, Larisa POSTOLACHI	
3D SIMILARITY SEARCH FOR PIN1 INHIBITORS	101
Daniela VARGA, Luminita CRISAN, Liliana PACUREANU	

IRON (III) ACETYL-ACETONATE-PVA-SILICA- INORGANIC-ORGANIC HYBRID NANOCOMPOSITE XEROGELS, THERMAL BEHAVIOUR 102

Cătălin IANĂȘI, Ana-Maria PUTZ, Paula SFIRLOAGA, Cecilia SAVII

INVESTIGATION OF DIFFERENT TYPES OF MATERIALS AS SORBENTS FOR THE REMOVAL OF DIRECT DYES FROM AQUEOUS SOLUTIONS 103

Maria Andreea NISTOR, Simona Gabriela MUNTEAN, Raisa NASTAS, Larisa POSTOLACHI, Maria Elena RADULESCU-GRAD

IONIC LIQUID CRYSTALS BASED ON SILVER(I) COORDINATION COMPLEXES 104

Angela M. SPIRACHE, Carmen CRETU, Viorel SASCA, Valentin BADEA, Elisabeta I. SZERB, Liliana CSEH, Otilia COSTISOR

IMMOBILIZATION OF LIPAZE FROM CANDIDA ANTARCTICA B BY COVALENT BINDING ONTO MAGNETIC SUPPORTS 105

Corina VASILESCU, Ioana BENEĂ, Cristina PAUL, Anamaria TODEA, Rodica TURCU, Francisc PETER

CORROSION OF ALUMINUM IN ALCOHOLIC SOLUTION – A PERMANENT CHALLENGE IN FOOD AND DRINKS PRODUCTION 106

Adrian PĂCURARIU, Delia-Andrada DUCA, Mircea Laurențiu DAN, Nicolae VASZILCSIN

STAINLESS STEEL CORROSION IN ETHANOL SOLUTIONS IN THE PRESENCE OF SULFITE IONS - A PERMANENT PROBLEM IN THE WINE INDUSTRY 107

Mihaela Alexandra LABOSEL, Cristian George VASZILCSIN, Delia-Andrada DUCA, Mircea Laurentiu DAN

DESIGN OF COORDINATION POLYMERS BUILT FROM POLYOXALAMIDE LIGANDS

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Since the eighties the synthesis of molecule based magnet is real challenge. Indeed, it is well known that the molecular precursors naturally favor isolated systems or low dimensional structures while it is compulsory to have at least 2D networks and ideally 3D networks to get magnetic ordering. Paradoxically the first attempts to obtain molecule based magnets were made with 1D coordination polymers. These low dimensional 1D compounds were chemically easier to obtain and later these 1D compounds have proved to be of particular interest for studying the magnetic properties of low-dimensional compounds such as the discovery of Glauber dynamic in 1D coordination polymers. We will describe in this lecture the strategies implemented to control the dimensionality of inorganic polymers using polyoxalamide ligands either to study low dimensional physics or to get magnetic ordering. We will specially focused on the quest of 3D networks with polyoxalamide ligands a thirty years old story but with particularly rich and diverse chemical systems.

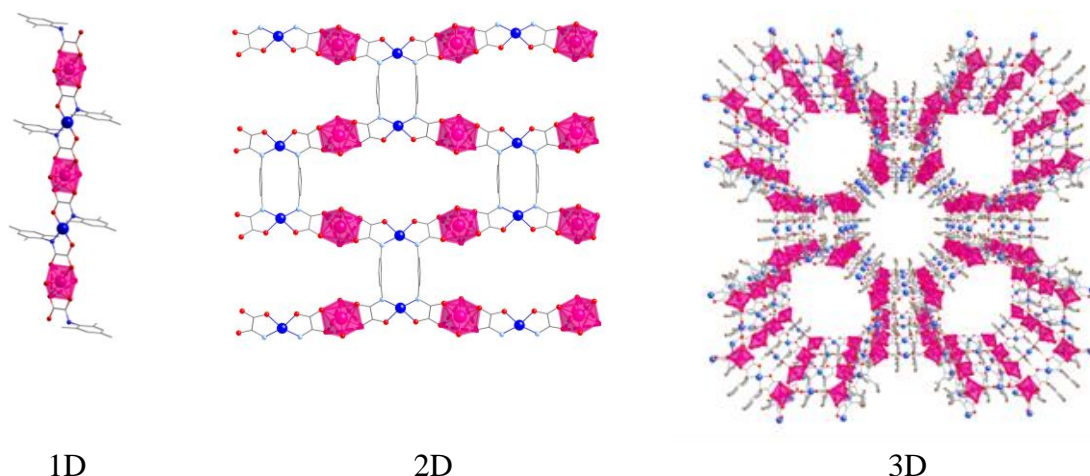


Fig 1. Molecular structure of coordination polymers synthesized from polyoxalamide ligands

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POLYMORPHISM, MESOMORPHISM AND ENANTIOMORPHISM IN LUMINESCENT Ir(III) CYCLOMETALATED COMPLEXES

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Development of luminescent metal complexes represents an important challenge with applications in many field, including catalysis, optoelectronics and biological imaging. Iridium(III) complexes are emerging as potentially valuable compounds since their emission is completely tunable via ligand modifications [1]. Many luminescent Ir(III) complexes incorporating cyclometalating (C[^]N) ligands exhibit excellent photophysical properties [2]. While, luminescent properties are normally investigated in solution, new materials for practical application are designed to be used in their solid state (both amorphous and crystalline). To this end, the comprehension of the molecular arrangements and interactions within a molecular material is fundamental in order to translate molecular properties into material properties (such as quenching or induction of luminescence due to aggregation effects) [3].

In this field, examples on the relationship between structures and properties of new ionic and molecular cyclometalated Ir(III) materials in their various aggregation states will be presented, pointing out the tight control between polymorphism, mesomorphism and enantiomorphism and the structure of the single metal containing unit.

Keywords: non covalent interactions, polymorphism, aggregation state.

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LIGAND-DIRECTED SELF-ASSEMBLY OF NANOPARTICLES

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Self-assembly of nanoparticles (NPs) into designed structures, with controlled symmetry and interparticular distances, is of relevance for engineering new materials with tuneable and reconfigurable functions, as well as for the subsequent bottom-up fabrication of devices. Such ‘metamaterials’, i.e. assemblies of building blocks or ‘meta-atoms’, are able to process incoming EM waves (light, sound) in a manner that is not achievable using regular materials directly built from atoms or molecules. For instance, for a metamaterial with optical properties, a requirement is that the building blocks be smaller than the light wavelength. They boast spectacular properties (i.e. negative refraction, magnetism, superlensing, ...) and are therefore much sought after for the design of innovative applications. Of importance, the nature and collective properties of such assemblies are crucially influenced by the surface functionalization (ligand shell). We recently developed bottom-up chemical routes for the preparation of such hybrids. With the help of some examples, we will show how the ligand shell affects both self-assemblies and certain physical properties.

Dendritic ligands of several generations tethered to the surface of NPs allow the control of their assemblies into 2/3D lattices, whereas the change in the dendritic generation allows a precise and stepwise control of NP separation. This offers potential for optimising collective responses for applications including optical and magnetic. Dual mixing of dendronized species further produces unprecedented binary superlattices, whose properties are intrinsically modulated at nm-scale distances.

Hydrophobic colloidal NPs are mainly synthesized and manipulated with commercially available ligands. These remain invaluable but surface functionalization is typically limited to a small number of molecules. We have recently proposed a robust method using polycatenar ligands for the direct synthesis of a wide variety of monodisperse NPs. Self-assembly into single and binary NP superlattices demonstrates the excellent monodispersity of the produced NPs. In addition, some NPs self-assemble into bcc lattices that deviate from conventional close-packed structures (fcc or hcp) formed by the same NPs coated with commercial ligands. The thorough study demonstrates that the molecular structure of the polycatenar ligands encodes interparticle spacings and specific attractions, engineering self-assembly, which is tuneable from hard sphere to soft sphere behaviour.

Polycatenar and dendritic molecules (mesomorphous or not) thus offer versatile modular platforms for the development of ligands with targeted properties, bringing organic functionality to inorganic NCs. This subsequently controls aspects such as solubility, interparticle spacings, self-assembly, liquid crystalline behaviour, biological and physical properties. It is expected that structural complexities and practical utilities be achieved through a thoughtful exploitation of organic chemistry and expanded to various inorganic systems.

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MULTIRESPONSIVE SUPRAMOLECULAR SYSTEMS BASED ON FLAVYLIUM / 2-HYDROXYCHALCONE DERIVATIVES

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Flavylium salts are 2-phenyl-1-benzopyrylium derivatives exhibiting large colour tunability and fluorescence quantum yields depending on the substituents [1]. They are the core of natural anthocyanin dyes responsible for the reds and blues of most flowers and berries. To attain these colours Nature developed intricate supramolecular structures where anthocyanins are involved in metal complexation and pi-pi stacking interactions [2]. Realizing that flavylium cations are electron poor guests they have been shown to form host-guest complexes through intercalation into neutral or negatively charged electron rich cavities such as those of molecular clips [3], cucurbiturils [4-6], or double-stranded nucleic acids [7].

In aqueous solution, flavylium cations establish a pH-dependent chemical reaction network involving several species. Among these species, *trans*-2-hydroxychalcones are of particular relevance because they can photoisomerize to the *cis* isomer that rapidly evolves to the strongly coloured flavylium species, allowing to exploit these compounds as pH-coupled photochromic systems [1]. Transfer of this solution photochromism to more organized matrices through immobilization of the systems in micelles, gels, polymers, zeolites or mesoporous silica is an ongoing project with the aim of developing photochromic and luminescent materials [8].

Examples of supramolecular systems and materials involving flavylium / 2-hydroxychalcone derivatives will be presented with a highlight on their photochromic properties.

Acknowledgements

Financial support from Portuguese funds from FCT/MEC (UID/QUI/50006/2013) and co-financed by the ERD under the PT2020 Partnership Agreement (POCI-01-0145- FEDER-007265).

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COLUMNAR LIQUID CRYSTALS IN CYLINDRICAL CONFINEMENT

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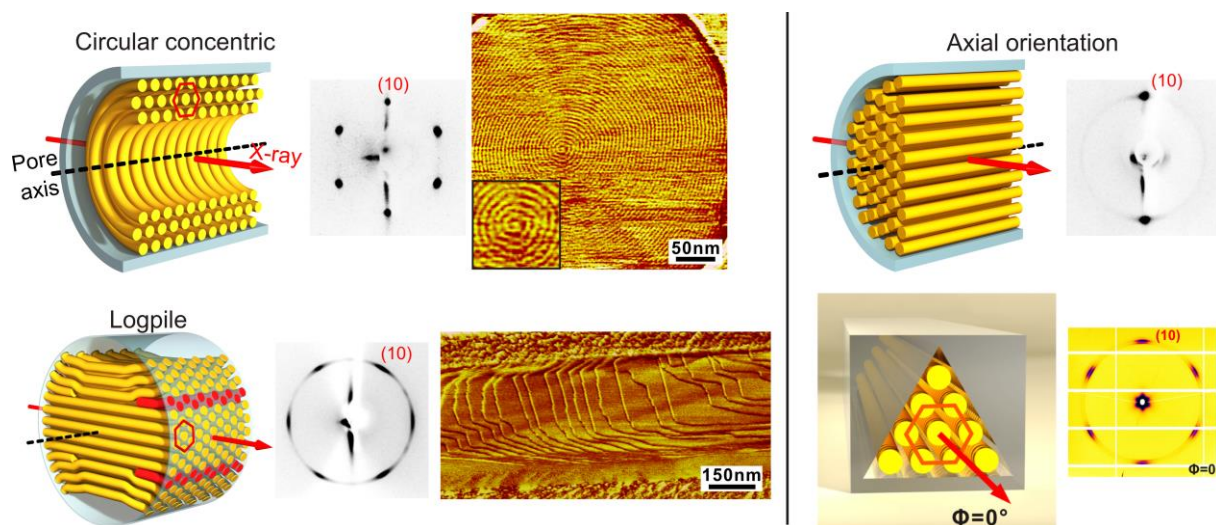
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The cylindrical confinement of columnar liquid crystals shows both rich physical phenomena and potential application in fabricating 1d organic nano objects. Most studies were done based on aromatic core discotics [1] but general rules that govern the orientation of the columns are still not clear. We studied compounds of structural diversity confined in circular pores from 20 nm to 100 μm . They include the supramolecular honeycomb phase of sidechain-bearing amphiphiles [2], a dendronized carbazole and discotics [3]. Using 2D X-ray diffraction and AFM we observed that under planar anchoring, the orientation of the columns are mainly circular concentric. Only for rigid columns, axial orientation can be achieved in small pores below 60 nm. We derive expressions for distortion free energy that suggest the lack of axial orientation results from the distortion energy of 2-D lattice and the mismatch of its crystallographic facets with the curved pore wall. We further used equilateral triangle and square shaped pores to reduce this mismatch and achieved axial orientation even in micron pores. Under homeotropic anchoring, however, logpile configuration is most common and axial one only shows up in large pores above 50 μm . The present findings should help in the design of low-dimensional semiconductor or ionic conductor devices based on oriented columnar phases.



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IONIC LIQUID CRYSTALS AS NEW ALIGNMENT MEDIA: A MULTINUCLEAR NMR INVESTIGATION

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Ionic Liquid Crystals (ILCs) are a class of molecular materials that have the peculiarity of combining the self-organization features of liquid crystals (LCs) with the solvent properties of ionic liquids (ILs) [1]. Since these materials have an anisotropic structural organization composed of only ionic units, they exhibit interesting potential applications as ion conductive materials in electrochemical devices as well as anisotropic reaction media [2,3]. In general, a typical structure of ILC consists of an organic cationic core which is attached to a long hydrophobic chain and paired with an anion. Understanding the relationship between the molecular structure and the type and stability of the mesophases formed by ILC's is of considerable importance for the study of these materials. In this context, the NMR spectroscopy is particularly suitable because allows to study these materials in their ordered phase. With this purpose, we report in this contribution a multinuclear NMR study conducted in two thermotropic imidazolium-based ILC: the 1-dodecyl-3-methylimidazolium chloride ($C_{12}mimCl$) and the 1-dodecyl-3-methylimidazolium tetrafluoroborate ($C_{12}mimBF_4$) [4,5]. These two salts are the firsts of the series that exhibit a mesogenic behaviour with a modified form of a smectic A phase, the so-called smectic A_2 phase (SmA_2), in a large temperature range making them suitable for investigations by NMR. We focused our attention on the investigation of orientational order of the two ILCs at different temperatures in their smectic phase by using the NMR anisotropic observables, such as quadrupolar splittings and residual dipolar couplings, measured directly on the compounds and indirectly on rigid solutes dissolved therein. Preliminary results regarding the partitioning of the solutes in distinct environments of the ILCs and the effect of counterions on the orientational order of the imidazolium ring will be outlined. Finally, to emphasize the versatility of these compounds, relatively to $C_{12}mimBF_4$, that is an highly ordering medium if used as such, we showed how a small addition of water makes it a promising easy-to-use candidate as weakly ordering alignment medium for polar solutes [6].

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TITANIUM AND ITS BIOMIMETIC REACTIVITY TOWARD METABOLIC PATHOPHYSIOLOGIES

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Diabetes mellitus exemplifies a host of metabolic disorders characterized by lack of insulin, defective insulin secretion and/or insulin resistance. Obesity, Diabetes mellitus, and insulin resistance emerge prominently as partners in disease onset and progression. The enhancement of insulin action and/or its complete replacement by insulin-enhancing or insulin-mimetic agents replacing insulin seems to improve the treatment of metabolic diseases. Over the past decades, intensive research has targeted the investigation of such insulin mimetic agents [1-4]. Titanium, in its Ti(IV) oxidation state, appears to be such a metal ion. It is a well-known early transition metal, widely used in a variety of industries, including the pharmaceutical industry (whitening agents), the food industry, the biomedical industry (component in medical devices to rectify skeletal malformation problems in humans, etc. In all such cases, Ti(IV) comes in contact with biologically important organic substrates of both low and high molecular mass. In an effort to probe the potential of that metal ion to divulge any biological role it might play in the biologically important cellular processes, synthetic efforts were launched in our lab to pursue such a goal. The focus was on binary complexes of Ti(IV) with low molecular mass α -hydroxycarboxylic acids, such as citric acid. The latter is a physiological ligand, with its involvement in the binary system with Ti(IV) providing the opportunity to examine the role of Ti(IV) in Diabetes mellitus II. To that end, the synthesis and isolation of the complexes $\text{Na}_6[\text{Ti}(\text{C}_6\text{H}_4.5\text{O}_7)_2(\text{C}_6\text{H}_5\text{O}_7)] \cdot 16\text{H}_2\text{O}$ (**1**) and $\text{Na}_3(\text{NH}_4)_3[\text{Ti}(\text{C}_6\text{H}_4.5\text{O}_7)_2(\text{C}_6\text{H}_5\text{O}_7)] \cdot 9\text{H}_2\text{O}$ (**2**) was achieved in aqueous media under pH-specific conditions. All complexes were characterized by elemental analysis, FT-IR, NMR, ESI-MS spectroscopy, cyclic voltammetry, and X-Ray crystallography [5-9]. Subsequently, the effect of a select title compound (**1**) was investigated on the a) survival of pre- and mature adipocytes (3T3-L1), b) endogenous cell motility, and c) insulin enhancing adipogenic capacity. The overall results suggest that a well-formulated and structurally characterized Ti(IV)-citrate complex a) is (a)toxic in a dose- and time- dependent manner, b) has no influence on cell motility and, c) can induce 3T3-L1 pre-adipocyte differentiation into mature adipocytes through influence of tissue specific biomarkers (Oil Red O, PPAR- γ , GLUT 4 and Adiponectin).

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SPIRO-CHROMENES AND ANTHOCYANINS – TWO FAMILIES REUNITED

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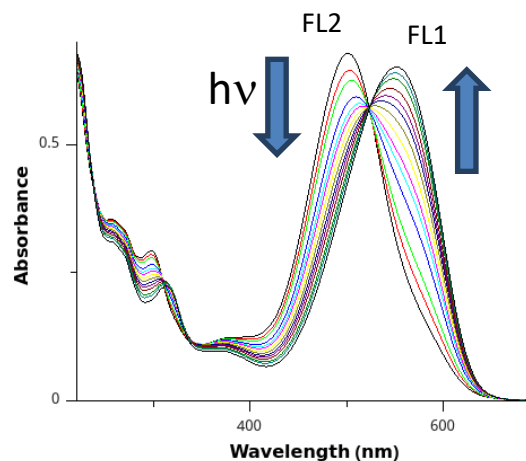
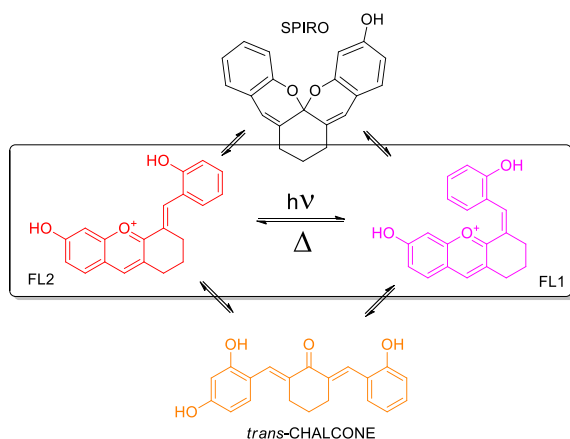
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In this work, we report our recent results concerning the new-found relation between two families of compounds: Anthocyanins¹ and Spiro-chromenes.² Our findings led to the discovery of specific structural features as essential for the stabilization of the Spiro-chromene form within the multi-equilibria network of reaction of anthocyanin derivatives (Flavylium).³



Our systems, bearing a propylenic bridge joining the α carbons from the trans-chalcone species, allowed us to obtain a new photochromic system through *cis-trans* isomerization, with the isomers being readily interconverted using light input.

Acknowledgements

Financial support from Portuguese funds from FCT/MEC (UID/QUI/50006/2013 and Post-doc grant SFRH/BPD/69210/2010) and co-financed by the ERD under the PT2020 Partnership Agreement (POCI-01-0145- FEDER-007265).

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PORPHYRINS – IN TANDEM WITH OTHER COMPOUNDS - NOVEL OPTOELECTRONIC APPLICATIONS

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Multifunctional materials containing assymmetrical A₃B porphyrins, namely: 5-(4-carboxyphenyl)-5,10,15-tris(4-phenoxyphenyl)-porphyrin (CTPOPP) or 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (CTPP) were developed for further advanced applications in detection and catalysis [1]. The organic–inorganic and organic-polymeric hybrids derived from CTPOPP porphyrin and the thin films of CTPP porphyrin obtained by MAPLE on screen-printed electrodes were synthesized and characterized by FT-IR, TEM, XRD, ¹H-NMR, HPLC, UV-vis and fluorescence spectroscopy and tested as catalysts for the Knoevenagel condensation of aldehydes [2], for CO₂ detection capacity and to design an electrochemically mediated by porphyrin sensor for histamine.

The development of new hybrids based on electrocatalytic effect of Mn(III) tetratolyl-porphyrin chloride (MnTTPCl) and gold colloids destined for the detection of ascorbic acid (AA) in the relevant range for medical investigations is also presented [3, 4].

Porphyrins and their corresponding metalloporphyrins are also recognized for their capacity to act as building blocks for achieving amazing supramolecular architectures with enhanced properties. Zn-metalloporphyrins derived from porphyrins grafted with at least one pyridyl group to favour generation of complex supramolecular assemblies by themselves and on ZnA₂O₆ (A = Ta and/or V) pseudo binary oxides films with the purpose to increase the corrosion protection efficiency of carbon steel were obtained and fully characterized. Some promising advancements are presented [5].

Acknowledgements

The authors kindly thank for the support of Romanian Academy of Programme 3 from Institute of Chemistry Timisoara and to UEFISCDI- Project 107PED/03.01.2017 in the frame of PN-III-P2-2.1-PED-2016-0524.

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MODIFIED BITUMEN: RHEOLOGICAL PROPERTIES AND PHYSICAL CHEMISTRY CHARACTERIZATION

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Modified bitumen (MB) is used extensively in thin asphalt surfacing and seals in order to improve specific performances [1]. However, the performances of MB are not easy to demonstrate with the conventional methods, such as penetration test, softening point etc [2]. In order to a better evaluation, different characterization methods are needed rather than ordinary empirical rheological tests. This work deals with the characterization of some modified bitumen systems by using conventional as well as advanced methods on bitumens. Dynamic rheological tests and advanced ¹H Magnetic Resonance analysis to evaluate the effect of modifiers on the bitumen structure, were used [3]. Moreover, morphological analysis by Scanning Electron Microscope (SEM) was performed on neat and modified bitumen and the effect of the filler addition on the supra-molecular organization of the bituminous binder was also investigated.

Additionally, properties of new kind of modified bitumen are presented. Bituminous binder was modified with mix modification using new stabilizing surfactants (NS). Terminal blend was the mixed modified binder. The properties of NS-B binder with comparison to neat bitumen and conventional surfactant modified bitumen were investigated.

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LITHIUM POLYPHOSPHONATES MEMBRANES-IONIC CONDUCTIVITY AND DIELECTRIC BEHAVIOUR

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Main-chain phosphorus-containing polyphosphonates can be prepared easily by the reaction of phosphonic dichloride with a diol.

Polycondensation of hexylphosphonic dichloride (HPD) with 4,4'-(1,3-phenylene-diisopropylidene) bisphenol was carried out under conventional heating and using a new green technique-polycondensation under microwave irradiation in similar conditions. The influence of the reaction temperature and reaction time on yield and inherent viscosity for polycondensation with bisphenol was considered. Polycondensation under microwave irradiation does not require an organic solvent and catalyst. Best results were obtained under microwave irradiation.

It could be concluded that microwave irradiation is a fast and efficient method for polyphosphonate synthesis. The polyphosphonate was characterized by FT-IR, ¹H and ³¹P-NMR spectroscopy, gel permeation chromatography, and thermal analysis. Ionic conductivity for membrane based on polyphosphonate and different Li salts was investigated. The results showed that these polymers are good candidates as membranes for Li polymer batteries. The flammability of polyphosphonate and membranes based on different Li salts was investigated by measuring limiting oxygen index values.

The experimental data indicated some associations between the conductivity, dielectric permittivity and salt type anions. These implied that the basis of dielectric behavior is affected by the conducting species and their interaction. The experimental data follow the Arrhenius relation and indicates that ion conductivity and ion pair relaxation are two components of the same process and should be described by the conductive model. The ions can be located all over inside the polymer matrix and present different mobility. The accumulation and depletion rate depends on the frequency of the applied electrical field and leads to relaxation processes. The relaxation times may be related to the mobility of the charge carriers the highest relaxation time pointed out to a lowest conductivity value.

SELF-ASSEMBLY IN SURFACTANT MIXTURES

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Surfactants are widely used in many fields: detergency, emulsification, lubrication, nanoparticle synthesis and specialized field of nanotechnology. They are usually dissolved as solute in suitable solvents; however, we have recently set-up an innovative approach involving the use of PURE liquid surfactants, with no solvent and mixed together to form binary mixtures. The absence of any solvent maximizes the surfactant concentration, therefore the merits of the system, deriving from the presence of the two surfactants, is obviously driven to their extreme. With no "solvent", the surfactant-based intermolecular structures are expected to be extremely concentrated and somehow percolated/interconnected leading to the formation of exotic organizations.

With this strategy we recently prepared surfactant-based liquid mixtures with striking properties: enhanced proton conductivity [1,2], anomalous 1D diffusion [3], exotic solubilizing properties towards inorganic salts [4], anti-Arrhenian behavior of proton conductivity [5]. Even smart materials fully responsive to an external stimulus (magnetic field) have been prepared [6].

We will show the physical and chemical reasons for all these peculiar properties as well as some future perspectives and potential applications.

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MESOPOROUS SILICA BASED DRUG DELIVERY SYSTEMS. THE LOADING CAPACITY AND THE RELEASE PROFILE OF THE KETOPROFEN FROM THE MATRIX

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In order to be tested for their drug loading and release properties, mesoporous silica particles were synthesised by sol-gel method, starting from mixed silica precursors, tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES). Nitric acid was used as catalyst and different alkyltrimethyl-ammonium bromides were used as pore templates. The specific surface areas were in the range of 883-1580 cm²/g, showing a maximum at an intermediate precursor composition, with MTES content 30mol%. The total pore volumes monotonically decrease with increasing MTES content, from 1.5 cm³/g to 0.45 cm³/g. The pore sizes show a clear trend to decrease with increasing MTES content, from pore diameter 5.7 nm for the sample synthesized with no MTES down to 2.5 nm, for 50% MTES. In parallel to the decrease of the average pore size, the interpore spacing is also decreasing as shown in SAXS measurements. TEM images show ordered arrays of very long tubules characteristic for MCM41 materials. The loading capacity for ketoprofen was found to be significantly improved as MTES content, within the prepared sample series, was the lowest or zero. The specific surface areas of the samples with the most efficient behavior were 1330.7 m²/g, and 1105.4 m²/g respectively; in the same time, these samples also have large pore volume, 1.499 cm³/g and 1.104 cm³/g, respectively. The sample with 30 mol% MTES content has one of the lowest loading capacity, even if it possesses the biggest SSA= 1580.4 m²/g. It exhibited relative low pore volume, 0.863 cm³/g, compared with the samples, with no MTES and 10% MTES. The ketoprofen release kinetics was observed to be dependent of MTES content. As MTES concentration of the prepared series of samples was increasing, the slower was the release process. The sample prepared with the highest MTES content (50% MTES) releases the drug 1.5 times slower than the matrix containing no MTES.

THE STUDY OF TRANSITION METAL SOAPS AS MODEL COMPOUNDS OF PAINTING ARTWORKS

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Almost all paintings change and degrade over time. One of the undesirable degradation processes of historical paintings is known as saponification. Its principle is slow reaction of fatty acids in binding media with some pigments. Product of this reaction are metal soaps, which can migrate and through other painting layer and damage them. We newly prepared several transition metal soaps (transition-metal dodecyl sulfates) as model compounds of product of these degradation processes. The compounds were characterized by chemical and physical methods and was determined their crystal structure.

SINGLE-STEP SYNTHESIS OF $\text{LaAl}_{0.95}\text{Cr}_{0.05}\text{O}_3$ PIGMENTS AND THEIR NIR-REFLECTIVE PROPERTIES

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Lanthanum aluminate based pigments, $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$, with low chromium content ($x = 0.05$) were prepared following a simple combustion synthesis procedure. The starting raw materials were $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, urea and glycine. The mineralization effect of CaF_2 was also investigated. The combustion process was ignited by heating the precursor solution inside a preheated heating mantle. The temperature evolution during the combustion reaction, measured by thermal imaging, indicated a decrease of the peak temperature from approximately 1700 °C ($x = 0$) down to approximately 1400 °C due to chromium nitrate replacing for aluminum nitrate and the presence of CaF_2 mineralizer. As a result, the specific surface area of the samples increased from 2.7 to 7.3 m^2/g . The X-ray diffraction analysis evidenced the formation of single-phase $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ solid solution having a perovskite structure. The presence of CaF_2 mineralizer had a massive positive effect on the color of the sample, which turned reddish-brown (CIEL*a*b* measurements without any annealing). The $\text{LaAl}_{1-x}\text{Cr}_x\text{O}_3$ reddish brown-pigment had a total solar reflectance of 48.5 %, which suggests it might be used as a NIR reflective pigment.

Acknowledgements

This work was supported by a Grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, Project number PN-II-RU-TE-2014-4-1587.

NEW CHIRAL FERROCENYLBISSPHOSPHINES AS LIGANDS FOR ASYMMETRIC CATALYSIS

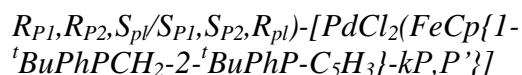
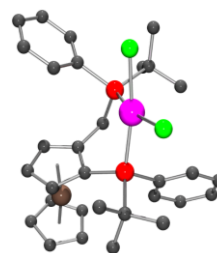
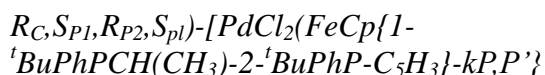
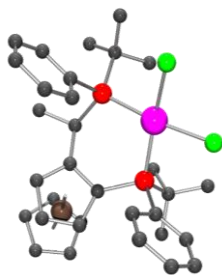
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Asymmetric catalysis is an important subject in synthetic organic chemistry. The design of new chiral catalysts is essential for exploring new classes of catalytic asymmetric reactions as well as for achieving high enantioselectivities. The chiral ferrocene ligands are becoming an extremely important alternative due to the interesting novel enantioselective applications in asymmetric synthesis [1].

We present the synthesis of new chiral ferrocenyl ligands and their complexes with metals relevant for the use as catalysts in organic asymmetric syntheses. The newly synthesized chiral ferrocenylbisphosphines were characterized by ¹H, ³¹P and ¹³C-NMR spectroscopy, X-ray diffraction, MS, IR and elemental analysis. NMR spectroscopy played an important role in determining the number of the obtained diastereomers.



The ligands were reacted with transition metals (Pd (see figures), Rh) and the catalytic activity of the obtained metal complexes is being tested in asymmetric hydrogenation and hydroformylation reactions as well as in C-C coupling reactions.

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF POLYNUCLEAR Co(II,III) ISOBUTYRATE CLUSTER

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Metal coordination complexes play a vital role in living systems as they participate in electron transfer, metal and oxygen transport, cell redox reactions, energy transfer, nitrogen fixation in photosynthesis, synthesis and degradation of fundamental biological molecules, blocking or substitution of functional groups. The preparation of new coordination complexes with biologically active ligands such as N,O-containing alcoholamines is a subject of considerable interest. The reaction of cobalt(II) isobutyrate with triethanolamine (H₃tea), pyrazine and azide ligands in acetonitrile under heating lead to a new pentanuclear mixed-valent [Co^{II}Co^{III}₄(is)₂(N₃)₄(Htea)₄] coordination cluster (Figure 1). A single crystal X-ray diffraction analysis revealed that the compound crystallizes in the monoclinic *C2/c* space group with *a* = 19.889, *b* = 18.556, *c* = 26.907 Å, and *V* = 9496.61 Å³. The cluster is composed of one Co^{II} and four Co^{III} atoms. The Co^{III} atoms are bridged by one isobutyrate ligand and two twice deprotonated Htea²⁻ ligands into dimers namely Co1-Co4, and Co2-Co3. The Co^{II} atom (Co5) connects these dimers in a pentanuclear mixed-valent cluster. The Co^{II} atom has a tetrahedral O₄ coordination environment being coordinated by O atoms from aminoalcohol ligands with Co–O bond distances of 2.005 – 2.016 Å. Each of Co^{III} atoms is six-coordinated adopting an octahedral N₂O₄ geometry by an O atom from isobutyrate, three O atoms and a N atom of two Htea²⁻ ligands, and a N atom from the azide anion. The Co–N bond distances are in the range of 1.929 – 1.977 Å and Co–O bond distances are 1.871 – 1.930 Å. The shortest Co^{III}...Co^{III} separations in the cluster are 2.832 and 2.853 Å, and Co^{II}...Co^{III} separations are in the range of 3.107 - 3.135 Å. The clusters are hydrogen-bonded via O...O and O...N hydrogen bonds into a 3D network.

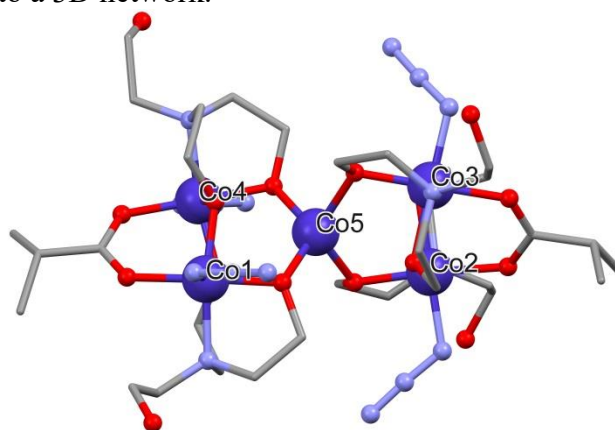


Figure 1. Structure of [Co₅(is)₂(N₃)₄(Htea)₄] cluster.

Acknowledgments

This work was supported by SCOPES IZ73ZO_152404/1 and the State Program of the Republic of Moldova (Project 16.00353.50.05A).

BIOLOGICAL PROMISCUITY MODELED USING *IN-SILICO* TOOLS

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Early stage drug discovery are highly dependable on cheminformatics to filter out undesirable molecules which lead to dead-ends in later stages. In this way, the risks of developing poor drug candidates are reduced and costs are optimized. Biological promiscuity, defined as the non-specific activity of compounds against a wide range of unrelated proteins, represents one major source of “bad” active compounds or false-positives. Consequently, novel cheminformatics tools are required to highlight promiscuous binders (frequent hitters, FHs) and to allow the reliable profiling of compound classes, e.g., kinases inhibitors are highly wanted and much efforts is invested in their development.

Here, we present the efforts that have been undertaken to recognize and quantify chemical properties responsible of the biological promiscuous behavior of the compounds [1,2]. Also, we have developed robust predictors for profiling kinase inhibitors [3]. These tools have been used to analyze a collection of bioselective flavonoids and related compounds (ColBioS-FlavRC set) gathered from the medicinal chemistry literature [4]. Thus, several potentially promiscuous derivatives showing undesirable selectivity against kinases have been highlighted [3].

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-0422 and Romanian Academy, Institute of Chemistry Timișoara, project number 1.2.4/2017.

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NEW 1-(1*H*-4-ETHOXYCARBONYL-3-METHYL-PYRAZOL-5-YL)-AZO-2,7-DIHYDROXYNAPHTHALENE AND ITS CYCLIZED DERIVATIVES OF 8-HYDROXY-2-METHYL-NAPHTHO[2,1-*E*]PYRAZOLO[5,1-*C*][1,2,4]TRIAZINE SYNTHESIS AND CHARACTERIZATION BY 2D NMR AND UV-VIS SPECTROSCOPY

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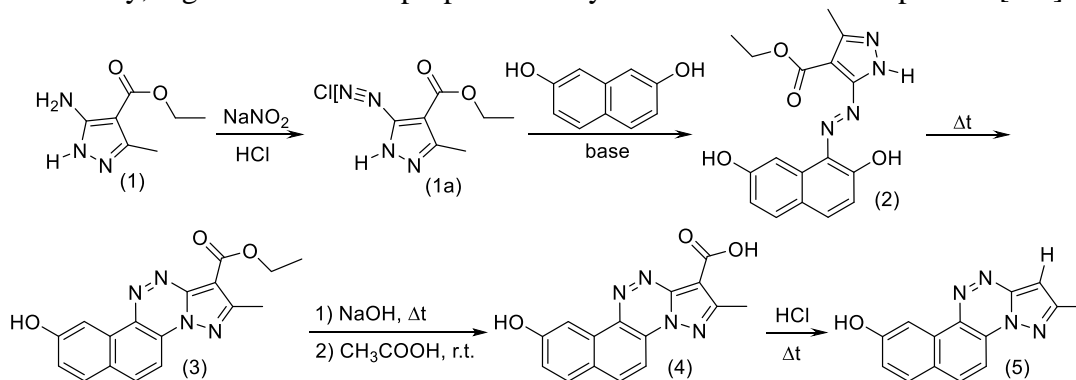
The coupling of the diazonium salt obtained from 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole (1) with 2,7-dihydroxynaphthalene in the presence of bases in organic solvent leads mainly to the coupling product 1-(1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-2,7-dihydroxynaphthalene (2).

The azo dye (2) cyclizes upon heating to 3-ethoxycarbonyl-8-hydroxy-2-methyl-naphtho[2,1-*e*]pyrazolo[5,1-*c*][1,2,4]triazine (3), which by alkaline hydrolysis yields 3-carboxy-8-hydroxy-2-methyl-naphtho[2,1-*e*]pyrazolo[5,1-*c*][1,2,4]triazine (4), and by hydrolysis in aqueous HCl at reflux gives 8-hydroxy-2-methyl-naphtho[2,1-*e*]pyrazolo[5,1-*c*][1,2,4]triazine (5).

¹H-¹⁵N correlation 2D NMR spectroscopy prove to be a valuable tool to characterize the above synthesized compounds and to evidence the closure of the azaheterocyclic rings.

All the synthesized compounds were characterized by m.p., TLC, IR, UV-VIS, 1D and 2D NMR spectroscopy. For the 8-hydroxy-naphtho[2,1-*e*]pyrazolo[5,1-*c*][1,2,4]triazines (3-5) obtained, their emission spectra were recorded.

Compounds in the pyrazolo-*as*-triazines class were synthesized and studied for their biological activity, together with their properties as dyes and fluorescent compounds [1-3].



Acknowledgements

This work was performed through the Partnerships in priority areas - PN II program, developed with the support of UEFISCDI, project no. PN-II-PT-PCCA-2013-4-0734.

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A NEW NMR SPECTROSCOPY APPROCH TO CHARACTERIZE DIFFERENT BITUMEN'S

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Bitumen is mixture of hydrocarbons and other substances, which can be obtained naturally or by distillation. The colloidal system depicts bitumen as a system divided into two principal class: malthenes and asphaltenes. The asphaltenes are present in the bitumen in a percentage of between 5% and 25% by weight and are composed of polynuclear aromatic molecules with attached alkyl chains. They are grouped into a structure composed of different molecular units organized in layers surrounded or immersed in the malthene fluid. The malthene fluid is composed of free saturated, mono- and diaromatics and resins which may be associated with the asphaltenes. For thermodynamic reasons, various units of these systems, asphaltenes sheets immersed in malthenes, lead to formation of macrostructures or “micelles”.

Recently, proton nuclear magnetic resonance (¹H NMR) spectroscopy has emerged as a very powerful and versatile tool for bitumen characterization [1]. It is possible with ¹H NMR spectrum to simultaneously detect and quantify a large number of components. Hence, the ¹H NMR spectrum analysis provides information on the bitumen chemical composition. Besides applying the ¹H NMR technique to bitumen as such, it is possible to separate the asphaltenes fraction from malthenes and analyze separately the two class of compounds, with the aim of standardizing bitumens from different sources to obtain a specific ligand with required characteristics.

Moreover, this research provides new insights into the chemical composition of the bitumen in order to correlate the chemical composition to its rheological properties.

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CHROMATOGRAPHIC ANALYSES OF ESSENTIAL OILS OBTAINED FROM DIFFERENT PLANT SPECIES CULTIVATED IN ROMANIA

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Essential oils (EOs) are formed in the secondary metabolism pathways of plants in the special cells or group of cells. Different compounds from essential oils are well-known antimicrobial agents that could be used to control food spoilage and food born pathogenic bacteria. They have been served as flavoring agents in food and beverages for long, and due to their versatile content of antimicrobial compounds, they exhibit properties suitable for food preservation.

In the present study we obtained essential oils by hydrodistillation from plants grown in western part of Romania: anise (*Pimpinella anisum*, *Apiaceae* family), cypress (*Cupressus sempervirens*, *Cupressaceae* family), thuja (*Thuja orientalis*, *Cupressaceae* family), and laurel (*Laurus nobilis*, *Lauraceae* family), in order to evaluate the chemical composition by gas chromatography-mass spectrometry (GC-MS) techniques. Results obtained indicate a significant amount of monoterpenes, oxygenated monoterpenes, sesquiterpenes, as well as aldehydes and ketones in all investigated EOs. The main constituents of anise essential oils identified are: L-fenchone, D-limonene, anethole, estragole, α -pinene; cypress essential oils: α -pinene and trans- β -ocimene; thuja essential oils: α -pinene, sabinen and cedrol; laurel essential oils: eucalyptol, α -terpinyl acetate, sabinen, linalool, and α -pinene. These results are in a good correlation with earlier reported studies.

Those essential oils could be used as alternatives to chemical preservatives in the food science development.

GRADUAL CHANGING OF THE PHYSICOCHEMICAL PROPERTIES OF HYBRID SILICA XEROGELS WITH THE VINYL SUBSTITUTION

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Organically modified silica (ORMOSIL) particles are organic–inorganic hybrid materials in which the organic moiety is chemically bonded to the silica matrix. The sol-gel process offers a proper way to produce ORMOSILs in desired forms and shapes with tailored porosity.

The present study deals with the synthesis and physicochemical characterization of the vinyl substituted silica gels using two different substituted precursors ($\text{CH}_2=\text{CH}-\text{Si}(\text{OX})_3$, X: O- CH_2 - CH_3 or OOC- CH_3) and varying amount of the substituents. Both the catalyst type and quantity has a strong effect on the properties of the resulted silica materials.

For a better understanding of the modification of the physicochemical properties with the substituents quantity, a series of complementary physicochemical characterization methods was employed. The texture, morphology, chemical composition and wettability of the hybrid materials were characterized by nitrogen adsorption, small angle neutron and X-ray scattering; electron microscopy (SEM and TEM); FT-IR and ²⁹Si-MAS-NMR spectroscopy; and contact angle measurements.

All the presented xerogels showed lamellar and porous structure with very high, up to 900 m²/g specific surfaces. The hydrophobicity and the degree of condensation were increasing with amount of added substituent

MANGANESE(III) PORPHYRIN A MULTIVALENT USEFUL MACROCYCLE FOR OPTICAL DETECTION OF H₂O₂ AND ASCORBIC ACID

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Novel approaches regarding the influence of H₂O₂ on photophysical behavior of Mn(III)-5,10,15,20-tetra(4-methyl-phenyl)porphyrin chloride (**MnTTPCl**) reveal its suitability as sensitive material in O₂ gas detection [1, 2]. This is due to the manganese porphyrin capacity to form all type of redox intermediates and highly reactive forms of oxo-Mn(IV) and Oxo-Mn(V). Increasing the concentration of the H₂O₂ solution produces the linear decrease of the absorption intensity of the Soret (V) band. The capacity of the manganese porphyrin to generate aggregates was investigated by AFM in different solvents THF and CHCl₃ before and after H₂O₂ introduction and put into evidence small triangular particles and platelets due to H aggregation and micro-structured ring geometries obtained by the side by side J-processes.

The same Mn-porphyrin was used for the development of new hybrids destined for the detection of ascorbic acid (AA) in the relevant range for medical investigations. **MnTTPCl**, spherical gold colloid (*n-Au*) and their hybrid (**MnTTPCl/n-Au**) were comparatively investigated by UV-vis spectroscopy in the presence of AA. The hybrid material (**MnTTPCl/n-Au**) has the best capacity to detect concentrations of ascorbic acid in the range of 2.6 x10⁻⁶ M to 4.38 x10⁻⁵M and is promising for sensor applications to improve medical test, because the amount of ascorbic acid (AA) contained in biological fluids can be used to determine the oxidative stress in human metabolism [3].

Acknowledgements

The authors from Institute of Chemistry Timisoara of Romanian Academy are kindly acknowledging the support from Program 3-Porphyrins/2017.

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NANOSTRUCTURAL INVESTIGATIONS ON CARBON NANOTUBES/EPOXY POLYMER COMPOSITES

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The first polymer nanocomposites using carbon nanotubes (CNT) as filler was reported in the early '90s. Since then a significant number of scientific reports have been published [1], [2]. While important insights have been achieved, there are still many unsolved questions concerning CNT based nanocomposites. CNTs have several characteristics, such as flexibility, low mass density, large aspect ratio that make them excellent for improving the mechanical, electrical, and thermal properties of polymers. Due to their reduced size and dimensionality, carbon nanotubes form complex networks of aggregates within the composite materials. The dispersion of nanotubes in host matrices is usually investigated by scanning electron microscopy (SEM) of fracture surfaces or transmission electron microscopy of thin slices from the composite. Although these methods provide local and partial information, consequently, provide little information about the internal structure of the aggregates themselves. In this work, the small angle neutron scattering (SANS) method has been used to characterize CNT nanocomposite material nanostructure providing information on the distribution patterns of the nanoscale filler materials representative for the whole volume of the sample. Many researchers have employed SANS to characterize composite structures to examine fractal behavior at specific length scales and to study changes in structure with respect to processing variables [3, 4]. Here, we have applied the method to characterize CNT reinforced epoxy composites revealing a power law behavior with decay rates indicating the surface fractal behavior of the nanotubes dispersed in the polymer matrix.

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THE USEFUL SIDE OF THE RESULTS OBTAINED BY NAA METHOD ON RAW PLANT MATERIALS FOR PHYTOPHARMACEUTICALS

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Medicinal crop plants represent the raw material for phytopharmaceutical forms, used as an alternative for conventional medicine. In many countries these raw materials are generally viewed only in terms of beneficial effects without considering the potentially toxic side. In this context in the present study, seven representative medicinal crop plants, such as, *coriander, dill, Echinacea, lavender, chamomile, mint and plantain*, cultivated in unpolluted areas in Romania, were analyzed concerning the elemental composition. One of our goals was to establish the expedience of a less often and more difficultly accessed analytical technique for plants, the neutron activation analysis (NAA). The principal advantage of the NAA is that does not require the digestion step of the plant matrix, step which generally can introduce errors in the obtained results for many of the usual analytical methods. We have validated the applied NAA procedure by statistical evaluation (ISO 13528 (2015)) of the results obtained for a known standard sample (IPE 205, of Tobacco leaf-mixture). So we have reached the conclusion that NAA, represents an accurate, specific and multielement analysis technique for medicinal plants. The results obtained for our analyzed medicinal plants provide a critical assessment of the beneficial, toxic, and potentially accumulating elements. Thus these plants may provide a useful contribution with essential macronutrients achieved by food intake. From the point of view of their contributions to intake and toxicity of metals for a person, the results remove concerns. Still, another conclusion is that a rigorous analytical control of the raw materials is advisable for some of the elements (among them aluminium) to avoid risks. In these circumstances the NAA method is differentiated as one with high potential to obtain internal plant standards in the phytopharmaceutical industry. These standards can be vegetable matrix, or plant specific, once achieved can be used a long period of time to verify and approve more routinely accessible analytical techniques, which in turn require a digestion stage. Hence a good evaluation of the element recovery by the used digestion technique can be verified and confirmed.

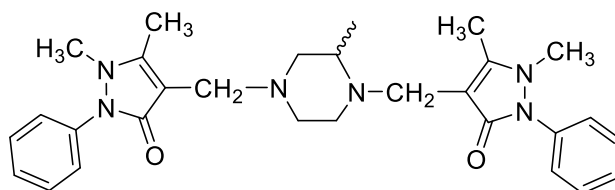
NOVEL ADAPTATION OF MANNICH REACTION IN THE SYNTHESIS OF NEW COMPOUNDS

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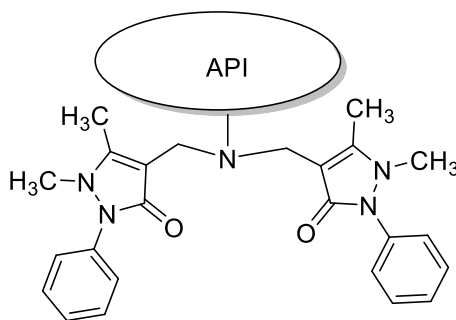
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Mannich bases obtained from antipyrine, such as N,N'-tetra(antipyrinyl-4-methyl)-1,2-diaminoethane (TAMEN) and N,N'-bis(antipyrinyl-4-methyl)-piperazine (BAMP) as well as their metal complexes have previously been reported and were found to be of potential pharmaceutical interest [1 - 5]. However, the Mannich reaction opens new opportunities to create novel, potentially bioactive compounds. We aimed at synthesizing chiral Mannich bases by the smallest modifications on the previously mentioned structures. Such modification could be the introduction of a methyl group on BAMP.



The introduction of an asymmetric center on BAMP

Either enantiomer selective synthesis or optical resolution of the so-obtained N,N'-bis(antipyrinyl-4-methyl)-2-methyl-piperazine results in an optically active Mannich base. The complexation behaviour and bioactivity of such compounds are to be investigated. Another goal of our research is the incorporation of existing Active Pharmaceutical Ingredients (APIs) in a Mannich base, preferably in an optically active form.



The incorporation of existing Active Pharmaceutical Ingredients (APIs) in a Mannich base

Acknowledgment

The authors are grateful for the financial support of the Hungarian Scientific Research Found (OTKA grant number K 104769 for E. Fogassy and K119202 for G. Keglevich).

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW SCHIFF BASE COPPER(II) COMPLEX

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The synthesis of polynuclear coordination complexes is of great interest for understanding the structural and chemical factors which determine the exchange coupling between paramagnetic centers [1]. Information on magneto-structural correlations in molecular systems is important for developing new functional molecular-based materials [2, 3].

In this work, we report the synthesis, structural characterization and thermal stability of a new copper(II) coordination complex $[\text{Cu}_2(\text{L})(\text{CH}_3\text{COO})_2]$ (**1**) with L = N,N'-bis[(2-hydroxy benzylideneamino)-propyl]-piperazine. (Fig. 1) Compound **1** was characterized by elemental analysis, FTIR, UV-Vis spectroscopy. Single-crystal X-ray diffraction analyses revealed that complex **1** consists of isolated units in which the two copper(II) ions are arranged symmetrically on opposite sides of the piperazine moiety. Each copper(II) ion is coordinated by two nitrogen and one oxygen atom of the hexadentate Schiff base ligand and two oxygen atoms from a bidentate acetate group. According to conductivity measurements, the copper(II) complex is not ionic. The infrared and electronic spectra are in agreement with the crystallographic data showing characteristic bands of the coordinated ligand and pentacoordinate copper(II) ions.

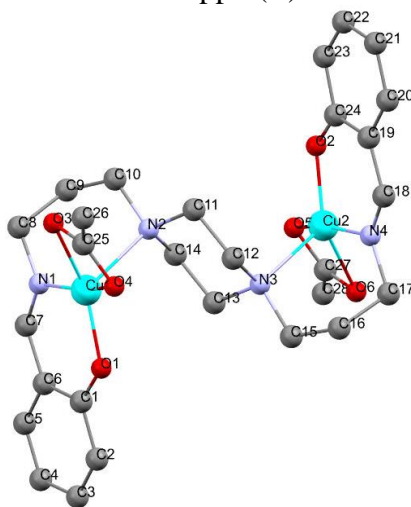


Fig. 1 Crystal structure of **1**

Acknowledgement

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RESEARCH ON OBTAINING ENOTANNINS FROM MOLDOVAN GRAPE SEEDS

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Research concerning the development of biologically active substances, preferably of natural origin, useful for protecting human health, is dictated by increasing the harmful factors impact on human body. A proper raw material for obtaining this category of substances is the grape seeds, which are a rich resource of condensed tannins with polyphenolic structure, called enotannins. They represent a complex mixture of catechol and epicatechol oligomers. The grape seeds constitute the most appropriate source of tannins in the Republic of Moldova. The enotannins content in the grape seeds depends on the grape variety as well as the geographical zones of grape cultivation [1]. The content of enotannins in studied grape seeds lies between 3.1 and 14.1 %.

As a raw material for obtaining enotannins, the grape seeds of the Black Fraga variety were chosen, because our previous research showed that just these seeds were characterized by a high content of enotannins. Initially the grape seeds contained various vegetal impurities. By multiple washings with tap water and subsequent decantation until a complete removal of impurities, the pure seeds were obtained, which then were dried in an oven at the temperature of 50°C till constant weight. The extraction of enotannins from grape seeds was carried out using the Soxhlet apparatus. Water and ethyl alcohol of 96% were used as solvents. The experiments were carried out both with the integrated and shredded seeds as well the seeds, from which the oil was previously extracted by hexane. The solutions of enotannins in water and ethyl alcohol of 96% were concentrated in a vacuum rotator at 65-70°C until the solution became rather viscous. The aqueous content was placed in the Petri dish and dried to constant weight in an oven at the temperature of 60°C.

Our subsequent research showed that the content of enotannins in the grape seeds of the Black Fraga variety soluble in ethyl alcohol of 96% was about 14%, while in those soluble in water was 2.6%.

Our investigations on the quality of enotannins soluble in alcohol of 96%, obtained from non- degreased seeds, have demonstrated that they contain large amounts of oil, up to 25%. Therefore, the enotannins can be extracted by ethyl alcohol with a concentration of 96% just after degreasing the seeds.

In order to improve the physical-chemical properties of enotannins, a new procedure for their solubilization in water has been developed in the Laboratory of Ecological Chemistry of the Institute of Chemistry of the Academy of Sciences of Moldova [2]. The solubility of enotannins is—changed by oxidation-reduction processes [3]. The obtained product, named Enoxil-A, has been tested on sugar beet seeds. Tests have shown that Enoxil-A increases the plant resistance toward various diseases caused by fungi and a number of bacteria.

Acknowledgment

The research is financially supported by Ukraine (ASŞIUI)-Moldova (ASM) bilateral project “Multi-component nanocomposites for stimulation growth of crops”, Nr. 17.80013.5007.02/Ua.

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THE STABILITY OF CALCAREOUS SUSPENSION IN PLUVIAL WATERS

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Rainfall intensity and aggressiveness have a major influence on the soil erosion. In order to develop efficient prevention and protection methods regarding the soil erosion, it is essential to comprehend the rainfall washing consequences in the presence of a series of mineral components (carbonates, sulfates, nitrates, nitrites, ammonium ion).

The continuous soil aridization in the Republic of Moldova results in changing dynamics of pluvial processes: rain becomes more intense, but shorter in time. Thus, the soil washing processes intensify, escalating erosion. Growing quantities of rainwater mineral components increases the aggressive capacity, further accelerating the degradation processes of soils (especially lands). Assessing the ability of soil erosion by rain and storage of the mineral particles in the suspended form for a long time allows elucidating the main effects of silting ponds and lakes and clogging the adjacent areas.

Using three models of rainwater and its diluted solutions, under laboratory conditions, the capacity of washing, hydration and maintaining of limestone particles in the suspended form has been investigated. The hydration of CaCO_3 particles, as one of the main causes of their storage in suspension for a long time, has been demonstrated by the pH-metric titration and quantitative determination of total calcium concentration in rainwater samples, containing the limestone particles.

The paper proposes a classification of rainwater, depending on the content of hydrogen carbonate, ammonium ion and anions of mineral acids. It has been found that after ten minutes of washing, the most aggressive is the “acidic” rainwater, in which the anions of strong acids prevail, along with HCO_3^- . By decreasing the concentrations of these components, the aggressiveness capacity of “acidic” rainwater becomes lower. The “moderate” rainwater (in which HCO_3^- anions prevail in comparison with the anions of strong acids) has a lower aggressiveness, decreasing much more slowly in comparison with “acidic” water. A slightly less aggressiveness, compared to that of “acid” water, has the “ammonia” rainwater, in which the NH_4^+ ion concentration exceeds the concentrations of anions of strong acids. Due to high concentrations of NH_4^+ , the accumulation of HCO_3^- takes place, by capturing the carbon dioxide in rainwater [1,2]. The dilution of the “ammonia” rainwater decreases more slowly the rainwater capacity of hydration, dissolving and keeping the suspended particles of CaCO_3 . The calcium carbonate particles are kept suspended for a longer time in the “ammonia” rainwater. At the same time, the suspensions are more unstable in the “acidic” rainwater, especially in its dilute solutions.

Therefore, the aggressiveness of “acidic” rainwater increases with increasing amounts of mineral components. At the same time, the strongest washing effect exhibits the rainwater with a predominant content of ammonia in the series of investigated main mineral components.

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FUNDAMENTAL INSIGHT ON DEVELOPMENT OF LOW DIELECTRIC CONSTANT QUATERNIZED POLYSULFONE/CELLULOSE ACETATE PHTHALATE BLENDS: ORIGIN OF DIELECTRIC RESPONSE

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Driven by growing demands of miniaturization, increased functionality, high performance in a wide variety of applications from biomedicine to electronics, new solutions concerning the polysulfones integration in a blend have been topics recently. One way to compensate the shortcomings of a conductive polymer is to use it together with another polymer, combining the positive qualities of both materials. In this context, new blend system of quaternized polysulfone (PSFQ)/cellulose acetate phthalate (CAP) for advanced applications was investigated, as to its electronic properties. Therefore, it is assumed that the quaternization effect and choosing of an appropriate additive, CAP, significantly improve the ionic conductivity and also could optimize dielectric properties required by ionic exchange membrane. In view of the above-mentioned, the dielectric spectra behavior over wide frequency (1 Hz-10⁶ Hz) and temperature ranges (-120°C and +120°C), respectively, was investigated according to chemical and micro-structural aspects.

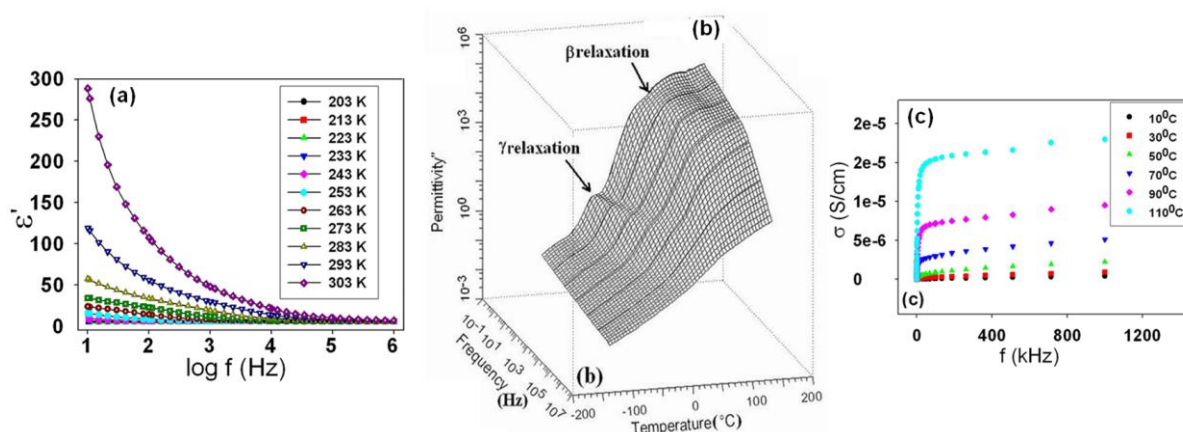


Figure 1. Dielectric response for 70/30 wt./wt. composition of PSFQ/CAP blend: (a) Frequency dependent dielectric constant at different temperatures; (b) Dependence of dielectric loss of frequency and temperature; (c) Electrical conductivity *versus* frequency at different temperatures

The dielectric constant takes low values for the studied blend, being dependent on the chemical characteristics of the blend compounds and also of free volume, and, consequently, with packing of the polymer chains and polarizable groups per volume units. The dielectric loss behavior exhibits two types of relaxation, γ and β , being due to temperatures at which the two processes occur in the case of pure components. The results obtained from conduction studies showed that the conduction mechanism in the PSFQ/CAP blend was based on the electronic hopping process, which can be explained in terms of band conduction mechanisms, through band gap representation. The study realized on new blend of PSFQ/CAP provides an insight into future approaches in industrial applications, due to the conductivity and implicitly, electron interactions which represent fundamental features to enhance their electrical performance.

HYBRID ENCAPSULATED ZINC COMPLEXES TOWARD ANTIMICROBIAL NANOTECHNOLOGY APPLICATIONS

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Zinc (Zn(II)) is a component essential to microorganisms and higher organisms. Moreover, Zn(II) carries important structural and chemical properties, which allow it to play a crucial role in a range of cellular reactions [1]. The latter reactions include metabolism, immune system, formation of red blood cells, organ, muscle and bone function, cell membrane stability, cell growth, division, differentiation and genetics [2]. Beyond the aforementioned usual function(s), Zn(II) has also been shown to possess antimicrobial properties [3-5]. Moreover, Zn(II) has been widely used for the treatment of a number of disorders including acute diarrhoea and its prophylaxis [6]. Therefore, Zn(II) deserves further scientific attention. In an effort to create improved Zn(II) nano-agents for advancement toward an antibacterial technology, acid-catalyzed silica gel matrices were synthesized. They were, subsequently, compared and evaluated as to their suitability as potential host-carrier materials for the controlled release of zinc sulphate and a newly-synthesized Zn(II) complex with a Schiff base. In addition, the physicochemical properties of these materials were investigated by different-complementary characterization techniques, aiming at unravelling the nature of Zn(II) species and their interaction(s) with the siloxane matrix. Concomitantly, the antimicrobial properties of the novel hybrid materials were tested against Gram-positive *S. aureus*, *B. subtilis*, *B. cereus* and negative *E. coli*, *P. aeruginosa*, *X. campestris* bacteria, using modified agar diffusion techniques. Overall, for the first time, the encapsulation and homogeneous dispersion of water-soluble Zn(II) complex species into sol-gel processed silica xerogels was successfully pursued targeting novel, well-defined hybrid organic-inorganic pharmaceutical nanomaterials. The physicochemical evaluation of the Zn(II) complex silica-nanoparticles was optimized and the nanomaterial configuration was linked to the delivery of the encapsulated zinc load. Afterwards, the antibacterial assessment of these novel hybrid nanoparticles was pursued compared to the common commercial antibiotic used widely, i.e. ampicillin. Specifically, Zn(II) sulfate nanoparticles showed greater antimicrobial activity than Zn(II)-Schiff nanoparticles. The Zn(II)-Schiff complex exhibited a better antimicrobial profile than zinc sulfate and the Schiff base applied alone. To this end, sol-gel encapsulation of binary zinc compounds in surface-modified silica nanoparticles projects the structure-activity correlations in hybrid materials, targeting zinc antibacterial use, and sets the basis for further study in the antibacterial nanotechnology field.

Acknowledgements

The authors would like to acknowledge IKY Financial Support of Excellence for Postdoctoral Researchers in Greece - NSRF 1st Cycle for 2014-2020.

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BETA-CYCLODEXTRIN CONJUGATED MAGNETIC IRON OXIDE NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

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In this study were synthesized iron oxides magnetic nanoparticles using the combustion method [1]. An aqueous solution containing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Roth) and combustible ($\text{C}_6\text{H}_{12}\text{O}_6$ (Riedel de Haën)) was heated to 400°C in the presence of air, in a round bottom flask. As the water evaporates, a smoldering combustion reaction occurs, leading to the formation of a black powder which consists of nanocrystalline $\gamma\text{-Fe}_2\text{O}_3$. The resulted black powder, impurified with carbon resulted from the combustion method, was hand crushed, washed with warm distilled water and dried at 80°C . An amount of the synthesized sample was sonicated for several hours and then the particles were coated with a double layer of oleic acid (Merck, 65-88%). The oleic acid double layer coated nanoparticles were dispersed in 25 mL of aqueous solution of β -cyclodextrin with a concentration of 18 mg/L (Oxford Lab. Chem.), leading to a stable colloidal suspension. The resulted $\beta\text{-CD-}\gamma\text{-Fe}_2\text{O}_3$ colloidal suspension has an iron oxide mass equally with 125 mg in 1 mL colloidal suspension.

Various concentrations of $\beta\text{-CD-}\gamma\text{-Fe}_2\text{O}_3$ colloidal suspension (5, 10, 25 and 50 $\mu\text{g/ml}$) were tested on two cell lines, A375 (human melanoma) and HaCaT (human keratinocytes). The effect was evaluated after 48h incubation with the probes. The colloidal suspensions increased A375 cells viability at all tested concentration, while on HaCaT cell line elicited at 10, 25 and 50 $\mu\text{g/ml}$ a decrease on cell viability. Our preliminary data suggest that 48h incubation stimulated the viability of tumoral cells, while showing at higher doses to be slightly cytotoxic for the keratinocytes. Further studies are required in order to elucidate the underlying mechanism.

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OCTANUCLEAR IRON(III) ISOBUTYRATE CAGE BASED ON TRIETHANOLAMINE LIGAND

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Abstract

A new octanuclear iron(III) isobutyrate cluster $[\text{Fe}_8\text{O}_3(\text{is})_6(\text{O}_2\text{CH})_3(\text{tea})(\text{teaH})_3] \cdot \text{teaH}_3 \cdot (\text{CH}_3)_2\text{CO}$ (**1**) (where His = isobutyric acid; teaH₃ = triethanolamine) has been prepared by the interaction of smaller trinuclear isobutyrate cluster $[\text{Fe}_3\text{O}(\text{is})_6(\text{H}_2\text{O})_3](\text{NO}_3) \cdot 2(\text{CH}_3\text{CN}) \cdot 2(\text{H}_2\text{O})$ with s-triazine and triethanolamine. Single-crystal X-ray analysis revealed that **1** crystallizes in the triclinic space group *P*-1 and comprises octanuclear $[\text{Fe}_8\text{O}_3(\text{is})_6(\text{O}_2\text{CH})_3(\text{tea})(\text{teaH})_3]$ clusters and solvate teaH₃ and acetone molecules. The iron centers in the {Fe₈} core are bridged by three μ₄-oxo atoms, and peripheral ligation of the core is provided by six isobutyrate and four triethanolamine ligands. Formate group is completed the coordination sphere of three metal atoms. Cluster **1** has been also characterized by elemental, infrared spectroscopy and thermogravimetric analyses.

Keywords: iron cluster, carboxylates, aminopolyalcohol ligand, structure.

Introduction

The design and investigation of polynuclear iron compounds with oxygen ligation continue to be of considerable interest due to their relevance to biological systems [1] and their potential serve as models for studying complex biological processes in nature. For example, a number of different polynuclear Fe oxide complexes found in non-heme metalloproteins and metalloenzymes [2]. Many metalloproteins play an important physiological role. Typical metalloproteins are proteins containing non-heme iron-transferrin, ferritin, hemosiderin, which are important in the metabolism of iron in the body. Thus, these compounds are being synthesized and examined in order to get information into the biomineralization process involved in the formation of metal core of the iron-storage protein ferritin [3]. Besides, a paramagnetic nature of Fe metals in polynuclear compounds affords interesting magnetic properties such as high-spin ground state or single molecule magnet behavior (SMM) [4, 5]. A large number of Fe-containing compounds have been synthesized and investigated over last decades [6-9]. The contribution to this area has been made by S. Baca and co-workers and consists in the preparation of new oxo/hydroxo bridged carboxylate clusters with various nuclearities {Fe₄} [10], {Fe₇} [11], {Fe₈} [12], {Fe₁₁} [13], {Fe₁₄} [14] and {Fe₁₆} [13]. The clusters with higher nuclearities {Fe₁₇} and {Fe₂₂} have been published by R. Winpenny [15] and G. Christou [16], respectively.

For the rational preparation of the polynuclear iron compounds several approaches have been employed [17-19]. One of these approaches includes the employment of the smaller clusters in order to obtain polynuclear Fe cages with higher nuclearity. Low nuclearity clusters such as {Fe₂O} [20, 21], {Fe₃O} [22-24] and {Fe₄O₂} [25, 26] are great starting materials to produce large clusters, they can be rearrange and bind to the larger systems. Herein is reported the reaction of trinuclear $[\text{Fe}_3\text{O}(\text{is})_6(\text{H}_2\text{O})_3](\text{NO}_3) \cdot 2(\text{CH}_3\text{CN}) \cdot 2(\text{H}_2\text{O})$ cluster with triethanolamine affording polynuclear octanuclear $[\text{Fe}_8\text{O}_3(\text{is})_6(\text{O}_2\text{CH})_3(\text{tea})(\text{teaH})_3] \cdot \text{teaH}_3 \cdot (\text{acetone})$ (**1**) isobutyrate cluster. Triethanolamine is commonly found in a number of cosmetic products and used in several different medical applications. In cosmetic uses, triethanolamine is used to raise the pH of certain mixtures, as well as acting as an emulsifier [27]. Furthermore, the effect of triethanolamine on an anthralin-induced inflammation was shown [28]. The performed experiment, where patients were treated with short-contact anthralin followed by 10% triethanolamine application, revealed that triethanolamine successfully inhibited anthralin-induced inflammation. The first octanuclear iron(III) compound

possessing similar structure with triethanolamine was reported by G. Christou [29], since than some structural analogues {Fe₈} have been reported by X. Murray [30] and A. Powell [31].

Experimental

Materials and physical measurements

All chemicals and solvents were obtained from the commercial sources and were used as received without further purification. All reactions were carried out under aerobic conditions. The precursor μ_3 -oxo trinuclear Fe(III) isobutyrate [Fe₃O(is)₆(H₂O)₃](NO₃)₂·2(CH₃CN)·2(H₂O) was prepared according to the previously published procedure [12]. Infrared spectrum for **1** was recorded on a Perkin-Elmer Spectrum One spectrometer using KBr disc in the region 4000–400 cm⁻¹. Elemental analysis of **1** for carbon, hydrogen and nitrogen was performed using an Elementar Vario El analyzer. TGA/DTA measurements were carried out with a Mettler Toledo TGA/SDTA 851 under a stream of dry N₂ (60 mL min⁻¹) in the temperature range from 25 to 600°C at a heating rate of 10 K min⁻¹.

X-ray crystallography. Diffraction dataset for compound **1** was collected on a Bruker APEX II diffractometer equipped with graphite-monochromatized Mo-K α radiation. The summary of the crystallographic parameters and structure refinement details of **1** are listed in Table 1. The structure was solved by direct methods and refined by full-matrix least squares on weighted F^2 values for all reflections using the SHELX suite of programs [32]. All non-hydrogen atoms in cluster **1** were refined with anisotropic displacement parameters, except the minor position of disordered O- and C-type atoms. Hydrogen atoms were placed in fixed, idealized positions and refined as rigidly bonded to the corresponding atom. Some ethanol groups of teaH₃ ligands in **1** were found to be disordered; application of restraints provided reasonable geometrical parameters and thermal displacement coefficients.

*Synthesis of [Fe₈O₃(is)₆(O₂CH)₃(tea)(teaH)₃]·teaH₃·(CH₃)₂CO (**1**)*

To the solution of [Fe₃O(is)₆(H₂O)₃](NO₃)₂·2(CH₃CN)·2(H₂O) (0.212 g, 0.24 mmol) in 5 mL acetonitrile were added s-triazine (0.058 g, 0.71 mmol) and teaH₃ (0.05 mL, 0.37 mmol). Resulted solution was stirred at room temperature during 3 hours and left for slowly evaporation. A month later 2 mL dichloromethane was added. In three weeks the obtained precipitate was dissolved in the mixture of acetone and acetonitrile (2.5:2.5 mL). The obtained red-brown crystals of **1** suitable for X-ray analysis were filtered off, washed with acetonitrile and acetone, and dried in air. (Yield: 13.2%). Elemental analysis for C₆₀H₁₁₈Fe₈N₅O₃₇: C, 36.98; H, 6.10; N, 3.59%. Found: C, 35.25; 35.24; H, 5.91; 6.31; N, 3.82; 3.74%. IR data (KBr pellet, cm⁻¹): 3355 (br), 3150 (w), 2966 (m), 2928 (sh), 2870 (m), 1629 (sh), 1576 (vs), 1471 (m), 1429 (m), 1377 (m), 1397 (m), 1094 (m), 1030(m), 1003 (w), 911 (m), 784 (w), 582 (m), 516 (m).

Results and Discussion

*Synthesis of **1***

An octanuclear cluster **1** was prepared using soft conditions: the solution of the μ_3 -oxo trinuclear iron(III) isobutyrate in acetonitrile solution with s-triazine and triethanolamine was stirred at room temperature, followed by the addition of dichloromethane. The obtained precipitate was recrystallized from the mixture of solvents (acetone and acetonitrile), giving red-brown crystals of [Fe₈O₃(is)₆(O₂CH)₃(tea)(teaH)₃]·teaH₃·(CH₃)₂CO (**1**). The additional amount of **1** was extracted with acetone and acetonitrile several times from the precipitate. The presence of s-triazine in the reaction is a prerequisite for the preparation of crystals of **1**.

Infrared spectroscopy

The IR spectrum of **1** displays the O–H stretching vibration at 3355 cm⁻¹, which corresponds to ethanol groups in teaH₃. Strong and broad bands of the coordinated asymmetric and symmetric carboxylate groups are observed at 1576 cm⁻¹ and 1429 cm⁻¹, respectively. The C–H

asymmetric and symmetric stretching vibrations of isobutyric groups demonstrate peaks in the range of 2966–2870 cm^{-1} , while the asymmetric and symmetric bending vibrations for these methyl groups produce a strong single band in the region of 1471 cm^{-1} and a doublet at 1377 cm^{-1} , respectively. The absorption peak found at 1629 cm^{-1} corresponds to C=O stretching vibrations of solvate acetone molecule in **1**.

Thermogravimetric analysis

The TGA data shows that the first weight loss of cluster **1** (Figure 1) begins at 40 °C and lasts up to 217 °C, corresponding to removal of solvent acetone and triethanolamine molecules (found: 10.05 %; calcd: 10.55%). The second step is accompanied by an endothermic peak at 236°C that indicates the loss of three formate and three isobutyrate groups (found: 20.13%; calcd: 20.35%). The next two consecutive steps in the range 300-410°C of TGA curve show an exothermic peak at 317°C that indicates the loss of remaining carboxylate ligands and all coordinated triethanolamine groups (found: 41.43%; calcd: 43.5%) with residual weight of 32.39 % suggests the final product of iron oxides (calcd: 35.7%).

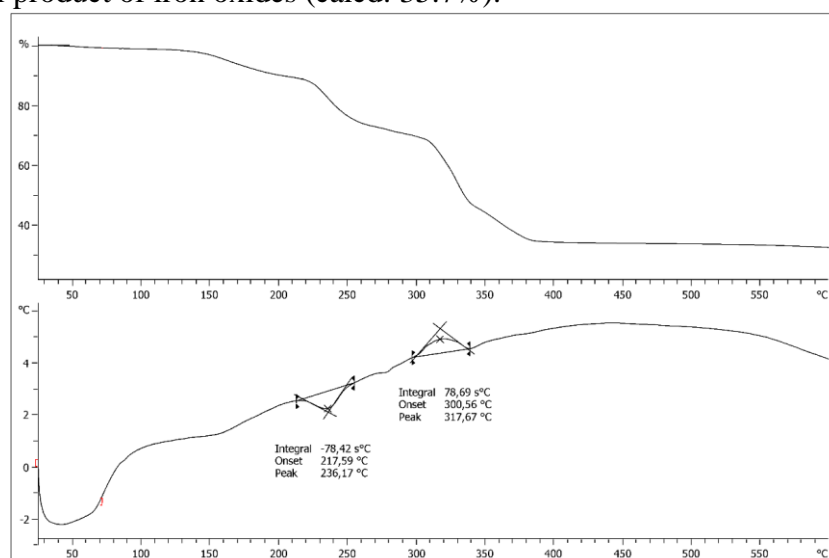


Fig. 1. The thermogravimetric spectrum of **1**.

Structure of **1**

Single-crystal X-ray analysis revealed that **1** crystallizes in the triclinic space group *P*-1 and contains an octanuclear $[\text{Fe}_8\text{O}_3(\text{is})_6(\text{O}_2\text{CH})_3(\text{tea})(\text{teaH})_3]$ cluster and solvate teaH_3 and acetone molecules. The $\{\text{Fe}_8\}$ core comprises two almost equilateral and parallel Fe_3 triangles ($\text{Fe}\dots\text{Fe}$ separations are 5.058(1), 5.083(1), 5.127(1) Å and 5.170(1), 5.225(1), 5.299(1) Å, dihedral angle between the planes of triangles is 1.91°), giving the appearance of a six-pointed star (Figure 2). Each triangle is capped by fourth iron atom, which displaces from the plane of triangle at 0.465 and 0.791 Å and situated at the distances 2.968-2.984 and 3.108-3.130 Å, respectively, from the iron atoms in the vertexes of triangle. The distance of 2.947(1) Å between these capped iron atoms is the shortest $\text{Fe}\dots\text{Fe}$ distance in the cluster. Selected bond distances are given in Table 2. The Fe(III) centers are bridged by three μ_4 -oxo, six isobutyrate and four triethanolamine ligands: three doubly deprotonated (teaH^{2-}) that coordinate in $\eta^2:\eta^2:\eta^1:\mu_3$ -bonding mode and one triply deprotonated (tea^{3-}) coordinating in $\eta^2:\eta^2:\eta^2:\eta^1:\mu_4$ -bonding mode. Three monodentate formate groups in **1** complete the coordination spheres of three Fe(III) atoms from one triangle. The replacement of these monodentate ligands can permit further linkage to form higher dimensionality clusters and cluster-based polymeric networks.

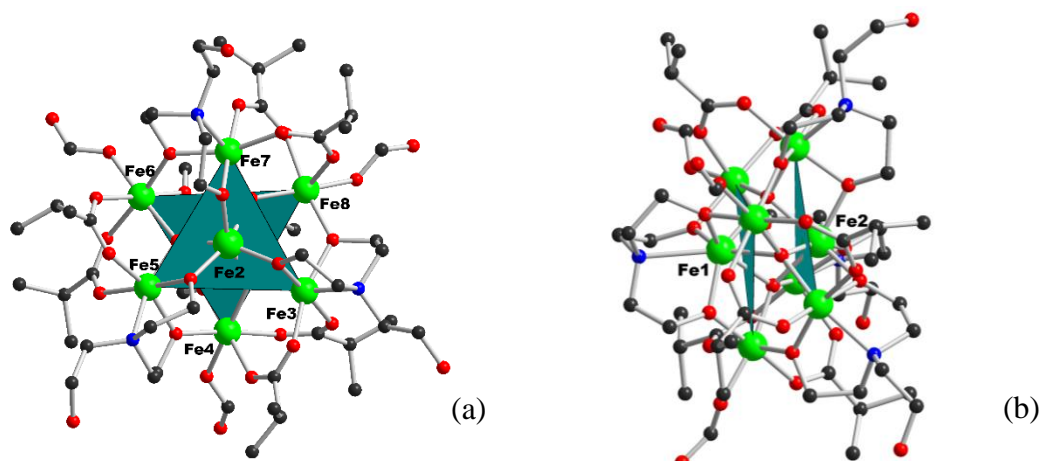


Fig. 2. Molecular structure of [Fe₈O₃(is)₆(O₂CH)₃(tea)(teaH)₃ (**1**): top view (a) and side view (b). Two triangles are highlighted in aquamarine color. Colour definition: Fe, bright green spheres; N, blue; O, red and C, black balls. Hydrogen atoms and solvent molecules were omitted for clarity.

All Fe(III) centers, except one (Fe1) are hexa-coordinated, displaying a distorted octahedral coordination sphere. The Fe(III) atoms in cluster have different coordination environments: Fe4, Fe6 and Fe8 atoms from one of above mentioned triangle have an O₆ donor set being coordinated by a μ_4 -O²⁻ atom, three O atoms from two bridging isobutyrate and one monodentate formate group, and two O atoms from one doubly deprotonated (teaH²⁻) and one triply deprotonated (tea³⁻) ligands. Each of the Fe3, Fe5 and Fe7 atoms from another triangle have an O₅N donor set arising from one μ_4 -O²⁻ atom, two O atoms from two bridging isobutyrate, and two O atoms and one N atom from one teaH²⁻. One of the central iron atoms (Fe1) is coordinated by three μ_4 -O²⁻ atoms, three alkoxide O atoms and one N atom from one tea³⁻, while another central iron atom (Fe2) is coordinated *via* three μ_4 -O²⁻ atoms, three alkoxide O atoms from three teaH²⁻. The Fe–O bond distances are in the range of 1.931(2)–2.477(2) Å (Fe– μ_4 -O: 1.940(2)–2.232(2) Å, Fe–O_{carb}: 1.985(2)–2.086(2) Å, and Fe–O_{tea}: 1.931(2)–1.993(2) Å. The Fe–N distances range from 2.243(2) to 2.267(2) Å for teaH²⁻ ligands and equals 2.477(2) Å for teaH³⁻. Packing diagram of **1** is shown in Figure 3.

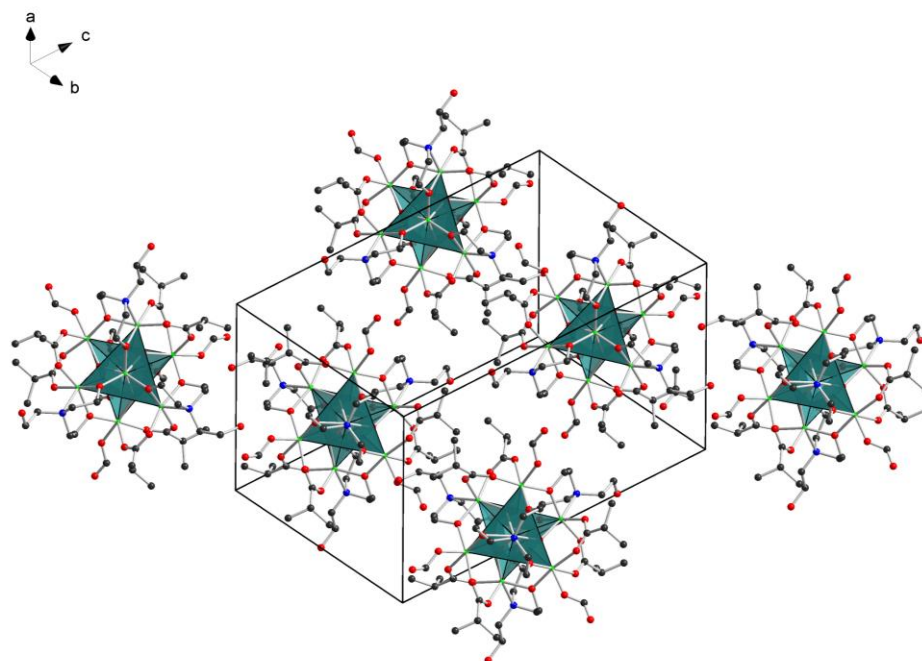


Fig. 3. View of the packing in **1**. Hydrogen atoms, solvate teaH₃ and acetone molecules are omitted for clarity.

Table 1. The main crystallographic data of **1**.

1	
Empirical formula	C ₆₀ H ₁₁₈ Fe ₈ N ₅ O ₃₇
Temperature (K)	123
<i>Mr</i> /g mol ⁻¹	1948.32
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	14.5428(9)
<i>b</i> (Å)	14.6907(9)
<i>c</i> (Å)	20.5757(13)
α (°)	73.1080(10)
β (°)	76.6520(10)
γ (°)	88.6330(10)
<i>Z</i>	2
<i>V</i> (Å ³)	4088.17
μ (mm ⁻¹)	1.468
<i>F</i> (000)	2018
<i>D</i> (calc) [g/cm ³]	1.575
reflns collected/reflns unique	39608/18580 [<i>R</i> _{int} = 0.031]
Reflections[<i>I</i> >2 σ (<i>I</i>)]	14252
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0399, 0.1230

Table 2. Selected bond distances (Å) for **1**.

Fe1–O1	2.211(2)	Fe3–O26	1.964(2)	Fe6–O15	2.066(2)
Fe1–O2	2.281(2)	Fe3–N	2.243(2)	Fe6–O17	2.037(2)
Fe1–O3	2.232(2)	Fe4–O	1.967(2)	Fe6–O19	1.985(2)
Fe1–O4	1.945(2)	Fe4–O	1.965(2)	Fe6–O30	1.995(2)
Fe1–O5	1.947(2)	Fe4–O	2.086(2)	Fe7–O3	1.948(2)
Fe1–O6	1.931(2)	Fe4–O	2.041(2)	Fe7–O18	1.980(2)
Fe1–N1	2.477(2)	Fe4–O	1.970(2)	Fe7–O19	1.980(2)
Fe2–O1	2.082(2)	Fe4–O28	2.023(2)	Fe7–O21	2.047(2)
Fe2–O2	2.054(2)	Fe5–O2	1.940(2)	Fe7–O23	1.998(3)
Fe2–O3	2.060(2)	Fe5–O11	1.993(2)	Fe7–N4	2.267(2)
Fe2–O12	1.939(2)	Fe5–O12	1.979(2)	Fe8–O3	1.973(2)
Fe2–O18	1.960(2)	Fe5–O14	1.985(2)	Fe8–O4	1.965(2)
Fe2–O26	1.931(2)	Fe5–O16	2.046(2)	Fe8–O22	2.040(2)
Fe3–O1	1.952(2)	Fe5–N3	2.248(3)	Fe8–O24	2.069(3)
Fe3–O7	1.995(2)	Fe6–O2	1.967(2)	Fe8–O25	1.979(2)
Fe3–O9	2.033(3)	Fe6–O6	1.963(2)	Fe8–O32	2.010(2)
Fe3–O25	1.982(2)				

Conclusions

In summary, an octanuclear Fe(III) isobutyrate cluster with triethanolamine ligand [Fe₈O₃(is)₆(O₂CH)₃(tea)(teaH)₃·teaH₃·(CH₃)₂CO (**1**) has been synthesized and structurally characterized by a single crystal X-ray method. Cluster **1** consists of {Fe₈} core in which iron atoms have different O₆, O₅N, or O₆N coordination surrounding and triethanolamine ligand performs different structural functions. Characteristic peaks in the IR spectrum confirms the presence of coordinating organic ligands in the structure. Thermogravimetric analysis showed that cluster **1** loses its weight at 40 °C and completely decomposes reaching a temperature of 410°C.

Acknowledgments

This work is supported by **SCOPES IZ73Z0_152404/1** and **CSSDT 16.00353.50.05A**. Author thanks Dr. Arkady Ellern from the Iowa State University (Chemistry Department) for performing X-ray measurements.

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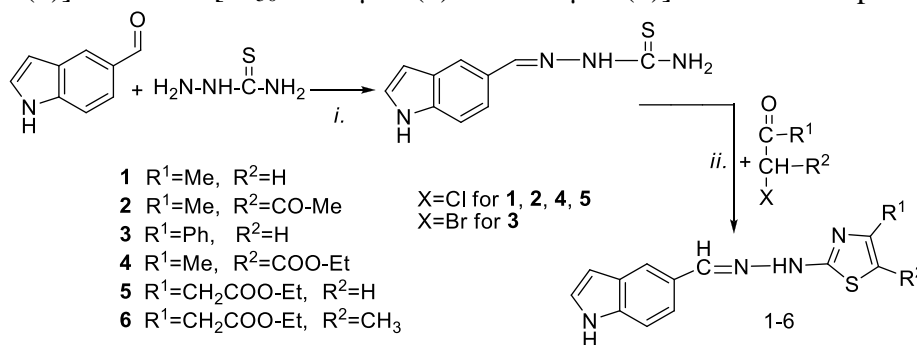
ANTI-PROLIFERATIVE ACTIVITY OF NOVEL 2-(2-((1H-INDOL-5YL) METHYLENE)-HYDRAZINYL)-THIAZOLE DERIVATIVES

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Newly synthesized 2-(2-((1H-indol-5yl)methylene)-hydrazinyl)-thiazole derivatives were evaluated for their in vitro cytotoxicity on two carcinoma cell lines A2780 and HeLa. Significant antiproliferative activity for 2-(2-((1H-indol-5-yl)methylene)hydrazinyl)-4-methylthiazole (**1**) and 2-(2-((1H-indol-5-yl)methylene)hydrazinyl)-4-phenylthiazole (**3**), on both A2780 [IC₅₀: 11.1 μM (**1**), and 12.5 μM (**3**)] and HeLa [IC₅₀: 22.4 μM (**1**) and 14.5 μM (**3**)] cell lines is reported.



i: EtOH, H₂O, v/v, 1/0.3, 3h, reflux; *ii*: EtOH/Acetone/AcOH v/v/v, 1/0.5/0.1, 24h, rt.

Their antioxidant potential was evaluated by spectrophotometric method, using DPPH radical or Fe(TPTZ)³⁺ complex, and EPR spectroscopy, therefore the compounds **1** and **3** showed remarkably antioxidant activity simultaneously with a cytotoxic effect on A2780 and HeLa cell lines. Furthermore, based on theoretical quantum chemical calculation the present study analyzed the chemoselectivity of the hydrogen extraction from the indolyl-hydrazinyl-thiazoles in reaction with free radicals [1,2].

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HYBRID BINARY Bi(III) COMPLEXES TOWARDS ANTIBACTERIAL APPLICATIONS

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The firm long lasting clinical applications of bismuth complexes have been widely reported for the therapy of a range of pathological conditions, including microbial infections, cancer, syphilis, diarrhea, gastritis and colitis [1-4]. These metal complexes have gained clinical interest due to their highest effectiveness and lowest toxicity in the individual affected compared to other metals [5]. Therefore, there is an increasing interest in making novel bismuth agents, which may be of importance in improving bismuth cure against a variety of diseases. Already, various bismuth containing antibacterial drugs, such as ranitidine-bismuth citrate, are already clinically available [6].

In the current investigation, metal ligands such as 1,10-phenanthroline (phen) and glycolic acid (Gly) were used to synthesize novel binary complexes of Bi(III). In brief, phen is a strong field bidentate ligand that forms very stable chelates with many first row transition metals that have been shown to disturb the function of a wide variety biological systems [7]. In addition, phen has long been known to possess antibacterial, antifungal and antiviral behaviour [8-10], and its metal complexes have been applied as topical antimicrobials [11,12]. Gly is a highly soluble in water monomer, which is widely used in organic synthesis, in a range of reactions, including oxidation-reduction, esterification and long chain polymerization. Furthermore, Gly possesses excellent metal chelator characteristics, reversibly allowing metal release, while its antimicrobial properties have been demonstrated in the past.

Herein, both ligands phen and Gly were employed for the synthesis of Bi(III) binary systems. Moreover, physicochemical characterization of these novel hybrid binary Bi(III)-organic compounds was carefully conducted in aqueous media. Last, but not least, their antimicrobial activity against a range of microorganisms was also put under scrutiny, using modified agar diffusion methods. In total, six microorganisms including Gram- positive *S. aureus*, *B. subtilis*, *B. cereus* and negative *E. coli*, *P. aeruginosa*, *X. campestris* bacteria were employed.

As a result, the Bi(III)-glycolic acid and Bi(III)-phenanthroline binary systems were stable throughout a wide pH-range, coupled with their emerging solid-state and solution properties. Furthermore, the new Bi(III) monomer and polymer Bi(III) complexes performed improved antimicrobial ability, while being more active than bismuth nitrate applied alone. Based on that, the current scientific work lays the groundwork for further investigations on the synthesis of more effective Bi(III) agents, with better antimicrobial characteristics, to be used in the therapy of a range of pathological conditions.

Acknowledgements

The authors would like to acknowledge IKY Financial Support of Excellence for Postdoctoral Researchers in Greece - NSRF 1st Cycle for 2014-2020.

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APPLICATION OF STYRENE-DIVINYLBENZENE COPOLYMERS FUNCTIONALIZED WITH PHOSPHONATE GROUPS AS ADSORBENTS FOR THE REMOVAL OF PHENOL FROM SYNTHETIC WASTEWATER

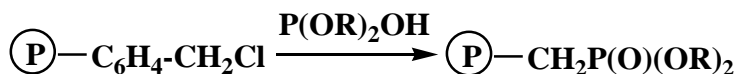
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Environmental protection and maintaining ecological balance are important topics nowadays for preserving the environment and quality of life [1,2]. Phenols are persistent pollutants and cause a lot of damage to the environment [1,3,4].

In this paper, we describe some results obtained from a preliminary study about the removal of phenol with phosphonate groups grafted on a styrene-divinylbenzene copolymer. The concentration of phenol in synthetic wastewater was analyzed by UV analysis performed on a Shimadzu UV-VIS Spectrophotometer with the wavelength at 270 nm. The variation of the residual concentration of phenol solutions and adsorption capacity of phosphonate groups grafted on styrene-7%divinylbenzene copolymer (Scheme 1) over time were studied.



Scheme 1. where: R= iso-C₈H₁₇ (1), -C₂H₅C₆H₁₂ (2), -C₆H₅ (3), -CH₂C₆H₅ (4).

A preliminary study of the removal of phenol showed that the samples tested had an adsorption capacity at 293 K. The adsorption capacity values are about 0.200 mg phenol / g copolymer.

The rate of the adsorption process at the beginning is very rapid for all the samples tested. After 4 hours, approximately 80% of the quantity of phenol is adsorbed. The adsorption capacity depends on the nature of the structure of the phosphonate groups grafted on the copolymer. From the samples tested it can be seen that the adsorption capacity is related to the radical of the phosphonate group in the following order R, -C₆H₅ < -CH₂C₆H₅ < -iso-C₈H₁₇ < -C₂H₅C₆H₁₂. It would appear that if the aliphatic radical is present in the phosphonate group, the adsorption capacity is greater. It can be observed that for 2-ethylhexylfosfonat grafted pe copolymer the adsorption capacity was best, 0.220 mmol/g copolymer after 24 hours of contact.

The phosphonate polymers are good effective in the removal of the phenol from wastewater.

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ANODIC OXIDATION OF 4-FLUOROBENZYLIDENEHYDRAZINO - PYRAZOLE IN ROOM TEMPERATURE IONIC LIQUIDS

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Aromatic rings containing one or more nitrogen atoms like pyrazoles or pyrazolo-triazoles can be found in countless natural products as well as pharmaceutical compositions. These structures are building blocks of more complex compounds with some outstanding properties like anticancer drugs [1], non-acidic analgesics and nonsteroidal anti-inflammatory drugs [2]. Pyrazole derivatives are often used as precursors in obtaining color photosensitive materials and photoconducting materials [3] azo-dyes; [4] as well as inks and toners [5]. All of the mentioned data have lead us to enquire for a more environmentally sustainable methodology of obtaining various pyrazolo[5,1-c]-1,2,4-triazoles through anodic cyclization of the corresponding hydrazino-pyrazoles, thus using imidazole-based room temperature ionic liquids as reaction medium [6].

In the present research we have analyzed the electrochemical behavior of 1H-3-methyl-4-ethoxycarbonyl-5-(4-fluorobenzylidenehydrazino)-pyrazole (I) in two types of room temperature ionic liquids (RTILs) both bearing the same anion and different cations based upon the imidazolium scaffold. The aim of the present study is mainly focused on finding the most suitable reaction medium for the anodic cyclization of compound (I). Electrochemical determinations were conducted using cyclic voltammetry as well as chronoamperometry at a polished platinum disk working electrode as part of a conventional three electrode system, with an Ag-wire as quasi reference electrode and a Pt-counter electrode mounted on a miniaturized undivided cell. Both RTILs used in this study contain the bis(trifluoromethyl)-sulfonylimide (TFSI) anion but incorporate different cations, i.e. 1-n-butyl-3-methylimidazolium (a) and the substituted 1-(2-hydroxyethyl)-3-methylimidazolium (b). The electrochemical investigation of the aforesaid substrate in the two solvents reveals a relatively similar behavior of the pyrazole derivative in both reaction media, as expected. Cyclic voltammograms of (I) recorded in the ionic liquid (a) reveals a sharp, completely irreversible one electron oxidation signal followed by another well-defined irreversible oxidation peak. The voltammogram recorded using ionic liquid (b) reveals the same two irreversible anodic signals, but in this medium they show a somehow broader shape. The first anodic peak occurs at a less positive potential in ionic liquid (a) compared to the first signal recorded in (b). Furthermore, the peak to peak separation between the two signals is lower in ionic liquid (b) meaning that in this medium the intermediate formed after the first oxidation step is less stable, thus facilitating the loss of a second electron. The obtained data led to the conclusion that ionic liquid (a) may better stabilize the intermediate formed after the first oxidation wave, hence being a more appropriate choice for the anodic cyclization of (I).

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Mn(II) COORDINATION COMPLEXES BASED ON 2,4,6-TRIS(2-PYRIDYL)-S-TRIAZINE

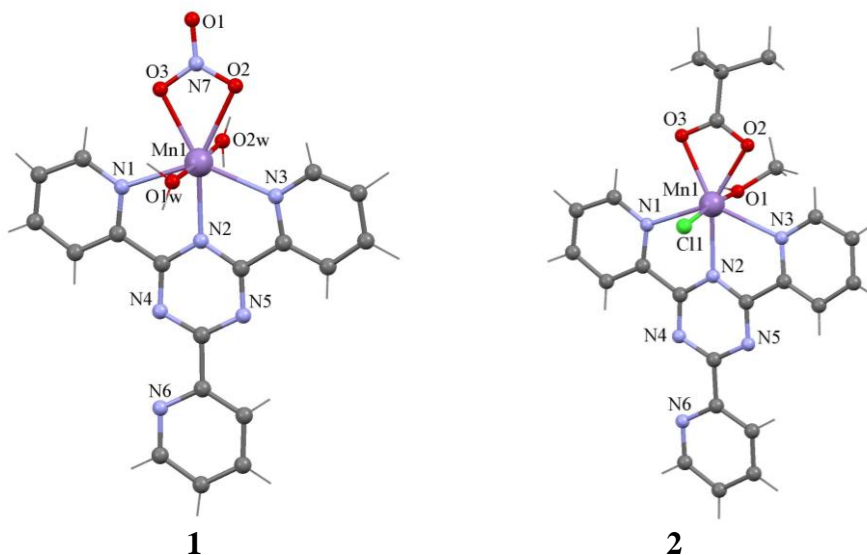
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Nitrogen containing 2,4,6-tris(2-pyridyl)-s-triazine (tpt) ligand and its metal complexes exhibit various pharmacological activities such as antiviral, antitumor, analgesic, antioxidant, antidepressant, antibacterial, and antimicrobial. In addition, they possess catalytic activities in some polymerization and oxidation processes and are used as analytical reagents in spectrophotometric determination of some species in pharmaceutical formulations.

Two new mononuclear manganese(II) complexes, cationic $[\text{Mn}(\text{tpt})(\text{NO}_3)(\text{H}_2\text{O})_2](\text{NO}_3)$ (**1**) and neutral $[\text{Mn}(\text{is})(\text{tpt})(\text{MeOH})(\text{Cl})] \cdot (\text{H}_2\text{O})$ (**2**), (tpt = 2,4,6-tris(2-pyridyl)-s-triazine, His = isobutyric acid), have been synthesized under ultrasonic irradiation by interaction of manganese(II) pivalate or manganese(II) isobutyrate with tpt in the presence of $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for **1** or 2-[bis(2-hydroxyethyl)amino]acetonitrile hydrochloride for **2** in ethanol and methanol solvent, respectively. Compound **1** crystallizes in the monoclinic $C2/c$ space group, $a = 20.436(1)$, $b = 13.361(1)$, $c = 16.727(1)$ Å, $\beta = 107.782(4)^\circ$, compound **2** - in the triclinic $P-1$ space group, $a = 8.813(1)$, $b = 10.955(1)$, $c = 15.129(1)$ Å, $\alpha = 71.115(4)$, $\beta = 81.894(4)$, $\gamma = 68.777(5)^\circ$.

In both complexes tpt molecule serves as a tridentate NNN ligand which forms two five-membered metallocycles with Mn–N distances 2.231 - 2.379 Å in cationic **1** and 2.295 - 2.412 Å in neutral **2**. Additionally, manganese atom coordinates NO_3^- anion and two water molecules in **1** or isobutyrate and chlorine anion and water molecules in **2**, resulting in pentagonal bipyramidal surrounding of the metal atom (Figures). The NO_3^- and isobutyrate anions coordinate in bidentate mode with Mn–O distances 2.269 and 2.412 Å (**1**) and 2.226 and 2.308 Å (**2**). The Mn–O distances with the water molecules in apical position in **1** equal 2.139 and 2.193 Å, and in **2** Mn–Cl = 2.486 Å and Mn–O(MeOH) = 2.294 Å.



Acknowledgement

This work was supported by the State Program of the Republic of Moldova (Project 16.00353.50.05A).

STRUCTURAL AND ELECTRICAL INVESTIGATIONS OF NEW TRANSPARENT CONDUCTORS WITH BIXBYITE STRUCTURE

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Much research has focused on the last years on transparent conducting oxide (TCO) semiconductors, in order to obtain new TCOs suitable for specialized applications. Among the various *n*-type TCOs that have been found up to now, the indium tin oxide (ITO) remain a reference due to its optical and electrical properties. Taking into account the potential economic benefit of reducing the amount of scarce and expensive indium oxide, coupled substitutions in indium oxide have to be investigated intensively. For this reason, we decided to check the ability for the substitution of the (Na/Sb) couple for indium in In₂O₃. We hereafter report the effect of coupled substitution of Na⁺/Sn⁴⁺ for In³⁺ in In₂O₃, upon the structural and electrical properties. New compositions with bixbyite structure have been synthesized by solid state reaction in air at 1300°C. X-ray powder diffraction (XRPD) analysis confirm the validity of the bixbyite structure model of In₂O₃, S.G. Ia3 with two sets of cationic positions 8(b) 1/4, 1/4, 1/4 and 24(d): x, 0, 1/4 and one set of oxygen positions 48(e) x, y, z. A small amount of unreacted SnO₂ was always identified. Electrical measurements show a decrease in resistivity for one of the compositions ($\rho_{RT} = 1.1 \times 10^{-3} \Omega \cdot \text{cm}$) by approximately one order of magnitude if compared to In₂O₃ ($\rho_{RT} = 2.2 \times 10^{-2} \Omega \cdot \text{cm}$).

***In vitro* ENHANCED ANTIOXIDANT PROPERTIES OF CATECHIN NANOPARTICLES AGAINST NEURODEGENERATIVE PHENOTYPES**

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In neurodegenerative diseases, neuronal synapses become dysfunctional or degenerate, thereby contributing to disease progression [1]. Synapse decline is the strongest exordium pathological hallmark of cognitive decline, indicating that synaptic degeneration plays a central role in dementias, such as Alzheimer’s disease (AD). Over the past decades, strong evidence has pointed out that pathological forms of tau [2] and amyloid precursor protein peptide act on the synapse to cause neural network dysfunction, and may act in concert to cause synaptic pathology. Although, copper is critical for the Central Nervous System (CNS) development and function, its dyshomeostatic imbalance is linked to oxidative stress, contributing to brain synapse deficits and compromised neurotransmission. So far, no cure has been found against AD. In this respect, contemporary molecular (nano)technology targeting proteins related to neuronal connectivity deficit, facilitating permeability through the blood brain barrier, arises as a prominent challenge.

Many *in vitro* studies on catechins report mechanisms consistent with protection against degenerative diseases [3,4]. Poised to investigate silica xerogel encapsulation of water-soluble antioxidant catechin drugs, targeting improved hybrid organic-inorganic pharmaceutical nanomaterials, we have a) synthesized base-catalyzed silica gel matrices surface-modified with i) PEG 3000, and ii) CTAB cationic surfactant, b) assessed the suitability of these matrices as potential carrier materials for the controlled release of the antioxidant flavonoid catechin (Ct) vs. other flavonoids such as quercetin (QC), and c) probed the cytotoxicity and potential protective effects on neuronal synaptic connectivity in *in vitro* primary neuronal cultures, under Cu(II)-induced oxidative stress conditions.

Acknowledgements

The authors would like to acknowledge IKY Financial Support of Excellence for Postdoctoral Researchers in Greece - NSRF 1st Cycle for 2014-2020.

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AN EVALUATION REGARDING THE CANNABINOID THERAPIES IN ONCOLOGY

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Cannabinoid refers to a group of chemicals naturally found in the marijuana plant *Cannabis sativa* L. and includes compounds that are either structurally or pharmacologically similar to D(9)-tetrahydrocannabinol or those that bind to the cannabinoid receptors. Cannabinoid therapies are varied and versatile, and can be offered as pharmaceuticals (nabilone, dronabinol, and nabiximols), dried botanical material, and edible organic oils infused with cannabis extracts. Cannabinoid therapy regimens can be creative, involving combinations of all modalities. Patients with malignant disease, at all points of their disease trajectory, could be candidates for cannabinoid therapies whether as monotherapies or as adjuvants. The most studied and established roles for cannabinoid therapies include pain, chemotherapy-induced nausea and vomiting, and anorexia. Moreover, given their breadth of activity, cannabinoids could be used to concurrently optimize the management of multiple symptoms, thereby reducing overall polypharmacy. The use of cannabinoid therapies could be effective in improving quality of life and possibly modifying malignancy by virtue of direct effects and improving compliance or adherence with disease-modulating treatments, such as chemotherapy and radiation therapy. Cannabinoids appear to have antitumor properties based on their ability to induce cancer cells apoptosis, reduce neoangiogenesis and tumor cell invasiveness. The literature has reported the antitumor effects of cannabinoids on various cancer types: glioma, breast, prostate, skin, lung, thyroid, gastric, colon, hepatocellular, pancreatic, lymphoma and leukemia. The endogenous signaling system of endocannabinoids, which share common receptors and manifest similar actions with cannabinoids, is also a promising field for the treatment of cancer. This paper presents the recent advances regarding ongoing research of cannabinoids and endocannabinoids in various cancer types.

COOKING AND REGENERATION OF PURE AND PALLADIUM DOPED $H_3PW_{12}O_{40}/SBA-15$ CATALYSTS

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The pure and Pd doped $H_3PW_{12}O_{40}$ (HPW) supported on SBA-15 were selected as the catalysts in gas phase dehydration of ethanol. HPW and PdHPW were introduced into the mesoporous silica molecular sieve SBA-15 by impregnation method. The synthesised catalysts were characterized by thermal analysis, FTIR, XRD, BET, XPS and SEM methods in order to establish their composition, structure, textural properties and thermal stability. In this paper, we focus on the effect of SBA-15 on the coke formation during the ethanol conversion at 275 and 300 °C.

The ethanol dehydration was performed in a flow reactor which was placed into an electric furnace, the composition of the reactor effluent stream being analyzed by gas chromatography equipment with a flame ionization detector (FID). Coking was analyzed by temperature-programmed oxidation (TGA/TPO) method using the thermoanalyzer system Mettler TGA/SDTA 851/LF/1100 in the range of temperature 25 - 650 °C.

The amount of coke precursor formed on the catalysts was calculated by the difference between the initial mass of spent catalyst sample after isothermal heating at 300 °C (temperature of reaction test) and the sample mass heated in nitrogen at 650 °C. The quantity of hard coke present in the catalysts was calculated as the difference between samples mass heated in nitrogen at 650 °C and mass loss of sample at 650 °C in air, when the coke was burnt out. The sum of coke precursor and hard coke represent the total coke.

The amount of total coke formed by ethanol conversion over catalysts at 275 and 300 °C was represented in figure 1. The quantity of coke formation (coke precursor and hard coke) increases with increase the temperature. By comparing the HPW/SBA-15 and PdHPW/SBA-15 catalysts was observed a decrease in amount of coke because palladium inhibits the formation of hard polyaromatic coke.

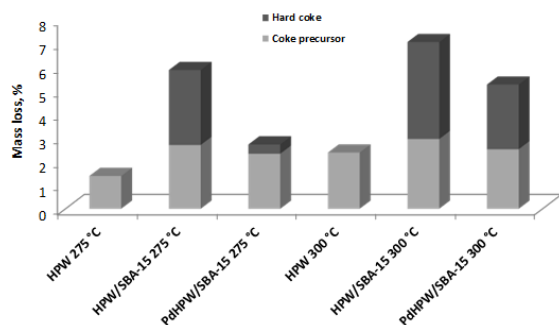


Fig. 1. Precursors and hard coke content for catalysts formed by ethanol conversion at 275 and 300°C.

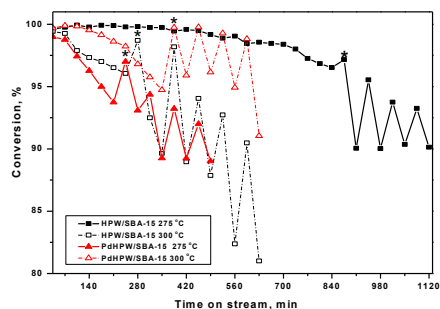


Fig. 2. Conversion and regeneration (*-starting to add air within 35 min.) at 275 and 300°C.

The ethanol conversion was studied as a test reaction for the deactivation/regeneration of the HPW/SBA-15 and PdHPW/SBA-15 at 275 and 300 °C. The effect of partial air regeneration on these catalysts was investigated and the results are presented in figure 2. As can see all catalysts regain for a short time the catalytic activity after regeneration under above conditions. PdHPW/SBA-15 exhibiting a good regeneration due to palladium which hinders the formation of hard coke at 300 °C. Optimization of catalyst regeneration will be accomplished by changing the amount of palladium from PdHPW/SBA-15.

PREPARATION OF PURE ENANTIOMERS BY SEPARATION OF DIASTEREOISOMERS

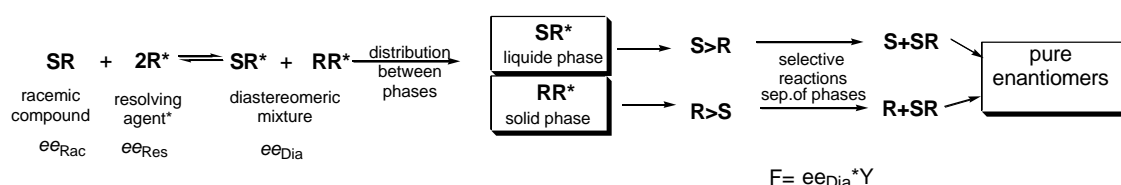
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The resolution still remains the most inexpensive and operationally simplest method for producing enantiopure substances on a large scale. It is still heavily dependent upon the separation of diastereomers obtained from the enantiomers and an optically active resolving agent. Methods for selecting optimal conditions of resolution and for the purification of obtained mixtures are also discussed.

Industrially the most common method for preparation of pure enantiomers is the exploitation of the distribution between two phases of diastereomers. These diastereomers are formed in the reactions of racemic compounds obtained in chemical syntheses and the resolving agent.



Scheme 1. General scheme of preparation of pure enantiomers

The efficiency of resolution (F) can be characterized by the enantiomeric purity (ee) and the yield (Y) of the enantiomeric mixture isolated from the corresponding diastereomeric salt ($F = ee_{Dia} \cdot Y$). The composition (stoichiometry) of diastereomeric salt in the solid phase can be influenced by the solvent applied, the time of crystallization, using structurally similar molecules, or achiral adduct, by the pH, temperature [1-4]. The composition of the solid phase can be stabilized using ultrasound irradiation [5].

Acknowledgment

The authors are grateful for the financial support of the Hungarian Scientific Research Found (OTKA grant number K 104769 for E. Fogassy).

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CALCIUM SILICATE BASED BIOMATERIALS FOR DENTAL CEMENTS

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Calcium silicate biomaterials are usually used as dental cements due to their hardening properties, chemical stability and biocompatibility replacing the Portland cement. In the present study, tricalcium and dicalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{SiO}_2$) and were synthesized by solid state reaction from calcium carbonate and calcium hydroxide and micronized silicon oxides and diatomite. The composition in a molar ratio CaO/SiO_2 of 3/1 respectively 2/1 were dry milled in a laboratory mill. The grain size is ranged in a nanometer scale, between 20nm and 200nm. For increasing the reaction rate, the granulated powder was pressed into pellets with 10.2 mm diameter and 2 mm height at a specific pressure of 500 kgf/cm^2 . The dried samples were thermal treated firstly at $700 \text{ }^\circ\text{C}$ and then at $1250 \text{ }^\circ\text{C}$ respectively $1300 \text{ }^\circ\text{C}$ in a Nabertherm type laboratory kiln. Phase composition of the tested biomaterials determined using a Bruker D8 Advance diffractometer revealed the presence of tricalcium and dicalcium silicate in all samples. Two compositions were prepared for testing. The first composition contains 80 % wt. C3S and 20 % wt. C2S and second composition 60 % wt. C3S and 40 % wt. C2S. The water and calcium chloride in different percent were added to the mixtures in order to obtain the slurry and accelerate the hardening time. The optimum hardening time, about 20 minutes, were obtained with 0.5 % calcium chloride. *In vitro* bioactivity of the calcium silicate cement was investigated by immersion in simulated body fluid (SBF) solution during 3 months in a water bath at $37 \text{ }^\circ\text{C}$. Hydroxyapatite formation on the surface of samples was shown using X-ray diffraction (XRD).

EXPERIMENTAL STUDY ON THE INTERACTION OF DICLOFENAC WITH SOME NATURAL SUPPORTS

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In this present work, the interaction of Diclofenac with *Citrus lemon L.* peel, *Ficus Carica* and *Olea europaea* leaves (three natural solid supports) was studied at several temperatures (namely 25, 35 and 45 °C). The main reason for the choice of these supports was grounded on their biomedical application, and thus their potential to be used as natural excipients in pharmaceutical formulations. The study involved a series of preliminary experiments in order to establish the time required for attaining the adsorption equilibrium, which ranged from 150 to 400 minutes. The adsorption studies were based on these durations, as well as on an experimental procedure which was established in previous studies [1]. The interaction of Diclofenac with the studied natural supports was also investigated by FTIR spectroscopy. The adsorption experimental data were analyzed in order to identify the optimal theoretical adsorption model. For this purpose, the data were fitted to the Freundlich and Langmuir classical adsorption models analysis by linear regression analysis. The obtained results showed that, for the three studied systems, the Langmuir model described better the interaction of Diclofenac with the investigated natural supports. It was noticed that the adsorption capacity of the three sorbents decreased in the order: *Olea europaea* leaves > *Ficus Carica* leaves > *Citrus lemon L.* peel, and these results indicate that the number of adsorption active centers of the investigated supports decreases in the same order. Further, for the Langmuir model, the free energy of Gibbs, the enthalpy and the entropy of the adsorption process were also calculated. The obtained values suggest the spontaneity and the exothermicity of the adsorption process of Diclofenac onto the three natural supports.

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COPOLYMERS OF VINYLPHOSPHONIC ACID WITH DIALKYL VINYL PHOSPHONATES AND THEIR PROPERTIES IN AQUEOUS SOLUTION

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Vinyl phosphonic (VPA) acid represents an important monomer in the synthesis of functional polymers bearing side chain phosphonic/phosphonate groups. Due to this structure, the main application of copolymers of VPA with various monomers refers to solid polymer electrolyte membranes for fuel cell, ion exchange membranes, and products for bone reconstruction. In the last decades, the anticorrosion property of copolymers based on VPA was investigated.

Functional synthetic copolymers based on dialkylvinyl phosphonates (alkyl = methyl, ethyl) have also gained applicative importance by the presence of phosphonate groups as anticorrosion agents and flame-retardants. The copolymerization of vinylphosphonic acid with dialkyl vinylphosphonates can be radically performed either in the presence of thermal initiators or by exposure to UV light in the presence of photoinitiators.

In this paper the properties in aqueous solution of copolymers of vinylphosphonic acid with dimethylvinylphosphonate were investigated regarding the surface protection of iron against corrosion.

The homopolymer of vinylphosphonic acid (VPA) and its copolymers with dimethyl vinylphosphonate (DMVP) were prepared by radical polymerization at different molar ratios from 1:1 to 4:1, respectively, by using UV light and photoinitiator. The evaluation of their spectroscopic, thermal and electrochemical characteristics was performed. The use of UV light to polymerize is an attractive technique from environmental point of view: formulations are free of organic solvents, and has the advantages of low energy consumption, low temperature operation (room temperature) and the possibility to coat various substrates (wood, plastics, paper).

The obtained polymers are soluble in water. Phosphonic acids and phosphonates, in general, inhibit steel corrosion in neutral and slightly alkaline solutions show promising application is the capacity of their inhibition against corrosion for iron surface in neutral aqueous solutions. The thermal analysis showed that these copolymers have good thermal stability until 320 °C. The polymers were tested as corrosion inhibitors for iron and their presence in aqueous solution decreased the corrosion current density by the formation of protective film on iron surface. The presence of phosphonate groups from dimethyl-vinylphosphonate in copolymers was beneficial and at a molar ratio VPA:DMVP 4:1 and 3:1 enhanced the anticorrosion property in comparison with homopolymer of vinylphosphonic acid.

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PORPHYRINS IN MEDICAL APPLICATIONS

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Porphyrins are well-known as versatile multifunctional biomimetic molecules which can be synthetically modified by either substitution with various peripheral functional groups or metalation [1]. Besides, porphyrins and their derived inorganic or polymeric hybrids are capable to form supramolecular tunable architectures by means of the association of more building block units.

The photobactericidal activity of diverse porphyrin based hybrids nanomaterials was evaluated against Gram positive and Gram negative strains bacteria and they represent an alternative to antibiotics in order to overcome the growing bacterial multiresistance [2].

Up-to-date researches reported polymer functionalization with porphyrin with the purpose to overcome some drawbacks such as self-quenching and photo-toxicity to the skin produced by the bare porphyrins, when used as photosensitizers in the non-invasive Photodynamic therapy of cancer (PDT) [3].

Different structures of porphyrins and their hybrids prepared either with gold and silver nanoparticles and also with biocompatible polymers are reviewed regarding their reported performance in medical applications, especially antibacterial activity and PDT [4].

Acknowledgements

The authors from Institute of Chemistry Timisoara of Romanian Academy are kindly acknowledging the support from Program 3-Porphyrins/2017.

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SOLIDE POLYMER ELECTROLYTES BASED ON POLYPHOSPHOESTERS

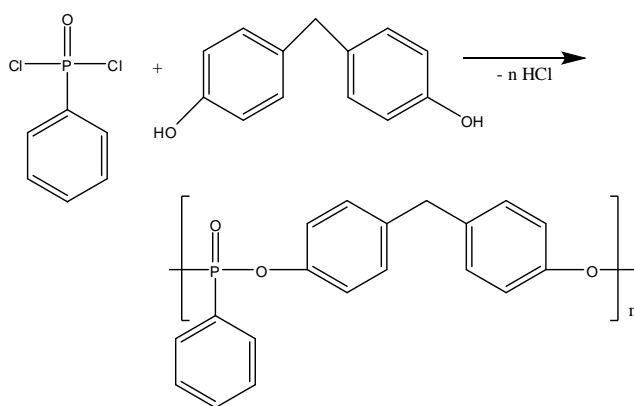
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This paper presents the synthesis of flame retardant solid polymer electrolytes based on phosphorus containing polymers. The new green technique synthesis, respectively polycondensation under microwave irradiation of phenylphosphonic dichloride (PPD) with bis(4-hydroxy)methane (bisfenol F) was described. (Scheme 1)



Scheme 1. Polyphosphonate P₁ synthesis

80 % yield and 0.90 dl.g⁻¹ inherent viscosity were obtained. The polyphosphonate P₁ was characterized by FT-IR, ¹H and ³¹P-NMR spectroscopy, gel permeation chromatography, and thermal analysis. The polymer presents thermal stability, begins to lose weight above 260°C. Membranes were obtained from the polyphosphonate complexed with different lithium salts using casting technique and the electrochemical properties were determined. The low activation energy of conduction determined for solid polymer electrolyte membrane with bis(oxalato)borate anions overcomes the activation energy request for relaxation process and this membrane presents the best conductivity. Also, the flammability of polyphosphonate and membranes was investigated by measuring limiting oxygen index values.

Acknowledgements

The work was financial supported by Program 2, Project 4 of Institute of Chemistry Timisoara of Roumanian Academy.

SUPRAMOLECULAR STRUCTURE OF DINUCLEAR Cu(II) ACETYLACETONATE COMPLEXES WITH BIDENTATE AROMATIC LIGANDS

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The interest in copper(II) complexes with aromatic ligands such as phen and 2,2'-bpy is originated from their potential application in the area of metal-based drugs which possess antimicrobial, antiviral, anti-inflammatory, antitumor activity [1]. The crystal structure of such complex reveals the variety of π - π stacking interactions, which may be responsible for intercalation mechanism of bioactivity, as well such interactions may be utilized for rational design of metal-organic materials with desired architecture [2].

Here, we report the synthesis and crystal structures of three new dinuclear Cu(II) complexes: $[\text{Cu}_2(\text{acac})_2(\text{phen})_2(4,4\text{-bpy})](\text{BF}_4)_2$ (**1**), $[\text{Cu}_2(\text{acac})_2(2,2'\text{-bpy})_2(4,4'\text{-bpy})](\text{BF}_4)_2$ (**2**) and $[\text{Cu}_2(\text{acac})_2(2,2'\text{-bpy})_2(\text{bpe})](\text{BF}_4)_2(\text{H}_2\text{O})_2$ (**3**) obtained by interaction of $\text{Cu}(\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ with 1,10-phenanthroline (phen) or 2,2'-bipyridine (2,2'-bpy) in the presence of acetylacetonate (Hacac) and bridging rigid rod-like 4,4'-bipyridine (4,4'-bpy) or flexible 1,2-bis(4-pyridyl)ethane (bpe) exo-ligands. All structures represent centrosymmetric dimers with square pyramidal 4+1 copper(II) environment, where the equatorial planes are fixed by the acetylacetonate and phen or 2,2'-bpy chelate ligands. Axial position is occupied by nitrogen atom of N,N-exo-ligand, which bridge two $[\text{Cu}(\text{acac})(\text{phen})]^+$ or $[\text{Cu}(\text{acac})(2,2'\text{-bpy})]^+$ moiety. In the crystal structures of all compounds these moieties reveal π - π stacking interactions, in which are involved chelating ligands attached to the copper ions and metallocycles (Fig.). Thus, our study proves the reliability of supramolecular synthon based on stacking interactions of square-planar Cu units. In the crystal two $[\text{Cu}(\text{acac})(\text{phen})]^+$ or $[\text{Cu}(\text{acac})(2,2'\text{-bpy})]^+$ units are related by center of symmetry and reside in parallel planes with an interlinear separation 3.459, 3.228, and 3.312 Å and Cu(II)⋯Cu(II) distances within the supramolecular synthon 5.198, 6.035, and 5.826 Å for **1**, **2**, and **3**, respectively. The difference in Cu(II)⋯Cu(II) distances is related with different type of face-to-face overlapping in stacking: in **1** both metallacycles and phen ligands are involved in stacking, while in **2** and **3** only 2,2'-bpy ligands and corresponding metallacycles. The distance between the copper ions within the binuclear entity are 11.652, 11.556 and 13.658 Å, in **1**, **2**, and **3**, respectively.

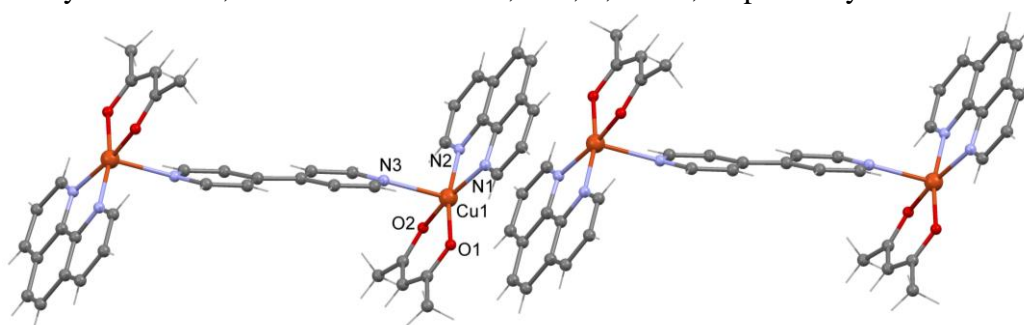


Fig. Stacking interactions between the dimers in **1**.

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Financial support was provided by the State Program of R. Moldova (Project 16.00353.50.05A).

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LIQUID CRYSTALLINE COMPLEXES BASED ON CU(I) METAL CENTRES

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Thermotropic metallomesogens are very attractive due to their various applications, the metal centres having the ability to add unique magnetic, spectroscopic or redox properties to a liquid crystal [1-3].

In this context we are focused on Cu(I) coordination complexes with N[^]N-chelating ligands, well-known for their excellent photophysical properties [4]. In order to induce liquid crystalline properties, one of the most used strategies is to functionalize the ligand with long alkyl chains, introducing thus the amphiphilicity needed for the microsegregation. Thus, herein we report the synthesis and characterisation of a new series of Cu(I) metallomesogens based on functionalised 2,2'-bisquinoline (Figure 1). The complexes were fully characterized structurally, and their mesomorphic behavior was investigated by a combination of polarised optical microscopy (POM) and differential scanning calorimetry (DSC). In particular, the complexes exhibited rich low temperature columnar mesomorphism whose symmetry depends on the number of alkyl chains grafted on the ligand.

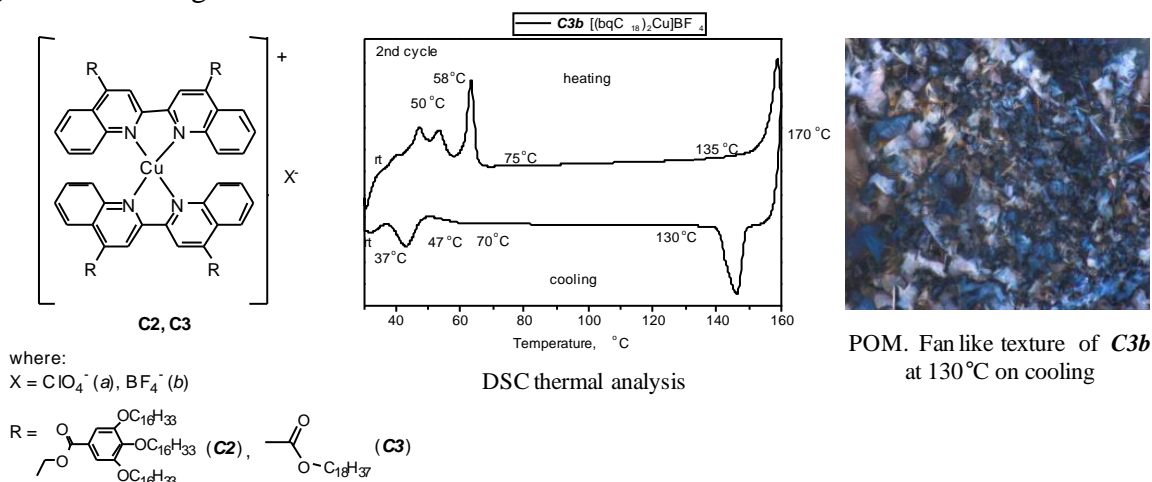


Figure 1. Cu(I) metallomesogens containing functionalised 2,2'-bisquinoline as ligand

Acknowledgment

We are thankful to the Romanian Academy (Project 4.1.) for the financial support.

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A NOVEL TOOL FOR THE CHEMICAL SPACE MAPPING OF BIOLOGICAL ACTIVE COMPOUNDS

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The chemical space is extremely large impairing the exhaustive search for molecules with very specific biological properties. Cheminformatics tools are able to efficiently contour regions of desirable molecules, based on the available the bioactivity data. During the last years, activity determination results have become largely accessible through the on-growing public databases, e.g., PubChem, ChEMBL etc. However, these data is heterogeneous and often limited to a number of small molecules tested against an arbitrary set targets.

In the present work, we attempt to develop an *in silico* tool to fill out the lack of bioactivity data for a significant number of protein kinases using proper validated predictors. Furthermore, we group compounds with similar kinase activity profiles allowing the analysis of chemically diverse structures sharing similar mechanisms of action. This tool can be further applied in drug discovery and development programs.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-0422.

INSULIN MIMETIC ZINC-INDUCED ADIPOGENESIS IN VITRO. STRUCTURE-SPECIFIC DESIGN AND SYNTHESIS OF A FAMILY OF BINARY AND TERNARY ZN(II)-SCHIFF BASE MATERIALS

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Zinc is abandoned in numerous (patho)physiological cellular functions, including gene expression, cell growth and metabolism. It is also involved in several diseases such as Diabetes mellitus, Alzheimer's disease, and cancer [1]. It is a constituent of many metalloproteins and metalloenzymes and also present in a loosely bound chelatable Zn(II), especially in the brain, pancreas, and spermatozoa. Schiff bases are generally bidentate, tridentate, tetradentate or polydentate ligands capable of forming very stable complexes with transition metals. They possess valuable characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties. Given the fact that properly designed Schiff bases may promote Zn(II) binding [2], thereby giving rise to bioactive binary Zn(II)-L and ternary Zn(II)-L-(L') insulin mimetic compounds capable of mimicking insulin action, efforts were launched to a) design new Schiff base organic substrates bearing systematically varying structural features, reflected in a variable number of terminal alcohol moieties attached to varying aldehyde cores, b) synthesize well-defined binary and ternary Zn(II)-Schiff base compounds of specific structure and characterize them physicochemically, c) investigate their ability to induce 3T3-L1 fibroblast differentiation to mature adipocytes, d) examine the insulin mimetic potency of such compounds and determine *in vitro* their arising biological activity profile(s), e) investigate the interactions of such molecules with closely related molecular targets (PPAR- γ , GLUT 4, GCK and adiponectin) in the insulin-induced glucose catabolic pathways known to date, and f) correlate chemical and structural features of the binary Zn(II) compounds with the observed activities at the cellular level, thereby formulating biological activity profile-physicochemical factor relationships that enable development of optimal Zn(II) insulin mimetic agents.

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COMBINED MOLECULAR DOCKING AND MLR STUDY OF NEONICOTINOIDS DERIVATIVES WITH INSECTICIDAL ACTIVITIES AGAINST PEA APHIDS

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A series of neonicotinoids analogues of hexahydroimidazo[1,2-a]pyridine, nitromethylene neonicotinoids containing a tetrahydropyridine ring with exo-ring ether modifications, cis-nitromethylene neonicotinoids and neonicotinoids bearing nitroconjugated double bond and five-membered heterocycles were found to be insecticides against the Cowpea Aphids (*Aphis craccivora*). The insecticidal activities of these compounds, expressed by experimental pLC₅₀ values, were modeled using docking and multiple linear regression (MLR) approaches. A conformer ensemble for each of the insecticide structure was generated using the MMFF94s force field. These conformers were further employed in a docking approach, to find out “active conformations” of the insecticide derivatives. The most “active conformers” from the docking study were further used to calculate 23 kinds of structural descriptors, which were related to the insecticidal experimental activity pLC₅₀ values by multiple linear regression (MLR). The dataset of compounds was split randomly assigning 78.6% and 21.4% of data into the training and test sets, respectively. Variable selection was performed using the genetic algorithm and several criteria were checked for model performance. The most stable and predictive MLR model with three descriptors had the following statistical parameters: $r_{\text{training}}^2 = 0.859$, $r_{\text{test}}^2 = 0.939$, $q_{\text{LOO}}^2 = 0.813$, $\text{RMSE}_{\text{tr}} = 0.278$, $\text{RMSE}_{\text{ext}} = 0.166$. The resulting model revealed that WHIM, molecular walk counts and 3D-MoRSE descriptors were found to influence to the insecticidal activity.

Acknowledgements

This project was financially supported by Project 1.1/2017 of the Institute of Chemistry of the Romanian Academy. The authors thank OpenEye Ltd., Prof. Paola Gramatica from the University of Insubria (Varese, Italy) and Chemaxon Ltd. for providing academic software license.

HETEROMETALLIC TETRANUCLEAR Fe-Dy PIVALATE CLUSTER BASED ON 1,1,1-TRIS(HYDROXYMETHYL)ETHANE

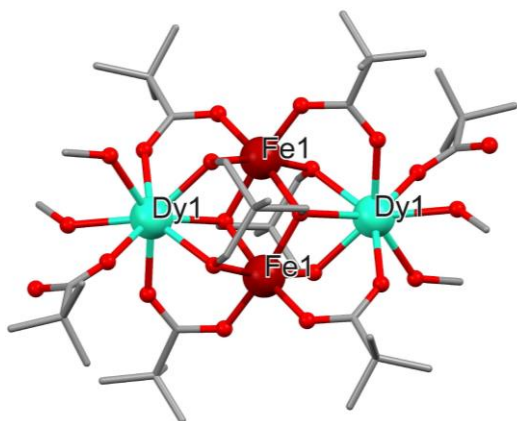
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Coordination complexes with biologically active ligands have a broad application in medicine and biotechnology. Pivalic acid (Hpiv) has found its use as a prodrug in carnitine homeostasis in human body [1]. In addition, drugs functionalized with pivalic acid increase their oral bioavailability. Moreover, pivalic acid has also been used in antibiotics synthesis [2] and for the preparation of polynuclear clusters as effective catalysts in organic synthesis [3].

In continue of our research on preparation of polynuclear coordination clusters of d-f metals with pivalic acid a new heterometallic tetranuclear coordination compound namely $[\text{Fe}_2\text{Dy}_2(\text{piv})_6(\text{thme})_2(\text{MeOH})_4] \cdot 2(\text{MeOH}) \cdot 2(\text{H}_2\text{O})$ was synthesized from the reaction of μ -oxo trinuclear iron pivalate with $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 1,1,1-tris(hydroxymethyl)ethane (H_3thme) ligand in methanol solution. Single-crystal X-ray diffraction analysis showed that the obtained pivalate compound crystallizes in the triclinic *P*-1 space group with $a = 11.2824(9)$, $b = 12.5156(7)$, $c = 14.8596(1)$ Å, $\alpha = 74.089(6)$, $\beta = 67.987(7)$, $\gamma = 70.593(6)^\circ$, $V = 1807.72$ Å³ and comprises the neutral cluster $[\text{Fe}_2\text{Dy}_2(\text{piv})_6(\text{thme})_2(\text{MeOH})_4]$ and solvent molecules. The cluster (Figure) contains a $\{\text{Fe}_2\text{Dy}_2\}^{12+}$ core, where two Fe^{III} and two Dy^{III} centers are connected by two thme^{3-} ligands with



$\text{Fe}^{\text{III}}\text{---Dy}^{\text{III}}$ distances of 3.427 and 3.434 Å, and a $\text{Fe}^{\text{III}}\text{---Fe}^{\text{III}}$ distance of 3.189 Å. Metal atoms reside in the vertexes of rhombus and are additionally linked by four pivalate ligands. Monodentate pivalate and two MeOH complete the coordination sphere for each of the Dy atoms. In cluster, Fe^{III} atoms are six-coordinated with a distorted octahedral O_6 geometry being coordinated by four O atoms from two thme^{3-} and two O atoms from two pivalate bridges (Fe-O , 1.954(4)-2.096(5) Å). The Dy^{III} atoms are eight-coordinated by three O bridging atoms of thme^{3-} ligands (Dy-O , 2.337(4)-2.436(4) Å), three O atoms from three pivalates (Dy-O , 2.306(5) □□2.370(4)

Å) and two O atoms from two methanol molecules (Dy-O , 2.407(5) and 2.419(7) Å). The coordinated methanol molecules and monodentate pivalates as well as solvent molecules establish a system of intra- and intermolecular hydrogen bonds joining heterometallic clusters into chains. The spectroscopic and thermogravimetric properties of $[\text{Fe}_2\text{Dy}_2(\text{piv})_6(\text{thme})_2(\text{MeOH})_4] \cdot 2(\text{MeOH}) \cdot 2(\text{H}_2\text{O})$ have also been studied and will be discussed in terms of the known structure.

Acknowledgements. This work was supported by SCOPES IZ73Z0_152404/1 and the State Program of the Republic of Moldova (Project 16.00353.50.05A).

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HETEROGENOUS CATALYST APPLICATION OF PHOSPHONATE METAL ORGANIC FRAMEWORK

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The requirement for new and enhanced properties has been a motivating force for the development of new materials beyond those available for conventional materials. Phosphonate metal organic frameworks exhibit a high range of applications and a rich synthetic and structural chemistry [1-3]. Novel catalytic materials are required in order to perform a variety of catalytic organic reactions. Phosphonates metal organic frameworks combine the benefits of heterogeneous catalysis like easy post reaction separation, catalyst reusability, high stability and efficiency, and mild reaction conditions. The group of active centers like organic linkers and metallic nodes displays potential to build up phosphonate metal organic frameworks constructed for catalytic experiments. A series of phosphonates metal organic frameworks were synthesized by solvothermal method was used as heterogeneous catalysts in methylation reactions of phenol, β -naphthol and aniline with dimethyl carbonate (DMC). The catalytic materials were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) and thermogravimetric analysis (TGA) measurements [4]. DMC, an environmentally mild reagent and solvent for chemical syntheses, has been used to *O*-methylation of phenol, β -naphthol and *N*-methylation of aniline [5]. Dimethyl carbonate serves also as a methoxycarbonylation agent and it was also the reaction solvent. The amount of catalyst used was 5% and syntheses were performed in two ways autoclave (180 °C) and at dimethyl carbonate reflux (90 °C). It was found that the Ni-VP show better conversion results between 56-71% in autoclave reactions. The catalysts are easy recoverable and can be reused.

Acknowledgments

This work was partially supported by Program no 2 from the Institute of Chemistry Timisoara of Romanian Academy and by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1398.

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POROUS COORDINATION POLYMERS OF Co(II) AND Zn(II) TRICARBOXYLATE WITH 1,2-BIS(4-PYRIDYL)PROPANE

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Porous coordination polymers are unique in terms of their good crystallinity, designable porosity and structural flexibility and play an important role in numerous application areas including gas storage, selective adsorption/separation, catalysis, luminescence, sensing, drug delivery, etc [1]. Being in line with these investigations we report herein the products of interaction of Co(II) or Zn(II) tetrafluoroborate with or 1,2-bis(4-pyridyl)propane (bpp) in the presence of 1,3,5-benzenetricarboxylic acid (H₃btc) which represent two novel polymeric compounds with the compositions $\{[\text{Co}_4(\mu_3\text{-OH})_2(\text{btc})_2(\text{H}_2\text{O})_8]\cdot 4\text{H}_2\text{O}\}_n$ (**1**) and $\{[\text{Zn}_4(\text{bpp})_4(\text{Hbtc})_3(\text{Me})\text{btc}]\cdot 2(\text{Me})_2\text{Hbtc}\cdot 2\text{H}_2\text{O}\}_n$ (**2**). These materials were obtained in similar solvo-thermal synthesis conditions and were characterized by single crystal X-ray method. Both compounds crystallize in centrosymmetric space groups: triclinic *P*-1, $a=7.7923(9)$, $b=8.7102(7)$, $c=10.7369(11)$ Å, $\alpha=101.043(8)$, $\beta=92.284(9)$, $\gamma=95.237(7)^\circ$ for **1**; orthorhombic *Cmcm*, $a=35.555(2)$, $b=14.9805(10)$, $c=19.9824(6)$ Å for **2**. The structural determination revealed that the coordination geometries around the metal centers are distorted octahedral for Co(II) and tetrahedral for Zn(II). Compound **1** consists of a tetranuclear Co₄(μ₃-OH)₂ cores bridged by btc³⁻ anions and are assembled to form a 2D coordination layer with Co···Co separations equal to 7.905 and 11.144 Å. In compound **2** each Zn(II) cation coordinates two bridging bidentate Hbtc²⁻ anions or one Hbtc²⁻ and one (Me)btc²⁻ anions and two neutral double-stranded bridge fashion bpp molecules with Zn···Zn separation of 11.677 Å, which are then linked by Hbtc²⁻ anions in a quadruple-stranded fashion with Zn···Zn separations equal to 8.305 and 10.585 Å with the formation of 1D ladder coordination polymer.

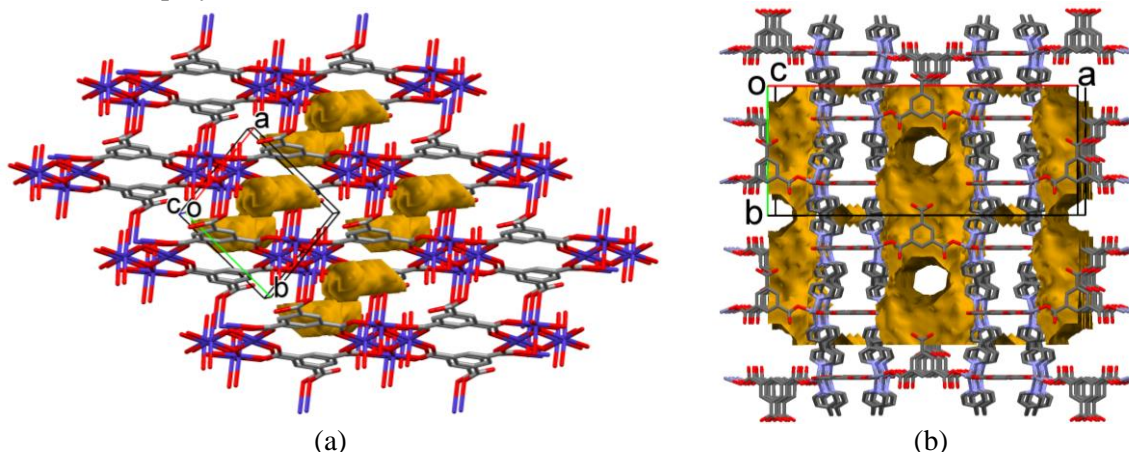


Figure 1. View of the SAVs in **1** (a) and **2** (b) generated using the MERCURY facilities

The both compounds represent predictable porous coordination polymers with negligible solvent accessible voids (SAVs) of 49.9 \AA^3 of the free volume (or 7.0% of total volume cell) for **1** and high cumulative solvent uptake with 3093.0 \AA^3 (or 29.1%) for **2** after the guest molecules evacuation (Fig. 1).

Acknowledgement

Financial support was provided by the State Program of R. Moldova (Project 16.00353.50.05A).

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COMPARATIVE ANALYSIS OF THE BINDING MODE AT ER α OF TWO DERIVATIVES OF 4-HYDROXY-TAMOXIFEN (4OHT)

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Estrogen receptor alpha (ER α) is involved in a large number of biological processes, as well as pathological conditions, e.g. breast cancer, the estimated leading death cause in 2016 for the female population worldwide [1]. Clearly understanding the binding mechanism of the small molecule modulators of ER α is a necessary step in the designing of newly potent ligands for this target, a continuous effort in pharma and academia.

Here, we present a comparative analysis of the binding mode for two small molecule modulators of ER α (Figure 1), using molecular docking [2,3]. For both ligands, the docking simulations were carried out on two conformations of the receptor, antagonist and agonist. The results analysis suggests that the ligands are better accommodated in the agonist conformation of ER α , with EtOXTPE being slightly favored over ZFREtOx through the formation of an additional H-bond with His524.

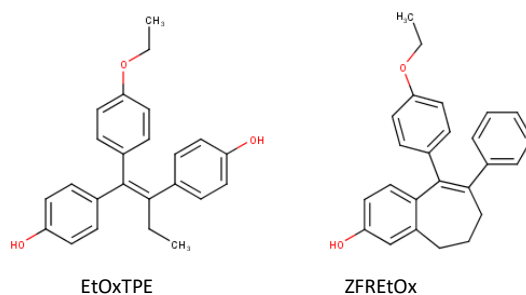


Figure 1 Compound structures

Acknowledgements:

This work was supported by Romanian Academy, Institute of Chemistry Timișoara, project number 1.1.2/2017.

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STRUCTURAL AND CONDUCTANCE STUDIES OF ETHYLETHANOLAMINE 4-NITROBENZOATE

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The crystals of alkanolamine 4-nitrobenzoates represented organic salts and revealed the variety of H-bonded supramolecular networks [1]. New single crystals of organic salt (EEA4NBA) of ethylethanamine with 4-nitrobenzoic acid were obtained by dissolution of components in acetone and slow evaporation at room temperature. Single crystal XRD revealed that the crystal belongs to the monoclinic system with the centrosymmetric space group $P2_1/c$: $a=6.8952(4)$, $b=8.3181(7)$, $c=21.9904(17)$ Å, $\beta=98.037(6)^\circ$. The protonated ethylethanamine cations interconnected by N–H \cdots O hydrogen bonds in the chain decorated by deprotonated 4-nitrobenzoate anions due to O–H \cdots O and charge assisted N–H \cdots O H-bonds, which form $R^2_2(9)$ graph set (Fig. 1a).

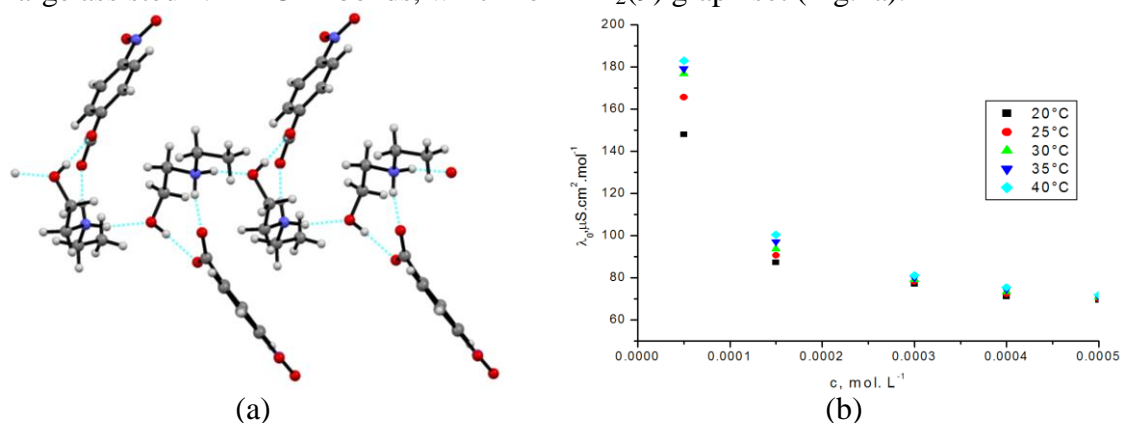


Figure 1. (a) The fragment of 1D supramolecular chain in EEA4NBA. (b) The variation of ionic conductivity with concentration of EEA4NBA in solution for given temperatures.

The electric conductivities of aqueous solutions of EEA4NBA were measured in the temperature range 20°C to 40°C at atmospheric pressure and in the concentration range $5 \cdot 10^{-3}$ - $1 \cdot 10^{-4}$ mol.L⁻¹, using the conductometric method (Fig. 1b). The limiting molar conductances, Λ_0 and the association constants, KA were calculated from conductometric data. On the basis of electrical conductivity measurements, it was found that, as the temperature increases, the capability of EEA4NBA to dissociate decreases, and that reduces the value of Kd . The process is exothermic.

Acknowledgement

Authors thanks the Romanian National Authority for Scientific Research and Innovation, CCCDI-UEFISCDI, project PN3-P3-217/24BM/19.09.2016 and the bilateral Moldova-Romanian project 16.80013.5007.04/Ro.

FLAVONOID NANOPARTICLES AS POTENTIAL ALZHEIMER'S DISEASE THERAPEUTIC AGENTS

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There has been an increasing interest in improving natural antioxidant agent actions by loading them in suitable nano-carriers in order to enhance their protective capacity without altering the quality of the antioxidant product. In other words, encapsulation plays an important role in drug delivery technologies by modifying drug release profile, absorption, distribution and elimination for the benefit of improving product efficacy and safety. Among drug encapsulation and delivery techniques, sol-gel has lately gained considerable ground. Besides its economical benefit, this encapsulation process is based on the chemical and physical interactions relying on a sol-gel reaction. The latter encounters the interconnecting configuration of colloidal nano-sized particles, sol, under increasing viscosity, until a rigid mass is formed with about half the density of glass, gel. Consequently, the design, desirable size, structure and properties of silica materials can be easily optimized. The advantageous applications of sol-gel materials rely on their biocompatibility with various natural or synthetic therapeutic agents for controlled drug delivery, while concurrently improving the efficacy, tolerability and safety of topical drugs [1,2]. They can be used as xerogel silica nanoparticles, which offer unique features, such as stable porous structures, large surface areas, tunable pore sizes and volumes, and well-defined surface properties for site-specific delivery and hosting drug molecules of various sizes, shapes, and functionalities [3]. Moreover, no side-effects of silica materials are detected, as Si(OH)₄ gradually degrades in the body through the kidneys [4]. Furthermore, the enhanced permeability and retention effect as well as the long blood circulation half-lives are of vital importance, especially for biological applications related to targeted delivery and sustained release of drugs through silica nanoparticles (NPs) [5]. In our efforts to employ such technology [6] encapsulating flavonoids in nanoparticles, toward potential therapies against neurodegeneration, PEGylation (PEG: poly(ethyleneglycol)) and CTAB (cetyltrimethylammonium bromide) surface modification of NPs in aqueous micellar systems were pursued [7]. Thus, natural antioxidant flavonoids were encapsulated in well-characterized and PEG or CTAB-modified silica NPs. Furthermore, the improved activity under cell environmental conditions was assessed and further demonstrated. As a result, the novel hybrid nanomaterials were shown to upgrade the antioxidant activity of the flavonoid against metal-induced neurodegeneration *in vitro*. Furthermore, decreased cytotoxicity was observed as a result of a slower yet efficient flavonoid release, counteracting oxidative stress in neurodegenerative processes. More importantly, flavonoid degradation was not observed suggesting that the silica nano-carriers employed possessed the ability to maintain optimal flavonoid pharmacokinetics, thereby, formulating its biodistribution behavior in a cellular environment. Further investigation into molecular mechanistic aspects of the *in vivo* function of such hybrid nano-materials is therefore warranted, thereby targeting potential preventive and therapeutic interventions in neurodegeneration.

Acknowledgements

The authors would like to acknowledge IKY Financial Support of Excellence for Postdoctoral Researchers in Greece - NSRF 1st Cycle for 2014-2020.

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QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS STUDY OF SOME FLAME-RETARDANT POLYPHOSPHONATES

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An important feature of most commercial polymers is to be non-flammable or flame retardant. Several studies reported quantitative relationship between the structure of polymers and their flammability. This paper presents a structure-flammability study for a series of 32 polyphosphonates, modelled by their monomers. Monomer structures were geometry optimized using the density functional theory (DFT) approach included in the Gaussian 09 software. Two types of chiral structures were found. Structural parameters were calculated for the two *R* and *S* chiral structures using the InstantJChem from Chemaxon Ltd. and Padel programs and were related to the limiting oxygen index to model the polymer flammability. Multiple linear regression (MLR) calculations were combined with genetic algorithm for variable selection. Several MLR stable models were obtained. External validation was checked for a test set of six compounds using several criteria. More stable and predictive models were obtained for the *S* isomers. Information on the nature of structural descriptors which influence the flammability was discussed.

Acknowledgements

This project was financially supported by Project 1.1/2017 of the Institute of Chemistry of the Romanian Academy. The authors thank Chemaxon Ltd. for providing academic software license.

SUPRAMOLECULAR ARCHITECTURES OF ISOMERIC METHYLETHANOLAMINE CHLORONITROBENZOATES

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Complexes between two organic compounds where components are underwent an intermolecular proton transfer, with complimentary acid and basic functional groups are known as molecular salts [1]. The interactions between the ionised species are often governed by a variety of intermolecular interactions, hydrogen bonding being maybe the most important critical force in directing the crystallization of organic molecules. Herein, we present the crystallization and single crystal X-ray structures of three new molecular salts using methylethanolamine (MMEA) and chloronitrobenzoic acids (2C4NBA=2-chloro-4-nitrobenzoic and 2C5NBA=2-chloro-5-nitrobenzoic acids) in 1:1 molar ratio. 2C4NBA presents dimorphism in the solid state which explain formation of two polymorphs (a, b) with MMEA. The analysis of supramolecular architecture of ionic compounds has revealed that chloronitrobenzoic acids are deprotonated and MMEA is protonated. Crystal packings of MMEA:2C4NBA are dominated by charge-assisted O–H···O[−] and N⁺–H···O[−] hydrogen bonding: –NH₂ hydrogen atoms connect to a carboxylate oxygen atom and the second oxygen atom of carboxylate group is also hydrogen-bonded to the hydroxyl group, leading to 1D supramolecular chains. In MMEA:2C5NBA crystal packing is directed and through N–H···O H-bond interactions with participation of ammonium NH₂ –donor centers and hydroxyl oxygen atoms acting as H-acceptors (Figure 1).

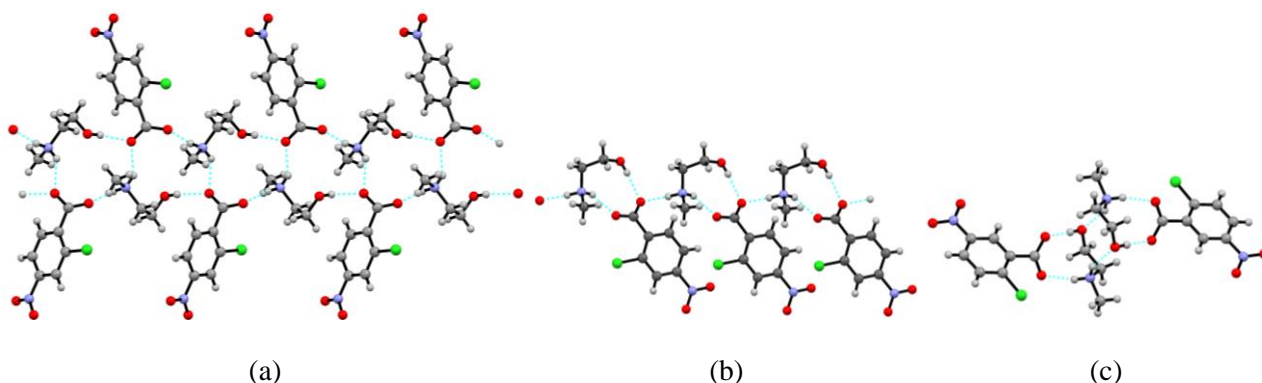


Figure 1. Fragments of supramolecular architectures formed by N–H···O and O–H···O hydrogen bonds in MMEA:2C4NBA (a), MMEA:2C4NBA (b) and MMEA:2C5NBA (c)

Acknowledgement. Authors thanks the bilateral Moldova-Romanian project 16.80013.5007.04/Ro and the Romanian National Authority for Scientific Research and Innovation, CCCDI-UEFISCDI, project PN3-P3-217/24 BM/19.09.2016

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A SURVEY OF ELECTRONIC PROPERTIES INFLUENCE ON BIOLOGICAL ACTIVITY OF FLAVONOIDS

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Flavonoids form a group of well-known natural compounds widespread in vegetables, fruits, flowers, seeds, and grains. The chemical structural modifications of these natural compounds are associated with various biological and pharmacological activities, e.g. anticancer activity, antioxidant activity, antibacterial, antifungal and antiviral activity [1]. In this light, flavonoids have been subjected to many chemical modifications in order to improve their pharmacological profile. To guide the process of designing new flavonoid derivatives with enhanced biological activity, we have investigated the influence of substituents on the flavonoid core for a set of 17 natural flavonoids. The reactivity and chemical profile was investigated by computing global descriptors within the semi-empirical and quantum chemical calculations with Jaguar package [2,3].

Acknowledgements: This work was supported by the Project 1.2 (Theme 1.2.2) of the Institute of Chemistry Timisoara of the Romanian Academy and by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-0422.

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ELECTROCHEMICAL EVALUATION OF COATINGS BASED ON MEDIUM ALKYD RESINS MODIFIED WITH AROMATIC POLYURETHANES ON METALS

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The use of organic coatings is the most frequent method for shielding metal surfaces against corrosion. It has been suggested that approximately one-half of corrosion control costs are related to the use of organic protective coatings [1].

The current study presents the results of the electrochemical measurements (EIS and anodic polarisation) concerning corrosion performance improvement of the coatings based on medium alkyd resin modified with aromatic polyurethanes on iron surface.

Four formulations were prepared with volumetric pigment content (VPC) between 15% and 76% and a nonvolatile content (NVC) 58-83%. The properties of the coatings were investigated by electrochemical methods. From polarization curve recorded in 3% NaCl solution the E_{corr} – corrosion potential and J_{crt} – critic corrosion current density were determined. The efficiency of the coatings based on the electrochemical parameters was evaluated. For the investigated resin it is observed that polarization resistance (R_p) increases with the decrease of pigment content (V5 versus V6), then decreases and tends towards a constant value (V7 and V8, respectively) (Figure 1). The lower value of R_p was obtained for the paint containing the largest amount of pigment (V5). The presence of a larger amount of pigment (VPC>37%) in coating formulation leads to the formation of a film containing micropores. The pores allow the access of the electrolyte through these pores to the surface of the metal.

The optimal amount of pigment that allows a uniform film adherent to the metal surface and without pores in order to prevent the penetration of corrosive species is at most 23.33% (V6).

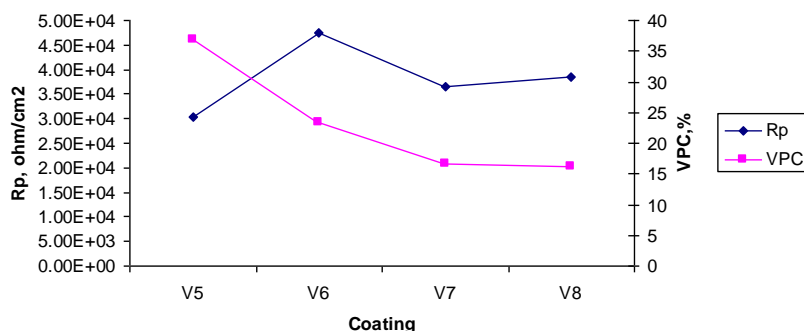


Figure 1. Polarization resistance and pigment content for V5-V8 polymer coatings

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EVOLUTIONARY RELATIONSHIPS AMONG G PROTEIN-COUPLED RECEPTORS USING LIGAND INFORMATION

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G-protein coupled receptors (GPCRs) is the largest and most diverse family of membrane proteins in the human genome. These receptors represent interesting biological targets for industry and academic research as such more than 35% of the marketed drugs target this family of proteins. GPCRs share a common structure with seven transmembrane segments (TM1-TM7) connected by three extracellular loops (ECL1-ECL3) and three intracellular loops (ICL1-ICL3). Commonly, GPCRs are classified based on their sequence homology GPCRs with six main classes, the homology between them being limited. In this work, we introduced a hybrid method which considers sequence and ligand similarities to find new relationships between orphans and characterized GPCR. Eighteen class A orphan GPCRs presented a significant relatedness with characterized GPCRs when binding site similarity and sequence conservation criteria were applied, and 9 class A orphan GPCRs presented relevant degrees of relatedness with characterized GPCRs when 2D similarity between known active ligands of orphans and characterized GPCR were calculated.

GRAFTING OF SnO₂ ON PHENYL-PHOSPHONIC ACIDS

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In this paper the attention is focused on the synthesis of phosphonic acid/esters and their compatibility with other functional groups or molecules. Then the types of inorganic surfaces which can be modified using phosphonic acid chemistry are summarized, as well as the related mechanisms involved when attaching phosphonate groups onto these surfaces. This paper finally goes on to outline the richness of applications which can be developed from the resulting functional materials.

The present work deals with the possible use of other organophosphorus coupling molecules such as phosphonic acids RR'PO(OH) and their ester derivatives. Indeed, grafting by phosphonic compounds would allow the introduction of more organic groups on the surface of SnO₂.

The modification of SnO₂ surfaces with phosphonic acids RPO(OH)₂ is currently attracting growing interest in different areas as self-assembled monolayers.

This synthetic approach has many advantages: films with optical quality and controlled thickness can be obtained using low temperatures and cheap raw materials.

Keywords: grafting, phosphonic acids, phosphonate, organophosphorus, stanium oxide

CHEMICAL AND BIOLOGICAL INVESTIGATION INTO BORON-HYDROXYCARBOXYLIC ACID BINARY SYSTEMS.

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Boron is one of the Periodic Table elements of particular interest. It is an essential micro-nutrient for plants, animals and humans [1]. The primary source of boron is through consumption of food and water. Extensive research in animals has concluded that sodium borate protects from the development of fatty liver [2]. In plants, it has an important role in sugar transport, regulation of metabolic functions, cell wall synthesis and membrane structure [3]. Moreover, it affects the activity of different enzymes, most of which are necessary for energy substrate metabolism [4]. In everyday life and human activities, boron is extensively used as an antimicrobial, insecticide, and constituent in pharmaceuticals [5,6]. In addition to that, there is evidence that boron is an inevitable nutrient for humans, involved in many mineral metabolism, hormone action and immune functions [7], with the exact biological function of boron, however, still remaining unexplained [8]. Being one of the most important forms of boron, boric acid and its behavior pertaining to Lewis acidity, in terms of electron donor-acceptor interactions, mark boron as an element stabilizing biological molecules by linking them through ester bridges [8]. In body tissue and fluids, boron exists as boric acid, which can affect bone growth and health as well as the skeletal and immune system, because of the regulatory role that boron has with minerals [9,10]. Based on the chemical and biological properties of boric acid and its unclear interactions in biological systems, research efforts were prompted in our lab leading to the idea of synthesizing materials from binary boron-hydroxycarboxylic acid systems in an aqueous environment. Physiological substrates, such as glycolic, 2-hydroxyisobutyric, and citric acid, reacted with boron and led to well-defined structures under pH-specific conditions. The isolated crystalline materials were characterized physicochemically by elemental analysis, FT-IR, TGA, NMR (in the solid state and in solution), X-ray crystallography, and Mass-Spectroscopy. Three crystalline materials with different substrates were used in biological studies, involving toxicity and proliferation. Selected structures were investigated in two different cell cultures, 3T3-L1 and Saos-2, at concentrations in the range 1-100 μM . The overall results confirmed the tetrahedrality of boron and the nontoxic effects in both cell cultures. All new compounds justify the potential of their application in the field of biochemistry and technology, concurrently suggesting further research using (O,N)- and (N,N)-containing ligands, capable of delivering new insight in the biological role of boron.

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DETERMINATION OF HEAVY METALS IN WASTE WATERS AND THEIR REMOVAL BY PHOSPHONATE METAL ORGANIC FRAMEWORKS

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Phosphonate metal organic frameworks exhibit a variety of applications and a rich chemistry are used nowadays for removal of heavy metals due to their ecofriendly nature. Wastewater pollution is a major concern due to their *toxicity* to many life forms. In order to decrease the heavy metals impact upon the environment numerous technologies of water treatment such as: electrochemical technology, ion exchange, chemical sedimentation, redox process and so on, are studied. The adsorption processes represent a very good alternative for heavy metals removal due to low costs and easy of operation.

The goal of this work involves batch types experiments investigating the effects of the solution pH, solid:liquid ratio, initial concentration of Cr(VI) and contact time upon the adsorption efficiency of phosphonate organic frameworks. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich were applied to adsorption equilibrium data to find the best amongst these models.

Phosphonate metal organic frameworks were obtained in our labs by the reaction of divalent inorganic salts (Co(NO₃)₂·6H₂O, NiSO₄·7H₂O), phosphonic acid (phosphonoacetic (CP), N,N-bis(phosphonomethyl)glycine (Gly) and unsaturated phosphonic acids (VP)) in hydrothermal conditions. The synthesized compounds were characterized by FTIR, X-Ray crystallography and thermogravimetric analysis [1-3].

The adsorption efficiency in the elimination process of Cr(VI) ions is in the following order: Co-CP < Co-Gly < Co-VP, while Ni-based metal phosphonates Ni-CP < Ni-Gly ≤ Ni-VP [4].

Acknowledgements

This work was partially supported by Program no 2 from the Institute of Chemistry Timisoara of Romanian Academy and by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1398.

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IDENTIFICATION OF ORIENTATION AND INTERACTIONS OF NEW 2-(TRIMETHOXYPHENYL)-THIAZOLES WITHIN COX-1/2 BINDING SITES

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Cyclooxygenase-1/2 (COX-1/2) inhibitors are common drugs used for the treatment of pain and inflammatory diseases i.e., rheumatoid arthritis and osteoarthritis. A series of 13 novel thiazole derivatives has been previously designed, synthesized and reported as COX-1/2 inhibitors. In order to highlight the structural requirements of these novel COX-2 inhibitors and relevant binding features which can afford guidance for the rational design of novel potent COX-2 selective inhibitors with reduced cardiovascular risks. The discussion concerns SAR analysis, 3D similarity overlay, the portrayal of binding site interactions by induced fit docking, and prediction of pharmacokinetic properties. Molecular docking and 3D shape similarity (Rapid Overlay of Chemical Structures (ROCS)) were used to determine the potential orientation and the interactions of thiazole derivatives **A1-13** within COX-1/2 binding pocket. The most probable binding mode of COX-2 selective compound **A3** showed hydrogen bond interactions with binding site key residues including Ser530, Arg120, and Tyr355, while hydrophobic contacts were identified with Val349, Leu352, Phe518, and Ala527. Pharmacokinetic profile of **A1-13** predicted by QikProp from Schrödinger software validate compound **A3** as lead candidate suitable for further structural optimization to design novel COX-2 selective inhibitors with appropriate pharmacokinetic profile.

Acknowledgements

The authors thank OpenEye Ltd. for providing academic license and to Dr. Ramona Curpăn (Institute of Chemistry Timisoara of Romanian Academy), for providing access to Schrödinger software acquired through the PN-II-RU-TE-2014-4-422 projects funded by CNCS-UEFISCDI Romania. This project was financially supported by the “Iuliu Hațieganu” University of Medicine and Pharmacy Cluj-Napoca, Romania through the internal research grant no. 1491/30/28.01.2014 and Project No. 1.2/2017 of the Institute of Chemistry of Romanian Academy, Timisoara.

QUERCETIN NANOPARTICLES PROTECT CELL SYNAPTIC CONNECTIVITY AND SURVIVAL RATE UNDER Cu(II)-LINKED OXIDATIVE STRESS IN NEURODEGENERATION

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Tremendous neurodegenerative defects of the brain temporal lobes occur during Alzheimer's disease (AD), affecting cognition and memory tasks of patients [1,2]. AD hallmarks include beta-amyloid (plaques) and protein tau (tangles) [3]. These changes are eventually accompanied by a gradual irreversible loss of synaptic connectivity, leading to the death of neurons [4]. At the molecular level, mounting evidence has implicated metal ions in aberrant beta-amyloid and tau protein function in the brain. However, with increasing age and/or oxidative stress, the BBB becomes compromised so that metal ions are more easily transported into and out of the brain [5]. Copper is a redox-active metal that can exist either in the oxidized or reduced oxidation state. Lack of copper in the organism increases oxidative damage through decrease of Cu-dependent antioxidant enzymes [6]. When electrochemically active copper is not bound to an enzyme as a cofactor, copper ions are able to catalyze the production of potentially dangerous reactive oxygen species (ROS) through Fenton reactions. To date, no therapy has been found to cure AD. Lately, intensive scientific efforts focus on and take advantage of the beneficial antioxidant properties of natural polyphenol agents, such as flavonoids, against neurodegenerative processes [7-9]. *In vivo* studies have shown improved learning and memory ability in AD mice upon flavonoid administration [10,11]. Therefore, in the present investigation, molecular approaches were brought up in order to develop more effective flavonoid agents by encapsulating flavonoids into PEG 3000, and CTAB-modified silica nanoparticles. Overall, our findings revealed increased protective effects of quercetin nanoparticles against Cu(II)-mediated neurodegeneration in primary rat neuronal and glial hippocampal cultures compared to previous studies using non-encapsulated quercetin. The latter functional biological reactivities of the novel flavonoid nanoparticles were in line with their physicochemical features, which reflect the a) differential nature of the structural assemblies of the new nanoparticles, thereby distinguishing them from other polymeric and liposomal drug carriers, and b) significance and impact of PEG vs. CTAB chemistry in the synthetic assembly of the nanocarriers. The encapsulated flavonoid nanoparticles deserve further perusal *in vivo* as they may be useful in encapsulating drugs of high therapeutic potency.

Acknowledgements

The authors would like to acknowledge IKY Financial Support of Excellence for Postdoctoral Researchers in Greece - NSRF 1ST Cycle for 2014-2020.

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SYNTHESIS AND STRUCTURAL STUDY 2:1 CLATHRATE INCLUSION COMPLEXES OF BIS(IMINOPHOSPHORANE)ETHANE WITH DIFFERENT SOLVENTS GUEST MOLECULES

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Iminophosphoranes are valuable building blocks in organic, organometallic and coordination syntheses, being key compounds with biological and pharmacological activity. Recently, it has been shown that triclinic (*P*-1 space group) crystal form of bis(iminophosphorane)ethane (**1**) represent 1:1 toluene solvate [1], in which the host molecules encapsulate toluene molecule in the cavity of $\sim 230 \text{ \AA}^3$. The solubility and bioavailability of crystalline compounds may strongly depend on the polymorph type or solvate forms therefore we have undertaken the investigation of different crystalline solvates of **1** with the smaller solvent molecules. Five new isomorphous 2:1 clathrate inclusion complexes of **1**, Fig.1, with water, ethanol, ethanol/acetonitrile, tetrahydrofurane, and acetone have been synthesized and structurally characterized by X-ray method. All compounds crystallize in the monoclinic *C*2/*c* space group, Table 1. The solvent molecule occupies the cavity with the volume only 82-115 \AA^3 . Thus, the size of solvent molecule influences on stoichiometry and the resulting crystalline form.

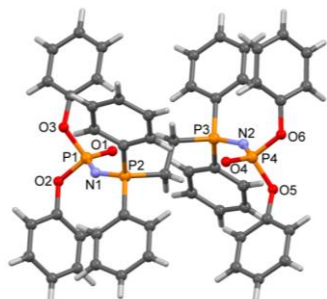


Fig.1. Molecular structure of **1**

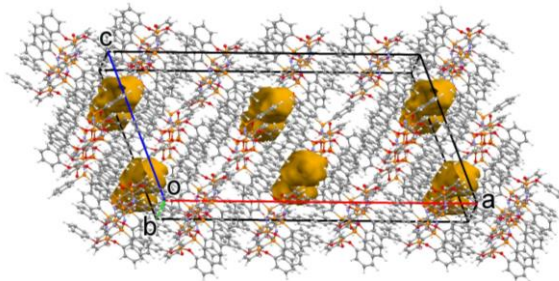


Fig.2. Crystal packing illustrates the voids formed by the host molecules

	Water	Etanol	Ethanol Acetonitrile	THF	Acetone
<i>a</i> (\AA)	41.022(3)	40.988(3)	41.103(2)	41.307(2)	41.503(3)
<i>b</i> (\AA)	11.152(1)	11.160(1)	11.206(1)	11.271(1)	11.186(1)
<i>c</i> (\AA)	20.929(1)	21.264(2)	21.062(1)	21.198(1)	21.178(1)
β (deg)	110.24(1)	111.86(1)	111.10(1)	111.23(1)	111.54(1)
<i>V</i> (\AA^3)	8984(1)	9027(1)	9051(1)	9199(1)	9146(1)
Void <i>V</i> (\AA^3)	82	99	98	115	110

Acknowledgement

Authors thanks the bilateral Moldova-Romanian project 16.80013.5007.04/Ro and the Romanian National Authority for Scientific Research and Innovation, CCCDI-UEFISCDI, project PN3-P3-217/24 BM/19.09.2016

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VANADIUM REDUCES AUTOPHAGY AND INHIBITS METASTATIC NICHE BY INDUCTION OF TRAIL-INDUCED APOPTOSIS IN CANCER CELLS

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The antitumor characteristics of vanadium and its ability to inhibit cancer cell growth and metastasis is known [1]. However, the precise mechanism by which vanadium inhibits carcinogenesis is not clear. The present study shows that a newly synthesized and characterized well-defined ternary vanadium-peroxido-betaine form down-regulates autophagy and EMT transition through augmentation of TRAIL-induced apoptosis in breast epithelial MCF-7 and lung adenocarcinoma A549 cells. Inhibition of autophagy by siRNA or 3-MA increases TRAIL-mediated apoptosis and inhibits the invasive phenotype of cancer cells. Moreover, vanadium reduces NF-κB binding to *Becn1* promoter, thereby preventing initiation of autophagy and abnormal proliferation. In search of a mechanistic insight into the above observations, it is demonstrated that vanadium directly targets autophagosome formation and reduces LC3-I and II expression, both of them important molecules involved in autophagy. The accruing results suggest that inhibition of autophagy by vanadium allows cancer cells to undergo apoptosis, thereby contributing to reduction in cancer cell invasion and metastasis [2,3]. Collectively, the work a) identifies a biologically active antitumor novel vanadofrom containing peroxido and betaine moieties, and b) reveals a crucial role for vanadium in autophagy inhibition, thereby providing new molecular perspective(s) into finely configuring vanadofroms for cancer drug research and therapy.

Acknowledgments

Financial support by “IKY Fellowships of Excellence for Post Doctoral studies in Greece – Siemens Program” is gratefully acknowledged.

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SYNTHESIS, CHARACTERIZATION AND EVALUATION OF ADSORPTION CAPACITY OF NEW MAGNETIC NANOCOMPOSITES

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Fe₃O₄/Ag/C nanocomposites have attracted much interest in many applications due to their valuable properties. These nanocomposites combine the good catalytic and antibacterial activity provided by silver and high adsorption capacity supplied by carbon with the advantage of easy magnetically manipulation given by magnetite. In this work magnetite/silver/carbon nanocomposites with different mass ratio were successfully synthesized by combustion method, working in controlled atmosphere. The structure and morphology of the Fe₃O₄/Ag/C nanocomposites were investigated by X-ray diffraction (XRD), FTIR, scanning electron microscopy (SEM)-energy dispersive X-ray (EDX) and N₂ adsorption-desorption technique. The obtained nanocomposites were tested as adsorbents for the removal of both anionic and cationic dyes from wastewaters, in selected working conditions. an adsorbent mass of 1 g/L, MSC demonstrated removal efficiency up to 99.6% for anionic dyes and 99.93% for cationic dyes, showing a decrease of the removal percentage with the increase of the silver content.

Acknowledgments

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1319.

STUDY ON CdSO₄ DECOMPOSITION IN THE PRESENCE OF CdO.

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The study of the oxidation of metal sulfides and sulfide concentrates is a very important problem for the optimization of its roasting process and also for to know its resistance to oxidation in photovoltaic cells, photocatalysts or light sensors used. The cadmium sulfides is known for a long time due to their semiconductor properties, thus dielectric diodes and triodes are made from the material based on cadmium sulfide, but in the last time its photocatalytic and photoemissive properties are studied intensively.

The oxidation of CdS to CdO is a complicate process that has generated controversial opinions on mechanism. The main theories, oxide formation or sulfate formation in the first stage, describe the final stage of process as the CdSO₄ decomposition in the presence of some CdO amount. The goal of this study is to determine the influence of CdO on the CdSO₄ decomposition in purpose to clarify subsequently the mechanism of CdS oxidation.

Samples of CdO and CdSO₄ (p.a. Reactivul-Bucuresti) were calcined at 943 K for 30 min. A sample of CdO: CdSO₄ in ratio 2:1 was prepared by mixing carefully the CdO and CdSO₄ in ratio of 2:1 and calcination at 943 K for 30 min also. All the samples were characterized by XRD and FTIR. The thermal decomposition of CdSO₄ and CdO: CdSO₄ = 2:1 was studied by thermogravimetry (Mettler-Toledo TGA/SDTA 851-LF 1100 apparatus) coupled with mass-spectrometry (Pfeiffer-Vacuum-Thermo Star mass spectrometer), with non-isothermal method at heating rates of 1, 2, 4 and 8 K/min and finally a heating at 943 K for 30 min. Typical thermal curves: TG, DTG and DTA are showed in Fig. 1 and 2.

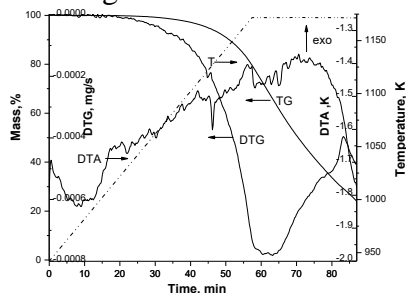


Fig. 1. Decomposition of CdSO₄, heating rate 4 K/min.

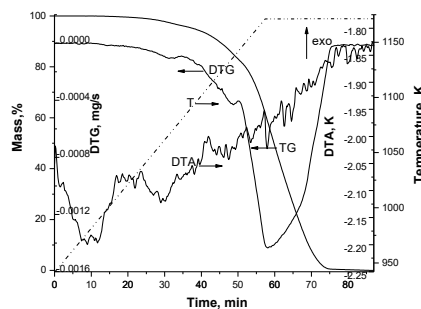


Fig.2 Decomposition of CdO: CdSO₄ = 2:1 heating rate 4 K/min.

The TG curves were processed with ASTM 1641 method (based on Flynn-Wall isoconversional method) for apparent activation energy calculation.

The activation energy of CdSO₄ decomposition at 10% conversion is 287.6 kJ/mole, similar to literature data (289 kJ/mole), which was nearly to the enthalpy of the CdSO₄ decomposition in nitrogen flow. The apparent activation energy for the CdSO₄ from CdO: CdSO₄ in ratio 2:1 is of the 320.6 kJ/mole, a significant higher value than for the CdSO₄ decomposition. An explanation could be the formation of a new phase between CdO and CdSO₄, more stable as CdSO₄. This phenomenon has to be stronger at CdS oxidation as the CdSO₄ and CdO are in a tighter contact having the same origin, CdS.

PRELIMINARY THEORETICAL INVESTIGATIONS OF SOME SELECTIVE COX-1 INHIBITORS

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In search for selective cyclooxygenase-1 inhibitors (COX-1), scientist tried to guide the development of small molecules which have significant effects on the analgesic activity without secondary gastric effects. Numerous studies conclude that minor modifications into the chemical structure of well-known COXs inhibitors (e.g. mofezolac, FR122047, valdecoxib) [1, 2] induce significant change in their COX selectivity and affinity. In order to identify the key structural features needed to achieve COX-1 selectivity, the electronic molecular properties: heat of formation, HOMO and LUMO energies, atomic Fukui indices and molecular electrostatic potential were computed by employing semi-empirical molecular orbital theory at the level AM1 and density functional theory quantum chemical calculations. The computational outcomes will be useful tools for an efficient design of new selective COX-1 inhibitors with enhanced pharmacological profile.

Acknowledgments

This study was financially supported by the Project No. 1.2/2017 of the Institute of Chemistry Timisoara of Romanian Academy. The authors thank to Dr. Ramona Curpăn, Institute of Chemistry Timisoara of Romanian Academy for providing access to Schrodinger software acquired through the PN-II-RU-TE-2014-4-0422 projects funded by CNCS – UEFISCDI Romania.

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3D STRUCTURE MODELING OF COMPOSITE MATERIALS USED IN 3D PRINTING BIOAPPLICATIONS

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A very important factor in tissue growth for biological applications is substrate cultures and their structure. Such applications may be associated with medicine, the development of implants or even applications involving animals and plants, in order to optimize and control food. In recent years research has been directed toward trying to model specific forms of 3D structures, which could help in the growth, development and shaping of soft and/or hard tissue for the above applications. During construction of structures, a number of important issues related to both life-conditions for the compatibility of the materials used need to be solved, including structural integrity during application, but also biological behavior to facilitate new tissue growth [1]. Important points in the relevant research are the a) structure and composition of the materials to be used, and b) internal geometric structure with reference to the distribution of materials in the model to represent the crux of tissue regeneration, according to the application which will result in the desired outcome (e.g. bone, muscle or biological mass, body organ, etc.). The structure in the design must combine good resistance to mechanical stress and an adequate space for growth, guidance and operation of the cellular structure so as to create the final tissue [2].

Key factors to be taken into consideration is the type of tissue to be grown, the initial and final biological structure or complexity, combined with the improved characteristics of the initial conditions, the growth rate when it pertains to industrial application in the food stuffs or elsewhere, and the end environmental conditions so that the final product is hygienically acceptable and environmentally friendly. The combination of systematically designing [3] materials with natural porosity for further use should be pursued in such a way that it is possible to create channels, through which to feed cells, remove debris, and create a vascular system [4]. This study investigates the above factors when fabricating 3D model components with specific biomaterial compositions. The building blocks have small dimensions, with a specific internal design and distribution of materials, which will be used to create tissue [5]. The implementation was based on a three-dimensional printing device (3D Printing) constructed in our laboratory. This was made possible by using a CAD system, wherein specific patterns that create surfaces and solids are used. The models are then printed and used in cultures. From the progress made so far, this study has gained ground toward promoting research, examining biological responses and compatibility to existing specific biological environments. The results show the importance of the promotion of reliable and well-defined (bio)materials through 3D printing processes.

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INVESTIGATIONS ON PHOTOCHROMIC PROPERTIES OF 2,6-BIS(2,4-DIHYDROXYBENZYLIDENE)CYCLOHEXANONE

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The development of novel photochromic materials has gained an increased interest in the last decades due to their industrial applications in optical memory devices, sensors, switches, intelligent windows and displays [1, 2]. Synthetic and naturally anthocyanins are of practical interest with the possibility of achieving reversible changes in color when submitted to different external stimuli, such as light, temperature and pH [3, 4]. Generally, all these compounds hold the same 2-arylbenzopyrylium (flavylium) core and follow the same pH-dependent network of reversible chemical reactions. It was reported that other three families of structurally related compounds such as xanthylium [5] follow an identical network of chemical reactions as flavylium derivatives. The aim of the present work was to discover novel photochromic systems based on xanthylium derivatives. The attention has focused on the isolation, identification and characterization of the species involved in the network of chemical reactions of 2,6-bis(2,4-dihydroxybenzylidene) cyclohexanone. The halochromic behavior of the compound considering the changes in color due to the pH shift has been studied. This ability can be attributed to the various species involved in the interconversion of the compound in acidic or basic conditions. In order to identify the stable species, the NMR analyses were performed in different pH media: neutral, acidic and basic. The color shift of the species as a function of pH has been also studied by UV-VIS spectroscopy.

Acknowledgements

The authors acknowledge the support of the Romanian Academy, Project 4.1.

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THE COMPUTATION OF PREDICTION INTERVALS IN KINASE-INHIBITOR MODELLING

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More than 500 kinases are included in the human kinome [1] and most of them present a highly conserved binding site, and therefore developing new compounds with an improved selectivity profile is very challenging. Cheminformatics can facilitate the efficient search for compounds with desirable selectivity pattern through machine learning algorithms. The prediction models developed so far for kinase inhibitors assess the model performance using external test sets, selected randomly from a given data set or from other activity data sources. This aspect, makes the models applicable to screen virtual libraries or to classify compounds but are limited to the training data.

In the present work, we estimate the variation of the prediction power provided by numerous kinase target sets recently published, [2] through the computation of statistical tolerance intervals for classification and virtual screening. The results indicate improved predictors for kinase inhibitors, with superior robustness and high ability to identify novel molecules with desirable kinome-wide profiles. These results offer a more clearer perspective of the prediction power of ligand-based virtual screen at a kinome-wide level.

Acknowledgments

This work was supported by Project 1.2.4/2017 of the Institute of Chemistry Timisoara of the Romanian Academy. We thank ChemAxon Ltd. for the free academic license to their software.

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INVESTIGATION OF MAGNETITE/CARBON NANOCOMPOSITES AS SORBENTS FOR REMOVAL OF METALS IONS FROM AQUEOUS SOLUTIONS

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Metal ions are reported as pollutants, due to their mobility in natural water ecosystems and due to their toxicity. The problem associated with metal ions pollution is that they are not biodegradable, cannot be metabolized or decomposed, and are highly persistent in the environment [1]. Adsorption proved to be a superior technique for metal ions removal from aqueous solutions, due to the cost, applications, simplicity of design, a wide range of adsorbents, low harmful secondary products, high effectiveness and facile regeneration of the adsorbents [2].

In this work, we investigate the capacity of new magnetic nanoparticles to remove metal ions (Cu^{2+} , Cd^{2+} , Zn^{2+}) from aqueous solutions. Magnetite/carbon nanocomposites (MNC) having different $\text{Fe}_3\text{O}_4/\text{C}$ mass ratios, were prepared by solution combustion synthesis [3]. The effect of solution pH, adsorbent nature and dose, initial concentration of metal ions, and contact time on adsorption process was investigated. The removal efficiency of pollutants depends on solution pH, increase with the adsorbent dose and decreases with initial concentration of the pollutants. The adsorption efficiency of investigated materials decreases in order: $\text{Cu(II)} > \text{Zn(II)} > \text{Cd(II)}$. Pseudo-second order kinetic model was fitted to the kinetic data. The experimental results suggest that as-prepared magnetite/carbon nanocomposites have the potential applications in the water purification management.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1319.

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SYNTHETIC DIVERSITY IN AQUEOUS BINARY Ga(III)-HYDROXY)-CARBOXYLIC ACID SYSTEMS. POTENTIAL BIOLOGICAL ROLES

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Gallium is a silver, glassy, semi-metal element, belonging to the group 13 and the fourth period of the Periodic Table. It is found mostly in a salt form in bauxite and zinc ore [1]. Albeit normally inert, growing industrial activity depends on it. As readily purified through the melting process, the predominant application of this trivalent "metal" is found in semiconductors of gallium arsenide and gallium nitride [2]. Considering the odds of these materials and the dependence on computers, high-speed communication by optical means, and photovoltaic elements, it is clear that the amount of gallium present in relevant applications will increase in the near future. As a result, the toxicological point of view cannot be ignored. Gallium is not known to possess a biological role. Historically, its low bioavailability has apparently excluded it from any biologically relevant function. However, it is known that Ga(III) can exert its effect by interfering with iron metabolism. The functions of the latter metal ion are quite diverse. Ga(III) with an ionic radius of 0.67 Å, is sufficiently similar to Fe(III) in an octahedral environment so as to be inserted into Fe-dependent biomolecules [1]. However, while Fe(III) is redox active, Ga(III) is not, and the replacement of iron by this ion often leads to inactivation of the target protein.

Hydroxycarboxylic acids are widespread in nature, playing an important role as metabolic intermediate products in plants and animals. Due to their role(s) as intermediate products in vegetable and animal metabolic pathways, they do not exhibit toxic properties [3]. The aliphatic hydroxycarboxylic acids have one or more alcoholic groups, with one or more carboxylic acid groups. In the simplest case, hydroxycarboxylic acids can be divided into three categories: 1) 2- or alpha-hydroxycarboxylic acids, 2) 3- or beta-hydroxycarboxylic acids, and 3) hydroxycarboxylic acids with the alcoholic group in position 4 or at even more remote carbon atoms from the carboxylic acid group [3].

The subject of the present work was the synthesis of new hybrid materials containing Ga(III) and organic substrates, (hydroxy)carboxylate ions, in order to impart suitable properties onto the emerging hybrid materials, thus making them amenable for investigation of their activities and applications in vivo. These materials formulate the basis for a thorough investigation of the biological properties of Ga(III) in the (patho)physiology of diabetes and its antimicrobial properties toward pathogenic organisms.

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3D QSAR MODEL BASED ON PHARMACOPHORE HYPOTHESIS FOR SMO RECEPTOR INHIBITORS

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The smoothened (SMO) receptor is a GPCR-like protein of the hedgehog (Hh) signalling pathway which has major implication in cancer development [1]. Some SMO inhibitors are already known to be effective as anticancer compounds [2, 3]. Taking into account this information, a 3D QSAR model based on the best pharmacophore hypothesis for SMO receptor inhibitors has been developed. The selected pharmacophore hypothesis has the following features: two hydrogen bond acceptors (A), one hydrogen bond donor (D), one hydrophobic (H) contact and one aromatic ring (R). The 3D-QSAR model built using this hypothesis shows good statistically parameters: a correlation coefficient, R^2 of 0.846 for the training set and a predictive correlation coefficient, Q^2 of 0.786. Subsequently, for AADHR hypothesis the best fitted compound has been used for flexible docking with the Induced Fit protocol of Schrodinger suite and the key amino acids important for ligand-receptor interaction have been highlighted. The residue Asn219 of SMO binding site has been found to contribute as hydrogen bond donor. Our current results are supported by the crystallographic data obtained by various groups of researchers that show the formation of an interaction between Asn219 and ligands in the binding pocket of SMO receptor [4, 5].

Acknowledgments

This work was supported by Romanian Academy, Institute of Chemistry Timisoara, project number 1.1.3/2017. The authors thank to Dr. Ramona Curpan, Institute of Chemistry Timisoara of Romanian Academy for providing access to Schrodinger software acquired through the PN-II-RU-TE-2014-4-0422 projects funded by CNCS – UEFISCDI Romania.

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NOVEL Zn-METALLOPORPHYRINS DERIVED FROM ASYMMETRIC A₃B PYRIDYL-*meso*-SUBSTITUTED PORPHYRINS

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The different peripheral substitutions on porphyrins are proven to induce significant conformational distortions of the planar ring skeleton minimizing steric interactions between the substituents and modifying the system electron density making it more or less nucleophilic. These macrocyclic deformations and mixed substitutions might drastically affect the optical and redox properties of the distorted porphyrins. Zn-complexes of A₃B mixed substituted porphyrins grafted with one pyridyl and three phenoxy or 3,4-dimethoxy groups are designed to favour generation of supramolecular assemblies between porphyrin molecules and with ZnA₂O₆ (A = Ta and/or V) pseudo binary oxides. These new organic–inorganic assemblies will be tested to evaluate their efficiency in corrosion protection on carbon steel samples obtained by PLD deposition of alternative thin layers. The classical metalation of porphyrins was performed in DMF bringing to reflux the porphyrins with twenty times excess of Zn(CH₃COOH)₂ salt in methanol. Samples were drawn every 5 minutes and the UV-vis spectra were recorded to monitor the reaction. Complete metalation took one hour. The UV-vis inspection proved the reduction of the four Q bands characteristic for porphyrin base to only two differently located Q bands characteristic for Zn-metalloporphyrins (Figure 1).

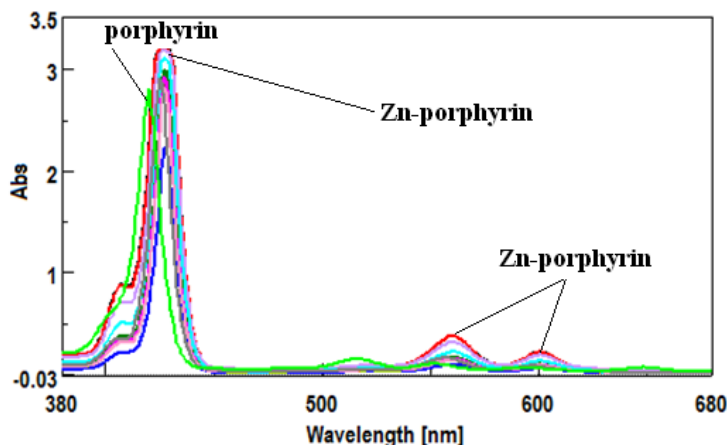


Figure 1. UV-vis monitoring of Zn-porphyrin syntheses

Acknowledgements

The authors are kindly acknowledging the support from UEFISCDI funded PED project CorOxiPor 107/03.01.2017 and Program 3-Porphyrins/2017 from Institute of Chemistry Timisoara of Romanian Academy.

CATALYTIC ACTIVITY IN TERNARY V(V)-DIPEROXIDO-BETAINE SPECIES

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Over the past few years, eluding correlations of ternary V(V)-diperoxido-betaine species with oxidation catalysis have attracted keen research interest in our lab. Synthetic approaches based on the physiologically relevant oxidation states V(IV) and V(V) were employed in pursuing the synthesis of well-defined complex forms of vanadium with physiological substrates and hydrogen peroxide, ultimately leading to ternary V(V)-H₂O₂-amino acid/betaine species, isolated and fully characterized in the solid state and in solution [1,2]. The employment of such vanadofoms in catalysis revealed the time and temperature-dependent effect that vanadium exerts on the selective transformation of organic substrates of well-defined catalytic systems (employing olefinic and aromatic compounds) compared to non-peroxido vanadate compounds [3-5]. The results project the chemistry of vanadium, when the latter is appropriately configured to promote organic substrate transformations under defined experimental conditions. Collectively, the synthetic chemistry of the adopted approach in the present work formulates a multidisciplinary strategy, which merits further perusal into the complex behavior and role of vanadium in organic substrate transformation catalysis.

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MLR AND PHARMACOPHORE STUDY OF DIBENZOYLHYDRAZINES INSECTICIDES

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The dibenzoylhydrazine non-steroidal ecdysone agonists have an unusual high affinity for the ecdysone receptor of lepidopteran insects. In this study we present a multiple linear regression (MLR) and pharmacophore study on a series of dibenzoylhydrazine insecticides with ecdysone agonistic activity against the silkworm *Bombyx Mori* lepidopteran species cell lines. Dibenzoylhydrazine structures were energy pre-optimized using the MMFF94s force field during a conformational analysis. Structural variables were derived from the minimum energy conformers and were correlated with the experimental insecticidal activity (expressed as pEC₅₀ values) using the multiple linear regressions (MLR) approach. Stable and predictive models were obtained. For the same series of compounds pharmacophore hypotheses were built and validated using the partial least squares (PLS) approach. Hydrogen bonding and hydrophobic compound characteristics contributed to the insecticidal activity.

Acknowledgements

This project was financially supported by Project 1.1/2017 of the Institute of Chemistry of the Romanian Academy. The authors thank OpenEye Ltd., Prof. Paola Gramatica from the University of Insubria (Varese, Italy), Chemaxon Ltd. for providing academic software license and to Dr. Ramona Curpăn (Institute of Chemistry Timisoara of Roumanian Academy), for providing access to Schrödinger software acquired through the PN-II-RU-TE-2014-4-422 projects funded by CNCS-UEFISCDI Romania.

CATALYTIC OXIDATION OF BENZENE WITH OXIDO-PEROXIDO-ZWITTERION VANADATE COMPOUNDS

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Vanadium exhibits a pluripotent role in abiotic and biological systems. Poised to explore the role of vanadium in both types of systems, binary and ternary systems of that metal ion in the oxidation state V(V) were explored in the presence of hydrogen peroxide and zwitter ionic substrates. The resulting ternary vanadium(V)-oxido-peroxido-betaine species were fully characterized physicochemically, including X-ray crystallography [1,2]. The emerging species were further employed in catalytic systems with defined organic substrates being exposed to vanadium. To that end, there have been various trial reactions with various stoichiometries within a “family” of ternary oxido-peroxido-vanadate compounds with ligands (betaine, zwitterions), as catalysts for the oxidation of the aromatic substrate benzene [3-5]. The results a) provide detailed information on the properties of the new materials in the solid and liquid phase, and b) distinctly demonstrate the structural and chemical characteristics that justify further perusal of the catalytic action of vanadium in epoxidation reactions of organic substrates. The collective results merit in depth investigation of the vanadium catalytic chemistry as providing insight into selective industrial applications, leading to catalytically derived products (e.g. phenol).

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COLOUR STUDY OF A DISAZO DIRECT SYMMETRICAL STILBENE DYE

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The worldwide standard method for color measurement is CIELAB 1976. The method it is based on numerical values, which takes the guess work out of color correction [1].

The 1976 CIELAB color space is an attempt at providing a perceptually uniform color space, the distance between two points also approximately tells how different the colors are in lightness (L^*), redness (a^*), yellowness (b^*), chroma or saturation (C^*) and hue angle (h°) calculated from the tristimulus values XYZ. The colour of an disazo direct symmetrical stilbene dye derived from the 4,4'-diaminostilbene-2,2'-disulphonic acid was evaluated in terms of above mentioned CIELAB parameters for the CIE D65 (natural day light), A (tungsten light), F2 (fluorescent light) and the standard 10° observer respectively. The used coupling component was N-(2-bromophenyl)-2-hydroxybenzamide. The colour differences: ΔE_{ab}^* and ΔE_{CMC} were calculated against a standard namely Pigment Black 7 (C.I. 77 266) and reveal a good colouring power of the studied dye.

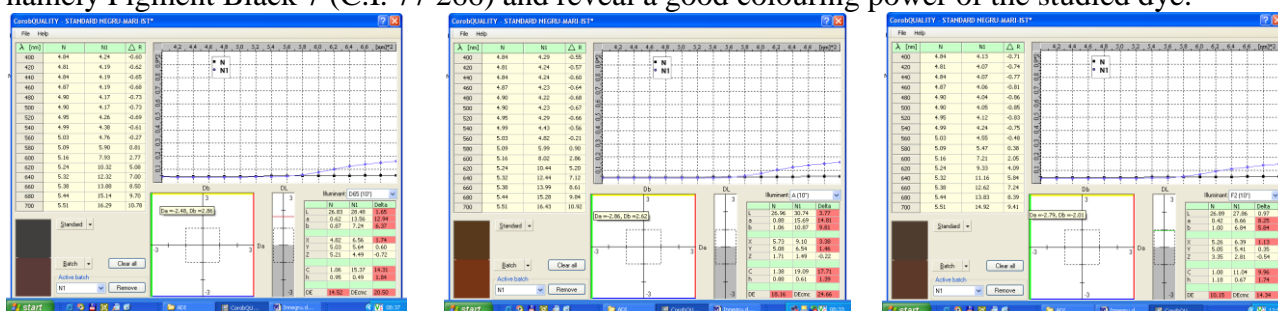


Figure 1. The reflectance curves of the azo-stilbene dye (2% dye concentration, D65, A, and F2 illuminants, 10° observer)

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SPHERICAL SILICA NANOPARTICLES OBTAINED BY STÖBER PROCESS. TETRA-ETHYL-ORTHOSILICATE CONCENTRATION INFLUENCE UPON SILICA NANOPARTICLES MORPHOLOGY

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Spherical silica nanoparticles were synthesized by sol-gel process using tetra-ethyl-orthosilicate as silica precursor. The Stöber route was used for the preparation of silica particles by TEOS hydrolysis and condensation of silicic acid in alcoholic solutions using ammonia as catalyst. The reactants mole ratio was n TEOS: H₂O: ETOH: NH₃ (where n=0.022÷0.31:0.43:0.789:0.06). The effects of TEOS concentration on the textural and morphology of silica powders were studied. The textural properties of silica powders were achieved by using N₂ adsorption-desorption isotherm measurements. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR) were used to reveal morphology and types of bond present within it. (TG-DTA) was carried out to analyze the thermal stability of the silica powders non-isothermal in the 25-800°C range. Under base catalyzed sol-gel process, the synthesized powders have the diameter between 3 and 9 nm (BJH) and the specific surface area (BET) of 13-112 m²/g. SEM images showed that almost spherical in shape silica nanoparticles were prepared. The FT-IR spectra of the compounds revealed the silica similar vibration bands corresponding to –OH and Si-O groups. Thermal analyses (TG-DTA) confirm the results obtained with FT-IR spectroscopy emphasized the mass loss associated with each type of bond on the corresponding temperature range (after 750°C the process was stable). Herein, has been studied the influence of TEOS concentration on the resulting silica particles size. The results obtained showed that the particles size decreases gradually as the concentration of the TEOS increases.

THEORETICAL ANALYSIS OF PAN-FGFR INHIBITORS

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In this study pharmacophore mapping and 3D-QSAR analysis has been performed on pyrazolylaminoquinazoline derivatives - pan-FGFR inhibitors. The best pharmacophore hypotheses including five features (Hypo-1 and Hypo-2) were generated using eight active compounds and six inactive compounds. Associated quantitative structure – activity relationships (QSAR) models at three PLS factors were generated for the best pharmacophore models Hypo-1 and Hypo-2, which show significant statistical parameters: the correlation coefficient of regression ($R^2 > 0.9$), cross validation coefficients ($Q^2 > 0.6$) and R-Pearson values for the test set greater than 0.8. Binding interaction pattern of pyrazolylaminoquinazoline derivatives with active site residues of FGFR2 were generated by rigid docking procedure with Fast Rigid Exhaustive Docking (FRED) software. The results obtained provided useful insight for the design of novel FGFR inhibitors with improved pharmacological profile.

Acknowledgements

The authors thank OpenEye Ltd. and BIOVIA Software Inc. for providing academic license for OpenEye package and Discovery Studio Visualizer v.4.5 program and to Dr. Ramona Curpăn (Institute of Chemistry Timisoara of Roumanian Academy), for providing access to Schrödinger software acquired through the PN-II-RU-TE-2014-4-422 project funded by CNCS-UEFISCDI Romania. This project was financially supported by Project 1.2/2017 of the Institute of Chemistry of the Romanian Academy.

TIME AND TEMPERATURE DEPENDENCE OF OLEFIN OXIDATION WITH PEROXIDO VANADATE CATALYSTS

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Vanadium is an essential element, which exists in all organisms at low concentrations. Nevertheless, it plays a catalytic role in metalloenzymes, such as haloperoxidases and nitrogenases. Recently, the discovery that vanadium possesses insulin mimetic activity has spurred considerable research activity. The spectrum of activities involving vanadium logically encompasses a variety of interactions that the metal ion in distinct oxidation states and complex coordination spheres develops in its predominant oxidation states (IV and V), in the presence of various physiological ligands. Furthermore, hydrogen peroxide is a physiological ligand and is well-known that vanadium-peroxido complexes exhibit an enhanced insulin mimetic action.

Todate, more than 163 peroxido complexes of vanadium have been reviewed and since the classical work by Mimoun et al., many results have been obtained in the field of oxidations of organic compounds through involvement of organic hydroperoxido vanadium compounds as catalysts. To that end, peroxido-vanadium compounds emerge as species able to oxidize aliphatic and aromatic hydrocarbons, sulfides, alcohols, etc. [1].

A new series of five complexes was synthesized involving vanadium in the oxidation state V(V) with zwitterionic ligands. In that framework of research activities, various trial reactions toward catalytic transformations were attempted, involving vanadium, with ternary oxido-peroxido-vanadate compounds, bearing suitable organic ligands (betaine, zwitterions), as catalysts for the oxidation of benzene. The results proved the catalytic ability of action of vanadium in oxidation reactions of organic substrates, such as olefins, meriting into further selective industrial applications leading to products of wide acceptance [2-5].

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PYRIMIDINE ANALOGUES AS TYROSINE KINASE INHIBITORS: A PARTIAL-LEAST-SQUARE DISCRIMINANT-ANALYSIS (PLS-DA) APPROACH

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The main purpose of this work is to investigate the abilities of Partial-Least-Square Discriminant-Analysis (PLS-DA) to discriminate between a novel series of thirty-eight pyrimidine derivatives and adequately selected inactives from the ChEMBL database, using Dragon descriptors.

The reliability of the generated PLS-DA model was confirmed by the good values of the statistical parameters, $R^2_{(CUM)}=0.882$ and $Q^2_{(CUM)}=0.816$, respectively. Additionally, the absence of data overfit for the final model was certified by Y-permutation test, using 999 randomizations. The $R^2_{rand}=0.205$ and $Q^2_{rand}=-0.309$ values indicate that the model complexity is adequate, and the obtained PLS-DA model is not overfitted.

The analysis of the model equation highlighted the positive influence of the GATS6m (Geary autocorrelation-lag 6/weighted by mass), Br-094 (Br attached to C1(sp²)), and nBr (number of Bromine atoms) descriptors with variable importance in projection (VIP) values greater than 3.0, for the model. These descriptors are expected to be useful structural features for achieving new potent and selective kinase inhibitors.

Acknowledgments

The L. Kurunczi laboratory thank to Dr. Eriksson for kindly providing access to SIMCA-P 9.0 package. This study was financially supported by the Project No. 1.2/2017 of the Institute of Chemistry Timisoara of Romanian Academy.

SEC-MALLS CHARACTERIZATION OF NEW SYNTHESIZED POLYMERS OF VINYLPHOSPHONIC ACID DERIVATIVES

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The vinylphosphonic acid homopolymer and the copolymers synthesized by using vinylphosphonic acid (VPA) and dimethylvinylphosphonate (DMVP) at different molar ratios (from 1:1 to 4:1), were characterized by size exclusion chromatography - multi angle laser light scattering (SEC-MALLS) [1-3].

SEC-MALLS method allows the determination of absolute molar mass averages, polydispersity, radius of gyration (R_g) and polymer conformation. According to the molar mass of the analyzed samples, three different SEC columns from Agilent were used: PL aquagel-OH MIXED-H 8 μm - 7.5 x 300 mm (PL1149-6800), PL aquagel-OH 50 8 μm - 7.5 x 300 mm (PL1149-6850) and PL aquagel-OH 30 8 μm - 7.5 x 300 mm (PL1120-6830). The MALLS detector used was Dawn Heleos II produced by Wyatt. It has 18 angular detectors ranging from 10° to 160° and it can detect molar masses from 200 to 10⁹ g/mol and radius of gyration from 8 to 500 nm. The measurements were performed by using 0.1M NaNO₃ aqueous solution as mobile phase (0.7 ml/min. at 25°C) [1-3].

After the polymerization, an average molar mass of 34200 g/mol was obtained for poly(vinylphosphonic acid) and in the range from 12700 to 19120 g/mol for copolymers. The SEC-MALLS measurements showed also polydispersity values between 1.19 and 1.51 for these polymers. The molar masses of the analyzed compounds were high enough to allow the formation of random coil conformation. This was confirmed by the determination of polymers conformation from Mark-Howink-Sakurada (MHS) plots. The coefficients calculated with SEC-MALLS from MHS plots were between 0.5 and 0.8 meaning that randomly coiled polymers were formed [1].

For the reason that the synthesized copolymers are soluble in water, one of the promising applications is their ability as inhibitors against corrosion for iron surface in neutral aqueous solution. Their presence in aqueous solution decreased the corrosion current density by the formation of protective film on iron surface. The presence of phosphonate groups from dimethylvinylphosphonate in copolymers was beneficial and at a molar ratio VPA:DMVP 3:1 and 4:1 enhanced the anticorrosion property in comparison with the homopolymer of vinylphosphonic acid [1].

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NEW N^N LIGAND FOR WATER SOLUBLE COORDINATION COMPLEXES BASED ON 3d METAL IONS

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Bioinorganic medicinal chemistry is a thriving interdisciplinary area of research, because it offers multi-purpose podia for drug design and development [1]. Although coordination complexes are excellent candidates as therapeutic agents, the insufficient solubility in water can affect the bioavailability of the drugs [2]. The solubility of the coordination complexes, and, hence, the bioavailability could be improved, amongst other, by varying the ligand architecture [1]. 2,2'-biquinoline is a well-known 1,4-diimine-type ligand [3], from the quinoline class, which are known to possess biological properties, such as antimicrobial, anti-inflammatory, etc [4].

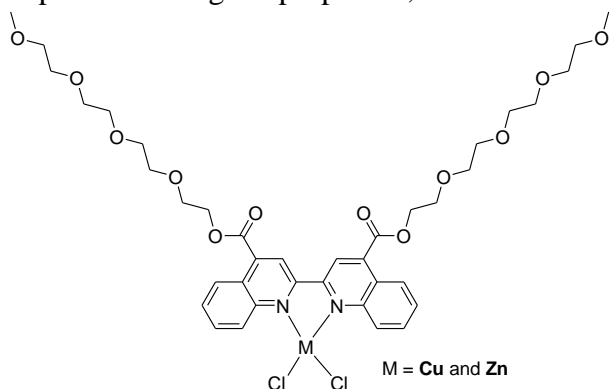


Figure 1. The proposed chemical structure of the complexes

Herein, we report the synthesis and characterization of a new 2,2'-biquinoline ligand substituted in the 4,4'-position with hydrophilic chains of tetraethylene glycol. The 2,2'-biquinoline derivative was further used for the synthesis of Zn(II) and Cu(II) coordination complexes. The proposed chemical structure of the complexes is presented in Figure 1.

The compounds were characterized by FT-IR spectroscopy, ¹H-NMR (ligand and Zn(II) complex), UV-vis spectroscopy and the metal content in the coordination complexes was determined by AA spectroscopy. Their antioxidant

activity was also investigated.

Acknowledgements

The authors from Institute of Chemistry Timisoara of Romanian Academy are kindly acknowledging the support from the Romanian Academy (Project 4.1).

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ASSESSMENT OF THE ADIPOGENIC POTENTIAL OF V(V)-SCHIFF BASE COMPLEXES IN 3T3-L1 PRE-ADIPOCYTES

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Vanadium serves as a multivariant biomimetic metal ion. In the regulation of intracellular signalling, energy metabolism and insulin mimesis, its exogenous activity stands as a contemporary challenge, currently under investigation, and a goal to pursue as a metallodrug against insulin resistance. Schiff bases are an important class of organic compounds and have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. Appropriately designed Schiff-bases promote vanadium binding and afford well-defined V(V)-Schiff ligand compounds [1,2]. To this end, the insulin-mimetic activity of vanadium linked to the development of well-defined anti-diabetic vanadodrugs has been investigated through: a) specifically designing and synthesizing Schiff base organic ligands L with 2-aminophenol as the basic primary amine, b) a series of well-defined soluble binary V(V)-L compounds designed, synthesized and physicochemically characterized, c) an investigation of their (a)toxic effect and establishment of adipogenic activity in 3T3-L1 fibroblasts toward mature adipocytes, and d) biomarker examination of a closely-linked molecular targets (PPAR- γ , GLUT 4, GCK and adiponectin) involving or influenced by the specific V(V) forms, cumulatively delineating factors involved in potential pathways linked to V(V)-induced insulin-like activity. The collective results a) project the importance of specific structural features in Schiff ligands bound to V(V), thereby influencing the emergence of its (a)toxicity and for the first time its insulin-like activity in pre-adipocyte differentiation, b) contribute to the discovery of molecular targets influenced by the specific vanadofoms seeking to induce glucose uptake and metabolism, and c) indicate an interplay of V(V) structural speciation and adipogenic biological activity, thereby gaining insight into vanadium's potential as a future therapeutical in metabolic pathophysologies.

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SYNTHESIS AND SPECTRAL CHARACTERIZATION OF COOPER(II) COMPLEX WITH CARBOXYLIC SCHIFF BASE AS LIGAND

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Schiff base ligands have been widely studied in coordination chemistry due to their facile syntheses, remarkable versatility and electronic properties [1]. The design and synthesis of new Schiff base ligands have been proven to be very important in constructing supramolecular architectures such as coordination polymers [2]. Because of their ability to possess unusual configurations, Schiff bases can accommodate different metal centers allowing synthesis of homo- and heterometallic complexes [3]. This feature is used for modeling active sites in biological systems. The metal complexes containing Schiff base ligand presents a variety of properties in medicinal and pharmaceutical fields like antimicrobial, antidepressant, anticancer and antioxidant activities [4]. This work presents the synthesis of a new copper(II) complex with Schiff base N,N'-bis(5-carboxy-salicylideneaminopropyl)-piperazine (CBPP). The complex was prepared by direct metal – ligand synthesis of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and CBPP in 2:1 molar ratios. The new compound was structurally characterized by FT-IR and UV-VIS spectroscopy and the thermal stability was determined by thermogravimetric and thermo-differential analysis (TG-DTA) under N_2 atmosphere.

Acknowledgement

The authors acknowledge the support of the Romanian Academy, Project 4.1.

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BETACAROTENE DETECTION WITH Mn(III)-PORPHYRIN-nanoAu PLASMONIC COMPLEX

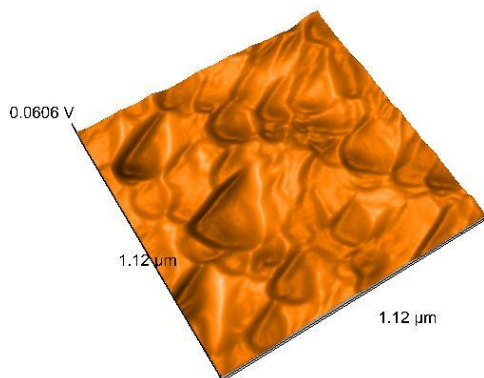
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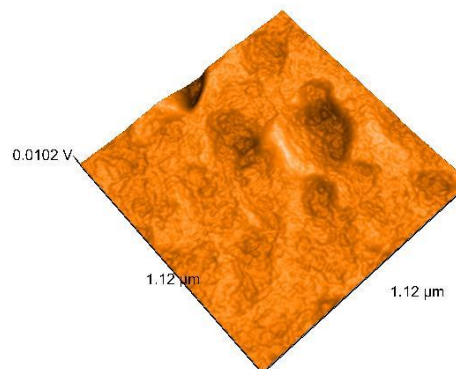
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The antioxidant properties of β -carotene are insufficiently investigated despite its well-known benefic actions [1]. Recent studies proved that higher concentrations of β -carotene can act as pro-oxidant, especially in the oxygenated tissues such as lungs favoring the incidence of lung cancer and this is the reason why its accurate dosage in human fluids is essential. A hybrid formed between Mn(III)-5,10,15,20-tetra(4-methyl-phenyl)porphyrin chloride (*MnTTPCl*) and gold colloidal nanoparticles (*MnTTPCl-nanoAu*) was tested for the detection of β -carotene from ethanol solutions [2]. This material gives rise to a wide absorption band, covering the range 425 nm to 581 nm after treatment with β -carotene. The investigated MnTTPCl-nanoAu organic-inorganic hybrid provides large β -carotene concentration interval detection by spectrophotometry ($9.80 \times 10^{-6} \text{M} - 1.15 \times 10^{-4} \text{M}$). A detailed comparative AFM investigation of the surfaces of both the bare MnTTPCl-nanoAu hybrid and its aspect after β -carotene exposure was done (Figure 1).

AFM images of the bare hybrid



AFM images of hybrid after β -carotene exposure



Acknowledgements

The authors from Institute of Chemistry Timisoara of Romanian Academy are kindly acknowledging the support from Program 3-Porphyrins/2017

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REMOVAL OF METAL IONS FROM AQUEOUS SOLUTIONS USING VARIOUS TYPES OF ADSORBENTS

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Metal ions are reported as pollutants, due to their mobility in natural water ecosystems and due to their toxicity. The problem associated with metal ion pollution is that they are not biodegradable, cannot be metabolized or decomposed, and are highly persistent in the environment [1]. In the recent years the NM were successfully tested as adsorbent materials for metal ions [2] removal.

With purpose to remove heavy metal ions from solutions, two types of adsorbents have been used: (i) mineral adsorbents-diatomite (D1) and modified diatomite with sulphuric acid (D2); (ii) carbonaceous adsorbents modified with manganese compounds and treated at 250 °C (E-3-1.0Mn-s-250, P1) and 450 °C (E-3-1.0Mn-450, P2). Batch experiments were performed in order to evaluate adsorption conditions for Cu²⁺, Zn²⁺, Co²⁺ and Ni²⁺. The metal ions adsorption equilibrium was established within 60 min, at normal temperature and pH ~6. The results indicated that the adsorption fitted well with the pseudo-second order kinetic model. The maximum adsorption capacities were determined, and the removal efficiency decrease in order: P1 > D1 > P2 > P1.

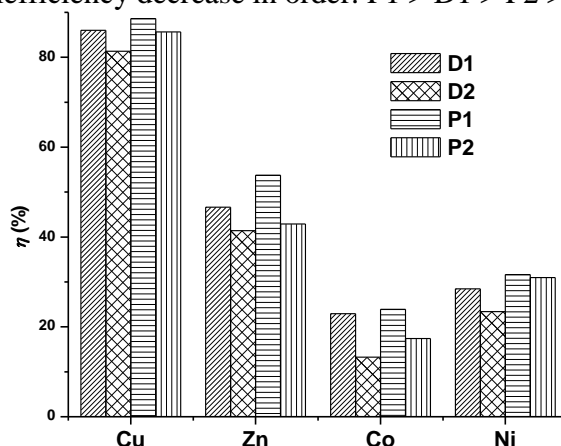


Figure 1. Effect of support's type on metal ions adsorption

Acknowledgments

This work was partially supported by Program no 2, Project no. 2.4 from the Institute of Chemistry Timisoara of Romanian Academy, by an inter-academic exchanges between Romania and Moldova, and by a grant of Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1319.

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3D SIMILARITY SEARCH FOR PIN1 INHIBITORS

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PIN1 (Protein interacting with NIMA 1 (never in mitosis A kinase 1)) is a member of the peptidyl prolyl cis-trans isomerase (PPIase) family which catalyze the isomerization of the amide bond prior to the proline in its target [1]. PIN1 plays critical roles in many types of cancer (breast, colon, prostate, esophagus, cervical, etc.) and is a potential therapeutic target in Alzheimer disease and cardiovascular diseases [2,3]. In order to obtain shape similar compounds with X-ray ligand used as query molecule (2R,4E)-2-[(naphthalen-2-ylcarbonyl)amino]-5-phenylpent-4-enoic acid (PDB code: JZI), a Rapid Overlay of Chemical Structures (ROCS) search was performed [4-6]. A dataset of 183 active compounds on PIN1 were downloaded from the ChEMBL database. Out of these, 126 compounds with experimentally determined IC₅₀ were involved in our study. These compounds were filtered for duplicates using InstantJChem resulting 118 unique compounds which were overlaid with ROCS. We screened these compounds using Gaussian-shape volume overlap filter which rapidly identify shapes that match the query molecule. The hits include 20 Compounds displaying Tanimoto Combo score higher than 1.2 and 34 compounds showing Combo Score higher of 1.2. The 3D Shape similarity alignment provide informations about the possible orientation of these compounds into PIN1 binding site and is useful to guide the rational design of novel compounds with enhanced affinity towards PIN1.

Keywords: PIN1, ROCS, shape-based screening

Aknowledgments

This work was supported by the Project 1.2 of the Institute of Chemistry Timisoara of the Romanian Academy. The authors thanks to OpenEye Scientific Software, Inc., and Chemaxon for for providing academic licenses (Simona Funar-Timofei laboratory).

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IRON (III) ACETYL-ACETONATE-PVA-SILICA- INORGANIC-ORGANIC HYBRID NANOCOMPOSITE XEROGELS, THERMAL BEHAVIOUR

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Three hybrid inorganic-organic nanocomposites xerogel samples were synthesized through one-pot acid catalyzed sol-gel method. The prepared xerogels mainly consisted in silica inorganic network physically mixed with polyvinyl alcohol (PVA) with a certain molecular mass. The iron (III) acetylacetonate precursor was confined in the hybrid matrix pores, along with aqua-alcoholic remains after the wet gel was dried at 60°C. The reactant mole ratio TEOS: H₂O: PVA:Fe(acac)₃:MeOH:HNO₃ = 1:10:n:0.1:18:0.01 was maintained constant, excepting PVA doping amount, with three molecular mass, of 45000(n= 1.89*10⁻⁵), 72000(n= 1.2*10⁻⁵) and 145000(n= 0.63*10⁻⁵), respectively. PVA was added as a constant percentage for each of sample. The three obtained hybrid xerogels were calcined at 220, 260, 300 °C, respectively. The xerogels and calcined samples have been investigated, in order to follow the thermal behavior of the xerogel precursors and also in order to find the optima conditions for obtaining a single crystalline and magnetically ordered iron oxide phase. Thermogravimetric analysis, FTIR and XRD spectra, N₂ adsorption desorption isotherms, SEM and magnetic measurements results were the mainly utilized as techniques of investigation. It was observed the behavior with temperature the samples for each PVA molecular mass, eventually it was studied the influence of PVA molecular mass upon structure and magnetic superparamagnetic behavior of the samples at each temperature of calcination. The average crystallite size of iron oxide was situated in 10 - 15 nm range, in dependence to PVA molar mass and calcination temperature. The maximum value of room temperature saturation magnetization of ~30 emu/g and 0.03 KOe coercive field was measured for the magnetic nanocomposite sample with 10% Fe₂O₃ and 145000 molar mass of PVA at 300°C that exhibited superparamagnetic behaviour. The highest surface area of 575 m²/g, which is a significant result, was obtained for the sample with 10% Fe₂O₃ with molar mass of PVA-72000.

INVESTIGATION OF DIFFERENT TYPES OF MATERIALS AS SORBENTS FOR THE REMOVAL OF DIRECT DYES FROM AQUEOUS SOLUTIONS

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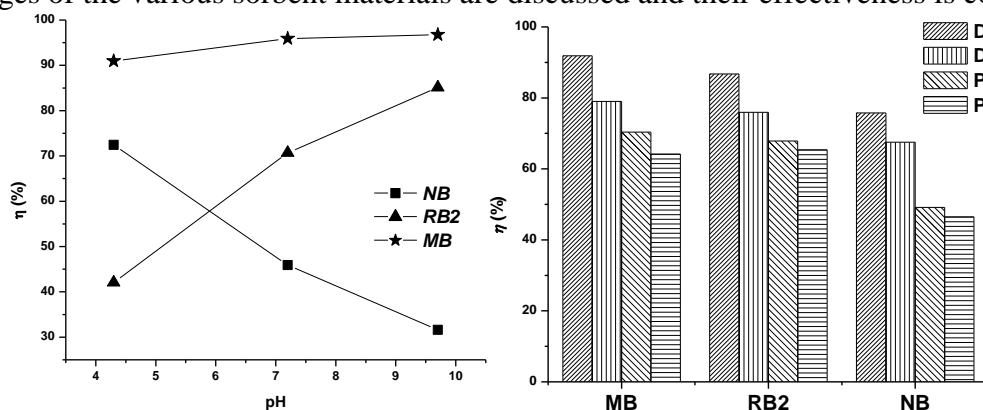
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Progress of various industries from the past decade led to a drastic increase in industrial effluent discharge, causing dramatically environmental pollution as well as serious life-threatening problems for environment in several regions. Colored wastewaters treatment by adsorption using alternative sorbents is a demanding domain. The efficiency of various sorbents under different process parameters and their comparative adsorption capacity towards dyes adsorption is presented.

In this paper adsorbents of different origin: (i) mineral adsorbents-diatomite (*D1*) and modified diatomite with sulphuric acid (*D2*); (ii) carbonaceous adsorbents modified with manganese compounds and treated at 250 °C (*P1*) and 450 °C (*P2*) were investigated for the removal of dyes from aqueous solutions. Three industrial dyes were selected as adsorbate: Methylene Blue (C.I. 52015, *MB*), Basic Red 2 (C.I. 50240, *RB2*), and Nylosan Blue (C.I. 62058, *NB*).

The parameters such as adsorbent nature, and solution pH, were studied. The advantages and disadvantages of the various sorbent materials are discussed and their effectiveness is compared.



Acknowledgments

This work was partially supported by Program no 2, Project no. 2.4 from the Institute of Chemistry Timisoara of Romanian Academy, and by an inter-academic exchanges between Romania and Moldova.

IONIC LIQUID CRYSTALS BASED ON SILVER(I) COORDINATION COMPLEXES

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Silver(I) based liquid crystals represents an interesting subclass of metallomesogens [1]. Their appeal lies in their mostly ionic character, promising for conductivity and charge transport properties. Moreover, their luminescence properties shown in the mesomorphic state at low temperatures, points toward the possibility of obtaining polarized light emission in anisotropic materials [2].

Herein, we report the synthesis and characterization of a new class of ionic silver(I) coordination complexes exhibiting thermotropic liquid crystalline behavior. Their proposed chemical formula is presented in Figure 1. The complexes were characterized by spectral (IR, UV-vis and ¹H NMR) and thermogravimetric methods (TGA). Their mesomorphic behavior was investigated by polarized optical microscopy (POM).

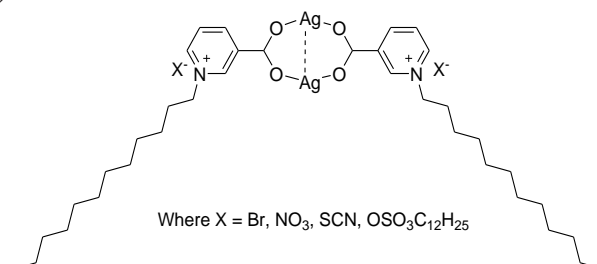


Figure 1. The proposed chemical structure of the complexes

Aknowledgements

The authors from Institute of Chemistry Timisoara of Romanian Academy are kindly acknowledging the support from the Romanian Academy (Project 4.1).

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IMMOBILIZATION OF LIPAZE FROM CANDIDA ANTARCTICA B BY COVALENT BINDING ONTO MAGNETIC SUPPORTS

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Although the use of isolated enzymes in biocatalytic transformations usually allows for high activity and product concentrations, their sensitivity to industrial conditions such as organic solvents, extreme pHs or elevated temperatures could be a significant drawback. One strategy to improve operational performances of enzymes in industrial processes is immobilization that might additionally improve enzyme properties such as selectivity, specificity or reduce substrate/product enzyme inhibition [1].

Several natural and synthetic supports have been reported for enzyme immobilization and among them, magnetic materials offered in addition to easy separation, large surface area, mobility, high mass transference, and recyclability. Regarding their excellent environmental compatibility, the use of magnetic composites represents an effective green chemistry approach, as well [2].

The aim of this work was a comprehensive screening of various magnetic supports [3] (nanoparticles/clusters) coated (activated) with poly(glycidylmetacrylate), 3-phosphonopropionic acid, phosphoetanolamine, polyacrylic acid, or polyacrylate, able to provide functional groups suitable for enzyme immobilization, such as carboxyl, amino, and oxiran. The immobilization conditions were fine-tuned by selecting the proper linker (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide or glutaraldehyde), the immobilization pH, and the enzyme loading amount.

The activity of the obtained biocatalysts was evaluated through the hydrolysis reaction of a model substrate, p-nitrophenyl palmitate. The highest activity was achieved by covalent binding through oxiran and amino groups. The results proved that thermal and pH stability was enhanced after immobilization.

Aknowledgements

This work was supported by a grant of the Romanian Authority for Scientific Research and Innovation, CNCS/CCCDI - UEFISCDI, project number PN-III-P22.1-PED-2016-0168, within PNCDI III.

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CORROSION OF ALUMINUM IN ALCOHOLIC SOLUTION – A PERMANENT CHALLENGE IN FOOD AND DRINKS PRODUCTION

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Nowadays, aluminium is the second most widely used metal in the world [1]. Currently, aluminum is present in food and drinks naturally, as well as additive or contaminant because of the contact with alloy-based aluminum materials used in the preparation and storage steps [2]. The essential feature of aluminum-based materials used in these industrial domains is metal ionization in contact with food in drink products. This process needs to be limited to the levels that do not endanger human health. Aluminum and its various alloys have many favorable properties and advantages such as good formability, machinability, thermal conductivity and have a high corrosion resistance [1,3]. Aluminum alloys used for food and drinks products may contain elements such as magnesium, silicon, iron, manganese, copper and zinc. The most commonly, aluminum alloys used in drinks industries are 3003 and 3004 types, which have very good corrosion resistance [3].

Worldwide or European international and national legislative and standardization agencies have laid down laws regulations, standards and guidelines with requirements that packing materials must please when they are used in direct contact with alcoholic or soft drinks.

Whereas pure aluminum is attacked by most dilute acids, his alloys used in food and, especially, in drinks industry are normally coated for packaging applications. The use of uncoated aluminum materials in direct contact with food and drinks is influenced by the acidity of the foodstuff and the solubility of the salt formed. Aluminum materials are most present in distinct types of cans and lids. Aluminum alloys are used as packaging material mostly for beer and soft drinks and less for wine and other alcoholic drinks. Beer is a corrosive media for aluminum alloys because it is an acidic solution and it contains microorganisms which can cause a significant biocorrosion [4]. Soft drinks are more aggressive than beer, these are extremely acidic, containing phosphoric acid, and the potential corrosion of packing materials became a serious problem and permanent challenge [4].

Aluminum alloys corrosion in the drinks industries is important from several major points of view: expenses, health and safety management.

This paper presents preliminary results obtained for corrosion process of different type of aluminum materials in alcoholic solutions. The influence of ethanol concentration from test solutions was studied by linear polarization, Tafel method in order to determine the kinetic parameters and electrochemical impedance spectroscopy, providing thus information about the corrosion mechanism. The morphology of aluminum samples after the corrosion attack has been studied by scanning electron microscopy.

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STAINLESS STEEL CORROSION IN ETHANOL SOLUTIONS IN THE PRESENCE OF SULFITE IONS - A PERMANENT PROBLEM IN THE WINE INDUSTRY

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Sulfur compounds such as sulfur dioxide and sulfites are used during several steps of the winemaking process, especially in common commercial final products [1]. Part of sulfur compounds can appear naturally in some types of wine due to the fermentation [2]. However, the greatest amount of sulfur compounds comes from various sulfiting agents (sodium sulfite, sodium bisulfite and sodium metabisulfite) added in wines as preservatives in order to avoid the microbial growth and wine oxidation by inhibiting oxidative enzymes which diminish wine quality and value [3]. From both enzymatic and non-enzymatic wine oxidation, quinones result as by-products. Another role of sulfur compounds is to reduce quinones present in wines. Sulfiting agents added in red or white wines participate in different reactions, producing various sulfur species. Two classes of sulfites, free and bound, are found in wine. Only the free ones react, exhibiting thus both germicidal and antioxidant properties [4]. Bound sulfites react reversibly or irreversibly with other molecules from wine, these processes depending mainly on the pH of wines [4]. Total sulfite concentration represents the sum of the free and bound sulfites.

The amount of sulfur compounds present in wines is limited for health reasons because they can generate allergic reactions that range in severity from minor to life threatening. This is a main reason why the sulfites concentration in wine must be closely monitored and legally regulated.

Stainless steel as material for tanks used in fermentation process and wine storage began since the mid-20th century [5]. Its intense use is based on many advantages such as high corrosion resistance, ease of cleaning, no addition of flavors or contaminants in wine and agreeable esthetically appearance [5]. However, stainless steel corrosion process has been noted in both red and white wines [5].

This paper presents preliminary results obtained for the corrosion attack of stainless steel in alcoholic solutions in the presence of different sulfite concentrations. Experimental studies consisting in cyclic and linear polarization, Tafel method and electrochemical impedance spectroscopy have been carried out in order to determine the kinetic parameters and elucidate the corrosion mechanism, all providing information about the studied process.

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AUTHOR INDEX

ACHOUR M. E.	24	FUNAR-TIMOFEI S.	46, 58, 65, 85, 88
ALMÁSY L.	13	FÜZI J.	24
ALMÁSY L.	22	GABRIEL C.	97
ANDELESCU A.	55, 83, 91, 96, 100	GAINĂ L. I.	39
ANESTAKIS D.	76	GHEONEA R.	70
ANTAL D.	25	GÓMEZ-RUIZ S.	16
ANTONOPOULOU M.N.	84	GONTARD G.	1
ARANICIU C.	73	GOREA M.	44, 49
ARDELEAN A.	27, 98	GROZAV A.	39
ARDELEAN R.	41	HADZOPOULOU-CLADARAS M.	76
AVRAM S.	18, 56, 67, 82, 94	Haidu D.	25
BABUȚĂ R. M.	15, 32	HALEVAS E.	31, 40, 45, 64
BACA S. G.	17, 43, 59	HALIP L.	18, 56, 62, 67, 69, 82, 85
BADEA V.	8, 19, 81, 96, 104	HANGANU D.	39
BAKER P.	5	HAR N.	49
BARABAS R.	13	HEY-HAWKINS E.	16, 27
BENEA I.	105	IANĂȘI C.	22, 91, 102
BERCEAN V.N.	19, 42	IANOȘ R.	15, 77
BEZDIČKA P.	14	ILIA G.	11, 51, 53, 70, 75, 95
BEZDIČKOVÁ J.	14	ILIESCU S.	11, 51, 53, 65, 95
BIRDEANU M.	86, 99	JACKSON G.	31, 40, 64, 74
BIZO L.	44, 49	JORDAN C. V.	62
BOLOGA C. G.	69	JOURNAUX Y.	1
BORA A.	18, 56, 58, 67, 79, 82, 85, 94	JULVE M.	1
BOROTA A.	62, 85, 88, 94	JURCAU D.	68
BÓTA A.	13	KEGLEVICH G.	26
BOTEZAT O.	33	KENDERESI V.	24
BOUKHEIR S.	24	KHAMOVA T.V.	13
BOUROSH P.	61, 63, 66, 75	KIM B.	5
BUSHBY R.	5	KIOSEOGLU E.	76, 87, 89, 93
BUTĂ I.	27, 98	KISS N. Z.	26
BUZILA S.	29	KOPITSA G.P.	13
CALANDRA P.	12	KRAVTSOV V.	54, 63, 75
CANO J.	1	KRAVTSOV V.Ch	17, 43, 59
CELEBRE G.	6	KURUNCZI L.	18, 25
CHAMOREAU L.M.	1	LABOSEL M. A.	107
COPOLOVICI D.	21	LASCU A.	23, 86, 99
COPOLOVICI L.	21	LAZĂU R.	15
COROPCEANU E.	61	LEN A.	22, 24
COSTA L. C.	24	LESCOUÉZEC R.	1
COSTEA L. V.	42	LI Y.	1
COSTIȘOR O.	27, 55, 81, 96, 98, 104	LISNARD L.	1
CRĂCIUN A.	73	LIVERI V.T.	12
CRASMAREANU E.C.	70	LLORET F.	1
CRETU C.	55, 96, 104	LÖNNECKE P.	27
CRISAN L.	73, 79, 88, 92, 94, 101	LOPES PEREIRA C.	1
CRISAN M.	63, 65, 66, 75	LUPA L.	72
CRISPINI A.	2	LUPASCU L.	28
CROITOR L.	63, 66, 75	LUPASCU T.	28
CSEH L.	8, 55, 81, 96, 104	LUPITU A. I.	21
CURPAN R.	18, 56, 62, 67, 82, 85	MACARIE L.	11, 51, 53, 68, 95
DABICI A.	15	MAFTULEAC A.	29
DAN M. L.	107, 106	MAGYARI K.	44
DARII M.	43	MAIUOLO L.	10, 20
DAVIDESCU C.M.	41	MARANESCU B.	60, 72
DE LUCA G.	6, 10, 20	MATSIA S.	71
DEHELEAN C.A.	32, 46, 50	MAXIMOV P.	62
DEVESELEANU-CORÎCI L.	81	MELNIC E.	54
DI PIETRO M.E.	6	MICLE A.	75
DONNIO B.	3	MIRICA M.	13
DUCA D. A.	107, 106	MOACĂ E. A.	15, 32
DUDÁS Z.	22	MORO A.J.	8
DUL M.C.	1	MUNTEAN E.	15, 77
DUMACHE R.	46	MUNTEAN S.G.	77, 83, 90, 100, 103
FAGADAR-COSMA E.	9, 23, 52, 86, 99	MUSCOI MÎNDRULEANU A.M	19
FERRANDO J.	1	NANDOR E.	24
FILIMON A.	30	NASTAS R.	100, 103
FILIP I.	16	NDAY C. M.	31, 40, 45, 64, 74
FLONDOR (IONESCU) D.	46, 58	NISTOR M. A.	77, 83, 90, 100, 103
FOGASSY E.	26, 48	OLIVIERO ROSSI C.	10, 20
FRINGU I.	23, 86, 99		

ONIGA S.D.	73	SHEN Z.	5
OTTENWAEELDER X.	1	SHIN K.	5
OUERIAGLI A.	24	SHOVA S.	8
OUTZOURHIT A.	24	SILAGHI-DUMITRESCU L.	16, 39
PĂCURARIU A.	106	SIMU G.M.	50
PĂCURARIU C.	15, 77	SIMULESCU V.	70, 95
PACUREANU L.	73, 79, 92, 94, 101	ȘOICA C.M.	32
PALADE A.	23, 86, 99	SPATARU P.	29
PALAGE M. D.	73	SPINU O.	28
PÁLOVICS E.	26, 48	SPIRACHE A.M.	104
PANA A-M.	8	STATI D.	17
PARDO E.	1	STEINHART M.	5
PÁRKÁNYI D.	25	STOICA C.I.	73
PAROLA A.J.	4, 8	SUBA M.	47, 78
PAUL C.	105	SUZUKI T.	58
PAUSESCU I.	8	SVERA P.	78
PAVEL I. Z.	32	SZELECZKY Z.	48
PEKAŘ M.	95	SZERB E. I.	55, 96, 104
PERCEC V.	5	TARA-LUNGA-MIHALI M.	51, 95
PETANIDIS S.	76	ȚĂRANU B.	13
PETER F.	105	TELTAYEV B.	20
PETRIC M.	63, 66, 75	TIAN Q.	13
PICIORUS M.	91	TIMBALIUC N.	28
PINA F.	4, 8	TIMIS L.	49
PLESU N.	11, 51, 53, 63, 68, 95	TODEA A.	105
PLOCEK J.	14	TOMOALA-COTIȘEL M.	49
PODGORNYI D.	59	TSAVE O.	57, 71, 84, 97
PONCET M.	1	TSCHERSKE C.	5
POP G.	21	TSCHIRSCHWITZ S.	16
POPA A.	11, 30, 41, 47, 51, 53, 68, 78	TUDOSE R.	26
POPESCU A.	50	TURCU R.	105
POSTOLACHI L.	100, 103	UNGAR G.	5
POVAR I.	28, 29	URSU D.	78
PREHM M.	5	VARGA D.	85, 92, 101
PUTZ A-M.	13, 22, 102	VASILESCU C.	105
RĂDULESCU-GRAD M.E.	83, 90, 103	VASZILCSIN C.G.	107
RIGO M.	13	VASZILCSIN N.	106
ROGOTIS K.	80	VERDES O.	47, 78
RUIZ-GARCÍA R.	1	VIK O.	14
RUSU L. R.	73	VISA A.	60, 72
SALAGEANU L.	52	VITIU A.	61
SALIFOGLOU A.	7, 31, 40, 45, 57, 64, 71, 74, 76, 80, 84, 87, 89, 93, 97	VOJTÍŠEK P.	14
SASCA V.	27, 47, 55, 78, 98, 194	WACHA A.	13
SAVII C.	13, 22, 25, 91, 102	YAVROPOULOU M.P.	57
SEBARCHIEVICI I.	9, 23	YOVOS J.G.	57
SFIRLOAGA P.	91, 102	ZENG X.	5
		ZHANG R.	5

