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Chimika Chronika, New Series, 26, 69 (1997)

Chemistry, Biology and Medicine of Natural and Designed Molecules

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ABSTRACT

Natural products with novel molecular structures and important biological properties provide exciting challenges and opportunities to synthetic chemists, biologists, and clinicians. The pursuit of such target molecules by chemical synthesis is often accompanied by the discovery and development of new synthetic technology and strategies, molecular design studies, and biological investigations with the natural and designed molecules. In this lecture, this philosophy of research will be exemplified with taxol and brevetoxin B as welll as other target molecules.

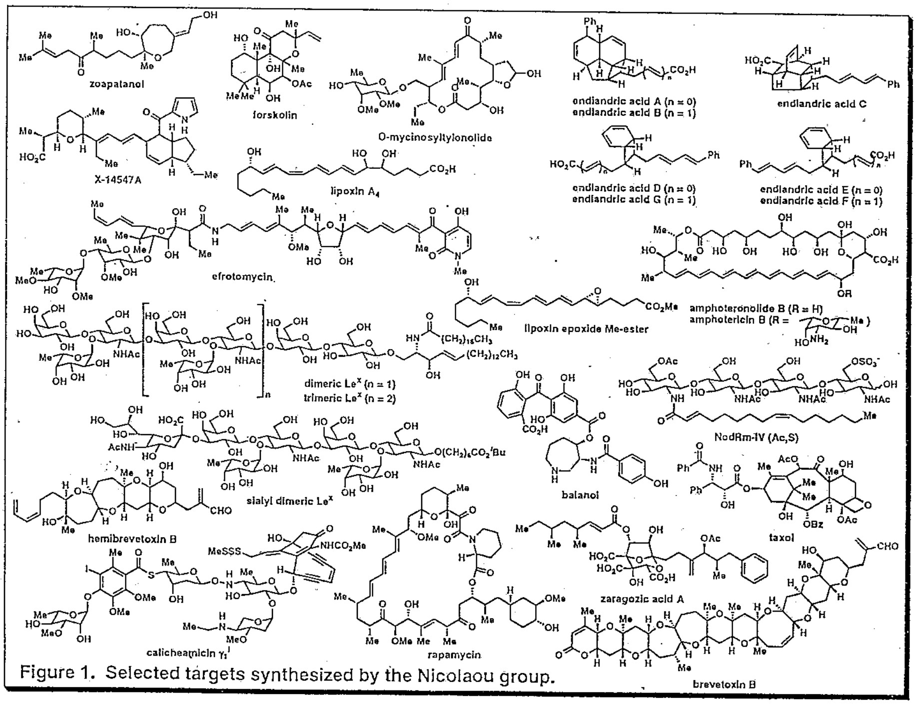

Figure 1. Selected targets synthesized by the Nicolaou group.

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Chemistry, Sustainability and the Quality of Life

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Massachusetts Institute of Technology

As we approach the year 2000, we are at an important crossroads with both the world's economy and environmental concerns becoming truly global in nature. The United Nations Conference on Environment and Development (UNCED) in Brazil concluded that the goals of development and environmental protection were not necessarily at odds, providing that institutions and people were committed to *sustainable* development. Industry, government, trade unions, environmental organizations and individual citizens are all important in fostering a transition to sustainability, but no one can deny the very central role that must be played by industry that creates economic wealth and has the ability to minimize, eliminate, and mitigate adverse effects of technology on health, safety and the environment. The chemical producing and using industries are at the very center of economic development in the modern industrial state and they have both created problems and are the source of many solutions. This is not to minimize the importance of government in providing an appropriate political environment and regulatory system to guide sustainable development, but both are necessary to achieve the desired goals.

The concept of sustainability must necessarily be viewed broadly. Since the firm or enterprise is connected to or affects the whole of society, discussion of the sustainable enterprise must include issues related to sustainable production, consumption, employment, livelihood (jobs which create purchasing power), and culture. To put it another way, health, safety and environmental concerns must be construed expansively to include both physical and economic security. Further, while discussion about the sustainable chemically-based enterprise tends to be centered on manufacturing, energy and services, it is important to note that chemicals are key to the extraction industries, agriculture, transportation, and information systems. Finally, the socio-economic impact of "industrial" activity, here broadly defined to involve all the activities that are undertaken to satisfy human needs, should also be viewed expansively to include ecological systems, biodiversity and environmental justice.

Chimika Chronika, New Series, 26, 71 (1997)

FREE RADICAL CHEMISTRY ASSOCIATED WITH THE C-1' POSITION IN MODEL NUCLEOSIDES

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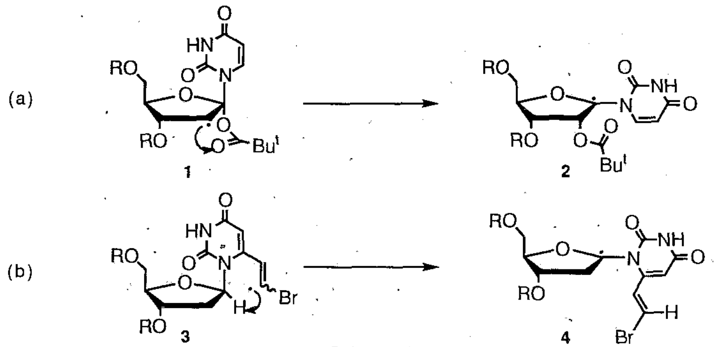
ABSTRACT

Two methods for the generation of ribosyl and deoxyribosyl C-1' radical species have been developed. These synthetically useful processes involve a novel type of a β-(acyloxy)alkyl radical rearrangement leading to the stereoselective production of an α-ribonucleoside and a 1,5-radical translocation reaction which furnishes anomeric spironucleosides.

Damage of DNA involving hydrogen abstraction from the C-1' position of a deoxyribonucleotide has been observed with almost every agent known to effect radical-induced DNA damage. We now report the successful generation of C-1' radicals in model nucleosides in two independent reaction schemes. A novel type of a β-(acyloxy)alkyl radical rearrangement leads, through the generation of a C-1' ribosyl radical species [Scheme 1, (a)], to the stereoselective preparation of an α-ribonucleoside. The rate of the above 1,2-migration has been estimated at $k_r = 7.0 \times 10^4$ s^{-1}. Similarly, a 1,5-radical translocation protocol has been developed for the generation of a C-1' deoxyribosyl radical from a protected 6-(2,2-dibromovinyl)-2'-deoxyuridine [Scheme 1, (b)]. A cascade of reactions ensues involving a rare *5-endo-trig* radical cyclization followed by fragmentation with expulsion of a bromine radical results in a synthetically useful preparation of anomeric spironucleosides.



Scheme 1

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SYNTHESIS AND REACTIONS OF 1-ARYL-2-NITROPYRROLES. STRUCTURAL AND CONFORMATIONAL STUDY OF ETHYL N-[2'-[1'-(2-NITROPYRROLYL)PHENYL]-N-TOLUENE-4-SULFONAMIDE GLYCINATE

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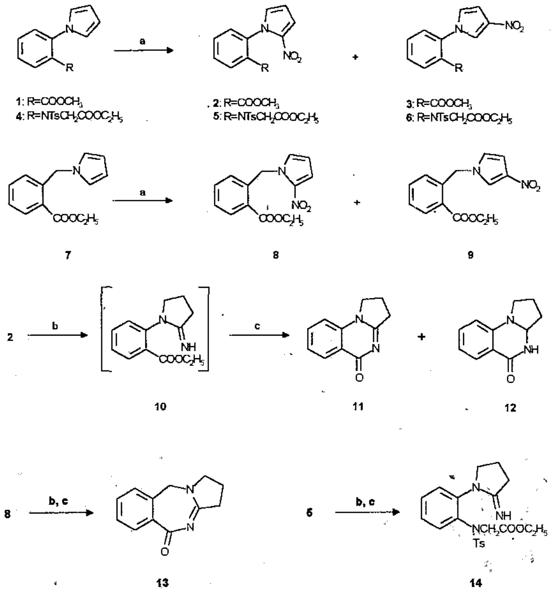
ABSTRACT

Nitration of 1-aryl(or 1-benzyl)pyrroles **1**, **4** and **7** has provided the corresponding 2- and 3-nitropyrroles **2** and **3**, **5** and **6**, and **8** and **9** in a 1:2 ratio. Reductive cyclisation of **2**, **5** and **8**, gave pyrrolo[1,2-a]quinazolines **4** and **12**, a mixture containing iminopyrrolidine **14**, and pyrrolo[1,2-b][2,4]benzodiazepine **13**, respectively. A conformational study of **5** in the solid and liquid state using X-ray diffraction analysis, molecular dynamics calculations and NMR spectroscopy, is described. In compounds **5** and **14** the $NCH_2COOC_2H_5$ chain takes up a position where one of the protons of the N-methylene group interacts with the adjacent sulfonyl oxygens. As a result in **14** the conformation adopted by the $NCH_2COOC_2H_5$ chain does not favour cyclisation.



Reagents:a) $(CH_3CO)_2O$, fuming HNO_3, -30°C to room temperature
b) H_2/Pd-C, MeOH
c) NaOEt, EtOH, reflux

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SYNTHESIS AND BIOLOGICAL STUDY OF NEW 4-(3′-1,2,4-OXADIAZOLO)-COUMARINS

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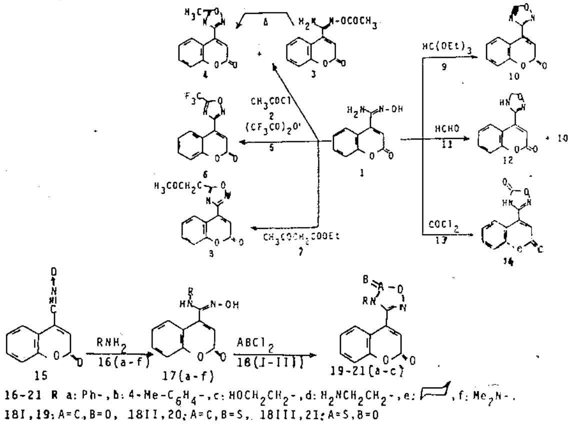
ABSTRACT

Reactions of 4-coumarinyl-amidoxime 1 with the acid derivatives 2, 5, 7, 9, 13 and the formaldehyde 11 resulted in 4-(3'-1,2,4-oxadiazolyl)-coumarins 4,6,8,10 and the 4-(3'-1,2,4-oxadiazolinyl)-coumarins 14 and 12. Reactions of 4-coumarinyl nitriloxide 15 with amines 16c-f gave the new amidoximes 17c-f. Further reactions of 17a-c with phosgene (18I) and thiophosgene (18II) afforded oxadiazolinones 19a-c and thiones 20a-c respectively. In addition reactions of 17a-b with $SOCl_2$(18III) gave the oxadiazolinones 21a-b. The above compounds were examined for antiproteolytic and reducing abilities. Compound 4 inhibits soybean 12-LO.



16-21 R a: Ph-, b: 4-Me-C_6H_4-, c: $HOCH_2CH_2$-, d: $H_2NCH_2CH_2$-, e: , f: Me_2N-.
18I, 19: A=C, B=O, 18II, 20: A=C, B=S, 18III, 21: A=S, B=O

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GENERAL APPROACH FOR THE SYNTHESIS OF CAFFRANE RINGS TOTAL ASYMMETRIC SYNTHESIS OF COMBRETASTATIN D-1

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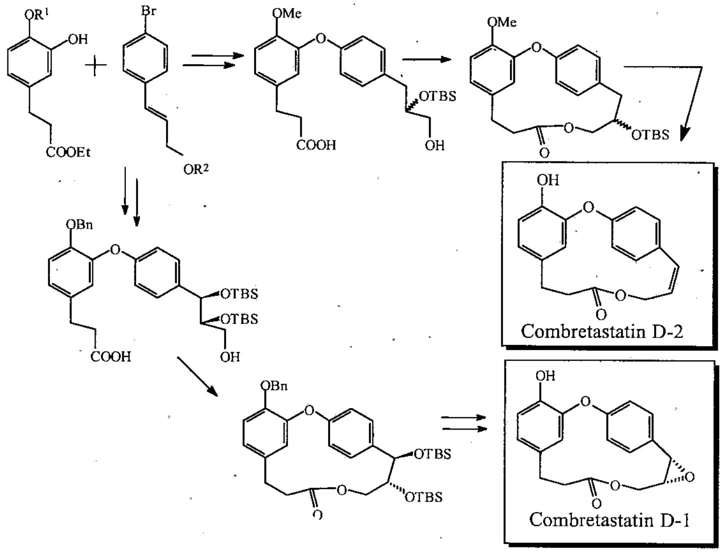
ABSTRACT

The total synthesis of naturally occurring Comrbretastatins D-1 and D-2 is described. The main problems associated with the construction of these substrates are: a) the introduction of the asymmetry and b) the cyclization leading to the medium sized macrolactones which have relative large strain energy. Our strategy involves the formation of suitably functionalized intermediates, which undergo a high yield macrolactonization and thus lead to a straightforward and efficient construction of the rest of the molecule. Accordingly Combretastatin D-1 was synthesized in 12 steps (total yield 29%) and Combretastatin D-2 in 13 steps (total yield 38%).



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DEVELOPMENT OF HIGLY POTENT AND SELECTIVE PHOSPHINIC PSEUDOPEPTIDE INHIBITORS OF ZINC METALLOPROTEASES

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Zinc Metalloproteases are an important group of enzymes responsible for many physiological and pathological processes.For example,degradation of the extracellular matrix components such as collagen and proteoglycans in normal embryogenesis and remodeling and in many diseases processes such as arthritis, cancer, periodonitis and osteoporosis.

Consequently, the development of synthetic inhibitors of these enzymes has considerable interest. It should be noted that pseudopeptides containing a phosphinic bond $\{PO_2CH_2\}$ were proved to be very potent inhibitors.

The synthesis of phospinic peptides by solid phase strategy using 2-chloro-trityl resin and Fmoc chemistry, requires to produce the Fmoc-Xaa{PO(OAd)CH2}Xaa′, where Xaa=Phe, Ala and Xaa′=Gly, Ala, Leu, were synthesized via five steps.

Some phosphinic pseudopeptides which are highly potent inhibitors of zinc-proteases are shown in table I..

Table I

Inhibitors	Bacterial Collagenase Ki (nM)	Endopeptidase 24-15 Ki (nM)	Endopeptidase 24-16 Ki (nM)
Z-Pheψ(PO2CH2)Gly-Pro-Nle	8	40	25
Z-Pheψ(PO2CH2)Gly-Arg-Met	-	0.35	135
Z-Pheψ(PO2CH2)Ala-Arg-Met	-	0.07	93
Pro-Pheψ(PO2CH2)Gly-Pro	-	8100	4

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SYNTHETIC INHIBITORS OF PHOSPHOLIPASE A_2

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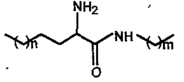
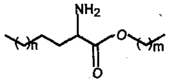
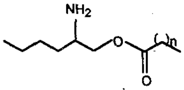
ABSTRACT

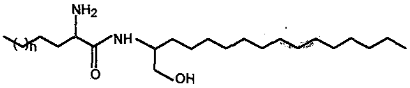
Phospholipases A_2 (PLA_2s) catalyze the hydrolysis of glycerophospholipids to release fatty acids and lysophospholipids. To date, the most widely studied phospholipases are the low molecular weight secretory proteins ($sPLA_2$) isolated from sources as mammalian pancreas, snake venom and human platelets. Since PLA_2s are involved to important processes (for example inflammation), inhibitors of PLA_2s have potential for the prevention and treatment of a range of common diseases. Altough a variety of natural and synthetic inhibitors have been reported in recent years, none with clinical potential has emerged.

We have designed , synthesized and tested against PLA_2 three groups of compounds :
A) A series of long chain α-amino acid amides and esters, esters of α-amino alcohols and lipidic peptide derivatives.

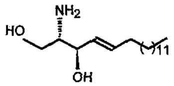


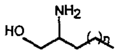


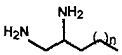




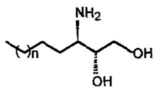
B) Sphingosine analogs

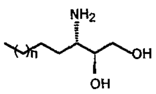






C) Chiral lipidic 3-amino-1,2-diols.





All the compounds synthesized were tested against pancreatic PLA_2 and some of them against human platelet PLA_2. The IC_{50} values for the most active compounds were between 1-10μM.

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STEPWISE MECHANISM IN THE [2+2] CYCLOADDITION OF TETRACYANO ETHYLENE (TCNE) TO 2,5-DIMETHYL-2,4-HEXADIENE. SYNERGISM OF CONJUGATION AND HYPERCONJUGATION IN THE OBSERVATION OF A REMOTE (ε) SECONDARY ISOTOPE EFFECT.

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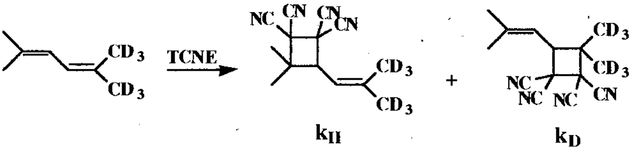
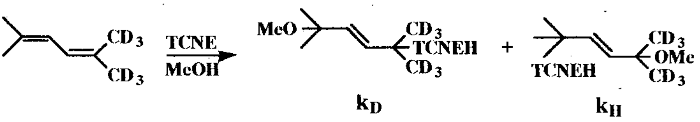
ABSTRACT

Tetracyanoethylene (TCNE) is a powerfull electrophile with a variety of [4+2], [2+2] and ene reactions. Addition of TCNE to 2,5-dimethyl-2,4-hexadiene (DMHD) in acetone and acetonitrile at 25°C, affords only the [2+2] cycloaddition product. No [4+2]π adduct is formed.

We studied the secondary kinetic isotope effects in the reaction of TCNE with 2,5-dimethyl-2,4-hexadiene-1,1,1,2,2,2-d_6 (DMHD-d_6) by ^{1}H NMR spectroscopy. In acetone-d_6 a $k_H/k_D = 0.77 \pm 0.04$ was found, while in acetonitrile-d_3 $k_H/k_D = 0.70 \pm 0.04$.



When the reaction was carried out in methanol the only product isolated was the trapping of the dipolar intermediate with methanol at position 4. In the case of DMHD-d_6, methanol captures the intermediate 1.30 times faster by attack at the double bond carbon which bears two -CH_3 groups, than the other terminal carbon which bears two -CD_3 groups.



The above results can be rationalized by a dipolar intermediate. In the case of DMHD-d_6, TCNE preffers to form the [2+2] adduct next to the geminal -CD_3 double bond. This result was rationalized in terms of a preferential charge stabilization of the two allylic carbocations by the geminal -CH_3 than the geminal -CD_3 groups. Consonant to this proposed mechanism is the isotope effect measured in the reaction of DMHD-d_6 with TCNE in methanol.

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OXIDATION OF AMINES BY THE ACTION OF $Cu/CCl_4/Et_3N$-SYSTEM

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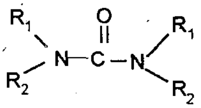
ABSTRACT

A numerous of some synthetic reactions, of amines and their derivatives with CCl_4 catalyzed by metal complexes.
We describe a successful study on the efficient selective formation of tetrasubstituted ureas in good yields (>70%) under mild condition from secondary amines by the action of $Cu/CCl_4/Et_3N$ systems. The reaction proceeds in the presence of O_2. The definite step for the reaction, is a copper promoted oxidation of CCl_4 to $COCl_2$ which rapidly reacts with the secondary amines affording an urea derivative.



Chimika Chronika, New Series, 26, 79 (1997)

IDENTIFICATION OF EPITOPE SEQUENCES AND LIGAND-BINDING DOMAINS ON THE BETA CHAIN OF THE INTERLEUKIN-2 RECEPTOR BY MEANS OF THE PEPSCAN METHOD

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ABSTRACT

Because of the central role of Interleukin-2 (IL-2) in both antigen-driven and non-specific immune responses, both the cytokine and its receptor (IL-2R) have long been the subject of intensive investigation. The IL-2R consists of at least three membrane proteins: the α chain (p55, Tac, IL-2Rα), the β chain (p75, IL-2Rβ) and the γ chain (p64, IL-2Rγ). The β chain of the Interleukin-2 Receptor (IL-2Rβ) binds IL-2 with intermediate affinity and is required for intracellular signal transduction, mediated by an associated nonreceptor protein-tyrosine kinase, which is activated in response to IL-2 binding on IL-2Rβ.

In order to identify antigenic sequences (epitopes) on the extracellular domain of IL-2Rβ, 239 overlapping dodecapeptides have been synthesized by means of the PEPSCAN method, often applied in epitope mapping studies. With this technique hundreds of peptides can be synthesized simultaneously, in a fully automatic fashion, and subsequently tested in regular ELISA assays, because the peptides are covalently linked on holders that fit in 96-well ELISA plates. The peptides are synthesized on polyethylene rods coated with derivatized polyacrylic acid, according to the standard methodology for solid-phase peptide synthesis. The large number of synthetic peptides prepared at low cost in a short time, and the possibility to test them against multiple monoclonal antibodies raised against the protein of interest, present the major advantages of the PEPSCAN method. Practically, all possible overlapping peptides of 8-12 amino acids corresponding to the primary sequence of a protein can be synthesized, thus enabling the detailed mapping of all linear/sequential epitopes on a protein antigen (e.g. antigenic sequences encompassing single continuous stretches of amino acids residues). On the other hand, discontinuous/conformational epitopes can hardly be identified by using synthetic peptides.

The monoclonal antibodies Mikβ1, HuMikβ1, TU27 and TU11 have been raised against the IL-2Rβ and characterized previously. Our results indicate that TU27 probably recognizes a conformational epitope, consisting of amino acid sequences that are located apart on the primary sequence of IL-2Rβ but are likely to come in close proximity when the IL-2Rβ polypeptide acquires its native conformation. This speculation is based on the fact that none of the 239 synthetic dodecapeptides tested was found to crossreact with TU27, although this antibody has been shown to bind on the IL-2Rβ native protein and inhibit the binding of IL-2. The Mikβ1 and HuMikβ1 monoclonal antibodies, which also inhibit the binding of IL-2, seem to recognize regions of a discontinuous epitope located throughout the IL-2Rβ primary sequence, since several non-neighbouring dodecapeptides crossreacted with these antibodies, although with moderate binding affinities. On the other hand, a sequential epitope recognized by the TU11 monoclonal antibody has clearly been identified. This epitope is comprised of several neighbouring dodecapeptides. The TU11 monoclonal antibody has been shown to inhibit the binding of IL-15, a novel cytokine cloned recently, on its high-affinity receptor complex consisting of the IL-2Rβ, IL-2Rγ and an unidentified subunit specific for the IL-15. This result raises the interesting possibility that the epitope crossreacting with the TU11 could constitute the IL-15 binding domain on the IL-2Rβ. All the immunoreactive peptides were tested for their ability to bind ^{125}I-IL-2 in solution, while still attached on the rods. Two peptides have been identified as candidate binding domains for IL-2 on the IL-2Rβ.

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STRUCTURAL MODIFICATIONS IN POSITION 5 OF ANGIOTENSIN II AFFECT DIFFERENTLY THE RELATIVE AFFINITY

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D.Theodoropoulos[2] and P.Cordopatis[1].

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ABSTRACT

Angiotensin II, a linear flexible octapeptide (H-Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-OH, Ang II), may obtain conformations related to the environment, structural features or overall molecular charges. Medium or long range lipophilic modifications in position 5 (x^5,Val, Leu, Ala, Gly, Chg), control the organization of the central sequence from tyrosine to proline including rotation and spatial distance of tyrosine and histidine side chains. These modifications satisfy more or less the receptor, but do not alter the biological activity. It seems that the binding sites (Arg^2, Tyr^4, His^6) are oriented in the one side of the molecule, whereas those imposing conformation (Val^3, Ile^5 or Val^5, Pro^7) occupy the other side. This arrangement of the hydrophobic and hydrophilic side chains in Ang II imitates somehow the spatial arrangement of the two sides of the oxytocin molecule around the backbone rigid structure of the disulfide ring. From our experience the balance of hydrophobic-hydrophilic moieties of the oxytocin molecule affects the biological potencies of this hormone. Furthermore increased hydrophobicity in position 5 converts weak agonists to weak antagonists, as we found out for the first time. This experience prompted us to investigate the 5-position residue of Ang II by replacing the hydrophobic side chain by another containing an electrophilic moiety.Along this line a number of sulfur-containing in side chains analogs were synthesized and tested for relative affinity. The results are discussed in terms of the proposed active conformation of Angiotensin II.

Chimika Chronika, New Series, 26, 81 (1997)

THE ROLE OF CADMIUM-INDUCED APOPTOSIS ON IMMUNE SYSTEM CELLS

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Cadmium, a potent toxic metal, poses a serious environmental threat that may alter homeostasis. Previous work in a human T cell line (CEM-C12) has shown that cadmium exerts its toxic effect via apoptotis. In contrast to stress-induced cell death apoptosis is a normal and strategic event with a crucial role in cell developmented processes which necessitate cell deletion. To investigate the role of cadmium-induced apoptosis in the immune system, we studied the cadmium apoptotic effect in two human cell lines, the immature T cell line CCRF-CEM and the B cell line Raji. Viable cell number and mortality (%) were assessed by methyl tetrazolium test (MTT). By that, cadmium was found to be dose-dependently toxic for both cell lines after 18 hrs incubation. The LD_{50} for CCRF-CEM was 50μM, while the LD_{50} for Raji was 24μM. As the morphological changes observed at apoptosis, provide the most reliable markers, we utilized the EtBr nuclear stain for the quantitative measurement of normal, apoptotic and necrotic cells after 18 hrs incubation with different cadmium concentrations (5μM to 100μM). We found that in both cell lines low cadmium concentrations induced apoptosis and high necrosis. In CCRF-CEM cells apoptotic cells were detectable at 10μM and reached a maximum at 30μM. In Raji, apoptotic cells were detectable at 5μM, while a plateau effect was observed from 20μM to 30μM Cd^{2+}. The above results showed that Raji cells were more sensitive to cadmium-induced apoptosis compared to CCRF-CEM cells, indicating that the differential cadmium triggered apoptotic cell death may disturb the normal developmental processes. In this regard, the apoptotic effect of cadmium suggests that another possible factor in the lymphocyte differentiation process exists.

Chimika Chronika, New Series, 26, 82 (1997)

SYNTHESIS OF THE FURANODITERPENES (±)-CORONARIN E AND (±)-DIHYDROCORONARIN E

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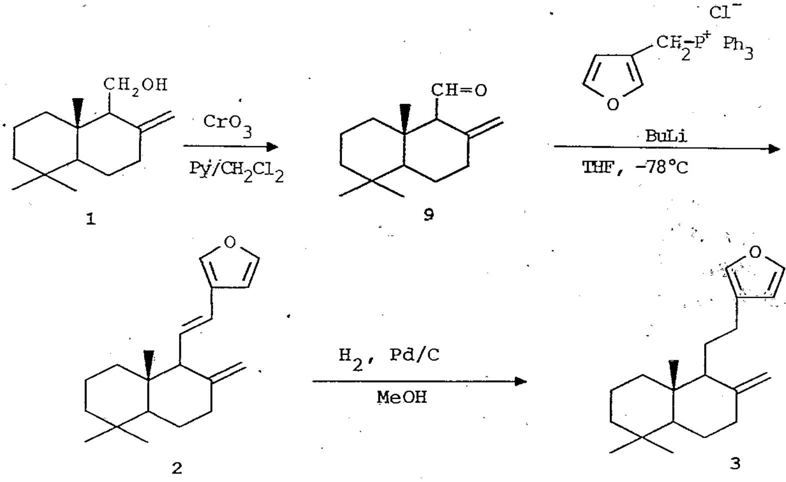
Summary : The first formal total synthesis of the furanoditerpenes (±)-Coronarin E **2** and (±)-Dihydrocoronarin E **3**, starting from the drimane sesquiterpene (±)-albicanol **1**, in three steps, is reported in this paper.

Coronarin E **2**, a cytotoxic furanolabdane diterpene, isolated from several Zingiberaceae species, is a significant chemical marker for these plants. Dihydrocoronarin E **3** is a suitable precursor for a biomimetic cyclisation to the marginatane skeleton, a recently discovered new class of tetracyclic diterpenes. Oxidation of synthetic (±)-**1** by PCC, gave quantitatively the albicanal **2**, which was subjected immediately to the Wittig reaction with the 3-furylmethyl-triphenyl phosphorane in THF at -78°C to give the unstable (±)-Coronarin E **2**, in 25% yield, as an oil. The spectral properties of the synthetic **2** are identical with those described for the natural Coronarin E. Selective reduction of the conjugated double bond of **2**, by catalytic hydrogenation gave quantitatively (±)-Dihydrocoronarin E **3**.



Chimika Chronika, New Series, 26, 83 (1997)

SYNTHESIS OF PYRANO[2,3-g]CHROMENE-2,7-DIONE DERIVATIVES AND ITS 3-AZA- ANALOGUE

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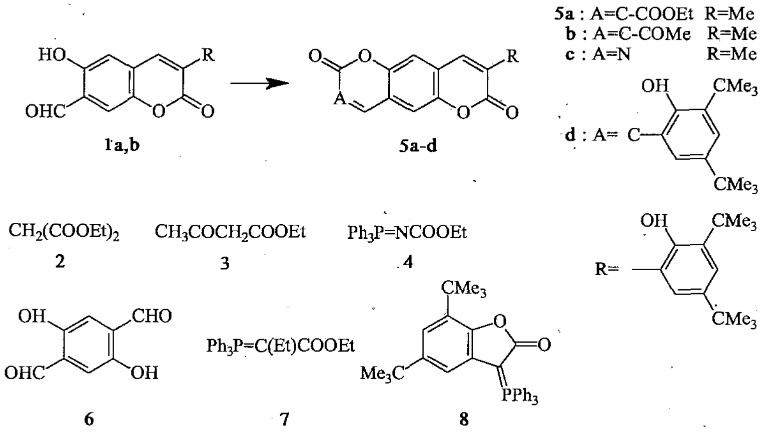
ABSTRACT

In connection with our previous work on the synthesis of pyranono-coumarins we report the facile preparation of compounds **5a-c** from the reaction of coumarin derivative **1a** (R=Me) with compounds **2**, **3** and **4** respectively, shown in Scheme 1. We also present an improved preparation of the coumarin **1b** (R=Et) as well as the synthesis of the new pyranono-coumarin **5d** by treatment of 2,5-diformylhydroquinone **6**, with phosphorus ylides **7** and **8** respectively. Similar other reactions as well as the study of their possible biological properties are under further consideration.



Scheme 1

Chimika Chronika, New Series, 26, 84 (1997)

SYNTHESIS OF 1,6-DIONE AND 1,6-DITHIONE OF [1,2,4]-BIS-OXADIAZOL[4,3-a:3′,4′-c]QUINOXALINE AND THE [1,2,3,5]-BIS-OXATHIADIAZOL[3,4-a:4′,3′-c]QUINOXALINE-1,6-DIOXIDE

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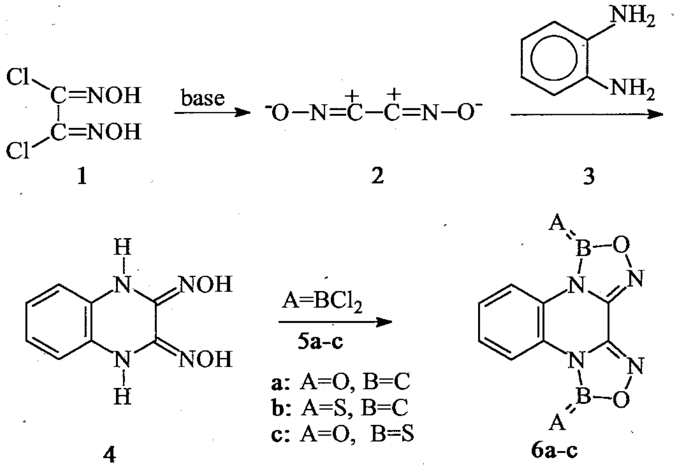
ABSTRACT

Quinoxaline derivatives are important for their interesting biological properties. In connection with our previous work in benzoxazines and quinoxalines, we report here the synthesis of some fused [4,3-a:3′,4′-c] and [3,4-a:4′,3′-c]quinoxaline derivatives **6a-c**. These new compounds are produced very easily by the reaction sequence depicted in the following Scheme, starting from the nitriloxide **2** and followed by the reaction of the obtained quinoxaline **4** with A=BCl$_2$ **5a-c**. The preparation of mono-fused derivatives as well as the study of their possible biological activities are under further consideration.



Chimika Chronika, New Series, 26, 85 (1997)

SYNTHESIS OF 4-SUBSTITUTED (BENZOXAZOL-2-YL)-, (BENZIMIDAZOL-2-YL)- AND (BENZOTHIAZOL-2-YL)- COUMARIN

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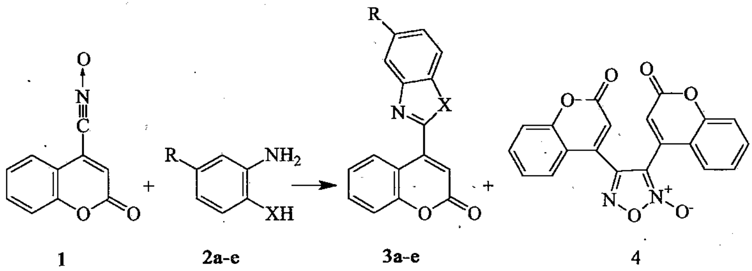
ABSTRACT

Treatment of nitriloxide 1 in refluxing chloroform solution with equimolar amounds of aminophenols **2a-c**, diamine **2d** and aminothiophenol **2e**, affords in 16-31% yields the corresponding 4-substituted (benzoxazol-2-yl)- **3a-c**, (benzimidazol-2-yl)- **3d** and (benzothiazol-2-yl)-2H[1]-benzopyran-2-ones **3e**, respectively. Dimerization of the nitriloxide 1 into the corresponding furoxan **4** also occurs. Similar coumarin derivatives are biologically interesting and our products obtained are to be also tested for biological activity.



2,3a: R=H, X=O, **b**: R=Cl, X=O, **c**: R= NO_2, X=O, **d**: R=H, X=NH **e**: R=H, X=S

Chimika Chronika, New Series, 26, 86 (1997)

A NEW CONVENIENT METHOD FOR THE SYNTHESIS OF BENZYL ESTERS

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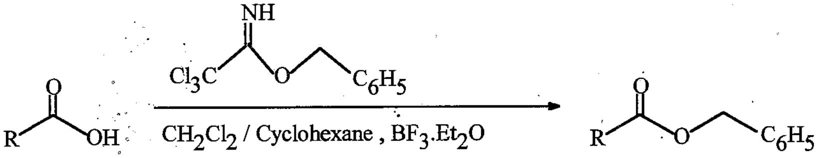
ABSTRACT

Benzyl esters are among the most common carboxylic protecting groups.Traditional methods as well as recent procedures for their preparation have been summarized by Kociensky.We now report an effective method for the conversion of carboxylic acids into the corresponding benzyl esters using benzyl 2,2,2-trichloroacetimidate under mild acidic conditions. The alkyltrichloroacetimidates may be prepared by the reaction of the alcohol with trichloroacetonitrile in the presense of a catalytic amount of an alkoxide. Benzyl 2,2,2-trichloroacetimidate has been used for the O-benzylation of hydroxy groups, while *tert*-butyl 2,2,2-trichloroacetimidate for the preparation of *tert*-butyl ethers and esters.

We found that carboxylic acids were readily converted to the corresponding benzyl esters by treatment with benzyl trichloroacetimidate in a mixture of cyclohexane / dichloromethane at room temperature on addition of a catalytic amount of boron trifluoride etherate. A variety of acids (propionic, iodoacetic, palmitic, linoleic, pivalic, benzoic, phenylacetic, cinammic, 9-fluorenylmethoxycarbonyl-L-leucine (Fmoc-Leu-OH), (1S)-(-)-camphanic) were benzylated in good to high yields.



Chimika Chronika, New Series, 26, 87 (1997)

CONVERSION OF L-THREONINE AND L-ISOLEUCINE TO THE CORRESPONDING ALDEHYDES VIA CURTIUS REARRANGEMENT

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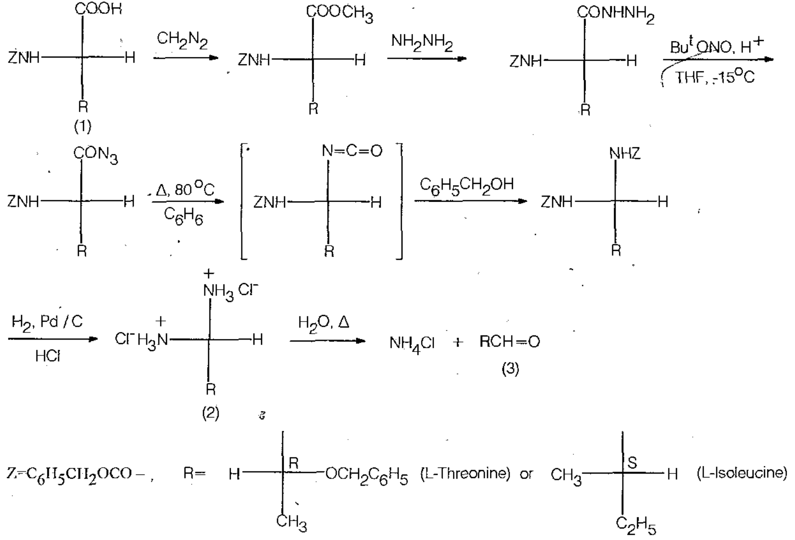
ABSTRACT

α-hydroxy propionaldehyde and 2-methylbutanal have been synthesized in their racemic form, from suitable derivatives of L-Threonine and L-Isoleucine respectively. The conversion of the amino acids to their corresponding aldehydes has been achieved by the application of Curtius rearrangement on their azides, properly protected. As shown in the following scheme, N-benzyloxycarbonyl-L-amino acid (1) is converted first to the gem-diamine (2), and finally to the aldehyde(3) by heating in aqueous acidic solution.



We have isolated aldehydes as racemates probably because of the enolization of the molecules (aldehydes with α asymmetric carbon atom), in the aqueous solution of the final conversion.

Both α-hydroxy propionaldehyde and 2-methylbutanal have been isolated as derivatives with 2,4-dinitrophenylhydrazine and characterized.

Chimika Chronika, New Series, 26, 88 (1997)

SYNTHESIS OF ACRYLIC ACID COMPOUNDS FROM COYMARINS

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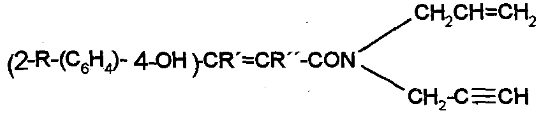
Abstract

It is known, that d-Lactones, in the presence of NH_3 or NaOH, open their ring, formatting respectively amides or sodium carboxylate salts. However, there is no sufficient report on more complexes Lactones such as coumarins especially by the action of $PdCl_2$.

The double bond of the d-lactonic ring of coumarins has the properties of a ethylenic bond, therefore is possible, a formation of a π-complex with $PdCl_2$. Nevertheless the expecting complexation do not occurs on the double bond but exclusively $PdCL_2$ coordinates of the 1-position of the d-lactone, leading to the spontaneous opening of the ring and the follow reaction with prepared N,N-allyl-propine-amine

$HC\equiv C\text{-}CH_2NHCH_2CH{=}CH_2$

forms some novel derivatives of acrylic acid



$$(2\text{-R-}(C_6H_4)\text{- }4\text{-OH})\text{-CR}'{=}\text{CR}''\text{-CON}\begin{matrix}CH_2CH{=}CH_2\\ CH_2\text{-}C\equiv CH\end{matrix}$$

R=OH, CH_3O R′=CH_3 R″=COOH

Chimika Chronika, New Series, 26, 89 (1997)

ISOTOPIC DIFFERENTIATION DUE TO 1,3- NON BONDED INTERACTIONS

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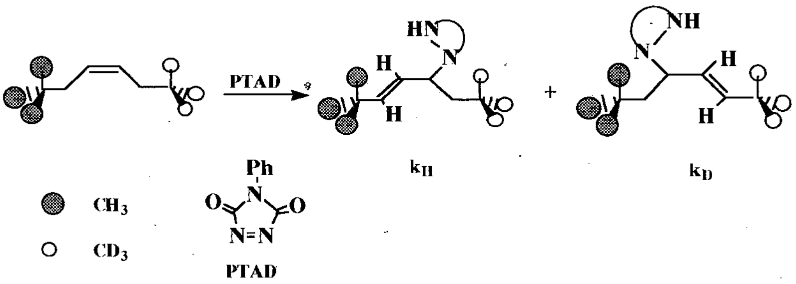
ABSTRACT

4-Phenyl-1, 2, 4-triazoline-3, 5-dione (PTAD) is a very powerfull electrophile. It reacts with conjugated dienes to give Diels-Alder products and with alkenes to afford *ene* or [2+2] adducts. In the *ene* reaction of PTAD with cis disubstituted alkenes the major or only product arises from the allylic hydrogen abstraction next to the larger alkyl substituent of the olefin. This regioselectivity has been explained in terms of 1, 3- non bonded interactions between the intermediate aziridinium imide and the alkyl substituents. We report here an isotope effect study of the *ene* reaction of PTAD with cis-2,2,7,7-tetramethyl-4-octene-d_9.



A remote isotope effect $k_H/k_D=1.16$ was measured by ^1H NMR spectroscopy. This δ- steric isotope effect can be rationalized in terms of unequal 1,3- steric interactions of the t-butyl-d_9 and t-butyl-d_0 groups with the incoming N of the PTAD molecule in the transition state.

Thus the C-N bond next to the t-butyl-d_9 is formed 1.16 times more than the other adduct with C-N bond next to t-butyl-d_0.

Chimika Chronika, New Series, 26, 90 (1997)

PRIMARY AND ß - SECONDARY ISOTOPE EFFECTS IN OXIDATION OF p - SUBTITUTED α- METHYLBENZYL ALCOHOLS WITH DIMETHYL DIOXIRANE (DMDO) AND PYRIDINIUM CHLOROCHOMATE (PCC).

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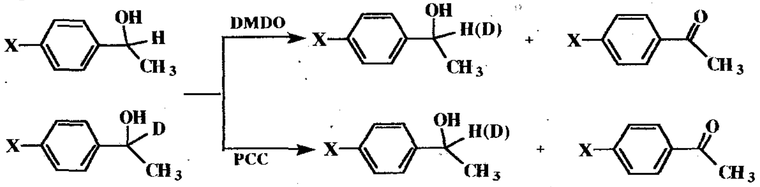
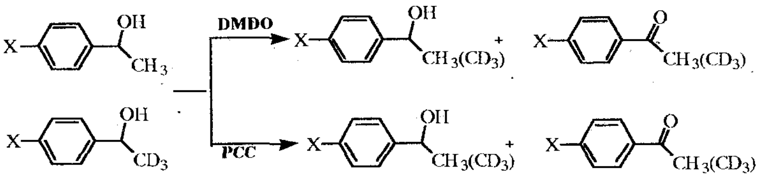
ABSTRACT

In the last decade, dioxiranes, three memberd ring cyclic peroxides, have been received intensive attention as oxidants. However, despite the huge amount of research efforts, there are still some uncertainties about the mechanism in which dioxiranes act in various oxidation processes. In this work, isotopic studies regarding the oxidation of secondary alcohols by dimethyl dioxirane (DMDO) and pyridinium chlorochromate (PCC), are presented.

The primary kinetic isotope effects (KIEs) which are observed for DMDO (k_H/k_D = 2,71) and PCC (k_H/k_D = 1,97) in the case of α - methylbenzyl alcohol, show that the rate determining step of the reaction is the abstraction of the α - hydrogen. Moreover the higher values of primary KIEs in the case of p - trifluoromethyl - α - methylbenzyl alcohol, (k_H/k_D = 4,42) for DMDO, and (k_H/k_D = 3,36) for PCC respectively, indicates the electrophilic nature of these reactions.



The ß - secondary KIEs show that the two oxidants act by different mechanisms. The absence of ß -secondary KIEs ($k_H/k_D \approx 1$) in the case of PCC indicates that the reaction mechanism is concerted. On the other hand, the normal values of ß -secondary KIEs (k_H/k_D = 1,15) when the oxidation reagent is DMDO suggest a stepwise mechanism, propably occuring via a radical caged proccess.



Chimika Chronika, New Series, 26, 91 (1997)

SYNTHESIS AND FLUORESCENT PROPERTIES OF NEW INTRAMOLECULARLY QUENCHED FLUOROGENIC PEPTIDES AS POTENTIAL SUBSTRATES FOR *CLOSTRIDIUM HISTOLYTICUM* COLLAGENASE

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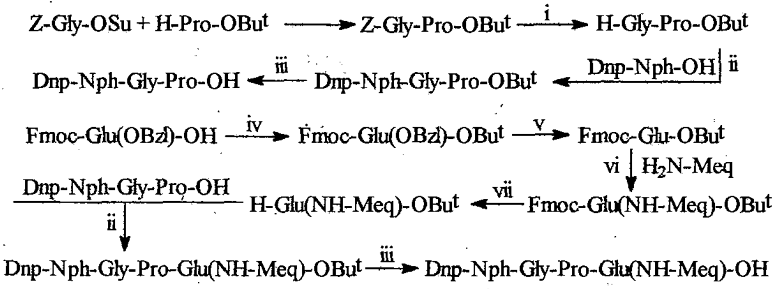
Athens 157 71, Greece

ABSTRACT

Three new intramolecularly quenched fluorogenic substrates for *Clostridium histolyticum* collagenase have been synthesized by using the fluorescent amine 7-amino-4-methyl-2-quinolinone (Ameq) as fluorophore F and the aromatic group 2,4-dinitrophenyl as quencher Q. The new substrates Dnp-Nph-Gly-Pro-Glu-NH-Meq (**1**), Dnp-Nph-Gly-Pro-Glu(NH-Meq)-OH (**2**) and Dnp-Nph-Gly-Pro-Leu-NH-Meq (**3**) were synthesized by conventional methods of peptide synthesis in good yield and purity and were identified by elemental analysis, IR and ^{1}H-NMR spectroscopy and mass spectrometry (FAB-MS). As an example, the synthesis of substrate **2** is depicted in the following scheme.



i) $HCOONH_4$, Pd/C, ii) WSC·HCl/HOBt, iii) TFA, anisole, iv) $Cl_3C-C(=NH)-OBu^t/BF_3 \cdot Et_2O$,
v) H_2/Pd-black, anisole, vi) $ClCOOCH_2CH(CH_3)_2/Et_3N$, vii) Et_2NH

The fluorescence properties of the substrates at $\lambda_{ex}=333$ nm and $\lambda_{em}=366$ nm (10^{-5}M solutions in 0.05M Tris, pH 7.8, containing 1% DMSO) were compared with those of the compound Ac-NH-Meq (**4**). The quenching of fluorescence of Ameq observed was 100.0, 99.1 and 99.9 % for substrates **1**, **2** and **3** respectively.

Enzymatic cleavage of the peptide chain at any point between the interacting groups F and Q will destroy the intramolecular quenching, resulting in an increase of fluorescence. Therefore, the synthesized substrates could be used for the direct determination of endopeptidases, such as *C.h.* collagenase or prolyl oligopeptidase, which hydrolyze the X-Gly or Pro-Y bonds respectively, by measuring the development of fluorescence.

Chimika Chronika, New Series, 26, 92 (1997)

SOLID PHASE PEPTIDE SYNTHESIS OF THYMOSIN β10 (43 AMINOACIDS) USING A NEW PARA - CYANO - TRITYL RESIN. CHEMICAL CHARACTERISATION AND IMMUNOCHEMICAL CONTROL OF THE SYNTHETIC PEPTIDE.

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[1]Immunochemistry Lab., Institute of Radioisotopes and Radiodiagnostic Products, NRCPS «Demokritos»; [2]Chemical Departement, University of Athens; [3]Pharmaceutical Technology Lab., Pharmaceutical Departement, University of Patras.

Abstract

Thymosin β10 (43 aminoacids) was synthesized using Fmoc-solid phase stategy. The new para-cyano-trityl resin used showed enhanced acid stability compared with the usual trityl ester resins, thus providing selective peptide synthesis with high yield and purity. After it had been cleaved from the resin, crude β10 was purified with gel filtration and reverse-phase semi-preparative high performance liquid chromatography (HPLC). The purified synthetic peptide was shown to co-elute with recombinant β10 in an analytical reverse-phase HPLC system. The amino acid analysis data were in agreement with the reported in the literature primary structure of β10. Furthermore, the synthetic β10 exhibited similar immunochemical characteristics compared with the recombinant material in an in vitro ELISA test using rabbit polyclonal anti-β10 antiserum.

Chimika Chronika, New Series, 26, 93 (1997)

THIOSEMICARBAZONES OF 2-AKETYL-IMIDAZO[4,5-b]PYRIDINE WITH ANTITUMOR ACTIVITY

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ABSTRACT

Thiosemicarbazones, a class of compounds possesing a wide spectrum of medicinal properties have been studied for antibacterial, antimalarial,antineoplastic and antiviral activities. This wide spectrum of action, of thiosemicarbazones, in combination with the biological properties of compounds which are derivatives of imidazo[4,5-b]pyridine system, was very encouraging in order to synthesize a series of N^4-monosubstituted and N^4N^4-disubstituted thiosemicarbazones derived from 2-acetyl-imidazo[4,5-b] pyridine. The title compounds were studied for their in vitro antitumor activity against 60 human tumor cell lines derived from nine cancer types by the National Cancer Institute. By increasing the size of N^4-substituent of thiosemicarbazone moiety enhancament of antitumor activity was observed.

Chimika Chronika, New Series, 26,94 (1997)

SYNTHESIS OF NOVEL ANTIARRHYTHMIC AGENTS WITH ANTIOXIDANT ACTIVITY

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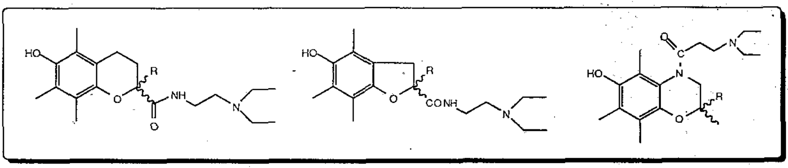
ABSTRACT

The majority of the persons who suffer cardiac arrest have a history of previous myocardial infarctions. Accumulating evidence suggests that the injury sustained by the heart following a case of acute myocardial ischemia occurs to a significant extent during reperfusion (reoxygenation) due to the production of a burst of active oxygen species (AOS).

In this paper we report the synthesis of three series of novel compounds which could act as bifunctional drugs which while reversing the arrhythmic state of the heart will also be able to trap any AOS generated during the reoxygenation process. The first two series utilize procainamide as a prototype for antiarrhythmic activity and tocopherol or its dihydrobenzofuran analog as the prototype for AOS scavengers. The third series combine in one skeleton benzoxazine for antiarrhythmic activity and structural features of lidocaine for antioxidant and antiarrhythmic activity.



Chimika Chronika, New Series, 26, 95 (1997)

ENANTIOSELECTIVE SYNTHESIS OF NEW MOLECULAR PROBES FOR THE CANNABINOID RECEPTORS

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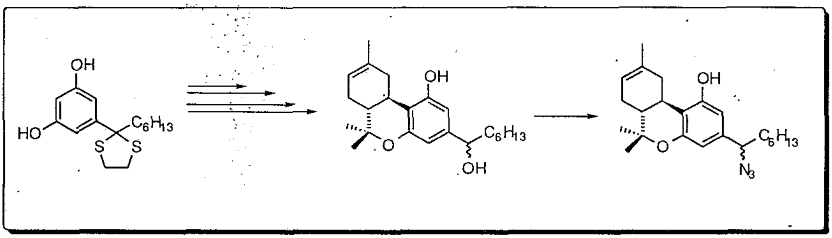
ABSTRACT

The successful preparation of a cannabinoid receptor affinity label will be described. The availability of this novel photoaffinity receptor probe constitutes an important development in cannabinoid research and should facilitate the full characterization of this receptor.

Photoaffinity labeling of a receptor involves the use of ligands carrying photoactivatable groups which covalently attach to reactive residues at or in the vicinity of the binding site(s), after equilibration and photoirradiation. This methodology has provided useful information on the distribution and molecular weights or amino acid residues at or near the active site(s) .

We present the total synthesis of a photoaffinity label, namely (-)-1'-azido-heptyl-Δ^8-tetrahydrocannabinol which was used to covalently label the cannabinoid receptor.



Chimika Chronika, New Series, 26, 96 (1997)

STUDY OF CANNABINOID:MEMBRANE INTERACTIONS USING A COMBINATION OF BIOPHYSICAL METHODS

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Since membranes are characterized by complexity and inherent instability they do not lend themselves to a detailed analysis of their structure and dynamics by a single biophysical method. It is therefore, preferable to use jointly several experimental techniques for such studies. A combination of three techniques (DSC, X-ray, stationary and high resolution solid state NMR) were used to study cannabinoid membrane interactions. A pair of analogs is chosen for this comparison which have a close structural resemblance but differ greatly in their biological activities. Specifically, Δ^8-tetrahydrocannabinol (Δ^8-THC) possesses a phenolic hydroxyl group and has psychotropic properties whereas its methylated analog Me-Δ^8-tetrahydrocannabinol (Me-Δ^8 -THC) is biologically inactive. The three biophysical methods demonstrated that the two molecules interact differently with membrane bilayers. Based on the experimental observations a model was proposed of their mechanism of action on the membrane level.

Chimika Chronika, New Series, 26, 97 (1997)

SYNTHESIS OF NOVEL NEUROSTEROIDS WITH ANXIOLYTIC AND ANTICONVULSANT ACTIVITY

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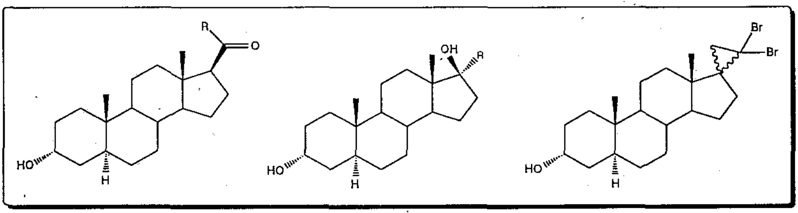
ABSTRACT

Neurosteroids are natural or synthetic steroids that rapidly alter the excitability of neurons by binding stereoselectively and with high affinity to receptors for the major inhibitory neurotransmitter in brain, γ-aminobutyric acid ($GABA_A$). Biochemical and electrophysiological studies have shown that these steroids markedly augment GABA-activated chloride ion currents in a manner similar (but not identical) to that of anesthetic barbiturates.

For neurosteroids to interact with the $GABA_A$ receptor, several structural requirements are essential. Thus, it has been found that the presence of a 3α-hydroxy group accompanied by the presence of an electronegative atom at C20 or C17, is necessary. *In vivo* experiments utilising neurosteroids possessing the above structural features suggest sedative-hypnotic, anxiolytic and spasmolytic activity accompanied by low toxicity. The present work describes the synthesis of a series of novel suitably substituted neurosteroids.



Chimika Chronika, New Series, 26, 98 (1997)

TACHYKININ SUBSTANCE P. SYNTHESIS AND BIOLOGICAL ACTIVITY OF C-TERMINAL FRAGMENTS

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Mammalian tachykinins e.g. Substance P (SP), Neurokinin A (NKA) and Neurokinin B (NKB) constitute a family of naturally occuring peptides, which have related primary structure and display high homology at the C-terminal pentapeptide amide.

	1 2 3 4 5 6 7 8 9 10 11
SP	Arg-Pro-Lys-Pro-Gln-Gln-Phe-Phe-Gly-Leu-Met-NH$_2$
NKA	His-Lys-Thr-Asp-Ser-Phe-Val-Gly-Leu-Met-NH$_2$
NKB	Asp-Met-His-Asp-Phe-Phe-Val-Gly-Leu-Met-NH$_2$

Tachykinins are widely disributed and active in both central nervous system (CNS) and perifery. They exert a variety of biological actions, like smooth muscle contraction (directly or indirectly), vasodilation, secretion of saliva, pain transmition and regulation of immune responce. Their receptors are designated as NK-1, NK-2 and NK-3 for SP, NKA and NKB respectively. This classification is based on the relative order of potency in various bioassays of tachykinins and their fragments. Specially SP biological activity depends mainly on the sequence of the C-terminal fragment. Substance P is also reported to implicate in diverse diseases like asthma, rhinitis, rheumatoid arthritis, migraine and others. Further elucidation of the biological actions of SP, NKA and NKB requires the synthesis of new agonists and antagonists capable for selective activity mediated through one of the three receptors.

Several structural modifications of the methionyl residue of SP by glutamic acid γ-esters, or replacement of other amino acids of tachykinin sequence have given SP C-terminal analogues (Table I) which showed remarcable agonist activity.

Table I. SP C-terminal analogues with agonist activity.

[Orn^{6},Glu(OBzl)^{11}]SP$_{6-11}$	[Glu(OBzl)^{11}]SP$_{6-11}$	[Glu(OBzl)^{11}]SP$_{5-11}$
[Orn^{6},Glu(OBu^{t})^{11}]SP$_{6-11}$	[Glp^{6},Glu(OBu^{t})^{11}]SP$_{6-11}$	[Glp^{5},Glu(OBu^{t})^{11}]SP$_{5-11}$

In the present study the analogues [Pro^{4},Glu(OBzl)^{11}]SP$_{4-11}$, [Hyp^{4},Glu(OBzl)^{11}]SP$_{4-11}$ and [cHyp^{4},Glu(OBzl)^{11}]SP$_{4-11}$ of the C-terminal octapeptide of SP have been synthesized by conventional solution methods using a stepwise chain elongation combined with fragment coupling. In each analogue the Met^{11} has been replaced by γ-benzyl ester of Glu and Pro^{4} by *trans*-4-hydroxy-L-proline (Hyp) or *cis*-4-hydroxy-L-proline (cHyp). The analogues have been purified by gel filtration on Sephadex G-15, semi-preparative HPLC and analyzed. Preliminary biological preparations, *in vitro*, on guinea pig ileum (GPI) showed that the analogues exert interesting agonist activity.

Chimika Chronika, New Series, 26, 99 (1997)

SOLID PHASE SYNTHESIS OF THE C- TERMINAL 16-PEPTIDES FROM *PSEUDOMONAS AERUGINOSA* (C-551) AND *HYDROGENOBACTER THERMOPHILUS* (C-552).

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ABSTRACT

The cytochrome C-552 from *Hydrogenobacter thermophilus* exhibits a much higher thermostability than the cytochrome C-551 from *Pseudomonas aeruginosa*,even though their amino acid sequences are 56% identical. This difference in stability could be due to their differences in their spatial structures.Therefore, it is interesting to investigate the "structure-stability" relationship for these two cytochromes.

An aproach to understand the process of protein folding is to obtain structural information on folding intermediates.There are data from structure-folding studies suggesting that the folding of N- and C- terminal helices of cytochromes, which takes place in the first 5ms, is used as a leader for the folding of the rest of the molecule.Based on the above informations, we have synthesized the C-terminal 16-peptides A and B of the cytochrome C-551 and C-552 respectively.

Peptide A	Ser-Asp-Asp-Glu-Ala-Gln-Thr-Leu-Ala-Lys-Trp-Val-Leu-Ser-Gln-Lys-OH
Peptide B	Thr-Asp-Ala-Glu-Ala-Lys-Gln-Leu-Ala-Gln-Trp-Ile-Leu-Ser-Ile-Lys-OH

The synthesis of the peptides was performed on a 2-chlorotrityl-resin utilizing the diisopropylcarbodiimide / N-hydroxybenzotriazole (DIPCD / HOBt) coupling procedure. The 9-fluorenylmethoxycarbonyl (Fmoc-) group was used for the temporary protection of the α-amino groups and *tert*-butyl-type groups for all side chain functionalities. After protecting group and resin cleavage, pure peptides were obtained by a semipreparative reversed phase HPLC and identified by ^{1}H NMR, ^{13}C NMR spectroscopy and FAB-MS spectrometry. The secondary structures of the synthesized peptides are now under investigation by 2D NMR and circular dichroism spectroscopy.

Chimika Chronika, New Series, 26, 100 (1997)

ANTIHYPERTENSIVE DRUGS

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ABSTRACT

The mechanism of antihypertensive action of timolol, a β-blocker, was studied using FT-IR spectroscopy and molecular modeling. The band at 1691 cm^{-1}, which corresponds to the absorption of the C6=O bond, shifts to 1652 cm^{-1}, after the adition of timolol β-blocker. Considerable changes were also observed in the region 1604 cm^{-1}, where the C8=N7 and C4=C5 bonds absorb. These results lead to the suggestion that the drug binds to 5'-guanosine monophosphate at O6 and N7 through hydrogen bonds. This binding was confirmed by conformational analysis with MODEL and BAKMDL programs, using MMX-force field.

Chimika Chronika, New Series, 26, 101 (1997)

INCORPORATION OF [^{3}H]-OLEIC ACID INTO PLATELET LIPIDS AND ITS MOBILIZATION AFTER STIMULATION WITH PLATELET ACTIVATING FACTOR (PAF) AND THROMBIN

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ABSTRACT

Oleic acid (cis-9-decaoctaenoic acid) is found esterified mainly in the sn-2 position of membrane glycerophospholipids. It has been reported that it is a potent inhibitor of platelet-activating factor (PAF) induced platelet aggregation and phosphoinositide metabolism. Furthermore oleic acid caused Ca^{2+} mobilization from internal stores in human platelets. In order to further investigate the possible role of oleic acid in rabbit platelets, in the present study we found that: (a) Incorporation of [^{3}H]-oleic acid into rabbit platelets was time dependent and reached a plateau within 75 min. (b) Oleic acid was rapidly incorporated mainly into phospholipids and mono-,di- and triglycerides as well. (c) Stimulation of labeled platelets with PAF or thrombin, both very potent activators of platelets, caused a rapid, transient release of oleic acid intracellularly, probably through activation of phospholipase A_2. The effect of PAF was more rapid: 10% of the incorporated oleic acid into phospholipids was released within the first 2 min. The mobilization of oleic acid caused by thrombin was pronounced and lasted longer. The released oleic acid could act as an intracellular messenger for these agonists in platelets and possible targets could be protein kinase C isoenzymes or other proteins as it has been recently reported by several investigators.

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ENZYMES IN LECITHIN MICROEMULSIONS. STRUCTURAL STUDIES

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ABSTRACT

The esterification reaction of lauric acid with propanol-1 catalysed by lipase from *Pseudomonas Cepasia* has been investigated in microemulsions formed with soya bean lecithin. The optima T, pH and water content, expressed in terms of $w_0 = [H_2O]/[\text{lecithin}]$, was determined. Time resolved luninescence quenching studies using $Ru(bipy)_3Cl_2$ as a lumophore and $K_3Fe(CN)_6$ as a quencher showed that the system is percolating. A dramatic variation of the water/oil interface occurs by increasing the water content.

Chimika Chronika, New Series, 26, 103 (1997)

STRAWBERRY FURANONES: THE CHEMISTRY OF THEIR BIOSYNTHESIS

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ABSTRACT

Two of the most important flavour compounds in strawberries are 2,5-dimethyl-4-hydroxy-2*H*-furan-3-one (DMHF) and its methyl ether, 2,5-dimethyl-4-methoxy-2*H*-furan-3-one. The biosynthesis of these two furanones is being investigated to obtain higher yields and therefore fruits with richer flavour. These flavour compounds have been analysed by HPLC-UV.

Plant tissue cultures of strawberries have been established. Immediate precursors of the above flavour compounds, i.e. 6-deoxy-hexoses, have been fed to callus cultures and the levels of the furanones are compared in the treated and control tissues. The increased levels of DMHF-glucoside in the precursor-fed cultures propose that 6-deoxy-hexoses have a key role in the formation of the two furanones.

The probable biosynthetic pathway of the two furanones is shown.

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BIOCONVERSION OF CHITIN TO CHITOSAN: ISOLATION AND CHARACTERIZATION OF CHITIN DEACETYLASE FROM *COLLETOTRICHUM LINDEMUTHIANUM*

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ABSTRACT

Chitin deacetylase, (EC 3.5.1.4), the enzyme that catalyzes the hydrolysis of acetamido groups of N-acetyl-D-glucosamine in chitin, has been purified to homogeneity from the culture filtrate of the fungus *Colletotrichum lindemuthianum* and further characterized. The enzyme exhibits a molecular mass of 150 kDa, it is a glycoprotein and its carbohydrare content was estimated to be 67% by weight. Chitin deacetylase is active on several chitinous substrates and chitin derivatives. The enzyme requires at least two N-acetylglucosamine residues (chitobiose) for catalysis, it is not inhibited by acetate while iτ exhibits a remarkable thermostability. When glycol chitin (a water-soluble chitin derivative) was used as substrate, the optimum temperature for enzyme activity was determined to be ~50°C and the optimum pH was ~8.5.

Chimika Chronika, New Series, 26, 105 (1997)

ENZYMATIC OXIDOREDUCTIONS OF NON-NATURAL SUBSTRATES-PARTIAL ENRICHMENT OF ALCOHOL DEHYDROGENASES FROM PSYCHROPHILIC BACTERIA.

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Abstract:

Enzymes from psychrophilic organisms exhibit low stability and increased catalytic capacity, when compared with thermophilic and mesophilic enzymes, presumably due to the flexibility of their stuctures, and are therefore expected to accept a broader spectrum of substrates.

In order to isolate alcohol dehydrogenases from psychrophilic bacteria, several purification schemes were employed. Dye ligand affinity chromatography was found to be inappropriate in the case of alcohol dehydrogenases from the psychrophilic organisms, although it is generally used for the purification of the corresponding mesophilic and thermophilic enzymes.

The purification proccess of alcohol dehydrogenases from psychrophilic bacteria is still in progress. The study of their specificity and mechanism is expected to lead in conclusions concerning the structure specificity relarionship.

Chimika Chronika, New Series, 26, 106 (1997)

ENZYMATIC HYDROLYSIS OF NON-NATURAL SUBSTRATES. SYNTHESIS OF OPTICALLY ACTIVE CARBONYL COMPOUNDS.

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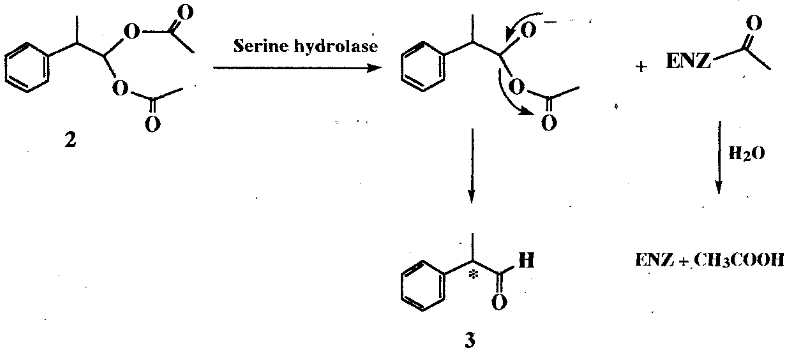
ABSTRACT

A new synthetic method for the preparation of optically active carbonyl compounds has been investigated. The enzymatic hydrolysis of the acylal **2** produced the desirable optically active 2-phenyl-propanal **3** with different values of enantiomeric excess, depending on the enzyme used. The best results came from lipase CCL.



Chimika Chronika, New Series, 26, 107 (1997)

THE ASSOCIATION OF PHOSPHORYLASE KINASE WITH SMOOTH ENDOPLASMIC RETICULUM MEMBRANES IN RAT LIVER

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ABSTRACT

A high percentage of rat liver phosphorylase kinase is directly bound to the membranes of smooth endoplasmic reticulum and it is easily extractable by washing procedures in absence of detergent. This binding is likely to involve both ionic and hydrophobic interactions. Moreover a small but significant amount of phosphorylase kinase is strongly associated with the microsomal fraction and can be partly extracted only by treatments with detergents. This second form of the enzyme could result from the population of reversibly associated kinase molecules through mechanisms involving alterations in the membrane or modification of phosphorylase kinase.

Chimika Chronika, New Series, 26, 108 (1997)

METAL IONS IN LIFE

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ABSTRACT

The metals of life are important and necessary elements of living processes. The quality of life depends to a great extent on the presence and physiological quantities of these metal ions in the body. The essential metal ions of life are: Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+} and Cu^{2+}. There may be other metal ions essential for some forms of life that have not yet been discovered. In this report the role of Mg^{2+} ions is discussed briefly together with its imlication in molecular recognitions and self-assembling systems through the formation of metal complexes in the double-stranded helices. Such systems may perform selective operations of recognition and structure generation at the molecular level.

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DNA INTERACTION WITH METAL IONS

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A study of interaction of various metal ions with calf thymus DNA has been carried out by ultraviolet, circular dichroism spectroscopies, polarography and thermal denaturation techniques. All studies were performed at different metal to DNA ratios, r, and various incubation times.

The results show that $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_6]Cl_3$, $[Rh(en)_2Cl_2]Cl$, $[Rh(NH_3)_5Cl]Cl_2$, $MgNO_3$, $CaCl_2$, $BaCl_2$, Mg(ATP), Ca(ATP) bind to the phosphate groups of DNA. The interaction of $Rh(acetate)_4$ with DNA takes place at high metal concentration and after long time of incubation; when the above conditions are not fulfilled the interaction is either negligible or can not be detected by the methods used. $RuCl_3$ is found to bind both to the phosphates and the bases forming cross-links between complementary bases. BaATP seems also to interact with both bases and the phosphate moieties. When r=0.5, Tl(I) interacts mainly with the phosphate groups of DNA, while at higher ratio values it binds also to the bases.

$RhCl_3$ and Sn(IV) induce appreciable alterations on the double-helix conformation. Rh(III) at low binding ratio causes a stabilization of the DNA B conformation, while at higher ratio structural changes are interpreted in terms of a B to C transition. Tin(IV) produces a C form geometry, while Tl(I) causes stabilization of the DNA double helical structure. The alkaline earth metal ions induce a stabilization of the B conformation, while their ATP complexes cause transitions which mainly belong to the B family. A contribution of the A form is observed in the case of CaATP-DNA system at the input ratio r = 0.6 and at the beginning of the reaction as well as in the Ba-DNA system at 22°C, for r = 5.

Chimika Chronika, New Series, 26, 110 (1997)

INTERACTIONS OF SMALL PEPTIDES WHICH CONTAIN CYSTEINE (CYS) OR HISTIDINE (HIS) WITH SALTS OF PLATINUM(II) AND PALLADIUM(II)

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ABSTRACT

NMR, 1D- and 2D- (^1H-, ^{13}C- and ^{195}Pt-) techiques were used to study the reactions of the peptides Cys-Ser-Ala-Cys (CSAC) containing two cysteine molecules and His-Ala (HA), His-Gly-Ala (HGA) containing histidine as the first aminoacid of the sequence, with the salts K_2MX_4, cis-, trans-DDP, cis-M(en)Cl_2,[M(dien)X]X, (M=Pd(II), Pt(II),X=Cl^-,Br^-,I^-).The results show the formation of complexes of 1:1 and 1:2 ligand to metal stoichiometry with these various salts, involving in bonding the two sulfur atoms of CSAC and the two nitrogen atoms of the histidine peptides.

Chimika Chronika, New Series, 26, 111 (1997)

SYN AND ANTI ISOMERISM IN MIXED LIGAND OXORHENIUM COMPLEX.

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ABSTRACT

As part of our work on mixed ligand complexes (SNS/S donor set) with rhenium or technetium, we report here the synthesis and the structural identification of the isomers of [4-(methoxy)thiophenolato][N,N-bis(2-mercaptoethyl)-N′,N′-diethylethylenediamine]-oxorhenium(V), $ReOL^1L^2$. The formation of two stereoisomers, syn and anti, upon complexation with the oxorhenium core, is expected. The N-substitution of the tridentate ligand, L^1H_2, can take either syn or anti conformations with respect to the ReO core.

The mixture of the isomeric complexes was prepared by a ligand exchange reaction using as precursor: a) $ReOCl_3(PPh_3)_2$, b) the intermediate Re(V)-citrate or c) via $[ReO(eg)_2]$ (eg=ethyleneglycole), in a ratio of tridentate to monodentate ligand, $[L_1H_2=(C_2H_5)_2NCH_2CH_2\text{-}\ N(CH_2CH_2SH)_2]$: $[L^2H=p\text{-}CH_3OC_6H_4SH]$, 1:1. The reaction produced a mixture of isomers which were separated by fractional recrystallization from $EtOH/C_5H_{12}$ as green (syn isomer) and orange crystals (anti isomer) in a 20:1 ratio respectively. Both complexes were characterized by elemental analysis and spectroscopic methods. The x-ray crystallographic analysis confirmed the syn and anti conformation (in relationship to the ReO core) for the two isomers of $ReOL^1L^2$. The geometry around Re(V) is trigonal bipyramidal for the syn isomer. The basal plane of the trigonal bipyramid is formed by the S1, S2 atoms of the tridentate ligand, L^1H_2, and the oxo group, while the N1 atom of L^1H_2 and the S3 atom of the monodentate thiol, L^2H, occupy the two apical positions. For the anti isomer, crystallographic analysis demonstrated that the coordination geometry is distorted square pyramidal. The S1, S2, N1 donor atoms of the L_1H_2 and the S3 atom of the L^2H form the basal plane, while the oxo group occupies the apex of the pyramid.

All sulfur atoms undergo ionization during complexation so that the complexes (syn and anti) are neutral.

Chimika Chronika, New Series, 26, 112 (1997)

METAL IONS ANTIINFLAMMATORY DRUGS INTERACTIONS. PREPARATION AND PROPERTIES OF QUADRUPLY DINUCLEAR COPPER(II) COMPLEXES OF DICLOFENAC.

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Abstract

Copper an essential element has received considerable attention with regard to its presence in normal blood plasma and serum components. Larger than usual mean serum copper concentration may be the result of an acute as well as chronic inflammation state. It is well known that copper complexes of inactive ligands and active anti-inflammatory drugs are more active than the ligands themselves. Because inactive compounds become active when administered as their copper complexes, and copper complexes of nonsteroidal anti-inflammatory drugs (NSAIDs) are more active than their parent ligands, the metal-ligand association seems to play a specific role, which sustains the hypothesis advanced by Sorenson that copper complexes are the active forms of these drugs. As part of our research on understanding drug-metal interactions in the present paper , we describe the reaction of diclofenac with copper and the x-ray structure of a symmetric dicopper(II) complex. The complexes $[CuL_2(H_2O)]_2 2H_2O$ and $[CuL_2(DMF)]_2$ were prepared by the reaction of a potent antiinflammatory drug, diclofenac sodium, and $CuCl_2$. The new symmetric dinuclear copper(II) complex $[CuL_2(DMF)]_2$ crystallizes in the monoclinic space group $P2_1/n$ with cell constants a=10.807(1), b=15.429(2), c=19.360(2), β=92.508(3), V=3225(1) Å^3, and Z=2. The crystal structure consists of a dinuclear quadruply-bridged neutral molecule. The four carboxylato groups from four ligands are in the familiar bidentate *syn,syn* $\eta^1 : \eta^1 : \mu_2$ bridging mode. The metal coordination geometry is described as perfect square pyramidal with the dimethyloformamide oxygen occupying the apical positions of both molecules. The optical, infrared, electron paramagnetic resonance and magnetic properties of these complexes are also reported.

Chimika Chronika, New Series, 26, 113 (1997)

EFFORTS FOR THE DEVELOPMENT OF SYNTHETIC METHODOLOGY IN THE CHEMISTRY OF POLYNUCLEAR METAL COMPLEXES: ARE THERE HOPES TO PASS FROM THE "SPONTANEOUS SELF-ASSEMBLY" TO THE "UNDER OPERATOR CONTROL" ERA?

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The synthesis and characterization of polynuclear metal complexes is an important current objective in transition-metal chemistry, magnetochemistry and bioinorganic chemistry. One of the goals in the area of polynuclear coordination chemistry is to control the nature of the final product and to escape from reliance on "spontaneous self-assembly". The elegant work of few groups coupling smaller metal fragments to make larger assemblies are rare examples of where such designed syntheses have been possible. In many cases the complex reaction products are unexpected.

Initial results are described in a new program designed to develop various synthetic procedures for the rational preparation of higher nuclearity species. One attractive approach is to simultaneously use anionic $n^1{:}n^1{:}n^1{:}\mu_3$ (e.g. deprotonated benzotriazoles) and bidentate chelating (e.g. β-diketonates) ligands, see for example eq. (1):

$$\underline{5}[\mathrm{Ni(acac)_2(H_2O)_2}] + \underline{5}\mathrm{btaH} \xrightarrow{\mathrm{Me_2CO}} [\mathrm{Ni_5(acac)_4(bta)_5(OH)(H_2O)_4}] + \underline{6}\mathrm{acacH} + \underline{5}\mathrm{H_2O} \qquad (1)$$

A second approach is to employ carboxylates (bases) and ligands possessing one or two acidic hydrogens that after overall or partial deprotonation can simultaneously chelate and bridge; an ideal such ligand is the *gem*-diol form ($dpk{\cdot}H_2O$) of di-2-pyridyl ketone, see for example eq. (2):

$$\underline{6}[\mathrm{Cu_2(O_2CMe)_4(H_2O)_2}] + \underline{6}\mathrm{dpk{\cdot}H_2O} \xrightarrow{\mathrm{MeCN}} [\mathrm{Cu_{12}(O_2CMe)_{12}(dpk{\cdot}O)_6}] + \underline{12}\mathrm{MeCO_2H} + \underline{12}\mathrm{H_2O} \qquad (2)$$

Our third strategy is *partial* carboxylate abstraction [eq. (3)] with Me_3SiCl from lower nuclearity M_x carboxylato species. The partial carboxylate removal can yield coordinatively unsaturated "fragments" which may aggregate either with deliberately added bridging ligands or with bound RCO_2^- groups themselves, converting from μ_2 to μ_3 or μ_4 modes for interfragment linking.

$$\mathrm{M{-}O_2CR} + \mathrm{Me_3SiCl} \longrightarrow \mathrm{M{-}Cl} + \mathrm{Me_3SiO_2CR} \qquad (3)$$

Chimika Chronika, New Series, 26, 114 (1997)

$[\{(P(OPh)_3)_2)Rh\}_2(\mu\text{-}MoS_4)]$: SYNTHESIS, CRYSTAL STRUCTURE, SPECTROSCOPY AND CATALYTIC ACTIVITY IN THE HYDROFORMYLATION OF ALKENES

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ABSTRACT

The synthesis and the X-ray crystal structure of $[\{(P(OPh)_3)_2Rh\}_2(\mu\text{-}MoS_4)]$ are reported. This compound shows an intense absorption in the Vis region (603 nm, ε_{max}=7.4 10^3 dm^3 mol^{-1} cm^{-1}), unsual for Rh(I) complexes. The ^{31}P and ^{95}Mo nmr spectra show low-frequency coordination chemical shifts, $\Delta\delta$, relative to the free $P(OPh)_3$ and $[MoS_4]^{2-}$, respectively. These are discussed with respect to the σ- and π-bonding ability of the phosphorus ligand, and, the influence of the "spectrochemical" factor on the dominant paramagnetic term for molybdenum. The reaction with CO (1 atm) leads to the formation of monocarbonylo species as found by using IR and ^{31}P nmr spectroscopy. Preliminary catalytic experiments proved that $[\{(P(OPh)_3)_2Rh\}_2(\mu\text{-}MoS_4)]$ is a catalyst precursor for the hydroformylation of terminal-alkenes, with high regioselectivity.

Chimika Chronika, New Series, 26, 115 (1997)

A MECHANISM OF THE REDUCTION OF CARBON-CARBON DOUBLE AND TRIPLE BONDS BY CHROMIUM (II).

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The kinetics and mechanism of the reactions between chromium (II) and some unsaturated ligands i.e. pyridine-3-acrylic acid, **paa,** 1,2-bis(2-pyridyl)ethylene, **bpe** and phenylpropiolic acid, **ppa**, have been studied at various conditions (large excess of chromium(II), large excess of ligand, excess of chromium (II) or ligand). The kinetic results (rate laws and activation parameters) suggest that binuclear species with chromium-carbon σ-bonds and carbon-carbon bridges (with single or double bonds) are discrete intermediates during these reactions. A first non-symmetric attack of a Cr^{2+} ion on the substrate leads to the formation of a 1: 1 Cr(II): substrate adduct which on a rate-limiting step reacts further after an attack on the far carbon[1] by a second Cr(II) ion to form a 2 :1 adduct. The 2:1 adduct by two electron transfer from both Cr(II) becomes a discrete binuclear σ-bonded organochromium complex with carbon-carbon single or double bond bridge [2]. The above mechanism is valid at various conditions irrespectively of the form of the rate-law. In the case of large excess of ligand the reaction is limited to the formation of the 1:1 adduct which upon electron transfer becomes an ion-radical [3].

Our experimental results are confirmed by semi-empirical calculations : the first attack of Cr(II) on unsaturated ligands is supported by ligand HOMO-LUMO calculations.

1. O. Eisenstein , R. Hoffmann, *J. Am. Chem. Soc.*, 102, 6148, (1980).
2. A.L.Petrou, *Chimika Chronika, New Series,* 24, 69-76 (1995)
3. D. Katakis, E.Vrachnou-Astra and J.Konstantatos, *J.Chem. Soc., Dalton Trans.,* 1986, 1491.

Chimika Chronika, New Series, 26, 116 (1997)

SYNTHESIS AND NEAR INFRARED PROPERTIES OF RARE EARTH IONOMERS

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Fully exchanged, anhydrous ionomers of ethylene-co-acrylic acid (EAA) and ethylene-co-methacrylic acid (EMAA) copolymers containing Dy^{3+}. Er^{3+}, Sm^{3+} and Yb^{3+}, and mixtures of them, were synthesized and studied in the near infrared region by reflection and Fourier Transform Raman spectroscopies. The EAA copolymers ranged from 1.4 to 8.7 mole percent acid and the EMAA copolymers were 7.3 and 16.2 mole percent acid. The ionomers were shown to be essentially free of carboxylic acid groups, water or other forms containing O-H groups and were characterized by infrared and other methods. They are light and heat stable, became thermoplastic and moldable at *ca.* 220°C under pressure. When excited at 1064nm with a Nd:YAG laser, these ionomers exibit novel, lanthanide-dependent near infrared luminescence and strong Raman scattering in the near infrared region. The strongest luminescence is observed with Sm^{3+} ionomers. The Dy^{3+} ionomer Raman-shifts this source to emit light most strongly in the 1.53 - 1.55μ range where the ionomer also transmits light well.

Chimika Chronika, New Series, 26, 117 (1997)

A POLYMERIC Cu^{II} CHAIN HAVING A TETRANUCLEAR REPEAT UNIT WITH S=2 GROUND STATE

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ABSTRACT

The synthesis, crystal structure and properties of compound $[Cu_4(dpk.CH_3O)_2Cl_6]_n$ [dpk.CH_3OH=unimethylated diol of di-2-pyridyl ketone] **(1)** the first example of a copper(II) polymer having a tetrameric repeat unit with S=2 ground state is reported. The synthesis of compound (1) has been achieved via the reaction of $CuCl_2$ with dpk in methanol. The base-catalyzed addition results in the formation of a unimethylated diol which may deprotonated. Crystal Structure data: $[C_{12}H_{11}N_2O_2Cl_3Cu_2]$, M_r=448.68; triclinic; space group $P_{\bar{1}}$; a=7.800(1) (Å); b=8.946(1) (Å); c=13.383(1) (Å); α=118.964(3)° ;β=92.693(3)°; γ=66.824(3)°; Z=2. Variable temperature magnetic susceptibility measurements indicate the presence of a ferromagnetic behavior with antiferromagnetic coupling below 15 K. The best fit parameters obtained are $J_1 = 71.32$ cm^{-1}; $J_2 = 1.43$ cm^{-1}; $J_3 = 0.07$ cm^{-1}; $J_4 = 0$(fixed); $J = -0.553$ cm^{-1}; g = 2.1(fixed). The energy levels obtained from the fitting procedure show a S=2 ground state. The polycrystalline powder EPR spectra at 4.1 K, show an intense broad signal spread over 3900 Gauss with g = 2.34, indicative of a bulk concentration of copper ions having strong ferromagnetic interaction.

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF DI-AMINOPYRIMIDINIUM TETRAPHENYLDICHLORO(μ-OXO) DISTANNATO

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Abstract.

Organotin complexes may interact with biological systems in many different ways as for instance bactericides, fungicides, acaricides and industrial biocides. In recent years, several investigations to test their antitumour activity has been carried out and has been observed that several organotin complexes are effective antineoplastic (mainly antileukaemic). The mechanism of their activity may involve the transportation of the complexed organotin compound into the tumor cells, followed by reaction of uncomplexed organotin and its hydrolysis product at the active sites. This suggestion is supported by the fact that the hydrolysis product is active. As an extension of our research on tin compounds with heterocyclic derivatives of biological and pharmaceutical importance, we report here the synthesis and solid state X-ray characterization of $(C_4H_6N_3)_2[SnPh_2OCl]_2$. To our knowledge this derivative provides the first example for five-coordinated anionic distannoxane.

The base-catalyzed hydrolysis of diphenyldicloride in the presence of diethylether proceeds *via* formation of an ionic monomeric diorganodistannoxane compound.

$SnPh_2Cl_2 + yC_4N_3H_5 + H_2O \rightarrow (SnPh_2Cl_2)_2(C_4N_3H_5)_3(H_2O)_2$ (1)

$(SnPh_2Cl_2)_2(C_4N_3H_5)_3(H_2O)_2 \rightarrow (C_4H_6N_3)_2[SnPh_2OCl]_2 + C_4N_3H_5 \cdot 2HCl$ (2)

The single-crystal X-ray diffraction study of $(C_4H_6N_3)_2[SnPh_2OCl]_2$ is reported, together with IR data. The dimmer consists of five coordinate tin(iv) units with di-μ-oxo bridging. The coordination geometry of the tin unit is a distorted trigonal bipyramid with two phenyl groups and one μ-oxo in equatorial positions and the other two μ-oxo and cloro atoms in axial position.

Chimika Chronika, New Series, 26, 119 (1997)

MIXED COMPLEXES OF OXORHENIUM(V) WITH CYCLIC AMINODITHIOLS AND p-THIOCRESOL

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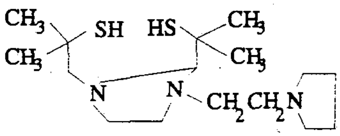
ABSTRACT

The aminodithiol derivatives I and II were designed, synthesized and used as ligands for the preparation of novel oxorhenium (V) complexes in the presence of p-thiocresol as co-ligand. The structure of these complexes is under investigation.



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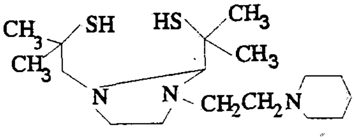

II

Chimika Chronika, New Series, 26, 120 (1997)

STUDY OF COMPLEXES Cu(II)-CYSTEINE CONTAINING OLIGOPEPTIDES WITH SPECTROSCOPIC METHODS

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ABSTRACT

The synthesis of the tetrapeptides Boc-Cys-Ser-Ala-Cys-$CONH_2$ (*I*), Boc-Cys-Gly-Ala-Cys-$CONH_2$ (*II*), Boc-His-Ser-Ala-Cys-$CONH_2$ (*III*) and Boc-Cys(Acm)-Gly-Ala-Cys(Acm)-OMe (*IV*) has been accomplished in liquid phase by applying the methods of DCC/HOBt, active esters and BOP. These peptides contain the sequence Cys-X-Y-Cys (X,Y amino acids) which has been found in the metal binding sites of many metalloproteins. The syntheses of complexes were depended upon the side chain protective group of Cys. Thus, when Bzl-group was used as SH protection, treatment of the peptide with Na/liq.NH_3 was preceded the complexation, while when Acm-group was used, the complexation was effected by direct interaction between peptide and metal ion. All complexes have been investigated by using IR, Far-IR, UV-Vis, CD, ESR and ^1H NMR techniques.Thus, the disappearance of the ν(S-H) vibration in the IR spectra of Cu(II)-peptides *I,II* and *III* complexes indicates the replacement of the corresponding bond by the Cu-S bond. Furthermore the Far-IR spectra of the complexes showed absorptions in the range 334-310 cm^{-1} which are assigned to ν(Cu-S) vibration. In the case of Cu(II)-peptide *III* the 445 cm^{-1} band is assigned to $\nu(Cu\text{-}N^{im})$ vibration. In the UV-Vis spectra the band around 314-325 nm is assigned to $S \rightarrow Cu(II)$ charge-transfer and in the case of Cu(II)-peptide *III* the same band must include and the $N^{im} \rightarrow Cu(II)$ charge transfer. The CD spectra of the complexes showed the corresponding $S \rightarrow Cu(II)$ and $N^{im} \rightarrow Cu(II)$ charge-transfer bands in the range of 330-400 nm. All the complexes gave isotropic ESR spectra with g values 2.25, 2.27, 2.29 and 2.34 respectively. Analoque values of g have also observed in other complexes Cu(II)-Sulfur compounds. Complexation of peptides with Cu(II) causes remarkamble chemical shifts in the ^1H NMR spectra. Most notably, resonances corresponding to the $C_\beta H_2$ of Cys^1 and Cys^4 residues and to the $C_\beta H_2$, C_2H and C_4H of His are influenced.Chemical shifts corresponding to the Acm group have not been found in the ^1H NMR spectrum of Cu(II)-peptide *IV*. Based on these results we conclude that interaction of Cu(II)-peptides *I,II* and *IV* takes place between S atoms of Cys^1 and Cys^4. In the case of Cu(II)-peptide *III* interaction occurs between S and N^{im} atom of Cys^4 and His^1 respectively.

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SYNTHESIS AND CHARACTERIZATION OF OXORHENIUM(V) COMPLEXES WITH N-(2-MERCAPTOETHYL)(2-PYRROLIDIN-1-YLETHYL)-AMINE AND A THIOPHENOL AS COLIGAND.

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ABSTRACT

Our efforts to synthesize new chelate systems for technetium(V) and rhenium(V) for subsequent use in in vivo diagnostic imaging and therapy led us to the development of a novel class of mixed ligand complexes with the general formula MO(NNS)(S).

In the present study, we describe the preparation and characterization of two novel oxorhenium(V) complexes with the general formula $ReOL^1L^2$ where L^1H_2 is the tridentate ligand N-(2-mercaptoethyl)(2-pyrrolidin-1-ylethyl)-amine and L^1H is thiocresol **1** or 4-mercapto-benzyl-ethyl-ester **2**. The complexes were prepared by a ligand exchange reaction using $ReOCl_3(PPh_3)_2$ as precursor and equimolar quantities of tridentate and monodentate ligands. The new complexes were isolated as red brown crystals and characterized by elemental analysis and spectroscopic studies. Infared spectra of each of the complexes **1, 2** showed a distinct absorption peak at 952 cm^{-1} corresponding to the Re=O stretching vibration.

The crystal structure of complex **1** was determined by x-ray crystallography. The crystallographic data demonstrated that the coordination geometry is square pyramidal with Re being 0.67 above the basal plane of the pyramid defined by the NNSS atoms.

Both sulfur atoms and the nitrogen atom undergo ionization during complexation so that the total net charge of the ReO(NNS)(S) core is zero.

Chimika Chronika, New Series, 26, 122 (1997)

SYNTHESIS AND CHARACTERIZATION OF MIXED COMPLEXES OF TECHNETIUM [TcO(SNS)(S)] WITH N-SUBSTITUTED AMINODITHIOLS FOR THE DEVELOPMENT OF POSSIBLE BRAIN IMAGING AGENTS

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ABSTRACT

The design and synthesis of mixed oxotechnetium(V)-99 complexes with N,N-bis(2-mercaptoethyl)(2-piperidin-1-yl)amine, and benzyl mercaptan (complex 1) or methoxybenzyl mercaptan (complex 2) as coligand are reported.

A general synthetic scheme developed for the synthesis of SNS ligands was used. The tridendate ligand was synthesized through the reduction of the benzyl protected thiol, which results from the alkylation of N,N-bis(2-benzylthioethyl)amine by 1-(2-chloroethyl)amine, in the presence of sodium iodide.

The ^{99}Tc complexes were prepared in high yield (85 %) by the reaction of ^{99}Tc(V)-gluconate with equimolar quantities of the tridentate ligand and the monodentate thiol. The novel complexes were isolated as red-brown crystals by crystallization from MeOH/H_2O 85:15. The complexes were characterized by elemental analysis and spectroscopic methods.

Chimika Chronika, New Series, 26, 123 (1997)

PREPARATION, PROPERTIES AND STUDY OF Cu(II) COMPLEXES WITH THE DIAMIDIC LIGAND N,N'-2,6-PYRIDINEDICARBOXAMIDE-BIS(2'-PYRIDINE)

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Spyros P. Perlepes[1] **and John M. Tsangaris**[2]

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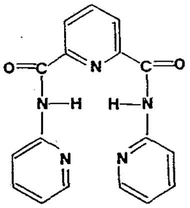
Over the last several years, we have expended a lot of time and energy in developing the coordination chemistry of ligands containing amide groups. These studies have been stimulated by the growing recognition that the inorganic chemistry of organic amides is a central theme in transition-metal chemistry; research in this area ranges from solution of pure chemical problems to biological modeling applications and advanced materials chemistry.

The synthesis of the new polydentate ligand N,N'-2,6-pyridinecarboxamide-bis(2'-pyridine) (LH_2) is reported in this work together with its employment as a ligand. The copper(II) complexes $[Cu(LH_2)X_2]\cdot H_2O$ (X=Cl, Br), $[Cu(LH_2)(NO_3)_2]$ and $[CuL(H_2O)_2]$ have been isolated. The complexes were characterized by a variety of physical and spectroscopic methods.



LH_2

The complexes of the neutral ligand acquire distorted octahedral polymeric structures with axial chloro, bromo or monodentate nitrato coordination. The LH_2 molecule behaves as a bis-bidentate ligand coordinating through both mono-substituted pyridine ring N-atoms and secondary amide O-atoms and bridging two Cu^{II} atoms. A mononeric structure with a trigonal bipyramidal geometry about the metal is proposed for $[CuL(H_2O)_2]$. The doubly deprotonated ligand acts as a tridentate chelating agent with the deprotonated amide nitrogens and the nitrogen of the di-substituted pyridine ring as ligating atoms.

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PREPARATION, PHYSICOCHEMICAL CHARACTERIZATION AND STRUCTURAL STUDY OF DIVALENT TRANSITION METAL COMPLEXES OF SINGLY AND DOUBLY DEPROTONATED N-METHYL-2-THIOOXAMIC ACID

Evy Manessi-Zoupa[a], Dimitris Xenidis[a], Marleen L. B. F. Hereygers[b], Herman O. Desseyn[b], Albert T. H. Lenstra[c] and Spyros P. Perlepes[a]

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In contrast to the great number of studies concerning complexes of oxamic acid ($H_2NCOCOOH$), very little is known about the corresponding 2-thiooxamato complexes, although this class of compounds could offer unique features in terms of structural, magnetic and spectroscopic properties.

Preparative procedures are described in this work that allow access to the new monomeric complexes *cis*-$[M(HA)_2(H_2O)_2]\cdot 2H_2O$ (M=Mn, Co), *cis*-$[M(HA)_2(H_2O)_2]$ (M=Fe, Ni, Zn) and *cis*-$[Cu(HA)_2]$, and to the polymeric compounds *trans*-$[MA(H_2O)]_n$ (M=Mn, Co, Ni, Zn) and *trans*-$[CuA]_n$, where $HA^-=(CH_3)HNCSCOO^-$ and $A^{2-}=(CH_3)\overset{-}{N}CSCOO^-$.

The X-ray crystal structure of *cis*-$[Mn(HA)_2(H_2O)_2]\cdot 2H_2O$ reveals a *cis* octahedral geometry around the metal ion; the ligand HA^- behaves as a bidentate chelate with ligated atoms being the thioamide sulfur and one of the carboxylate oxygens. The complexes were characterized by elemental analyses, conductivity measurements, X-ray patterns, magnetic susceptibilities and spectroscopic (FT-IR, FT far-IR, FT-Raman, UV/VIS, EPR) studies. The vibration analysis of the complexes is given using OH/OD, NH/ND. CH_3/CD_3 and metal ($^{58}Ni/^{62}Ni$, $^{63}Cu/^{65}Cu$) isotopic substitutions. All data are discussed in terms of the known structure of the manganese(II) complex, the nature of bonding and assigned structural types. The dianion A^{2-} behaves as a bridging O,N/O,S bis-bidentate ligand yielding square planar (Cu^{II}) and octahedral (Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}) polymeric compounds.

Chimika Chronika, New Series, 26, 125 (1997)

A DISTINCTION BETWEEN THE S-cis AND S-trans CONFORMATION OF FREE AND COORDINATED DITHIOOXAMIDES BY INFRARED (IR) SPECTROSCOPY

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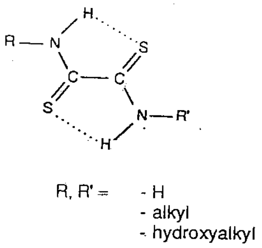
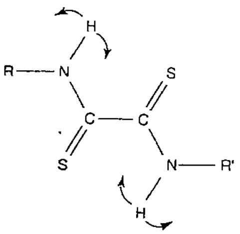
The general structure of planar dithiooxamides is shown in I. As long as one hydrogen atom remains on each nitrogen these molecules have a planar structure with the sulfur atoms positioned *trans* to each other, *i. e.*, they adopt a S-*trans* conformation. When dithiooxamides are used as ligands in metal complexes, they frequently act as bidentate chelates coordinating through both sulfur atoms, thus adopting a S-*cis* conformation. However, no spectroscopic evidence for the S-*cis* conformation of the ligands has been found.



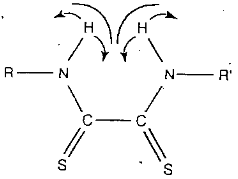
I

Careful re-analysis of our previous studies, in combination with new results, show that the shift of the i.r. in-plane δ(NH_2) (when R or/and R'=H) and δ(NH) deformations to higher frequencies in the spectra of the complexes, which remained unexplained in the past, can be correlated with the change from the S-*trans* to the S-*cis* conformation upon coordination. The reason why this transformation has such a remarkable effect on the frequencies of δ(NH_2) or/and δ(NH) in dithiooxamides, becomes clear when these vibrations are depicted as below. Due to the increased sterical hindrance in the S-*cis* conformation the δ(NH_2) or/and δ(NH) vibrations require more energy, resulting in a frequency increase of these modes.

S-trans



S-cis



Chimika Chronika, New Series, 26, 126 (1997)

REACTIONS OF TRANSITION METAL NITRATES WITH N,N'-BIS(2-PYRIDYL)UREA (LH_2)

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[1]*Laboratory of Pharmacognosy and Chemistry of Natural Products, Department of Pharmacy, University of Patras, 265 00 Patra;* [2]*Institute of Materials Science, NRCPS "Demokritos", 153 10 Aghia Paraskevi Attikis;* [3]*Laboratory of Inorganic Chemistry, Department of Chemistry, University of Patras, 265 00 Patra*

The development of the coordination chemistry of urea (H_2NCONH_2) and substituted ureas is an important theme in transition-metal chemistry. Research in this area ranges from solution of pure chemical and spectroscopic problems, to biological modeling applications, pharmaceutical and advanced materials chemistry. In contrast to the great number of studies concerning complexes of simple ureas, little is known about the complexes of pyridylureas. In pursuit of the latter subject, we have isolated the new complexes *trans*-$[M(ONO_2)_2(LH_2)_2]$ (M=Mn, Fe, Co, Ni, Cu, Zn), where LH_2=N,N'-bis-(2-pyridyl)urea.

The complexes were characterized by microanalyses, IR spectroscopy and single-crystal X-ray crystallography (see, for example, Fig. 1). The six mononuclear complexes are isostructural. LH_2 behaves as a bidentate chelate with ligated atoms being the amide oxygen and one of the pyridyl nitrogens. The six-coordinate metal ion sits upon a crystallographic centre of symmetry, with the axial positions being occupied by two oxygen atoms from two monodentate nitrato groups. It is worth noted that the pale green Fe(II) complex was obtained by the reaction of $Fe^{III}(NO_3)_3 \cdot 9H_2O$ with LH_2 in MeOH/TEOF/Et_2O. This redox reaction is under investigation.

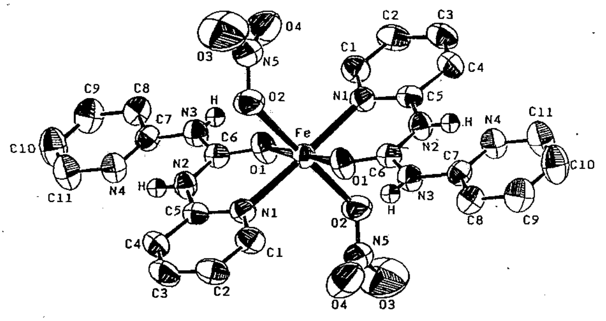

Figure 1. The molecular structure of *trans*-$[Fe(ONO_2)_2(LH_2)_2]$.

Chimika Chronika, New Series, 26, 127 (1997)

COMPLEXES OF L-PIPECOLIC AND N-METHYL-PIPECOLIC ACIDS WITH PALLADIUM(II) AND PLATINUM(II)

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ABSTRACT

L-pipecolic acid is related to several not common inherited metabolic diseases(1). The complexes of L-pipecolic acid with transition metal cations and especially with Pd(II) and Pt(II) are relatively not enough explored. In the present paper the following complexes: [1] K[Pd(L-pipe)Cl_2], [2] Pd(L-pipe)$_2$, [3] K[Pt(L-pipe)Cl_2, [4] Pt(L-pipe)$_2$, [5] Pd(N-Me-L-pipe)$_2$, [6] Pt(N-Me-L-pipe)$_2$ were prepared (where L-pipe=L-pipecolic acid and N-Me-L-pipe=N-methyl-L-pipecolic acid). The signs of the circular dichroism (CD) d-d bands of these complexes can be explained by the hexadecant rule(2). CD measurements reveal trans configuration for the [2],[4],[5],[6] complexes in water solution. ^{1}H-NMR measurements of the prepared complexes provide useful informations about the positions of the protons of the piperidine ring in the conformers of the complexes, by application of Karplus equation(3).

(1) J.M.F. Trijbels et al, *J.Inher.Met.Dis.* 10(2), 182 (1987).
(2) J.M.Tsangaris and R.B.Martin, *J.Am.Chem.Soc.* 92, 4255 (1970).
(3) M.Karplus, *J.Am.Chem.Soc.* 85, 2870 (1963).

Chimika Chronika, New Series, 26, 128 (1997)

REACTIONS OF THE GROUP IIB METAL HALIDES ($ZnCl_2$, $CdCl_2$, $HgCl_2$) WITH DIHYDROTHIAMINE AND TETRAHYDROTHIAMINE

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ATHANASSIOS GIANNOPOULOS[2]

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ABSTRACT

The reactions of the group II_B metal halides ($ZnCl_2$, $CdCl_2$, $HgCl_2$) with dihydrothiamine (DHTH) and tetrahydrothiamine (THTH) produce the complexes of formulae ML_2Cl_2 and M_2Cl_4L (M = Zn(II), Cd(II), L=DHTH, THTH) and $[HgCl(L'H)]_2^{+}[HgCl_4]^{2-}$ and $HgL'Cl.HCl$ (L′=a rearrangement product of DHTH). As the IR and ^1H NMR spectra show, Zn(II) and Cd(II) bind DHTH through the N_1 site of pyrimidine and THTH through thw S atom of thiazolidine. Hg(II) is bound through S in its complexes while the N_1, is protonated in both complexes with this metal.

Chimika Chronika, New Series, 26, 129 (1997)

STUDY OF THE COMPLEX $[Hg_2I_4L_2]$ WHICH WAS SYNTHESIZED BY THE REACTION OF CH_3HgI WITH 2-(2'-PYRIDYL)QUINOXALINE (L): CLEAVAGE OF THE Hg(II)-C BOND DUE TO THE COMPLEXATION OF THE METAL WITH A CHELATING LIGAND

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ABSTRACT

The 2:1 and 1:1 reactions of CH_3HgI with 2-(2'-pyridyl)quinoxaline (L) leads to Hg-C bond cleavage and yields the dinuclear complex $[Hg_2I_4L_2]$ as one of the products. The X-ray crystal structure and some spectroscopic characteristics of the dimer as well as the biological relevance of this reaction are also reported.

Chimika Chronika, New Series, 26, 130 (1997)

SYNTHESIS, STRUCTURAL STUDY AND PHYSICOCHEMICAL CHARACTERIZATION OF Pd(II) AND Pt(II) COMPLEXES WITH THE HETEROAROMATIC LIGAND 2-(2'-PYRIDYL)QUINOXALINE (L)

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ABSTRACT

The new complexes [$PdCl_2L$], [$PdBr_2L$], [$PtCl_2L$], [$PtBr_2L$] and [PdL_2]Cl_2 have been isolated and characterized by a variety of physical and spectroscopic techniques. L behaves as a N(pyridyl), N(quinoxaline) bidentate chelating ligand.

Chimika Chronika, New Series, 26, 131 (1997)

PREPARATION, MOLECULAR AND CRYSTAL STRUCTURE, MAGNETIC STUDY AND REACTIVITY OF A NOVEL OCTANUCLEAR COPPER(II) CLUSTER

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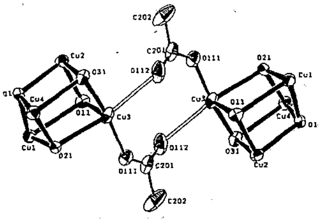
The synthesis and characterization of di- and poly-nuclear complexes in which the ligands maintain the metal centers in close proximity is an important current objective in transition-metal, magnetochemistry and bioinorganic chemistry.

In the present work we report a particularly straightforward preparation of the remarkable octanuclear Cu^{II} cluster $[Cu_8(dpk{\cdot}OH)_8(O_2CMe)_4]\ (ClO_4)_4{\cdot}9H_2O$ ($dpk{\cdot}OH^-$ =the monoanion of the hydrated, *gem*-diol form of di-2-pyridyl ketone, dpk), and describe its structure, magnetic properties and chemical reactivity. The doubly-bridged double cubane cation (the core structure is shown in the picture) has a novel structure in the solid state and it is one of the rare examples of a magnetically-characterized Cu_8^{II} cluster.



The anion $dpk{\cdot}OH^-$ functions as a $\mu_3{:}n^1{:}n^3{:}n^1$ ligand. The ground state of the complex-based upon the order of its energy levels obtained from the analysis of the temperature dependence of the magnetic susceptibility-is a triplet. However, an overall antiferromagnetic interaction results, depending on the relative magnitudes of the antiferromagnetic and ferromagnetic interactions, related to structural features. The reaction of $[Cu_8(dpk{\cdot}OH)_8(O_2CMe)_4](ClO_4)_4{\cdot}9H_2O$ with an excess of Me_3SiCl in MeCN yields the interesting chain polymer $[CuCl_2(dpk)]_n$.

Chimika Chronika, New Series, 26, 132 (1997)

THE REACTION OF $Hg(ClO_4)_2$ AND 2-(2'-PYRIDYL)QUINOXALINE (L) IN ACETONE: ISOLATION AND CHARACTERIZATION OF A REMARKABLE COMPLEX OF Hg(II) WHICH CONTAINS THE 2-OXOPROPYL ANION AS A LIGAND

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ABSTRACT

The 1:1 reaction of $Hg(ClO_4)_2.3H_2O$ and 2-(2'-pyridyl)quinoxaline (L) in CH_3COCH_3 leads to the isolation of the remarkable product $[Hg(CH_2COCH_3)(ClO_4)L]_2$; the single-crystal X-ray structure and the NMR (^{1}H-, ^{13}C-) study of this complex reveal the presense of the coordinated 2-oxopropyl anion and show a bidentate, highly assymetric behaviour of L.

Chimika Chronika, New Series, 26, 133 (1997)

NEW ORGANOMETALLIC COMPLEXES OF THE GENERAL TYPE $[[Cp(CH_2)_2N(CH_3)_2M]^+X^-$ AND $[Cp(CH_2)_2N(CH_3)_2]MX_2$ (M= Rh, F, Co etc, $X^-= PF_6^-$ Cl^-) WITH THE LIGAND N,N-DIMETHYLAMINOETHYLCYCLOPENTADIENE.SYNTHESIS AND CHARACTERIZATION.

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ABSTRACT

New metallocenes and metallocene dihalides complexes of Rh (III) containing the N,N-dimethylaminoethylcyclopentadiene ligand are described.

$Na_3RhCl_6.xH_2O$ reacts with $Cp(CH_2)_2N(CH_3)_2$ in methanol giving the cationic complex (A), where the $-N(CH_3)_2$ group is protonated. The addition of solid NH_4PF_6 in an aqueous solution of (A) at ambient temperature leads to the formation of a white-yellow solid (B).

Also the reaction of anydrous Na_3RhCl_6 with the sodium salt of the ligand $NaCp(CH_2)_2N(CH_3)_2$ gives the complex (C) where the $-N(CH_3)_2$ group is coordinated to the rhodium. These complexes have been characterised by IR, NMR, MS and elemental analyses. The obtained complexes will be screaned for antitumour activity.

Chimika Chronika, New Series, 26, 134 (1997)

PHOTOCHEMICAL STUDY OF Ag(I) COMPLEXES WITH TRIPHENYLPHOSPHINE AND HETEROCYCLIC THIONES AS LIGANDS

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ABSTRACT

Mixed ligand mononuclear silver(I) complexes of the general formula $[Ag(PPh_3)_2(L)_2]NO_3$ (where L= pyridine-2-thione, thiazolidine-2-thione and benzthiazolidine-2-thione) were prepared by treating $AgNO_3$ with PPh_3 and the appropriate thione in ethanol at 50 °C. The used silver nitrated solution was labelled by means of a small amount of ^{110m}Ag ($T_{1/2}$=256 days) prepared by neutron activation of $AgNO_3$. The microcrystalline substances obtained were characterized by elemental analyses and by their IR and UV-Vis spectra. UVB irradiation of the complexes in chloroform solutions at room temperature provokes decomposition in two stages. The percentage of the photolyzed complex was determined by measurement of the 656 keV gamma radiation emitted by ^{110m}Ag using a NaI(Tl) detector connected with a standard gamma-ray spectroscopy set-up (Nucleus, PCA 4K).

Chimika Chronika, New Series, 26, 135 (1997)

RHODIUM(I) COMPLEXES CONTAINING THE ENOLATE OF N-ACETYL-3-BUTANOYLTETRAMIC ACID (NABTH) AND THE CRYSTAL STRUCTURE OF [Rh(NABT){P(OPh)$_3$}$_2$].

Chris-Kriton Skylaris,[a,b] **Brian T. Heaton,**[a] **Chacko Jacob,**[a] **John Markopoulos,**[b] **Olga Markopoulou,**[c] **Jens Nähring**[a] **and Anthony K. Smith**[a].

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ABSTRACT

N-acetyl-3-butanoyltetramic acid (NABTH) is readily deprotonated when it reacts with [Rh(acac)(CO)$_2$] (acac = acetylacetonate) in a 1:1 ratio, in CH_2Cl_2, and [Rh(NABT)(CO)$_2$] **1** is produced. Monitoring this reaction by IR shows that the CO stretch bands due to [Rh(acac)(CO)$_2$] at 2085 and 2014 cm^{-1} are replaced completely within one hour by two equally intense bands at 2095 and 2027 cm^{-1} due to the formation of **1**. **1** undergoes displacement of CO by P(OPh)$_3$ or PPh$_3$ to give [Rh(NABT){P(OPh)$_3$}(CO)] (2020 cm^{-1}) **2**, [Rh(NABT){P(OPh)$_3$}$_2$] **3**, [Rh(NABT)(PPh$_3$)(CO)] (1990 cm^{-1}) **4**; the reaction of **4** with PPh$_3$ gives the penta-coordinate complex [Rh(NABT)(PPh$_3$)$_2$(CO)] (1960 cm^{-1}) **5** which has a trigonal bipyramidal structure with axial phosphines. ^{13}C and ^{31}P NMR spectra are consistent with the presence of two isomers for **2**, as expected for a square planar complex with an asymmetric bidentate ligand like NABT. Two isomers are also found for **4**. The solid state structure of has **3** been determined by X-ray diffraction, in which rhodium exhibits a slightly distorted square planar geometry with the NABT enolate ligand adopting an η^2-O,O' mode of coordination via the functionalities associated with C^4 and the acyl group at C^3 in the pyrrolidine ring. The room temperature ^{31}P NMR of a solution of **3** containing one equivalent of P(OPh)$_3$ indicates fast exchange of phosphite. Under ^{13}CO, **3** is in equilibrium with **2** and **1** as shown by ^{13}C NMR. No evidence has been found for the formation of 5-coordinate complexes through the addition of P(OPh)$_3$ to **2**.

Chimika Chronika, New Series, 26, 136 (1997)

SYNTHESIS AND MOLECULAR STRUCTURE OF A COMPLEX OF URANIUM-(VI) WITH CHLORANILIC ACID

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ABSTRACT

Chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone=CAH_2) forms complexes with several transition metal cations.This paper deals with an U(VI) complex of chloranilic acid, synthesized and structurally investigated for the first time. Quinone derivatives were used in a multistage process leading to enriched $^{235}U^{(1)}$ .The crystalline complex $[UO_2(CA)_2]Na_2{\cdot}6H_2O$ was prepared from uranyl(VI)-nitrate hexahydrate and sodium chloranilate in acidic solution. The crystal structure of the complex reveals a pentagonal bipyramidal geometry for both uranyl moiety and sodium atom in the lattice,whilst the six water molecules form an hexagonal cluster via hydrogen bonding. The structure of the complex resolved by X-ray crystallography is consistent with the spectroscopic measurements (IR, UV-Visible, ^{13}C-NMR). The thermal decomposition of the complex was also investigated from the TG, DTG, and DTA curves. Pentagonal bipyramidal structures are usual geometries for the U(VI) complexes$^{(2)}$.

(1)- M.Seko, et all, Brit.Patent, **1**, 565, 392 (23-4-1973).

(2)- V.N.Serezhkin,et all,Russ.J.Inorg.Chem.,**27**,2727,(1982).

Chimika Chronika, New Series, 26, 137 (1997)

TRINUCLEAR $Mn^{III}Mn^{II}Mn^{III}$ SCHIFF BASE COMPLEXES WITH CARBOXYLATE BRIDGING LIGANDS

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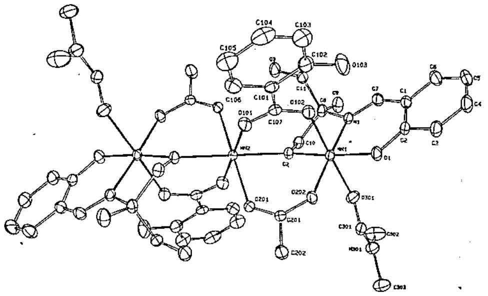
ABSTRACT

Two mixed valence, trinuclear manganese complexes of general stoichiometry $Mn^{III}Mn^{II}Mn^{III}L_2(AcO)_2(Hsal)_2X_2$, where L is a tridentate Schiff base ligand and X is a neutral monodentate donor, have been structurally characterised by using X-ray crystallography. The structurally characterised complexes have strictly 180° Mn^{III}-Mn^{II}-Mn^{III} angles as required by crystallographic inversion symmetry. The complexes are valence trapped with two terminal Mn^{III} ions showing Jahn-Teller distortion along the salicylate-Mn^{III}-X axis. The manganese separation is 3.52 Å. The complexes have S=3/2 ground state with small antiferromagnetic exchange J coupling. The e.s.r. spectra show a broad low field signal with $g \approx 4.3$. Crystal data for $[Mn_3(Hsaladhp)_2(acetato)_2(salicylato)_2(dmf)_2$: triclinic, $P_{\bar{1}}$, a=10.775(2)Å, b=11.587 (2) Å, c=11.742(2) Å, α=87.77(2)° β=72.15(2)°, γ=86.34(2)°, μ=7.1 cm^{-1}, V=1392.4(4) Å^3, R=0.0387, R_w=0.0463, ρ_{obsd}=1.38 g·cm^{-3}, ρ_{calcd}=1.40 g·cm^{-3}: crystal data for $Mn_3(Hsaladhp)_2$ $(acetato)_2(5\text{-}Cl\text{-}salicylato)_2(thf)_2$: monoclinic, $P2_1/n$, a=8.776(3) Å, b=22.182(7) Å, c=13.575(4) Å, β=94.443(12)°, ρ_{obsd}=1.47 g·cm^{-3}, ρ_{calcd}=1.493 g·cm^{-3}, μ=8.83 cm^{-1}, V=2635.0(14) Å^3, R=0.0378, R_w=0.0957



ORTEP Diagram of the $[Mn_3(Hsaladhp)_2(acetato)_2(salicylato)_2(dmf)_2$

Chimika Chronika, New Series, 26, 138 (1997)

COPPER(II)-HERBICIDES INTERACTION. SYNERGIC EFFECT. PART I

C. Dendrinou-Samara[1], G. Psomas[1], C. P. Raptopoulou[2], V. Tagoulis[2], A. Terzis[2], I. Samaras[3], D. P. Kessissoglou[1]

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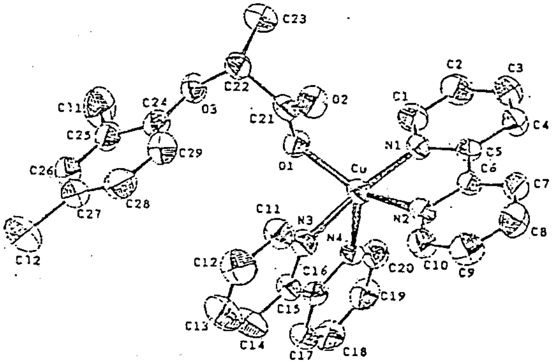
ABSTRACT

The copper(II) complexes with the commercial auxin herbicides 2,4-D, 2,3-D, 2,4,5-T, MCPA and 2,4-DP and 2,2'-bipyridyl were prepared and characterised. The complexes have the general formula $[Cu(L_2)(L_1)_2]Cl$ where L_2 are the herbicides and L_1 is the 2,2'-bipyridyl. Crystal data for $[Cu(2,4\text{-}DP)(bipy)_2]Cl\cdot 2MeOH\cdot 3H_2O$: triclinic, $P\bar{1}$, $a=12.803(2)$Å, $b=15.011(3)$Å, $c=10.734(2)$Å, $\alpha=109.464(7)°$, $\beta=107.750(6)°$ and $\gamma=96.155(7)°$, $\mu=8.8\ cm^{-1}$, $V=1801.7(5)$ Å^3, $\rho_{obsd}=1.38\ g\cdot cm^{-3}$, $\rho_{calcd}=1.407\ g\cdot cm^{-3}$, $R=0.0542$, $R_w=0.1513$. The antibacterial activity of the complexes was evaluated against Bacillus subtilis, Escherichia coli, Staphylococcus aureus and Proteas vulgaris by the Minimal Inhibitory Concentration (MIC).



ORTEP Diagram of the $[Cu(2,4\text{-}DP)(bipy)_2]Cl\cdot 2MeOH\cdot 3H_2O$.

Chimika Chronika, New Series, 26, 139 (1997)

COPPER(II)-HERBICIDES INTERACTION. SYNERGIC EFFECT. PART II

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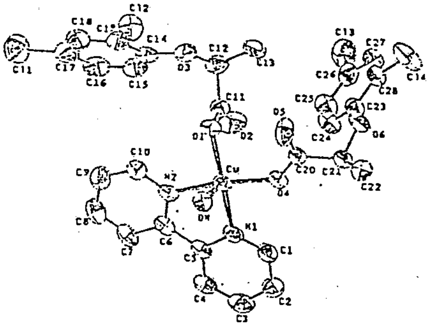
ABSTRACT

The copper(II) complexes with the commercial auxin herbicides 2,4-D, 2,3-D, 2,4,5-T, MCPA and 2,4-DP and 2,2'-bipyridyl were prepared and characterised. The complexes have the general formula $Cu(L_2)_2(L_1)(H_2O)$ where L_2 are the herbicides and L_1 is the 2,2'-bipyridyl. Crystal data for $Cu(2,4\text{-}DP)_2(bipy)(H_2O)$: triclinic, $P\bar{1}$, a=11.468(6)Å, b=14.095(8)Å, c=10.887(6)Å, α=89.28(1)°, β=62.05(1)°, γ=76.4(1)°, μ=8.8 cm^{-1}, V=1501.0(8) $Å^3$, ρ_{obsd}=1.32 $g{\cdot}cm^{-3}$, R=0.0542, R_w=0.1513. The antibacterial activity of the complexes was evaluated against Bacillus subtilis, Escherichia coli, Staphylococcus aureus and Proteas vulgaris by the Minimal Inhibitory Concentration (MIC).



ORTEP Diagram of the $Cu(2,4\text{-}DP)_2(bipy)(H_2O)$.

Chimika Chronika, New Series, 26, 140 (1997)

CONFORMATIONAL STUDIES OF MIXED-LIGAND COPPER(II) CHELATES. CRYSTAL AND MOLECULAR STRUCTURE OF (N,N-DIMETHYL-N'-ETHYL-1,2-DIAMINOETHANE) (1-PHENYL-1,3-BUTANEDIONATO)COPPER(II) PERCHLORATE

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ABSTRACT

The preparation, the IR and ligand field spectra and the structure of the mixed-ligand compound [N,N-dimethyl-N'-ethyl-1,2-diaminoethane(1-phenyl-1,3-butanedionato)(perchlorato)copper(II)], [Cu(dmeen)bzac($OClO_3$)], are reported. The structure was determined by single crystal X-ray diffraction analysis (triclinic, space group $P\bar{1}$, a=8.581 (6), b=9.669 (6), c=12.664(6) Å, α = 103.32(6)°, β=103.33(6)°, γ=91.43°, Z=2, R=0.0628, R_W=0.1607). The structure is square pyramidal with the nitrogens of the substituted 1,2-diamine and the carbonyl oxygens of the β-dione forming the basal plane. The apical position is occupied by one oxygen of the tetrahedral perchlorato group (distance from copper 2.452(5)Å). The U(Z,Z) conformation of the β-dione leads to half-chair conformation of the β-dionato chelate ring. The plane of the phenyl ring is tilted forming an angle of 16.72(14)° with the plane of the β-dionato moiety. The nitrogenous base adopts the ***gauche*** conformation with torsional angle of 108.72(14)°. The ethyl group is *cis* relative to the phenyl group, occupying *equatorial* position.

Chimika Chronika, New Series, 26, 141 (1997)

VARIABLE COORDINATION AND CONFORMATION OF THE 3-CYANO-2,4-PENTANEDIONATO ANION IN A MIXED-LIGAND BINUCLEAR COPPER(II) CHELATE

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The preparation and structure of $\{[Cu(NC\text{-}acac)dipyamH](NC\text{-}acac)\}_2$ are reported. The structure of this binuclear compound was determined from a single microcrystal (monoclinic, space group $P2_1$, a=7.894(7), b=25.550(24), c=11.661(13) Å, b= 106.10(8)^o, Z=2, R=0.0592, R_w=0.0592). In the [Cu(NC-acac)dipyamH](NC-acac) entities when the NC-acac$^-$ anion acts as chelating and bridging ligand assumes the commonly observed U(Z,Z) conformation, whilst behaviour as weakly N-coordinated unidentate counteranion imposes the rarely encountered S(Z,E) conformation. One of the copper(II) centres is a 4+2 Jahn-Teller complex while the other is a square-based pyramid.

Chimika Chronika, New Series, 26, 142 (1997)

STUDY ON SOLUTIONS OF VANADIUM (V) WITH 3,4-DIHYDROXYPHENYLACETIC ACID AND 3,4-DIHYDROXYBENZOIC ACID

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Oxygen is a powerfull oxidising agent but it is also kinetically inert in many reactions, under normal conditions. In biological systems several enzymes are able to catalyse such reactions e.g. ring openning of aromatic molecules. Oxygenases are such enzymes, that catalyse the breakdown of the Carbon-Carbon bond in benzol derivatives,usually in phenols or catechols [1]. These enzymes remain active in the presence of various transition metal complexes [2]. Here we present a study on the interaction of alkoholic (MeOH or EtOH) solutions of Ammonium Vanadate with aqueous solutions of carboxylic derivatives of o-catechols in the presence of $K_2S_2O_5$. The ligands we used were: (i) 3,4-dihydroxyphenyl acetic acid (3,4-DHPA) and (ii) 3,4-dihydroxybenzoic acid (3,4-DHB).

Four basic routes of reaction were carried out, the following:
(i) Neutrallization of the 3,4-DHPA aqueous solution with $K_2S_2O_5$ and additon of the EtOH solution of ammonium Vanadate in metal:ligand ratio 1:5. A blue solid (A) is isolated.
(ii) Similar to route (i) with metal:ligand:EtOH ratio 1:3:3 and a blue precipitate is isolated (B).
(iii) Similar to (i) with metal:ligand:MeOH ratio 1:4:4.
(iv) Metal:ligand ratio is 1:5, the alkohol is MeOH and the pH of the aqueous solution is 9<pH<10. An orange solid is isolated.
With the ligand 3,4-DHB the route (i) is followed, and a blue solution is obtained.

The solid complexes as well as the mother solutions were studied by IR, ^1H, ^{13}C and ^{51}V-NMR and by UV-Vis spectroscopies.

In the complex A the Vannadium is reduced, with most probable oxidation state being the V(IV). In the coordination sphere the existence of bidenate Suplhur anions is indicated by the IR spectra as well as the appearence of a V=O band. The most important is the dissapearence of the resonance bands in the aromatic region of the NMR spectra, indicating the break of the aromatic ring, while Vanadium is bound to the degradation products.

In routes (ii) and (iii) the ligand coordinates reduced Vanadium, but the products, as the NMR spectra reveal, are slowly decomposed with degradation of the benzene ring with the simultaneous production of muconic acid.

Finally in route (iv) in alkaline pH, the ligand is obviously oxidised and present as quinone in the mother solution.
Further study and analysis of the results of these complexes is under way.

[1] a. M. Rogic and T. Demmin, J.Am.Chem.Soc, 100, 5472(1978).
b. O. Hayaish, "Molecular Mechanism of Oxygen Activation", N.Y. Academic Press, N.Y. 1974.
[2] J. Freemen and J. Leohr, J.Am.Chem.Soc, 98, 28009(1976).

Chimika Chronika, New Series, 26, 143 (1997)

APPLICATION OF THE ELECTROSPRAY MASS SPECTROMETRIC TECHNIQUE TO MOLYBDENUM AND TUNGSTEN DITHIOLENES

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ABSTRACT

The measurement of electrospray mass spectra from neutral molybdenum and tungsten tris dithiolenes is reported. Normally, the electrospray technique works for charged in solution species, and one shouldn't expect to see a signal from a neutral molecule.

The neutral complexes, though, give negative ions during the electrospray vaporisation process because they can easily pick up an electron from the negatively charged metallic tip. The reverse procedure, an oxidation, has been reported in the literature, and was considered to be due to an electrochemical oxidation of the studied species.

The process, in this case, is considered to be either an electrochemical one or an electric discharge. The peaks observed appear at lower potentials for acetone than acetonitrile, i. e. they appear easily in the solvent that favours charge separation. Moreover, the process takes place at very high potentials, very unusual for normal electrochemistry.

The fragmentation with respect to the focus and skimmer lenses potentials is also discussed. Normally, there is no fragmentation in the spectra, as electrospray is a soft ionisation technique. Though, collisionally induced dissociation (CID) takes place when the focus and skimmer lenses potentials are increased, leading to the appearance of fragments in the spectrum. The fragments can be assigned formulas confirming the structure of the complexes.

Chimika Chronika, New Series, 26,144 (1997)

COMPLEXES OF THE CATECHOL AND SEMIQUINONE TYPE OF THE LIGANDS 2,3- AND 3,4-DIHYDROXYBENZOIC ACIDS WITH Zn(II) AND Cu(II), ISOLATED IN ALCOHOL SOLUTION.

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The Cu(II) complexes of 2,3- and 3,4-dihydroxybenzoic acid (2,3- and 3,4-dhbH_3) are prepared in n-propanol solution, adding a Pr^nOH solution of salt $CuCl_2.2H_2O$ to a solution of the ligand in this solvent and also by addition of some base (KOH). The compounds are isolated as solids.

The elemental analysis of the complexes of Cu(II) correspond to the formulas: (i) the tetramer $[Cu_4L_5Cl_6(H_2O)_6]K_{10}$ (1) ($L=2,3\text{-dhb}^{3-}$), analogue of the known structures [1], and (ii) $[Cu_4L_8Cl_9]K_{15}.2H_2O$ (2) ($L=3,4\text{-dhb}^{3-}$).

The ligand exists in two forms, the catecholate and the semiquinone-form, as indicated by spestroscopic methods, conductivity measurements and oxidative titrations. The ligand in (1) is simultaneously coordinated via: (a) both phenolic oxygens (catecholate-type) and (b) the 2-OH and carboxylate groups (salicylate-type of coordination) [2], with two ligands being semiquinones and the remaining three are catecholes, while in (2) two ligands are quinones and the rest are semiquinones.

The Zn(II) coordination stabilizes the semiquinone radicals of the ligands as indicated by the signals in the ESR-spectrum of the complexes, in the solid state at room temperature [3]. The Zink complexes are prepared and isolated in a way analogue to the synthesis of the Copper compounds.

Further structure analysis of the compounds is under way.

[1] R.M. Buchanan, B.J. Fitzgerald and C.G. Pierpont, Inorg. Chem., 18, 3429(1979).
[2] C. Bianchini, P. Frediani, F. Laschi, A. Meli, F. Vizza, and P. Zanello, Inorg. Chem., 29, 3402 (1990).
[3]a.D.R. Eaton, Inorg. Chem, 3, 1268 (1964).
b.S. Bhattacharya, S.R. Boone, G.A. Fox, and G.G. Pierpont, J.Am.Chem. Soc., 112, 1088 (1990).

Chimika Chronika, New Series, 26, 145 (1997)

COMPLEXES OF PLATINUM WITH 2,3- AND 3,4-DIHYDROXYBENZOIC ACID

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The ligands 2,3- and 3,4-dihydroxybenzoic acid are used as Iron chelators [1]. Such ligands could help in the removal via chelation of the excess of platinum which is can harm, when deposited,several organs e.g. the kidneys. On the other hand, water soluble platinum compounds consist the so called third generation of antitumor platinum complexes [2].

We synthesised several platinum complexes with these two ligands in water starting from the aquated form of cis-platin cis-$[(NH_3)_2Pt(OH_2)_2](NO_3)_2$.

The 2,3-dihydroxybenzoic acid reacts even in acidic solution with Pt(II), producing green solutions. From this solution we isolated a diamagnetic platinum green complex in crystalline form. This compound has the empirical formula $[(NH_3)_8Pt_4L_6].4H_2O$, where L=2,3-dhb^{3-}, according to the elemental analyses of the fresly prepared complex. Analogue polymeric complexes are the platinum pyridone blues and greens [3].This solid complex is decomposed upon remaining in the air, giving at the end as products elemental platinum and free ligand, losing all its nitrogen. The electronic spectra of the complex gives two bands in the visible region, with maxima at 506 and 600 nm, with the latter beinga MLCT band. The diamagnetism of the complex is explained if the metal is in the 3+ or 4+ and 2+ oxidation forms or if the ligand is present in its oxidised forms, semiquinone or quinone.

As solid another complex of Pt with this ligand could be isolated in neutral solution, being stable under the air.

In slightly acidic solution, the ligand 3,4-dhbH$_3$ upon reacting with aquated cis-platin gives blue complexes, which are isolated as solids.

For the blue complex with Pt:3,4-dhbH$_3$ ratio 1:2 in the preparation, the formula: $[(NH_3)_4Pt_2(3,4\text{-dhb})_2].4H_2O$ agrees with the elemental analysis results.

Further analysis of the compounds is under way.

[1] J. Raymond, K.M. Raymond and B.R. Myers, J. Inorg. Biochem., 51, 103(1993)
[2] N. Farell, "Transition Metal Complexes as Drugs and Chemotherapeutic Agents", 1st ed., Kluwer ed., London, 1989.
[3] J.K. Barton, D.J. Szalda, H.N. Rabinowitz, J.V. Waszczak and S.J. Lippard, J. Am. Chem. Soc, 101, 1434(1979).

Chimika Chronika, New Series, 26, 146 (1997)

COMPLEXES OF Ni (II) WITH 2,3- AND 3,4-DIHYDROXYBENZOIC ACID

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Complexes of metals with dihydroxybenzoic acids serve as models of the interaction of organic humic acids with metals. As a second part of our work in progress [1], we present here the synthesis of Nickel (II) complexes of 2,3- and 3,4-dihydroxybenzoic acid.

The syntheses were carried out by the following routes:

Route (a)

$$Ni(NO_3)_2.6H_2O + 2,3\text{-}dhbH_3 \xrightarrow[pH=4(NaOH)]{25^\circ C, 2hr} [(H_2O)_2Ni(2,3\text{-}dhbH_2)]NO_3.H_2O\ (1) + HNO_3 + 3\ H_2O \qquad (\underline{i})$$

$$2\ Ni(NO_3)_2.6H_2O + 3,4\text{-}LH_3 \xrightarrow[pH=6(NaOH)]{25^\circ C,\ 2hr} [(H_2O)_2Ni(\mu\text{-}L)Ni(OH_2)_3](NO_3)_2\ (2) + 2\ HNO_3 + 7H_2O \qquad (\underline{ii})$$

Route (b), in n-PrOH

$$5\ NiCl_2.6H_2O + 5\ LH_3 + 14\ KOH \xrightarrow{2hr,\ 25^\circ C} [Ni_5L_5(OH)_7]K_4.\ 13H_2O\ (3) + 24\ H_2O + 10\ KCl \qquad (\underline{iii})$$

$$4\ NiCl_2.6H_2O + 2\ LH_3 + 10\ KOH \xrightarrow{2hr,\ 25^\circ C} [Ni_4L_2(OH)_4(OH_2)_8]K_2.2H_2O\ (4) + 20\ H_2O + 8\ KCl \qquad (\underline{iv})$$

The compounds are rather polymeric, and an extended hydrogen bonding makes them slightly soluble in common organic solvents and water. In (1) and (3) the ligand exposes the salicylate coordination, and in (2) and (4) acts like a bridge between two nickel atoms. In compound (2) 3 ligands are quinones and two semiquinones and in (4) there are two catecholes and four hydroxyl-bridges or two semiquinones and two hydroxyl and four oxo-bridges. Further study of the compounds is under way.

[1] M. Kamariotaki, A. Karaliota, D. Stambaki, T. Bakas, V. Papaefthymiou, S.P. Perlepes and N. Hadjiliadis, Transition Met. Chem, 19, 241 (1994).

Chimika Chronika, New Series, 26, 147 (1997)

INFLUENCE OF BIDENTATE NITROGENOUS BASES ON THE SPECTRA AND STRUCTURE OF MIXED - LIGAND NICKEL(II) CHELATES CONTAINING β - DIONES. CRYSTAL STRUCTURE OF Ni[dpamH)$_2$ acac]NO$_3$. CH3OH.

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ABSTRACT

The chelates of β-diones(βH) exhibit unusual and interesting properties that find many laboratory uses and have a variety of industrial applications. Regarding spectroscopic and stereochemical features the significance of substituents attached to the methylene and the carbonyl carbon atoms is elegantly illustrated in the case of the Niβ$_2$ chelates. Due to the strong tendency of Nickel(II) to achieve coordination numbers exeeding four and octahedral stereochemistries, addition compounds are readily obtained from the reaction of Niβ$_2$ with Lewis bases , such as substituted 1,2-diimines and α-diamines(enR). The resulting compounds are the neutral adducts [Niβ$_2$(enR)] and the products were the [Niβ(enR)]$^+$ entity predominates. Oxyanions, such as nitrates may compete with additional molecules of the nitrogenous base for the occupation of the recent coordination sites leading to the formation of octahedral chelates.

In this work the infrared and electronic excitation spectra of a series of new Nickel(II) chelates containing a nitrogenous base (enR) and the anion of β-dione (βH) with formula [Niβ(enR)ONO$_2$] or [Ni β (enR)$_2$]NO$_3$ were obtained in the solid state and in solution. The composition and the overall structure of the new chelates depends on ligand concentration, on the substituents within the β-dionato moiety and the coordination mode of the nitrate counteranion, which can interact covalently or electrostatically. Based on physiochemical measurements (conductivity and magnetic) and spectroscopic data, it is deduced the bidentate charecter of the ligands, the coordination mode of the nitrate group and the octahedral stereochemistry of the studied chelates. The existence of the Ni(II) in an octahedral environment is confined by the structure of [Ni(dpamH)$_2$ acac]NO$_3$. CH$_3$OH that was determined from a single microcrystal (monoclinic, space group $P2_{1/n}$, a = 7.296(1), b = 7.462 (1), c = 21.604(3) A°, β = 95.65(1)°, Z = 4, R = 0.053, Rw = 0.06).

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SYNTHESIS OF COMPLEXES OF MANGANESE AND CHROMIUM WITH DIHYDROXYBENZOIC ACIDS

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Mangenese and Chromium are metals with an important role in biological systems. Mn is the central metal atom of many metalloenzymes, in its +2, +3 and +4 oxidation states [1], while chromium participates in biological processes like the insuline metabolism. On the other hand, the catecholic ligands we used in this study are good chelating agents providing as an additional site for metal coordination the carboxylate group.

The synthetic route followed for the complexes studied is:

A hydrated metal salt, either nitrate or chloro, is dissolved in alkohol, and a solution of the ligand in the same solvent is added in proportion metal:ligand 1:1 in the case of Mn and Cr, and 1:3 only in the case of Cr.

The solids we isolated after the reaction took place, evaporation of the solvent and recrystallization, are characterized by means of IR, UV-Vis and NMR spectroscopies, and their empirical formulas were calculated according to the results of elemental analyses.

Another alternative preparation route being studied under way is in aceton solutions for the Mn(VII) and water solutions for the Cr(VI) complexes. The ligands we used were 2,3-dihydroxybenzoic acid (**2,3-DHB**), 3,4-dihydroxybenzoic acid (**3,4-DHB**) and 3,4-dihydroxyphenylacetic acid (**3,4-DHPA**).

The formulas of the products isolated are depended on the acidity of the mother solution. In acidic solutions polymeric complexes are obtained, being dimeric or trimeric for Cr and tetrameric for Mn. In less acidic or even alkaline solutions, monomeric complexes with metal to ligand ratios 1:2 and 1:3 were isolated as solids.

In the Mn complexes the 2,3-DHB can be bound to the metal in the salicylate mode, oxidising Mn(II) to Mn(III), especially in the presence of KOH. The ligand exists in its semiquinone form, as electronic and IR spectra indicate. The NMR peaks are broadened because of the paramagnetism of the metal. The carboxylate, as well as both catecholic oxygens, are coordinated to Mn in the 3,4-DHB complex.

The Cr complexes isolated from acidic solutions are green solids insoluble to common solvents if the starting compound is the nitrate salt of the metal, while for the case of the chloro salt, green complexes soluble in polar solvents are isolated. In the presence of alkali (KOH), solid complexes with metal:ligand ratios 1:2 and 1:3 were isolated. The ligand is bound in its catecholic mode, but when the complex remains in the presence of air is first oxidised to semiquinone and finally to quinone [2].

Further analysis of the complexes is presently under way.

[1] R.M. Buchanan and C.G. Pierpont, J. Am. Chem. Soc., 102, 4951(1980).
[2] R.M. Buchanan, J. Claflin and C.G. Pierpont, Inorg. Chem., 22, 2552(1983)

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SYNTHESIS AND ELECTROCHEMICAL CHARACTERIZATION OF DITHIOLENE COMPLEXES OF TUNGSTEN AND MOLYBDENUM

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Nonsymmetric dithiolenic complexes of the general formula $[RR'(C_2S_2)]_3M$, M=Mo or W and R, R' = H, Ph, p-ClPh, p-BrPh, p-CH_3Ph, p-CH_3OPh, p-$(CH_3)_2$NPh were synthesized. Their electrochemical properties were studied by cyclic voltammetry in order to elucidate their role in photochemically induced redox reactions (i.e. these complexes have been used as catalysts for the photochemical cleavage of water by visible light).

For each complex, two quasi-reversilble electron transfer reactions were observed, assigned to the one electron transfer between neutral and monoanionic and monoanionic and dianionic species. The half-wave potentials ($E_{1/2}$) are highly dependent on the nature of the central metal ion and on the nature of the ligand. In the case of ligands bearing the phenyl group, $E_{1/2}$ depends on the nature of the ring substituent.

The voltammetric data showed that the molybdenum dithiolene complexes are more easily reduced than the equivalent tungsten complexes. Complexes with ligands containing the phenyl group instead of hydrogen have a more positive $E_{1/2}$ due to the electron-attracting character of the phenyl group. On the other side, for both tungsten and molybdenum complexes differing only in the phenyl ring substituent, the ease of reduction is the folowing: Cl > Br >H > CH_3 > OCH_3 Trends of this kind are not unusual and follow in general the electron-withdrawing ability of the ligand. Thus, complexes with ligands of greater electron-attracting ability can accommodate more easily the incoming electron. The above results have to be taken into account in order to explain and better clarify differences in the catalytic efficieny of these dithiolene complexes for the photochemical splitting of water.

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ELECTRONIC SPECTROSCOPY OF COMPLEXES OF THE TYPE $[(L_2Rh)_2(\mu\text{-}MoS_4)]$, L=PHOSPHINE, PHOSPHITE

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ABSTRACT

The novel rhodium(I) tetrathiomolybdato-complexes $[(L_2Rh)_2(\mu\text{-}MoS_4)]$, L=phosphine, phosphite, exhibit unsual electronic spectra. EHMO calculations performed on the model-molecule $[\{(PPH_3)_2Rh)_2(\mu\text{-}MoS_4)]$, show that the lower-energy absorption band can be assigned to Rh→Mo electron transfer transition(s). The band maxima of the v(Rh→Mo) bands for the complexes with five different phoshorus ligands show perfect linear correlation with Tolman's electronic factor.

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DIRECT SYNTHESIS OF ACETALS IN THE LOW PRESSURE HYDROFORMYLATION OF ALKENES WITH RHODIUM CATALYSTS IN THE PRESENCE OF ORTHOFORMATE

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ABSTRACT

The two catalyst precursors $[Rh_2(\mu\text{-cysteine})_2(CO)_4](OTf)_2$ and $[Rh_2(\mu\text{-penecillamine})_2(CO)_4](OTf)_2$ in the presence of 4 equivalents of $P(OPh)_3$ in triethyl orthoformate as solvent and reactant, permit the low pressure hydroformylation of various alkenes into the corresponding acetals. Apart from a few low-yield by-products resulting from isomerization of the substrates, the carbonylated products obtained directly and exclusively are acetals.

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DRAMATIC VARIATIONS OF THE REGIOSELECTIVITY OF THE LOW PRESSURE HYDROFORMYLATION OF TERMINAL ALKENES CATALYSED BY RHODIUM(I) SPECIES CONTAINING A THIOAMINOACID LIGAND

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ABSTRACT

Dinuclear tetracarbonyl rhodium(I) complexes containing cysteine or penicillamnine as bridging ligands have been synthesized. Addition of phosphite ligands results in a good catalytic activity in the hydroformylation reaction of 1-octene. NMR investigations have shown that according to the phosphite to rhodium molar ratio, mononuclear and dinuclear species interconvert in solution. The regioselectivity in linear aldehyde can range from 40 to 90%.

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METAL COMPLEXES OF OROTIC AND ISOOROTIC ACID

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The interaction of metal ions with orotic and isoorotic acid is investigated in this work. Ten compounds of a number of metal ions (Mn^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, VO^{2+}, Co^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+}, Ag^{+}) were precipitated in aqueous solutions. The metal to ligand molar ratio is found to be 1:1 for the compounds of Ag^{+}, Co^{2+} and Fe^{3+}, 1:2 for the compounds of Mn^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, VO^{2+}, Hg^{2+}, Cr^{3+}. The compounds were characterized by infrared, diffuse reflectance spectra, magnetic susceptibility and conductivity measurements. Co^{2+} is coordinated to orotic acid through the carboxylate group and the adjacent deprotonated N(1). Mn^{2+}, Cu^{2+}, VO^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+}, are coordinated to orotic acid through the carboxylate group and Ag^{+}, Zn^{2+}, Cd^{2+}, form ionic compounds.

Nine complexes of a number of metal ions (Mn^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Pd^{2+}) with isoorotic acid were precipitated in aqueous solutions. The metal to ligand molar ratio is found to be 1:1 for the complexes of Pd^{2+} and Hg^{2+} and 1:2 for the complexes of Mn^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}. The complexes were characterized by infrared, diffuse reflectance spectra, thermal studies, magnetic susceptibility and conductivity measurements. The crystal structure of the Mn^{2+} complex was determined. The 1:2 complexes have pseudooctahedral centrosymmetric structures with the metal ion chelating to isoorotic acid through the carboxylate group and the adjacent amidic O(4). The axial sites of the octahedron are occupied by two water molecules. The 1:1 complexes have square planar structures with the metal ion chelating to isoorotic acid through the carboxylate group and the adjacent deprotonated enolic O(4). The other two sites are occupied by two water molecules.

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PENTANUCLEAR Cu(II) CLUSTERS: MODELS FOR THE CORROSION INHIBITION OF COPPER BY BENZOTRIAZOLES

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The coordination chemistry of neutral and deprotonated benzotriazoles is currently an area of great activity. This is due to a variety of reasons, not least of which is the anticorrosion action of benzotriazole and substituted benzotriazoles towards certain metals, particularly copper and its alloys. Chemical, physical and structural studies on realistic model complexes are needed to undestand the complex surface chemistry that leads to corrosion inhibition.

The novel hexakis(benzotriazolato)tetrakis(β-diketonato)pentacopper(II) clusters $[Cu_5(acac)_4(bta)_6]\cdot Me_2CO$, $[Cu_5(bzac)_4(5Mebta)_6]\cdot MeNO_2$, $[Cu_5(dbm)_4(bta)_6]$ and $[Cu_5(hfac)_4(bta)_6]$, where acacH=acetylacetone, bzacH=benzoylacetone, dbm=dibenzoylmethane, hfacH=hexafluoroacetylacetone, btaH=benzotriazole and 5MebtaH=5-methylbenzotriazole, have been prepared (see, for example, eq. 1).

$$\underline{5}\,[Cu(bzac)_2] + \underline{6}\,5MebtaH + MeNO_2 \xrightarrow[20\ °C]{MeNO_2} [Cu_5(bzac)_4(5Mebta)_6]\cdot MeNO_2 + \underline{6}\,bzacH \qquad (1)$$

The complexes have been characterized by single-crystal X-ray crystallography and by a variety of other physical and spectroscopic methods. The pentanuclear copper(II) assemblies are composed of distorted tetrahedral arrangements of four Cu^{II} atoms centered on the fifth. Each of the six benzotriazolato ligands spans an edge of the terahedron and is ligated to the central Cu^{II} atom through its central nitrogen. The four peripheral Cu^{II} atoms are each coordinated to oxygens of a bidentate chelating diketonato anion and to nitrogens of three different benzotriazolato ligands. The pentanuclear clusters are excellent models for the corrosion inhibition of Cu by benzotriazole and its derivatives, with the diketonato oxygens modelling the chemical species O^{2-}, OH^- or/and H_2O which are bound to the oxidized metallic surface.

Chimika Chronika, New Series, 26, 155 (1997)

NONANUCLEAR Ni(II) CLUSTERS: PREPARATION, STRUCTURAL CHARACTERIZATION AND MAGNETIC STUDY

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3d-metal benzotriazolates encompasses a range of interesting structural types and, quite frequently, possess unusual magnetic and spectroscopic properties. More recently, we have developed an interest in nickel(II) benzotriazolates, an area that has been relatively unexplored for this otherwise well-studied metal and we report in this work the preparation (eq. 1) of some novel nonanuclear Ni(II) clusters of the general formula $[Ni_9L_{12}(bzac)_6(MeOH)_6]\cdot 6H_2O$, where LH=benzotriazole, 5-methylbenzotriazole, 5,6-dimethylbenzotriazole and bzacH=benzoylacetone (yields:~80%).

$$\underline{9}[Ni(bzac)_2]\cdot EtOH + \underline{12}LH + \underline{6}MeOH + \underline{6}H_2O \xrightarrow{MeOH} [Ni_9L_{12}(bzac)_6(MeOH)_6]\cdot 6H_2O + \underline{12}\ bzacH + \underline{9}\ EtOH \qquad (1)$$

The novel single-crystal X-ray structure of the representative compound $[Ni_9(5,6diMebta)_{12}(bzac)_6(MeOH)_6]\cdot 6H_2O$ (Fig. 1), together with the results of variable-temperature magnetic susceptibility studies will be described.

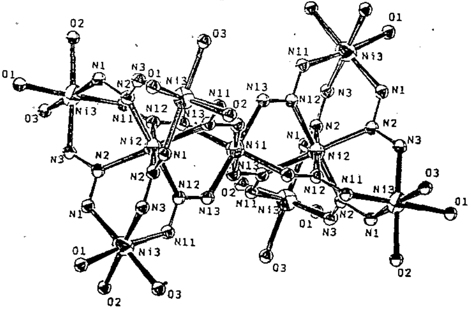

Figure 1. The molecular structure of the nonanuclear $Ni^{II}/5,6diMebta^-$ cluster. All C atoms and solvate H_2O molecules have been omitted.

Chimika Chronika, New Series, 26, 156 (1997)

E.S.R. AND IR SPECTROSCOPIC STUDIES OF LAYER ALUMINOSILICATE MINERALS

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ABSTRACT

Electron Spin Resonance and Infrared spectroscopy have been used in order to characterize a Greek clay taken from the island Milos and designated as Zenith, in conjunction with other familiar layer structured smectites. The E.S.R. spectra show a similar distribution of the structural Fe^{3+} for all clays studied. All spectra reveal sites of near rhombic symmetry ($g=4.3$) with crystal parameters $E/D=1/3$ and $D=1.2$ and also sites deviating from rhombic symmetry ($g=8.3$, $E/D=0.12$) probably due to a different orientation, cis or trans of hydroxyl surrounding structural Fe^{3+}. The presence of Fe^{3+} in adjacent cation sites leads to a very broad resonance ($\Delta B>1000G$) centered near $g=2$. Other lines in the spectra are attributed to trapped holes located at oxygen sites next to silicon.

The infrared spectra exhibit significant changes after thermal treatment at 250°C. These changes have been attributed to the Hofmann-Klemen effect. The effect which arises from the migration of small cations into the vacant octahedral sites in dioctahedral clays, seems to disturb the AlOHAl vibrations in Li^+ saturated samples. The behaviour of lithium saturated Zenith clay suggests the existence of vacancies in the octahedral sheets and shows that at least a fraction of its cation exchange ability originates from the substitution in the octahedral sheet. In addition we report that changes associated with absorption of the Si-O-Si bridges in the vibrational spectra can be used for a better understanding of Hofmann-Klemen effect.

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REDUCTION OF TRANS, TRANS-2,4-HEXADIEN-1,6-DICARBOXYLIC ACID (TRANS, TRANS-MUCONIC ACID) BY CHROMIUM (II) IN ACIDIC SOLUTIONS

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The kinetics of the reaction between Cr(II) and trans,trans-2,4-hexadien-1,6-dicarboxylic acid were followed at 750 nm at various temperatures, chromium(II) and $[H^+]$ concentrations. The pseudo-first order rate constants give a linear dependence on [Cr(II)]. A rate equation $k_{obs}=k_o+k_1[H^+]^{-1}$ is valid at 22^{0}C at [Cr(II)]=constant. Recording spectra at time intervals of 5 msecs a decrease in absorbance is first observed due possibly to a decomposition/transformation of a precursor complex assumed to be formed by a non-symmetric[1] first attack of Cr(II) on muconic acid. A following intense increase in absorbance in the UV region is attributed to a formation and chelation of a Cr-C σ-bond bearing intermediate [1-4]. A second attack by chromium(II) takes place in a rate-limiting step leading finally to reduction of a double bond of the substrate.

Semi-empirical calculations were carried out for the possible isomers of muconic acid,and the LUMOs of all the forms,which may be considered as the directly related orbitals to the redox reaction, are almost identical in constitution ; they are mainly localised on the central conjugate part of the molecule,while their energetic difference is also small,implying that all forms, if present in solution , would react similarly. The picture regarding LUMO constitution is generally the same for the corresponding muconic acid anions. The LUMO energies of the anionic isomers lie between 2.36eV and 2.76eV,while the corresponding ones for the acids vary from -1.41 to -1.37eV,being more susceptible to electrophilic attack.

1.D.Katakis, E.Vrachnou-Astra and J.Konstantatos, *J.Chem.Soc., Dalton Trans.,* 1986, 1491.
2.A.Petrou, E.Vrachnou-Astra and D.Katakis, *Inorg.Chim.Acta,* 39,161,(1980).
3.A.Petrou, E.Vrachnou-Astra, J.Konstantatos, N.Katsaros and D.Katakis, *Inorg.Chem.,* **20**,1091 (1981).
4.A.L.Petrou, *J.Chem.Soc., Dalton Trans.,* 3771,1993.

Chimika Chronika, New Series, 26, 158 (1997)

POSSIBILITY OF PEAT UTILIZATION FOR ORGANIC FERTILIZERS PREPARATION

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ABSTRACT

We attempt to make an organic fertilizer using a mixture of peat-melasse-vinasse. We formed mixtures with combination of these materials in different proportions, we diluted them into water of the town network.

Subsequently after observing their pH changes in the extract, the macro, micro nutrients content was determined and the electrical conductivity was measured.

We kept those mixtures that contain sufficient organic matter and macro micro nutrients. We apply them to see the theory in practice in pot seedling culture with two different soils.

Three treatments are studied (the comparative pot and two portions of the mixtures) replicated three times. Especially, observations on plants are taken, the wet and dry weight of the plants are measured and finally analysis of the vegetative stems, soils and mixtures are carried out.

In the end we will make deductions concerning the organic fertilizer (mixtures) efficiency.

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UTILIZATION OF GREEK COALS FOR AGRICULTURAL USE

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The purpose of the study is to determine which of the Greek coals (peat and lignite) are apropriate for agricultural uses. They have been studied samples from nine different deposits of coal from several areas of Greece.

It has been concluded that part of the Greek peat and lignite deposits is very good raw material for organic fertilizers, mainly because of the high concentration in humic substances.

For example most of the samples from peat and lignite from Megalopolis, Drama, Ptolamais and Filippi, contain about 25 and 40 % humic substances in dry basis.

Not only the high concentration in humic substances, is a strong reason for using the Greek coals as organic fertilizers, but they also contain the appropriate amount in other nutrients such as iron, calcium, manganese etc.

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STUDY ON COMPLEXES OF MOLYBDENUM WITH CARBOXYLIC DERIVATIVES OF CATECHOLS AS LIGANDS.

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Molybdenum is part of many enzymes containing multiple oxidation-reduction centers and catalyse reactions of atom transfer from or to the metal atom. Mo hydroxylases take part in reactions of hydroxyl transfer [1]. In the active centers of the enzymes, a key chemical reaction involves the oxidation of the catechol to semiquinone and quinone (flavone) with simultaneous reduction of the metal to Mo(VI) [2]. Carboxylic derivatives of the catechols are basic metabolites of neurotransmitters and they are involved in glucose metabolism [3] and metal uptake.

In the present study, we prepared complexes of the ligands 2,3- and 3,4-dihydroxybenzoic acids (2,3- and 3,4-DHB) and of 3,4-dihydroxyphenylacetic acid (3,4-DHPA) with Mo(VI).

Two series of experiments were carried out. In the first one, we studied the type of complexes formed using as starting materials $(NH_4)_2MoO_4$ in water and a water or methanol solution of the ligands, and we found that their formulas depend on the kind of the ligand, the metal:ligand proportion we used every time, the acidity of the solution, as well as the proportions of the mixture of solvents(methanol to water ratio) and the sequence of the addition of the reactants and finally form the reaction time. With 2,3-DHB and 3,4-DHPA as ligands, in propanol/water mixture, red solutions are obtained, from which yellow complexes are precipitated. The compounds are unstable in the air, as indicated by UV-Vis, IR, and ESR spectroscopies, turning to green. Green complexes stable in the air are isolated in more alkaline solutions. Raise of the pH causes ligand oxidation by the metal with simultaneous polymerization.

In the second set of experiments, relatively stable compounds were isolated as solids, with the same starting compounds but with addition of reductant ($K_2S_2O_5$) and in the absence of alkohol. The stable yellow complexes formed were isolated by precipitation with the aid of the heavy (bulky) cation $P(ph)^{4+}$, beiing dimer for metal:ligand ratio 1:1 and trimer for M:L=5:1. The electron spray mass spectra of these complexes in CH_3CN solution indicate that the monomeric unit of both compounds is $[MoO_2(H_2O)_2L]^{1-}$. The ligand is chelated as catechol and quinone, as indicated by IR, UV-Vis and NMR spectroscopic data. For the dimer the empirical formula is $[Mo_2O_5L_2(H_2O)_4]^{2-}$, with ligand and oxygen bridges [4].

Further study and results analysis involving these complexes is currently under way.

[1] E.I. Stiefel, Progr.Inorg.Chem., 221(1977).
[2] K.N. Raymond et al., Coord.Chem.Revs, 106, 171(1990).
[3] C..G Pierpont et al., Coord.Chem.Revs, 38, 45(1981).
[4] B. Borgias et al., Inorg.Chem., 23, 1009(1984).

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MICROPHASE STRUCTURES IN NOVEL MACROMOLECULAR ARCHITECTURES OF BLOCK COPOLYMERS

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ABSTRACT

The synthesis of novel non-linear block copolymers of the A_2B (3-miktoarm* star copolymers), A_3B (4-miktoarm star copolymers), $(AB)_2(BA)_2$ (inversed 4-miktoarm star block copolymers) and A_3BA_3 (bridged miktoarm star copolymers) type was achieved. A is polyisoprene (PI) and B polystyrene (PS). The synthetic approach involves the reaction of methyltrichlorosilane or tetrachlorosilane with monofunctional or difunctional macroanions of B, under conditions unfavorable to chain coupling or linking, followed by addition of the monofunctional macroanion A. Characterization carried out by size exclusion chromatography, low angle laser light scattering, laser differential refractometry, membrane and vapor pressure osmometry, NMR and UV spectroscopy indicated that these new materials have a high molecular and compositional homogeneity.

The microphase separation was studied by transmision electron microscopy, small angle x-ray scattering and image simulation. Comparison of A_2B and A_3B stars with the corresponding linear block copolymers, showed that the macromolecular architecture not only affects strongly the morphological domain borders but it can introduce new morphologies as well. In the case of the $(AB)_2(BA)_2$ stars, ordered bicontinuous double diamond structure (OBDD) was observed, despite the fact that the volume fraction of PS was 50%. The A_3BA_3 bridged stars exhibit new interesting morphologies which are under investigation.

*mikto from the greek word μικτός meaning mixed.

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CRYSTAL ARCHITECTURE AND PHYSICAL PROPERTIES OF POLYMERIC COMPLEXES OF α,ω- DICARBOXYLIC ACIDS. CONSTRUCTION OF MOLECULAR ZEOLITES.

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ABSTRACT

We have constructed infinite frameworks by linking silver or lanthanum cations with flexible α,ω dicarboxylic acids. The polymers obtained are formulated as Ag_2(succinate), 1, Ag_4(glutarate)$_2$, 2 and La_2(adipate)$_3$ $10H_2O$, 3. X-ray analysis shows that 1 and 2 are composed of Ag_4 clusters linked by organic dianions, but the crystal architecture depends on the conformation of the ligand. In 1 the succinate anions adopt a "linear" conformation leading to an interpenetrated 3D super-diamandoid structure, while 2 is a 2D polymer owing to the gauche-gauche conformation of the glutarate anions. In 3, adipate adopts a "linear" conformation and a 3D porous solid is formed, with infinite channels in the three directions. Interestingly, this compound presents zeolitic properties.

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ELECTRICALLY CONDUCTING ISOMERIC POLYPHENYLENES

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ABSTRACT

One of the most valued properties of polymers is their ability to act as very good electrical insulators. However, there has been interest for many years to produce electrically conducting polymers. The ease and low cost of preparation and fabrication of polymers especially in films and fibers, compared to semiconductors and metals, and their mechanical properties are very important attractions of polymers to the electrical/electronic industries. Ellectrically conducting polymers have been found application as batteries, electrochromic devices, chemical sensors etc. Polyphenylenes are one of the most important class of conjugated polymers, that become electrically conducting after treatment with electron acceptors such as $FeCl_4^-$, AsF_6^-, I_3^- or with electron donors such as alkali metals.

o,m,p-polyphenylenes were synthesized by oxidation cationic polymerization by using biphenyl as the monomer, $CuCl_2$ as the oxidant and $AlCl_3$ as the catalyst. The insoluble in chlorobenzene fraction was selected after several extractions with appropriate solvents. Then, the polymers were doped with different doping systems ($FeCl_3$-acetonitrile, $FeCl_3$-nitrobenzene and $SnCl_4$-acetonitrile). Heat treatment of polymers at 90 or 115°C was occured being followed by a second doping.

All doped polymers were semiconductors with higher conductivity values after the second doping, while heat treated at mild conditions remained semiconductors and at more intense conditions became insulators. SEM studies of doped polyphenylenes showed crystallized and amorphous areas. FTIR measurements did not show serious changes between the undoped and doped stage.

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PROCESS OPTIMIZATION OF AN EPOXY BASED CHEMICALLY AMPLIFIED RESIST FOR SUB-QUARTER-MICRON E-BEAM LITHOGRAPHY

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ABSTRACT

The use of ultrasensitive resists is highly desirable in e-beam lithography for both direct and mask writing applications. Cresol epoxy novolac based chemically amplified negative resists have been introduced by M. Hatzakis and his IBM coworkers[1] as having the highest reported sensitivities for subquarter-micron e-beam lithography.

A new advanced epoxy novolac resist formulation, "EPR" in the following, is presented in this paper. Aspects of the resist formulation and the optimization of critical process parameters for high resolution lithography are discussed. Specifically the post-apply bake (PAB) and post-exposure bake (PEB) conditions have been optimized to achieve resolution at the 0.1 μm regime. Process lattitude issues are also reported.

A commercial epoxy novolac polymer of Shell Chemicals which is fractionated before use and an e-beam sensitive hexafluoroantimonate triphenylsulphonium salt are the resist basic components. A Bronsted acid is produced during the e-beam exposure which catalyses crosslinking reactions of epoxy functionalities during the subsequent PEB step.

The bulk sensitivity (E_{80}, dose for 80 % resist thickness retention) of EPR is 0.9 $\mu C/cm^2$ at 40 KV. Resist contrast increases significantly with increasing PEB temperature (increase from 2.3 at 90°C to 4.3 at 130°C). However, resolution capability and the contrast are not maximized at the same processing conditions[2]. High aspect ratio (6:1) columns with a diameter of 70 nm have been written at 90 °C PEB with a 50 nm full width half maximum beam. Patterns of 0.2 μm equal lines/spaces and high aspect ratio 0.1 μm doubly spaced lines have been written at the same conditions. PAB temperature increase in the same as above range improves resist adhesion and stability of <2μm lines.

EPR shows also very good process lattitude characteristics. The dose lattitude (for a ±10% linewidth variation) is ± 20% in the case of 0.5 μm lines. The according value for 0.2 μm lines is ±10%. The PEB time process lattitude is very good as it has been shown by single exel exposures. At 90 °C a 2 min PEB time is enough for the completion of the chemical change and longer PEB times do not increase the diameter of the written cylinders[3].

1. M. Hatzakis , K. Stewart, J. Shaw and S. Rishton, *J. Electrochem. Soc.*, **138**, 1076(1991) and references therein.
2. P. Argitis, I. Raptis, C.J. Aidinis, N. Glezos, M. Baciocchi, J. Everett, and M. Hatzakis, *J. Vac. Sci. Tecnhnol.* **B14**, to appear December 1995.
3. I. Raptis, L. Grella, P. Argitis, M. Gentili, N. Glezos, *Microelectronic Eng.* **29** , to appear 1996.

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HYDROXYMETHYLATED LIGNIN FROM AGRICULTURAL BYPRODUCTS WITH NOVOLAC AS ION EXCHANGER RESIN

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ABSTRACT

Phenol (P)- formaldehyde (F) resin, commonly sulfonated are used as ion exchanger. On the other hand, lignocelluloses promise improved products for material industries. In the past ca. 20 years progress has been made in developping new engineering materials from lignocellulosic wastes, including wood-polymer composites and wood plastics. Lignin (L),the phenolic polymer matrix in wood, is a high impact-strength thermally resistant thermoset polymer. Lignin was isolated from olive stone biomass by Kraft method. The biomass was treated by alkaline hydrolysis of weak ether bonds with NaOH and Na_2S in an autoclave at about 180°C, 9 Atm. for 1.5 h. Kraft lignin was precipitated by solution of H_2SO_4. Novolac (N) was synthezised from phenol-formaldehyde under acidic conditions. Lignin was also hydroxymethylated (HL) and then incorporated with phenol-formaldehyde during the polymerisation. The polymers contained HL or not, sulfonated with conc. H_2SO_4 and crosslinked with formaldehyde, were called as resin N-HL-S and N-S, respectively. The various products were characterized by IR spectroscopy. The sorbability of metal ions from standard aq.solutions determined by Atomic Absorption Spectroscopy is increased : N-S<N-HL-S and $Cu^{2+}<Ni^{2+}<Co^{2+}$.

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1 ACCELERATED WEATHERING TEST
QUALITY COMPARISON THROUGH MECHANICAL PROPERTIES TEST

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ABSTRACT

When new coating materials are developped it is often important to determine how durable they will be when exposed to the weather. Will they chalk, crack or peel? Or will they retain a reasonable percentage of original appearance, physical and chemical properties? Today, the chemist can no longer afford to wait one or two years for outdoor exposure tests to show whether his latest "improved" formulation is really an improvement. In these times you need weatherability data in a matter of weeks, not years.

With today's accelerated weathering testers, it is possible to generate reliable weatherability data in a matter of days or weeks-provided you understand the mechanisms of outdoor weathering and use a tester of proper design. It is widely recognized that sunlight and moisture are the most widespread and important causes of weathering damage to polymers.

In our approach we propose the QUV Tester for accelerated weathering stress on pwoder coated samples-sheets by different producers' powders, under the same conditions. Then, measure gloss and mechanical properties retention. We realized that although different powders do not show big differences in gloss retention, they do show huge differences in mechanical properties retention. We propose therefore the mechanical properties measurement after QUV exposure as more reliable criterium of quality comparison between powders.

The method could be extended by measuring the chemical properties and corrosion resistance retention. We also propose to compare mechanical, chemical and corrosion properties retention after real time exposure, like the FLORIDA test, etc.

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EFFECTIVENESS OF NON - IONIC SURFACTANTS ON THE DYEING OF COTTON WITH DIRECT DYES

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The effectiveness of non - ionic surfactants [poly(oxyethylenated) p - alkylphenols (NPE 10, NPE 12) and stearylamin (Rokamin 11)] on the dyeing (40°—> 98 °C) of cotton fabrics with direct dyes (C.I. Yellow 106 and C.I. Blue 78, 1 % o.w.f.), concerning the dye uptake and levelling, was studied. Various molar ratios of surfactants to dye (0: 1, 0.5:1, 1: 1, 2: 1) were applied. Dye adsorption was indirectly determined spectrophotometrically (λ_{max}) and dye content on the dyed fabrics was also determined directly by a reflectance spectrophotometer. The presence of surfactants caused a low decrease of dye uptake, no change of the hue (h*) and an increase of dye levelling mainly in presence of NPE 12. A preliminary study to correlate the evaluation of levelling by objective and reflectance spectrophotometric measurements (ΔE) showed consistent results.

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MECHANISM OF THE ACTION OF A N-HEROCYCLIC ORGANIC ACID DURING THE A-C COLOURING OF ANODIZED ALUMINIUM IN NICKEL SULFATE SOLUTIONS

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ABSTRACT

After extensive investigation on the coloration of the anodized aluminium with A-C electrolytic treatment in nickel sulfate baths with the presence of certain organic additives it has been concluded that : The presence of piperidine-4-carboxylic acid in concentration 0.07 g/l in a colouring bath which contains 30 g/l $NiSO_4.6H_2O$, 30 g/l H_3BO_3 has a positive influence on colour uniformity and intensivity of anodized aluminium probes treated in this solution at 15 V AC.

The mechanism of the action of this additive on the ac electrolytic colouring of anodized aluminium from nickel sulfate solutions was investigated. The boat conformation of this additive which permits its opposite charges to have the right distance was correlated with the ability of the additive to be adsorbed on the electrode surface in spite of the alternating current and to interfere in the re-anodizing process and in the nickel deposition rate and distribution.

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THE INFLUENCE OF MECHANICAL ACTIVATION OF FRANCOLITE ON THE AMOUNT OF AVAILABLE P_2O_5.

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ABSTRACT

Francolite (Carbonate apatite) is separated by Silverman method from Epirus deposit phosphorite. The chemical analysis and the XRD pattern confirmed that the separated sample was almost pure francolite. The mechanical activation of francolite were carried out by a planetary mill for activation times of 1, 2, 4, 8, 16 and 32 h. We determined the amount of available P_2O_5, particle size distribution and specific surface area of raw and activated samples.

The results showed that the amount of available P_2O_5 is increased from 11.93 % to 69.73 % during the mechanical activation up to grinding time of 16 h in two individual sharp steps from 0 to 2 h and from 8 to 16 h respectively. The above mentioned increase does not closely depend from the increase of specific surface area and the mean particle size of the activated francolite. A coagulation process occurs after 4 h grinding treatment, as indicated the particle size distribution results. The ratio of the change of available P_2O_5 amount with the change of specific surface area during the activation, had a maximum at 2 h activation time. Thus the optimum activation time seems to be the 2 h which led in an available P_2O_5 amount of about 51%.

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PRODUCTION OF Mo POWDER AND Fe,Ni,Mo ALLOY POWDER BY A HYDROMETALLURGICAL PROCESS OF FERROUS SCRAP

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ABSTRACT

The recovery of metals from industrial wastes or byproducts such as slags,scraps e.t.c. has consisted the scope of continuous recearch.Development of metal recovery process is imposed by the decrease of ores deposit as well as by the enviromental problems caused by the rejection of such waste materials.

In this study the development of a hydrometallurgical process is presented according to which the recovery of Mo and Fe,Ni,Mo alloys from ferrous scrap in powder form,appropriate for powder metallurgical purposes is feasible.Experiments have been performed on the dissolution of scrap,solvent extraction and reduction of metal chlorides to Mo powder.Metal chlorides (Fe,Ni,Mo) were used as raw materials for the production of Fe-Ni, Fe-Mo alloys by simultaneously reduction of the material and the parameters of the process have been estimated.

The dissolution of the ferrous scrap was carried out by HCl 20% w/w at T=80°C,t=1.5h,solvent extraction was studied according the pH of the solution and the concentration of metals.Silicon powder and hydrogen were the reductants used during the experiments for the production correspondigly of Mo and alloy powder at T=400-450°C and t=4-7h.Physicochemical characteristics measured were the chemical purity (99.8%) and the granulometric distribution (-200+56μ,80%) and were of very satisfactory values.

The low cost of the initial raw material, the use of commercial grade chemicals,the advantange of recycling the byproducts of the process and quality of the final product are some economical aspects which makes the described process quite attractive.

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TEMPERATURE DEPENDENCE OF THE VISCOSITY OF DILUTE POLY(CYCLOALKYL METHACRYLATES) SOLUTIONS

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ABSTRACT

Actual viscosity measurements of dilute solutions of poly(cyclopentyl-), poly(cyclooctyl-) and poly(cyclododecylmethacrylate) in different solvents and temperatures were carried out. The polymethacrylates studied here cover a molecular weight range from 0,29 10^5 to 48 10^5 and polydispersity M_w/M_n from 1,2 to 1,4.

The temperature dependence of the actual viscosity is described by an Arrhenius expression

$$\eta = A \exp (Q / RT) \qquad (1)$$

where Q is the apparent energy for the viscous flow and A is a pre-exponential term with an activation entropy significance. The plots of ln η against 1/T support the validity of equation (1).

In equation (1), Q varies with solvent, polymer concentration and polymer molecular weight according the equation

$$Q = Q_o + K_e M C \qquad (2)$$

where Q_o is the activation energy of viscous flow for the pure solvent, K_e is a constant for a particular polymer- solvent system, M is molecular weight and C is concentration.

The A term in equation (1) also depends on molecular weight and concentration. For flexible chains Moore suggested

$$A = A_o \exp (K_\beta M^\beta C) \qquad (3)$$

where A_o refers to the solvent and K_β and β are characteristic system-dependent constants.

The K_e constants are obtained from the plots of K_eM against M and was found that the difference of K_e are in agreement with the differences in the flexibility of these flexible macromolecular chains. All the experimental results were found to fit the emperical relationships suggested by Moore for flexible polymer chains.

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STABILIZATION PROGRESS OF POLYACRYLONITRILE FIBERS AND ITS COPOLYMERS BY DSC AS FIRST STEP FOR CARBON FIBER PRODUCTION

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ABSTRACT

The production of carbon fibers based on polyacrylonitrile (PAN) fibers consists of a low temperature oxidative stabilization, usually in air, and a high temperature pyrolysis, in inert atmosphere. The stabilization occurs at temperatures between 200°C and 300°C for sufficient time and proper stretching while the pyrolysis step takes place at temperatures between 800°C and 1500°C or more according to applications.

PAN fibers (homopolymer and copolymer) were stabilized in an air circulated furnace under proper conditions keeping constant length. The stabilization-oxidation process of polyacrylonitrile fibres and copolymer fibres was investigated by Differential Scanning Calorimetry (DSC). The cyclization of nitrile groups is the main reaction during the oxidation of PAN fibers, leading to a ladder type polymer. Cyclization is followed by an exotherm, different for each type of fiber.

The homopolymer shows a higher onset temperature T_0, stronger peak-intensity, more narrow temperature width and higher ΔH. By increasing the oxidation temperature of homopolymer fibres the T_0 and T_{max} are shifted to higher temperatures and the peak-intensity as well as ΔH decrease. The exothermic curves of the copolymer fibres, as the oxidation temperature increases, range from 273-305°C, the peak-intensity and ΔH decrease. In addition, stabilization at temperatures lower than 200°C needs long periods of heating for suitable cyclization.

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MACROMOLECULAR ARCHITECTURE WITH POLAR MONOMERS. METHACRYLIC ESTERS

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ABSTRACT

The synthesis of polymers with well defined architectures (stars, combs, cyclic) is possible by the use of anionic polymerization of non polar monomers, such as styrene, isoprene, butadiene, and the use of chlorosilane chemistry. Such polymers are of great academic and industrial interest, because they are used to study the relationship between the structure of the polymer and its properties.

In the case of polar monomers, such as methacrylic esters, macromolecular architecture is much more difficult. Anionic polymerization of polar monomers takes place in different conditions comparing to non polar monomers. Non polar monomers are polymerised using s-BuLi as initiator, non polar solvents such as benzene and room temperature. In order to polymerise anionically methacrylic esters bulky initiator systems such as diphenylhexyllithium, polar solvents such as tetrahydrofuran and low temperatures (-78°C) are used. In such conditions, side reactions, like the reaction of the initiator (s-BuLi) with the carbonyl group of the ester, are avoided. The carbanions of the methacrylic esters are less reactive and less stable compared to the carbanions of the non polar monomers. So chlorosilane chemistry can not be applied at -78°C. Instead of chlorosilanes, bromomethylated aromatic compounds are used for macromolecular architecture with polar monomers.These compounds can react fast enough with the less reactive, less stable carbanions of the methacrylic esters, at -78°C, conditions favoring prolonged linking reaction duration. Post polymerization reactions such as the hydrolysis of poly (tert- butyl methacrylate) lead to model polymethacrylic acid. This method can be used for the synthesis of block copolymers with one hydrophobic (such as PS, PI, PBd) and one hydrophilic (PMAA) block. The profound advantage of such chemistry is the synthesis of ion containing polymers (polyelectrolytes / ionomers) with complex architectures.

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SYNTHESIS AND CHARACTERIZATION OF 16-MIKTOARM STAR COPOLYMERS OF THE A_8B_8 TYPE. VERGINA STAR POLYMERS.

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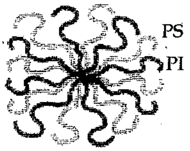
ABSTRACT

Model star polymers are best prepared by coupling of anionic living polymers with multifunctional electrophilic coupling agents. Except from multifunctional chlorosilane compounds other coupling agents do not extend the functionality of the stars beyond f=6. Even with the chlorosilane compounds incomplete coupling was observed. This was avoided by limiting the number of chlorine atoms per silicon atom to two and by seperating the silicon atoms by ethylene spacers. The reaction of such chlorosilane compound with 16 reactive chlorine atoms and ω-functionalized macromolecules prepared from anionic polymerization resulted the synthesis of well-defined, near monodispersed miktoarm star copolymers of the A_8B_8 type where A is polystyrene and B is polyisoprene.

The synthetic approch involves the synthesis of a coupling agent with 16 chlorine atoms $Si\{(CH_2)_2Si(CH_3)[(CH_2)_2Si(CH_3)Cl_2]_2\}_4$, the reaction of this compound with an appropriate quantity of polystyryllithium in order to incorporate only 8 polystyrene branches and finally the reaction of the produced $(PS)_8SiCl_8$ with a small excess of polyisoprenyllithium. After linking the excess of the polyisoprenyllithium was terminated with methanol and removed by fractionation. Characterization of the copolymers was carried out by size-exclusion chromatography, low-angle laser light scattering, laser differential refractometry, membrane osmometry, NMR and UV spectroscopy. The results indicated that the prepared copolymers have a high degree of molecular and compositional homogeneity.



The name "Vergina star" copolymers was given because of the similarity to the 16-rayed star discovered by Professor M. Adronikos of the University of Thessaloniki, in the ancient tomp of Philip of Macedonia in Vergina, a place close to Thessaloniki.

Chimika Chronika, New Series, 26, 175 (1997)

SYNTHESIS OF A HIGH MOLECULAR WEIGHT PS-b-PI
A unique material for polymer physics

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ABSTRACT

High molecular weight block copolymers are very usefull materials for physical properties studies such as structure factor by light scattering, which are not possible in the case of low molecular weight materials. Although linear diblocks with relatively low molecular weight have been prepared, the synthesis of a high molecular weight diblock was not accessible, due to the very low initiator concentration. By using anionic polymerization and extra purification procedures for monomers, initiator and solvent, the synthesis of a linear diblock with more than one million molecular weight has been accomplished.

Initially, the polystyryllithium block was prepared and a small aliquot was removed for characterization. The polymerization was completed after the addition of the isoprene monomer. Typical polymerization times were one day for each block polymerization. The sec trace of the final polymer revealed some termination of the living polystyryllithium due to the trace impurities present in isoprene monomer. This amount of terminated polystyrene precursor was removed by fractionation. The fractionation was preformed, in many cycles, by adding methanol in a mixture of toluene and hexane. The presence of hexane promotes the selective precipitation of polystyrene. Characterization of the diblock and the precursor was carried out by size-exclusion chromatography, low-angle laser light scattering, laser differential refractometry, mambrane osmometry, NMR and UV spectroscopy. The results indicated that the diblock has a high degree of molecular and compositional homogeneity and a small molecular weight distribution as well.

The properties of such a material are currently investigated and the results will appear soon in the literature. Photon correlation spectroscopy is been used to investigate the dynamics of concentration fluctuation in disordered semidilute solutions of the diblock. Also the diblock's phase behavior is studied because this material, due to its high molecular weight, is expected to form highly oriented lammelar structure with a large domain size.

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Synthesis, Characterization and Aggregation Phenomena of $(PE)_2(PEP)_2$ Miktoarm Star Copolymers

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ABSTRACT

The synthesis of partially deuterated $(PE)_2(PEP)_2$ miktoarm star copolymers was carried out using anionic polymerization and hydrogenation techniques. The synthetic approach involves the reaction of tetrachlorosilane with styrene capped macroanions of polyisoprene (PI) so that only two chains are incorporated in the star. This stage is followed by the addition of a small excess of d-polybutadiene living chains. The $(PI)_2(d\text{-}PBd)_2$ star thus obtained is converted to $(PE)_2(PEP)_2$ by hydrogenation.

Due to the ability of PE to crystallize, these stars are expected to form micelles in solution. The aggregation phenomena of these copolymers in decane were studied using SANS. "Hamburger" like micelles were found to be formed. The core was consisting of the crystalline PE, while the brush was consisting of the amorphous PEP. The exact structure of these micelles was determined by fitting of the experimental scattering profiles with theoretical curves. We found that by increasing the molecular weight of the PEP arms, the lamellar thickness of PI was decreasing, while the degree of extension of the PEP chains was increased.

Chimika Chronika, New Series, 26, 177 (1997)

LIQUID CRYSTALS DERIVED FROM AMPHIPHILIC QUATERNARY AMMONIUM SALTS FUNCTIONALIZED WITH CHARACTERISTIC GROUPS

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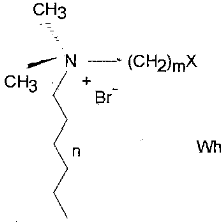
ABSTRACT

It is well established that the amphiphilic character is directly associated with the appearance of liquid crystallinity. In the present study we examine certain amphiphilic quaternary ammonium salts that exhibit smectic thermotropic liquid crystalline phases. The variation of the properties resulting from their functionalization with characteristic groups inducing intermolecular binding of the molecules is investigated.

Specifically we have synthesized by the standard quaternization reaction a series of quaternary ammonium salts bearing cyano- carboxy- and hydroxy-groups at the end of a side carbon chain of variable length (m) and having an equally variable main chain (n) as depicted below.



Where n = 12-18
for X = CN m = 3 - 6
for X = OH m = 2, 3, 6
for X = COOH m = 1, 10

All the quaternary ammonium salts exhibited liquid crystalline behavior as observed in the polarized microscope, with the exception of those with the hydroxy group having m=2 that decomposed before melting. The liquid crystalline character was proven by Differential Scanning Calorimetry (DSC) and X-Ray analysis. The variation of the transition temperatures and enthalpies as revealed by DSC was indicative of the different organizational characteristics induced by the functional groups and the length of the alkyl chains. The X-Ray diffraction patterns at increasing temperatures were indicative of a transition from the crystalline single layered lamellar structure to the double layered smectic structure.

Chimika Chronika, New Series, 26, 178 (1997)

AMPHOTROPIC CHARACTER OF DIALKYL PHOSPHATE SALTS

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ABSTRACT

The preparation and characterization of synthetic vesicles, monomeric and polymerized, have received significant interest for both scientific and technological reasons. The most widely investigated representative of vesicles is dixehadecylphosphate (DHP). In the present investigation the cationic counter ion is changed and its effect on the amphotropic properties of dihexadecyl phosphate salts is investigated. The cationic ions employed are Li, K, Na and Cs.

Dihexadecylphosphate was prepared by the interaction of $POCl_3$ with a threefold amount of hexadecanol. The precipitated material was recrystallized from methanol. The salts were prepared by the reaction of equimolar quantities of dihexadecylphosphate and alkali hydroxides which subsequently were recrystallized from ethanol.

The liposomes were prepared by the vaporisation method of Deamer and Bangham. The liposomes were characterized using AFM microscopy. It has been found that these salts form vesicles in water which are smaller than the ones originating from the dihexadecylphosphate. Specifically, dihexadecylphosphate liposomes have sizes ranging between 90 to 300 nm while the liposomes derived from the salts range from 50 to 200 nm. The liposomes exhibit very good stability.

Additionally, the same compounds exhibit thermotropic smectic liquid crystalline phases which are stable over a wide temperature range, i.e., from 80^0 C up to 300^0 C. An exception is the lithium salt which exhibits a liquid crystalline phase up to 85^0 C.

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NOVEL LIQUID CRYSTALS INDUCED BY MOLECULAR RECOGNITION THROUGH HYDROGEN BONDING.

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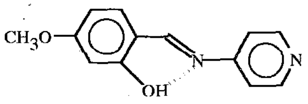
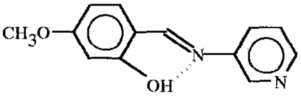
ABSTRACT

Hydrogen bonding interaction between similar and, dissimilar molecules has extensively been used for the formation of liquid crystals in the recent years. The pair of acceptor-donor molecules used for the formation of the complex may or may not be mesomorphic. Molecules bearing pyridyl and carboxylic moieties have been proven very useful for the formation of rid-rod type liquid crystals through hydrogen bonding.

In the present study, two new acceptors bearing the pyridyl group were synthesized, i. e., N-(p-methoxy-o-hydroxybenzylidene)-p-aminopyridine (I) and N-(p-methoxy-o-hydroxybenzylidene)-m-aminopyridine (II). The interaction of these anils with p-alkoxy-benzoic acids results in the formation of liquid crystals. Specifically, as established by optical microscopy, DSC and X-ray diffraction studies, complexes of I with short-chain acids afford nematic phases, complexes with long alkyl chain acids exhibit smectic and nematic phases while only smectic phases are induced with acids bearing a very long alkyl chain. In the complexes derived from anil II only the acids with long alkyl chains induce the formation of nematic and smectic phases.



I



II

Chimika Chronika, New Series, 26, 180 (1997)

DYEING OF COTTON AND WOOL FIBRES WITH NATURAL PIGMENTS. EFFECT OF ENZYMATIC TREATMENT ON THE DYEING

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ABSTRACT

Cotton and wool samples were dyed with the natural pigments crocin and a mixture of shiconin esters. Dyeing was also carried out after treatment of the cotton and wool samples with amylase and trypsin respectively. Wash fastness of the dyed samples was also studied. Enzymatic treatment resulted in an increase in crocin uptake in both cases, compared to the corresponding untreated samples, whereas it didn’t affect wash fastness.

Chimika Chronika, New Series, 26, 181 (1997)

Parameter Estimation of an Abrasion Model for Wool Fabrics Treated with Polymers

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ABSTRACT

Shrink-resist treatment of wool fabrics with polymers can improve also resistance to abrasion. In this paper, the following three parameter model of asymptotic dependence of abrasion resistance Y on polymer content X of fabrics is suggested:

$$Y = Y_\infty - (Y_\infty - Y_0) \cdot e^{-kX}$$

where Y_0, Y_∞, are the Y-values for X=0, X→saturation, respectively, and k is the constant of Y-change. Fitting of this model to experimental values by means of non-linear regression (through a new version of the Complex algorithm based on internal constraints forming local optima) gives satisfactory results; nevertheless sensitivity analysis proves k to be quite insensitive in some cases due to accumulation of experimental points near the asymptote as data were extracted from experiments on shrink-resist treatment where low-polymer content measurements were not carried out because of lack of industrial interest. The estimated parameter values show that treatment with the DLH-polymer can increase abrasion resistance from 84% to 643% for light-weight-worsted and flannel fabrics, respectively.

Chimika Chronika, New Series, 26, 182 (1997)

A NEW COLORATION OF ANODIZED ALUMINIUM BY THE A-C COLORING IN THE PRESENCE OF AN ORGANIC DYE.

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ABSTRACT

The A-C coloring of anodized aluminum from acidic tin (II) sulfate solutions with the presence of the dye with C.I. 63010 gave colored probes with a blue hue and high fastness properties. It was observed that the presence of the dye decreased the deposition rate of tin, as well as the throwing power of the coloring bath. The optimum conditions of concentration of the dye and the time of coloring treatment were determined. Thus the dye concentration shall not exceed the 7.5 g/l in the case where the coloring treatment takes place in a bath containing 2.75% w/v H_2SO_4 and 1.5% w/v $SnSO_4$ at 15V A-C for 1 minute.
The mechanism of the action of this organic dye was also investigated.

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IMPROVEMENT OF GROUT PROPERTIES BY ADDITION OF SULPHONATED NAPTHALENE-FORMALDEHYDE ADMIXTURE

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ABSTRACT

Grouts are extensively used for the enforcement of foundations, underground works, tunnels, abutments, core of dams and soils. The water to cement ratio for the preparation of grouts varies within the range of 5:1 to 1:2 according to the application. Lower ratios give better mechanical and physical properties to the grout but affect negatively its workability. To give the required workability to the grouts with low water to cement ratios, specific admixtures, containing usually organic surfactants substances are added.

The studied admixture is containing sulphonated naphthalene-formaldehyde. This admixture, when added in low percentages in hydraulic cement (type II/45, Blain specific surface above 4500 cm^2/g) grouts, with small water to cement ratio, found to be very effective, affecting positively their efflux, setting time and mechanical strength. The optimum additions determined were 2, 5 and 6 %wt of cement, for grouts with 1:2.5, 1:3 and 1:3.5 water to cement ratio, respectively. The values obtained for efflux, setting time and mechanical strength, (determined according to ASTM and Greek cement-concrete regulations), were in the optimum region and within the required limits for grout applications.

Chimika Chronika, New Series, 26, 184 (1997)

STRENGTH DEVELOPMENT OF PORTLAND LIMESTONE CEMENTS

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ABSTRACT

The European Prestandard ENV 197-1(1995) specifies the properties of the constituents of common cements and the proportions in which they are to be combined to produce a range of types and classes of cement. It also specifies the mechanical, physical and chemical requirements for these types and classes and states the rules for accessing their conformity to these requirements. According to the above Standard the cements containing limestone are Type II/A-L, permitting 6-20% limestone and II/B-L permitting 21-35% limestone. The Greek Standard allows the incorporation of up to 3% by mass of limestone in cements as filler. The main advantages of the production of Portland limestone cements are the decrease of the fuel consumption and the corresponding environmental relief.

In this paper the strength development, in relation to the cement fineness and the limestone content and quality, is investigated. Portland limestone cements of different fineness (3300-5900cm^2/g) and limestone content (5-35%) have been produced by intergrinding of clinker, gypsum and limestone. Three types of limestone, with different content of calcite, dolomite and clay, have been used. The compressive strength of the cements after 1, 2, 7 and 28 days has been measured according to the Greek Standard.

It is shown that the cements II/A-L satisfy the requirements of the strength classes 52.5, 42.5R and 42.5, while the cements II/B-L satisfy the requirements of the strength classes 42.5R, 42.5, 32.5R and 32.5. The limestone quality, if it meets the European requirements, does not significantly affect the strength development of cements.

Chimika Chronika, New Series, 26, 185 (1997)

SHRINKPROOFING TREATMENT OF WOOLLEN FABRIC BY GRAFTING WITH METHACRYLATES

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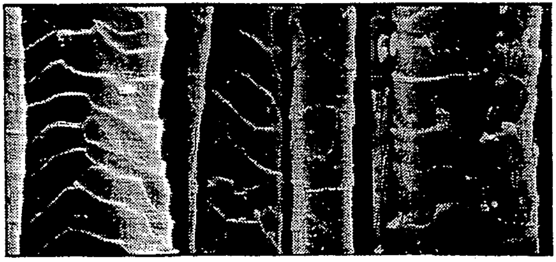
Abstract

The dimensional stability of woollen fabric in washing is one of the most important factors affecting the fabric's serviceability.

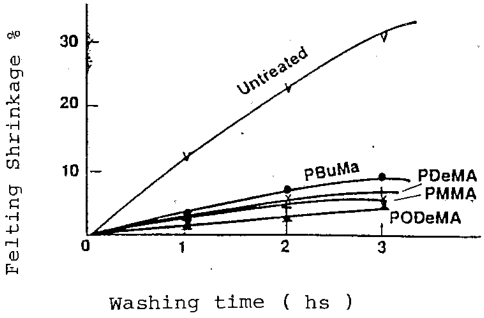
In this paper woollen fabric becomes shrinkproofing after grafting with methyl (MMA), n-butyl (BuMA), n-decyl (DeMA) and n-octadecyl methacrylate (ODeMA).

The evidence of grafting was provided by scanning electron microscopy.



Untreated Wool Wool-g-PMMA

The measurements of felting were carried out according to method of the International Wool Secretariat.



Effect of washing time on felting shrinkage.

Chimika Chronika, New Series, 26, 186 (1997)

SYNTHESIS OF BLOCK COPOLYMERS OF N-SUBSTITUTED METHACRYLAMIDES BY LIVING RADICAL POLYMERIZATION

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ABSTRACT

Radical polymerization of N-substituted methacrylamides in benzene (initiated by UV-high pressure Hg lamp , ditertbutylperoxide as initiator) leads to the formation of stable "living" propagating radicals. These "living" radicals react with a second monomer to produce block copolymers. As a second monomer were used:.methyl acrylate, methyl methacrylate, butyl methacrylate, styrene, isoprene, acrylnitrile, vinyl acetate. When the second monomer is a solvent of polymeric radicals, they "die" and the heterogeneous mixture becomes homogeneous. When the second monomer is not solvent for the first monomer, the radicals remain stable and "live". The addition of a third monomer (styrene or isoprene) gave the propagating radicals of this third monomer. High vacuum techniques were used during all homo- and co- polymerizations.

After precipitation of the polymers in ether, followed Soxhlet extraction of the copolymer as the insoluble residue. Benzene and methanol were used as solvents.

Homo and copolymers were characterized by Infrared Spectroscopy (IR), Nuclear Magnetic Resonance Spectroscopy (NMR),Size Exclusion Chromatography (SEC), Laser Defraction Refractometry(LDR), Low Angle Laser Light Scattering (LALLS) and Differential Scanning Calorimetry (DSC).

Chimika Chronika, New Series, 26, 187 (1997)

CHEMILUMINESCENCE ARISING FROM THE OXIDATION OF BILIRUBIN IN AQUEOUS MEDIA

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ABSTRACT

Chemiluminescence (CL) can be defined as the production of electromagnetic radiation by a chemical reaction. CL is observed in solid-, gas- and liquid-phase reactions and all have been used analytically. In solution, CL finds many applications in analytical chemistry for the determination of metal ions, inorganic anions, biomolecules, carcinogens and drugs in a variety of environmental and clinical matrices. The advantages of CL for analysis include high sensitivity and a wide linear dynamic range, both of which can generally be achieved with simple instrumentation.

Bilirubin, a catabolic product of hemoglobin and heme proteins, is a compound of great biological interest since it is found in human plasma. Analytical methods currently used for the determination of bilirubin are, usually, spectrophotometric (direct or after diazo reaction), enzymatic and HPLC methods, but are prone to interferences and they lack simplicity and sensitivity. Thus, a simple, fast and reliable method is required for the assay of the compound.

It was found that bilirubin generates chemiluminescence during the action of various oxidizing agents, such as N-bromosuccinimide, hypochlorite and ferricyanide. The first two oxidants generated the most intense radiation and the corresponding reactions were monitored kinetically by using a batch chemiluminometer. The fast reaction of bilirubin with N-bromosuccinimide was established in a flow injection system and the slow reaction with hypochlorite was established in a continuous flow system, so that the procedure could be automated. The results indicate that both procedures are very sensitive since bilirubin at concentrations of less than 1 μg ml^{-1} can be easily and reproducibly measured.

Chimika Chronika, New Series, 26, 188 (1997)

ATOMIZATION MECHANISM OF CHROMIUM IN ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

The atomization mechanism of chromium was investigated with ETAAS experiments. The kinetic parameters of atomization (such as the activation energy, E_a, and the order of release, x) were calculated from atomic absorption signals using Arrhenius-type plots. The influence of the pyrolysis temperature (T_{pyr}), heating rate (dT/dt), sample mass and the condition of the pyrolytic surface of the graphite tube on these parameters was investigated. It was found that chromium atoms are produced in the gas phase by thermal desorption of adsorbed chromium and that this is a first-order process. Used graphite tubes and/or $T_{pyr} \geq 1300°C$ probably promote the formation of Cr_3C_2 and therefore the atomization mechanism includes two steps: (I) the thermal decomposition of chromium carbide and (II) the thermal desorption of adsorbed chromium.

Chimika Chronika, New Series, 26, 189 (1997)

ORGANOMETALLIC COMPOUNDS AS CARRIERS IN CHEMICAL SENSORS

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ABSTRACT

The search for selective anion carriers has recently directed to coordinating organometallic agents, some of which containing cobalt, mercury and manganese. Different organotin compounds have also been used as carriers for various anions like chloride, salicylate, thiocyanate and phosphate. The main interest of this presentation will be focused on inorganic phosphate selective electrode based on multidentate organotin compounds. Structural parameters that determine selectivity of these carriers towards phosphate as well as other sensor characteristics will be discussed.

Chimika Chronika, New Series, 26, 190 (1997)

QUALITY CONTROL OF PROTEINS LABELLED WITH ^{99m}Tc. DETERMINATION OF RADIOCHEMICAL IMPURITIES

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Ag. Paraskevi Attikis, 15310

ABSTRACT

Technetium-99m still remains the most attractive radionuclide for the diagnostic application of radiolabelled biomolecules. Technetium-99m labelled Monoclonal Antibodies have been widely used in diagnosis. We have previusly investigated two labelling methods for the preparation of ^{99m}Tc-antiCEA. These were protein coupling with 2-iminothiolane and protein reduction by 2-mercapto-ethanol. Although both of them had a high labelling yield (>95%) and resulted to immunoreactive and stable derivatives, we have found that partial modification of the protein was caused during the labelling reaction, as revealed by HPLC, PAGE and animal studies.

In the present study we have focused our interest on the above protein modification, as well as on radiochemical impurities formed by the methods applied. Using radiochemical and radiobiological techniques, we have studied the impurities consistently produced during the labelling.

Further on we have experimentally reproduced in high yield the impurities usually formed and we have studied labelling factors, in order to avoid or eliminate their formation. The detailed investigation of each species will resul in improved labelling procedures, leading to more specific radiolabelled MoAbs.

Chimika Chronika, New Series, 26, 191 (1997)

APPLICATION OF A EUTROPHICATION MODEL IN THE MANAGEMENT OF COASTAL AREAS

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ABSTRACT

Eutrophication, the result of human-induced nutrient enrichment of sea-water is one of the most common causes for the deterioration of coastal ecosystems. The assessment of eutrophication levels is rather complicated because of the ecosystem complexity, the seasonal trends and the biological variations. However, the identification of discrete states of anthropogenic pollution is required by policy-makers for the implementation of different management strategies on the coastal zone. The determination of different levels of eutrophication is usually based on ecological parameters, but more recently multivariate statistical analysis and simulation models have been used for the understanding of the relationships between nutrients and the resulting phytoplanktonic growth. In the present work, a eutrophication model has been applied on two different coastal ecosystems in Greece, based on the available data sets from oceanographic surveys. Temperature, irradiance and nutrient loadings were the most important driving forces. A time step of 1- day was used and a zero-dimensional spatial resolution was applied for each of the sampling locations. Simulation on the ten stations on the coastal area of the city of Rodos (island of Rodos), resulted into three different seasonal patterns according to the maximum phytoplanktonic growth. Similar differences were observed at the two stations on the coastal area of the city of Mytilini (Lesvos islsnd) and the evaluation of the differences between the observed and the simulation values was performed with a non-parametric method. The examination of the modelling procedure at different ecosystems with satisfactory results suggests the further application of the model at water quality studies and the testing of its performance under different management strategies.

Chimika Chronika, New Series, 26, 192 (1997)

VOLATILE SECONDARY METABOLITES OF MARINE ORGANISMS

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1] School of Pharmacy, Division of Pharmacognosy
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ABSTRACT

The volatile secondary metabolites produced by a number of marine organisms were isolated by means of dynamic head space methods and identified by spectroscopic methods. The importance of them as potential tools for chemotaxonomic purposes is discussed.

The volatile constituents of terrestrial plants, over the past decades, have been proven valuable tools for biosystematic and chemotaxonomic investigations. In this work the volatile secondary metabolites of several marine organisms is studied. Care was taken so that the methods used would be as much as possible artifact-free and the trapped chemicals would represent the volatile emissions of the live organisms. A closed loop stripper system was modified according to the needs of this work so as to host the organisms in sea water and allow us to efficiently collect the chemicals that the organisms would liberate in their in their natural environment.

The structure of the compounds was elucidated mainly by means of Mass Spectrometry and Nuclear Magnetic Resonance Spectrometry. The chemical classes of the identified metabolites range from very small linear hydrocarbons to oxygenated terpenes. Very interestingly it was found that a green algae produced significant quantities of small toxic halogenated hydrocarbons.

Chimika Chronika, New Series, 26, 193 (1997)

DETERMINATION OF DMS BY GAS-CHROMATOGRAPHY AND IT'S RELATIONSHIP WITH PHYTOPLANKTON IN SARONICOS GULF

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NATIONAL CENTER FOR SCIENTIFIC RESEARCH "DEMOKRITOS"

ABSTRACT

The biogenic sulfur gas, Dimethyl sulfide (DMS), is the major volatile compound in the sulfur cycle. The oceans contribute ›50% of the global emission of DMS, therefore, the biogeochemical cycling of DMS in seawater is of great interest.

DMS was investigated in two stations (one eutrophic and one oligotrophic) of Saronicos Gulf, Aegean Sea. Water samples were collected from the surface microlayer (upper 1mm) and the bulk water and they were analyzed for DMS by Gas Chromatography as well as for physical (temperature, salinity), chemical (phosphates, nitrates, ammonia, silicates) and biological (chlorophyll α, primary production, phytoplankton cells) parameters. DMS is removed from water samples by sparging with a He carrier gas stream. The volatile DMS is trapped cryogenically with liquid nitrogen on a chromatography column thus serves as both the trapping and the separation mechanism. After the separation DMS is detected by a flame photometric detector (F.P.D.)

The concentration of DMS+DMSP showed a significant trend from eutrophic to oligotrophic conditions. Thus the mean concentration in the eutrophic station ranged from 7.2 to 12.79 $nmol.l^{-1}$ and in the oligotrophic station 1.94-8.93 $nmol.l^{-1}$. The correlations between DMS+DMSP and chlorophyll α and temperature were statistically significant.

Chimika Chronika, New Series, 26, 194 (1997)

CHEMICAL CHARACTERIZATION OF ORGANIC AEROSOLS EMITTED FROM AN OLIVE-STONE PRESS INDUSTRY. DISPERSION TO THE SURROUNDING ATMOSPHERE.

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ABSTRACT

It is well known that olive's elaboration produce solid, liquid and gases wastes. The purpose of this work was a)the chemical characterization and b)the dispersion of organic aerosols emitted from an olive-stone press industry in Heraclion,Crete.

Samples collected at the middle of the chimney and from two different posistions near the industry during winter. Qualitative and quantitative determinations have been done using gas chromatography eqquiped with mass spectroscopy and flame ionization detector. For the dispersion model adapted Sutton equations to predict Pasquill curves. For the origin determination diagnostic ratios calculated from the analysis: a)Carbon Preference Index(CPI) b)Unresolved Complex Mixture/Total Resolved Alkanes (UCM/TRA) c)PAHs diagnostic ratios have been used.

Organic aerosols emitted from the chimney contained n-alkanes, polycyclic aromatic hydrocarbons, n-alkanals and n-alkanols, free fatty acids and their salts. Their distribution and diagnostic ratios values are characteristic of biogenic origin and confirmed biomass burning as the major source. The presence of low molecular polar compounds is responsible for the odour. In contrast, organic aerosols collected from the surrounding gave a different profile. The distribution of each homologue and the diagnostic ratios values indicate two main input sources, continental higher plants and petroleum and more or less complete combustion of organic matter.

Using Sutton equation for the organic aerosols emitted from the industry to predict aerosols concentrations at the two positions and compared with measured concentrations concluded that there is no obvious direct influence to the surrounding atmosphere.

Chimika Chronika, New Series, 26, 195 (1997)

DETERMINATION OF CARBAMATE PESTICIDE RESIDUES BY HPLC AND AND POST COLUMN DERIVATIZATION IN NATURAL WATERS OF GREECE

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ABSTRACT

In the past years organochlorine and organophosphorus pesticide residues were monitored in natural surface waters of Greece and determined by the use of gas chromatography. In the present study the solid phase extraction technique combined with liquid chromatography-post column derivatization, that was first applied by Moye et al., were used for the determination of 11 N-methyl carbamate compounds in natural waters of Greece. The limit of determination of the method used was between 0.1 and 0.5 μg/L for the above compounds, while the MRLs that have been set by the European Community for the surface waters are 1-3 μg/L. 44 samples of water samples taken from various rivers and lakes all over Greece were analyzed according to the method and propoxur was found in the water of the lakes Pamvotis and Orestiada, at concentrations 1.3 and 2.7 μg/L respectively. Since propoxur has approved uses in Greece for the control of insects in houses and storage areas, and the area around the two lakes has not been used for extensive agricultural production, the detection of propoxur in these lakes may be attributed to such uses rather than to agricultural ones.

Chimika Chronika, New Series, 26, 196 (1997)

APPLICATION OF A CHEMILUMINESCENT REACTION TO THE ESTIMATION OF THE ORGANIC CONTENT OF SOIL

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Various soil samples from the outskirts of Ioannina, Greece, were collected and analysed for their organic content by means of the chemiluminescent reaction of KIO_4 with the pyrogallol groups contained in humus. Prior to the analysis, the samples were suspended in 0.5 M NaOH solution for the extraction of humic acids. The supernatant liquid was then injected into a flow injection system, which allowed the acids to react with KIO_4 in front of the detector (photomultiplier tube). The signal corresponding to the power of the light emitted was recorded and the samples were ranked according to their organic content. The analysis-of-variance technique was used on the results obtained to calculate the effects of the factors: origin and sampling homogeneity. These factors as well as their interaction were found to be significant at the $p=0.0001$ level.

The samples were also ashed and the correlation between the two methods was estimated by way of the Spearman test. Correlation was statistically significant at the $p=0.137$ level. From the UV-VIS spectrum of humic acid it was evident that the spectrophotometric analysis of the samples is difficult at the wavelengths suggested in the literature ($\lambda \approx 350$ nm).

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DETERMINATION OF CARBAMAZEPINE AND VALPROIC ACID IN HUMAN HEAD HAIR

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The determination of drugs by enzymeimmunoassay techniques in the hair of human subjects is an effective mean to toxicologists and clinicians. Carbamazepine and valproic acid are two of the important antiepileptic drugs and have been evaluated in the management of various psychotic disorders together with other antipsychotics drugs and lithium. We study some techniques to determine these drugs in hair of patients. The experiments were positive for the detection of the drugs. The relation between the drug dose and drug levels of the hair has to be enlighted with further study.

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SIMULTANEOUS VOLTAMMETRIC DETERMINATION OF MOLYBDENUM AND COPPER IN BIOLOGICAL SAMPLES

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ABSTRACT

This paper deals with the development of a voltammetric method for the simultaneous determination of molybdenum and copper in biological samples. The method is based on the formation of molybdate and copper complexes with 8-hydroxyquinoline (oxine) as a chelating agent, and on the application of the adsorptive stripping voltammetry (DPAdSV) in an 0.45 M acidic chloride media. The molybdenum complex gives two reduction peaks at -0.52V and -0.58V, respectively, while the copper complex only one at -0.14V. Heavy metals commonly present in biological materials do not interfere at all. The detection limit is 0.29 ng for molybdenum and 0.14 ng for copper *per* ml of cell solution; the RSD at concentration level of 10 ng/ml is 5.3% for molybdenum and 3.8% for copper; especially for the copper, the results obtained by the proposed method are well compared with those taken by atomic absorption spectrophotometry. Thus, the method may be considered selective, sensitive and reliable. Besides, the method can be applied successfully in biological materials, such as liver and various animal foodstuffs, after appropriate wet digestion by a mixture of concentrated sulfuric, nitric, and perchloric acids.

Chimika Chronika, New Series, 26, 199 (1997)

DETERMINATION OF ASCORBIC ACID IN DIETARY SUPPLEMENTS BY MEANS OF THE CHEMILUMINESCENT SYSTEM OF KIO_4 - PYROGALLOL

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Ascorbic acid became known through scurvy and the possible cures for the disease. Scurvy was common among early sea travellers and it is now known to be a deficiency disease that produces haemorrhaging into the tissues, bleeding gums, loose teeth, anaemia and general weakness. It can be fatal if left untreated, but the patient can easily recover after he has being dosed with small amounts of ascorbic acid. The biochemistry of vitamin C is complicated and has not been fully understood. Among other reactions, ascorbic acid participates in the hydroxylation of certain amino acids, leading to the formation of hydroxyproline and hydroxylysine. These hydroxy compounds are constituents of collagen and this fact alone explains most of the symptoms of scurvy: in the absence of vitamin C the two hydroxylated amino acids and collagen are not formed properly, thus resulting in skin lesions and blood vessel fragility.

Due to the importance of ascorbic acid to humans, various preparations of the vitamin can be found in the market. Most of them are in the form of tablets (usually effervescent), which present the analyst with a complex matrix due to the substances added to bind the ingredients and improve the strength of the tablet or to produce the fizz. Among the various analytical methods available, there are the expensive and time consuming bioassays (which involve the use of animals), the 2,6-dichlorophenolindophenol titrimetric method (applicable when ascorbic acid is the only reducing substance in the sample), the spectrophotometric determination of vitamin C in the UV region (where most substances have absorption bands as well), expensive chromatographic methods (mainly HPLC), etc.

In the present work, we propose a method for the determination of ascorbic acid, in which the vitamin is oxidised by periodate and the excess of the oxidant is estimated by means of its reaction with pyrogallol and measurement of the power of the light emitted. The suggested method requires inexpensive equipment (a flow injection system was used) and its main advantage lies in the principle that IO_4^- attacks C-C bonds in vic polyalcohols. Therefore, the results are not affected by any partial oxidation of vitamin C to dehydroascorbic acid.

Chimika Chronika, New Series, 26, 200 (1997)

PRINCIPAL COMPONENT ANALYSIS FOR RESOLVING COELUTING SUBSTANCES IN GC/MS DOPING CONTROL ANALYSIS

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ABSTRACT

The application of Principal Component Analysis (PCA) in the deconvolution of coeluted substances in doping control analysis was examined. PCA was applied on a real urine sample containing an etilefrine derivative and an artifact (BHT antioxidant), which were coeluted in the same GC peak. The mathematical analysis of the data set and the graphical presentation of the results were carried out with the MDA (Multivariate Data Analysis) program, called PONTOS. This program runs under the Microsoft Windows environment. Currently, the program includes the techniques of Principal Component Analysis, Discriminant Rotation and Canonical Correlation Analysis. PCA was applied on 7 spectra in the GC-MS peak under investigation. Clear full spectra of the two component substances were extracted from mixture spectra. PCA was used as an exploratory method of data analysis.

Keywords: Principal component analysis; Chromatographic analysis; Doping control analysis.

Chimika Chronika, New Series, 26, 201 (1997)

CHARACTERISATION OF CHEMICALLY MODIFIED PEAT AND COKE RESIDUES AS ION EXCHANGERS.

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ABSTRACT

The products of chemically treated peat and coke present good cation exchanging abilities. The modification process requires relatively inexpensive chemicals in small amounts and only simple procedures are involved. This factor in conjunction with the availability of peat and coke residues makes these modified products well suited for large scale applications.

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EVALUATION OF A GLASSY CARBON ELECTRODE MODIFIED BY A BILAYER LIPID MEMBRANE WITH INCORPORATED DNA

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ABSTRACT

The objective of the present work was the evaluation and characterization of a glassy carbon electrode modified by a bilayer lipid membrane (BLM) with incorporated ss-DNA. Various procedures were developed and tested for the incorporation of DNA at the electrode modified by the lipidic membrane:

1. Adsorption of DNA at the electrode, followed by immersion of the electrode with adsorbed DNA in a lipid solution in an organic solvent and subsequent immersion into a DNA solution.
2. Formation of self-assembled BLMs [H. Ti Tien and Z. Salamon, Bioelectrochem. Bioenerg. 22 (1989) 211] over ss-DNA adsorbed on the electrode surface.
3. Direct adsorption of DNA from an electrolyte solution (0.1 M KCl) at a metal-stabilized BLM [H. Ti Tien and Z. Salamon, Bioelectrochem. Bioenerg. 22 (1989) 211].
4. Formation of a BLM with incorporated DNA at the electrode surface using the monolayer folding technique [D. P. Nikolelis and U. J. Krull, Talanta, 39(1992) 1045].

Differential pulse voltammetry (i.e. oxidation guanine and adenine residues) was used to monitor the incorporation of DNA at the glassy carbon electrode modified by the BLM. The results have shown the lipid membrane enhances the stability of DNA towards a "medium-exchange" transfer of the electrode and prohibits diffusion of DNA from the electrode surface. They also have shown that the adsorption of DNA at the electrode surface can occur much faster using smaller amounts of DNA than previously established protocols [C. M. A. Brett, A. M. Oliveira Brett and S. H. P. Serrano, J. Electr. Chem. 366 (1994) 225].

Acknowledgements

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ELECTROCHEMICAL TRANSDUCTION OF INTERACTIONS OF ATRAZINE WITH BILAYER LIPID MEMBRANES (BLMs)

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ABSTRACT

This work investigates the interactions of atrazine with bilayer lipid membranes (BLMs) that can be used for the direct electrochemical sensing of this herbicide. Egg phosphatidylcholine (PC) and dipalmitoylphosphatidic acid (DPPA) were used for the formation of solventless BLMs. The interactions, of atrazine with these membranes were found to be electrochemically transduced by BLMs in the form of a transient current signal with a duration of seconds, which reproducibly appeared within 1 min after exposure of the membranes to atrazine. The sensitivity of the response was maximized by use of BLMs composed of 35% (w/w) DPPA, and by alteration of the phase distribution within membranes by the introduction of calcium ions in bulk solution. The mechanism of signal generation was related to the adsorption of atrazine with a consequent rapid reorganization of the membrane electrostatics due to atrazine aggregation at the surface of BLMs. Hydrogen bonding between atrazine and the carbonyl group of the lipid was explored by addition of platelet-activating factor (PAF; an ether analog of PC) in BLMs composed of PC. Differential scanning calorimetry of vesicles composed of 15% DPPA was used to study the aggregation of atrazine in membrane domains enriched in the charged lipid.The magnitude of the transient current signal was linearly related to the concentration of atrazine in bulk solution with submicromolar detection limits. This electrochemical transduction of atrazine interactions with BLMs holds prospects for flow injection monitoring of triazine herbicides.

Acknowledgements

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Chimika Chronika, New Series, 26, 204 (1997)

BIOSENSORS BASED ON LIPID FILMS FOR DIRECT MONITORING OF ENVIRONMENTAL POLLUTANTS

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ABSTRACT

The objective of the present work was the development of a technology for biosensors based on lipid films which are used for on-line monitoring of environmental pollutants in field and eventually can replace costly analytical devices (i.e. chromatographic instruments). This work was directed to develop a novel type of biosensoric technique which will be cost efficient, easy-to-use, fast responding alternative to mostly expensive, time consuming standard laboratory analytical and screening methods. In a single device a primary transducing element, very similar to biological recognition mechanisms will merge to form a unique sensing system.

Stabilized systems of lipid films prepared on a solid support serve as a basic transducing element. Techniques to prepare stable assemblies based on the present thin film technology are presented herein. Bioactive material isolated and purified from biological sources was incorporated into these membranes and the sensing system can be directly compared to biological recognition systems. Such a sensor is able to "see" the environment the same way the living cell does.

Potential application of these future sensors aims to the detection and quantification of environmental contaminants as toxins of bacterial and fungal origin, insecticides, pesticides, herbicides and other hazardous substances. The control of processes of industrial interest is another possible field of application. The potentiality of these devices was shown by results of construction of an ammonium minielectrode based on BLMs using gramicidin as an ionophore with improved characteristics as compared to the commercial devices such as fast response times (to ms speeds), ease of construction, high selectivity to ammonium ions in the presence of volatile amines and potassium ions and capability of analyzing small volume of samples. The same principle was used to develop a carbon dioxide sensor (by using hemoglobin as a carrier) and sensors for other gases. Examples of toxin and herbicide monitoring by using BLM-based sensors are also provided herein. Present achievements include the construction of stabilized BLMs for flow-through applications were used as electrochemical detectors for flow injection analysis of mixtures of herbicides. Present research is currently focused in the preparation of DNA sensors based on DNA hybridization on lipid membranes for the direct and selective determination of environmental contaminants.

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Chimika Chronika, New Series, 26, 205 (1997)

OZONE DEPLETION AND FIRE EXTINGUISHING AGENTS

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ABSTRACT

Halon-1301 (CF_3Br) and Halon-1211 (CF_2ClBr) were the main chemical fire extinguishing agents used, until their manufacture was banned recently. The compounds act as flame inhibitors but their extended lifetime allows their carry-over to the stratosphere where they absorb UV radiation and decompose to chlorine and bromine atoms, as simplified shown for CF_3Br (Halon-1301)

$$CF_3Br + h\nu \rightarrow CF_3 + Br$$

The reaction is followed by a sequence of reactions

$$Br + O_3 \rightarrow BrO + O_2$$
$$BrO + O_3 \rightarrow Br + 2\,O_2$$

which are responsible for the consumption of stratospheric ozone.

A special apparatus was built in order to estimate the atmospheric impact of halogenated compounds and various substitutes. Ozone is generated from oxygen by UV absorption. The concentration of ozone is followed by UV absorption and chemiluminescence. The reactivity of the halogenated compounds is established by introducing the compound into the stream of oxygen before irradiation. If ozone is depleted by the fragments of the halogenated compound, then the absorbance and the chemiluminescence signals are reduced. The % reduction of signals is proportional to the ability of the compound to deplete ozone and to the concentration introduced into the apparatus.

Formation and depletion of stratospheric ozone will be discussed in this lecture. Current research on ozone-depleting compounds and substitutes will be presented.

Chimika Chronika, New Series, 26, 206 (1997)

SPECTROFLUORIMETRIC DETERMINATION OF SILVER IN ALLOYS WITH 2-HYDROXYQUINOLINE

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ABSTRACT

Silver, at a limiting concentration of $5x10^{-6}$ M, was determined in its alloys spectrofluorimetrically using 2-hydroxyquinoline as a fluorescent reagent. No separation was necessary and this determination was performed in an alkaline solution (0.02 M KOH) in the absence of any masking agent. Metal ions such as cadmium, copper, nickel and zinc, found in brazing silver alloys, didn't interfere even when their concentration in the measured solution were many times larger compared with the concentration of silver. The fluorescence was measured at 376 nm (excitation at 320 nm). Two standard reference silver alloys (D165 and E170, Thorn Smith) were used to check the accuracy and precision of this method. Good agreement of the results with the value of the standards was found. The relative standard deviation of a typical calibration graph for silver was 1.61%, corresponding to confidence limits of 3.00±0.04 (arbitrary units of fluorescence per μM of silver) at the 95% level. The correlation coefficient was 0.9995 (n=7). One mg of alloy would be enough to determine silver.

Chimika Chronika, New Series, 26, 207 (1997)

A COMPARATIVE STUDY OF TERNARY COMPLEXES OF TERBIUM IONS WITH AMINOPOLYCARBOXYLIC ACIDS AND SEVERAL AROMATIC LIGANDS

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ABSTRACT

A systematic spectrofluorimetric study on the ternary complex formation of Terbium (Tb) with EDTA and a variety of bidentate organic ligands has been performed. Twenty different aromatic ligands were examined after their structures were carefully selected according to their ability to act as efficient energy donating chelators for Tb. More specifically, three major ligand groups that belong to salicylic acid, hydroxysulfonic acid and quinolones derivatives were tested. Excitation and emmision spectra of the ligands alone as well as of their ternary complexes with Tb and EDTA have been examined. Optimisation experiments for complex formation including the effect of pH, buffer systems, EDTA analogues and Tb and EDTA concentration were performed and analytical features for all the complexes are reported. A possible relationship between the ligand structure and its ability to act as an efficient absorbing and energy donating chelator for Tb is discussed. The results of the present study could be useful for: I) the development of highly sensitive lanthanide sensitized fluorimetric methods for the determination of organic ligands and ii) the design of novel substrates for enzymatically amplified time resolved fluoroimmunoassays after an appropriate modification of the chelator's molecule.

Chimika Chronika, New Series, 26, 208 (1997)

SECOND DERIVATIVE SYNCHRONOUS FLUORESCENCE SPECTROMETRY FOR THE SIMULTANEOUS DETERMINATION OF DIFLUNISAL AND SALICYLIC ACIDS IN BIOLOGICAL FLUIDS

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ABSTRACT

By using second derivative synchronous scanning fluorescence spectrometry the simple resolution of two nonsteroidal, antiinflammatory drugs diflunisal and salicylic acid, as ternary *complexes with terbium and EDTA, is accomplished. The method developed* is simple, sensitive and rapid, and has been successfully applied for the determination of both compounds in 10μL of untreated human serum and urine samples. The detection limits for diflunisal were 0.9 and 1.8mg/L, and for salicylic acid 1.2 and 1.7mg/L, in serum and urine respectively. The mean analytical recoveries from serum and urine samples spiked with diflunisal (25-100mg/L) and salicylic acid (28-138mg/L) were 99±8% (serum) and 102±8% (urine) for diflunisal and 102±9% (serum) and 95±8% (urine) for salicylic acid. The precision of all determinations varied from 2.5 to 10%.

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COMPUTERIZED ENZYMATIC KINETIC METHOD FOR GLUCOSE DETERMINATION IN FOODSTUFF USING IMMOBILIZED GLUCOSE OXIDASE IN GEL BEADS

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ABSTRACT

A simple, quick and low cost kinetic method of analysis for glucose determination, employing glucose oxidase (GO) immobilized in calcium alginate beads, is presented. The enzymatic glucose oxidation reaction is monitored photometrically at 460 nm, by means of an indicator reaction based on the oxidation of o-dianisidine by hydrogen peroxide in the presence of peroxidase. Under optimum conditions, the enzyme beads show a good behaviour for 45 days and for at least 20 consecutive measurements on the same sample. The method was applied to the determination of glucose in foofstuffs like honey, glucose-containing refreshments, ice-cream toppings and the results were compared with those obtained by a standard photometric and a standard titrimetic method.

Chimika Chronika, New Series, 26, 210 (1997)

PARTITION OF ANIONS INTO ORGANIC SOLVENTS OF POLYMERIC MEMBRANES

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ABSTRACT

The partitioning of anions between aqueous and lipophilic organic matrices is a very important parameter since it effects the selectivity of the ion carriers employed in potentiometric Ion-Selective Electrodes (ISEs) and of membranes in active ion transport. Equally interesting is the mobility of anions in organic matrices which are used for plasticizers of membranes as 1-N-Octanol, DOS, TOP, and NPOE.

In this talk a complete series of partitioning data and relative mobilities of anions into plasticizers are presented. The method used is based on a sensitive electrochemical system in conjuction with a newly designed planar conductivity cell.

ANIONS	NPOE	N-OCTANOL	DOS	TOP
SAL^-	0,33	0,088	0,01098	0,295
F^-	0,065	0,038	-	0,097
SCN^-	0,21	0,085	0,00154	0,77
ClO_4^-	0,17	0,0584	0,01944	0,094
NO_3^-	0,0119	0,048	-	0,33
Br^-	0,01125	0,052	-	0,059.
Cl^-	-	-	-	0,031
OH^-	0,0598	0,032	-	0,084
NO_2^-	0,0058	-	-	0,022
$H_2PO_4^-$	-	-	-	0,15

Table I

Partition Coefficient for Anions into some Plasticizers

ANIONS	NPOE 1.00E-21	N-OCTANOL 1.00E-21	TOP 1.00E-21
SAL^-	0.0464	149,490	0.05191
I^-	1.6582	217	0.59436
SCN^-	0.6230	1,097	0.01989
ClO_4^-	11.208	105	0.362
NO_3^-	2.4711	42.7	0.0464
Br^-	3.3482	58.2	0.41708
Cl^-	-	-	0.49398
NO_2^-	0.7334	-	0.59329
$H_2PO_4^-$	-	-	0.009057

Table II

Relative Mobilities of Anions into some Plasticizers

$u\,/(cm^2 * s^{-1} * V^{-1})$

-: CAN NOT BE MEASURED

Chimika Chronika, New Series, 26, 211 (1997)

STUDY OF THE EFFECTS OF FIRE RETARDANTS ON THE PYROLYSIS OF CELLULOSE BY THERMAL METHODS

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ABSTRACT

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were used for studying the effects of various fire retardants on the pyrolysis of cellulose. Salts and oxide hydroxide additives, such as $(NH_4)_2HPO_4$, NaH_2PO_4, $(NH_4)_2SO_4$, $NaHCO_3$, $KHCO_3$, $(COONa)_2$, $Ca(OH)_2$ and $Na_2O.CaO$ were used as retardants at concentrations of 4%w/w. DSC and TGA showed that the addition of $(NH_4)_2HPO_4$, NaH_2PO_4 and $(NH_4)_2SO_4$ on cellulose causes a significant shift to lower pyrolysis temperatures (i.e. 50-80°C), as well as significant increase in char residues (i.e. more than three times at 500°C). The effect of $NaHCO_3$, $KHCO_3$, and $(COONa)_2$ on the pyrolysis of cellulose was also found significant, in terms of DSC profile, while the increase in char residues was moderate (i.e. about two times at 500°C). In contrast the effect of $Ca(OH)_2$ and $Na_2O.CaO$ on the pyrolysis of cellulose was found minor, under the above mentioned criteria.

KEY WORDS: Fire retardants, Cellulose, Pine-needles, Pyrolysis, DSC, TGA.

Chimika Chronika, New Series, 26, 212 (1997)

MODIFIED ELECTRODES. ELECTROCATALYTIC REACTIONS WITH POLYOXOMETALLATES

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Polyoxometalates (POM) have a long and interesting redox chemistry, acting as electron and oxygen relays that find diversified applications, including commercially important catalytic processes [1].
The ability of POM to accept and release electrons, i.e., to serve as multielectron relays, has been recently exploited in electrode modification [3]. Quaternary butyl ammonium salts of $P_2Mo_{18}O_{62}^{6-}$ and $P_2W_{18}O_{62}^{6-}$, having a redox range from about 0.5 to -0.7 Volt vs. sce, have been immobilized on the surfaces of wax impregnated graphite electrodes, using methyl methacrylate.
The electrolytic behavior of these POM in solution and immobilized on the electrodes is compared and their electrocatalytic behavior toward reduction of BrO_3^- and NO_2^- ions has been studied.

References

1. a. M.T. Pope and A. Muller, *Angew. Chem. Int. Ed., Engl.*, *30* (1991). b. E. Papaconstantinou, *Chem. Soc. Rev.*, *18* (1989) 1.
3. α. D. Ingersoll, P.J. Kulesza, and L.R. Faulkner, *J. Electrochem. Soc.*, 1994, *141*, 140. b. B. Wang, F. Song, and S Dong, *J. Electroanal. Chem.* 1993, *353*, 43. c. B. Keita, D. Bouaziz L. Nadjo and A. Deronzier, *J. Electroanal. Chem.*, 1990, *279*, 187.

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PHYSICOCHEMICAL MEASUREMENTS IN THE STROFILIA LAGOON SKIATHOS ISLAND - NW AEGEAN SEA

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ABSTRACT

The Strofilia lagoon situated at the SW part of Skiathos island (Sporades-N.W. Aegean Sea), is a small (500x250m), shallow lagoon with depths between 0.8 and 2m, which communicates with the Aegean Sea through a long channel 2.2m deep.

A few years ago an attempt was made to change the use of the lagoon into an internal port for small boats. Due to the evident effects of the works on the natural environment, which were immediately seen, the works stopped and the wetland was saved.

In order to assess the existing situation and to estimate the result of human intervention on this environment, some physical and chemical parameters were measured on a seasonal basis from September 1993 to June 1994. Hydrographic measurements (temperature and salinity) were carried out with the use of a CTD unit manufactured by Sea Bird Electronics. Moreover surface samples were collected for dissolved oxygen and nutrients determinations. The DO was measured on board according to Carritt and Carpenter while the analysis of nutrients was performed on a Technicon CSM6 Autoanalyser.

The results did not show any permanent disturbance in the water masses. This must be attributed to the water renewal which was estimated to be satisfactory, due to the good circulation of the Aegean Sea water masses.

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STUDY OF Hg-ADSORPTION IN NATURAL CLAY

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ABSTRACT

Mobilities of trace metals in surface and subsurface environments associated with environmental polution and accidental spills from landfill repositories, forms a field of ongoing recearch interest in everywhere. Within this framework a laboratory experimental study of Merkury sorption in a natural clay in presence of artificial groundwater was done. The results were expressed with the parameter Kd (Distribution Coefficient), which is the amount (mass or activity of ^{203}Hg) bound on the clay divided by the amount remaining in the water. We observed that the most important variable affecting on Kd and concequently on the Hg-adsorption appears to be pH. Temperature, and Ratio (Clay/Water) seem to have a lower influence on Kd.

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REVIEW OF OIL SPILL CLEANUP TECHNIQUES WITH EMPHASIS ON BIOREMEDIATION

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Today, there is a plethora of different oil spill cleanup techniques. These include means to prevent the spread of oil spills, techniques to recover the oil from the water surface and a wide variety of chemicals to treat the spilled oil. During the last few years emphasis has been placed on bioremediation methods. They were used for the first time on a large scale at the Exxon Valdez oil spill.

The first and probably most important step towards an oil spill cleanup is oil containment to avoid spreading of the oil over a large area. The most common way to do so is through the use of floating booms. Sorbent booms, bubble barriers or chemical barriers are other oil containment options, but their use is not common.

There are three approaches to oil recovery from water: the use of mechanical skimmers, the use of sorbing materials and manual recovery. All three of them are commonly used, each one under different conditions or at different phases of a cleanup effort.

Oil treatment methods include, in addition to bioremediation, the use of dispersants, sinking agents, burning agents and gelling agents. In general all oil treatment methods are considered a last resort because they can pose a greater threat to the environment than the oil itself. Thus they should only be used if all other methods have failed.

Part of the natural oil degradation is a result of the action of "oil-digesting" or "oil-oxidizing" microorganisms found in the environment. There are estimated to be more than 200 such species. The rate of biodegradation is usually very slow and depends considerably on temperature and availability of oxygen and nutrients, especially phosphorous and nitrogen. The natural biodegradation process can be artificially enhanced in two ways: by adding phosphorous and nitrogen containing fertilizers to stimulate the growth of oil-degrading microorganisms already present in the area or by actually adding new microorganisms, usually in the form of dried bacterial cocktails.

The main problem associated with the application of nutrient mixtures has to do with nitrogen and phosphorous being very water soluble. This in addition to the nutrients being lost in the water, can lead to algal blooms due to eutrophication. To overcome this problem three options are available: metered application of soluble fertilizers, the use of slow release granules or briquettes and the use of oleophilic fertilizers in which nitrogen and phosphorous are in compounds that can actually stick to or dissolve in the oil instead of the water.

Despite the fact that numerous other energy sources are available, the use of petroleum products is not predicted to decrease in the near future. As a result the threat oil spills will be always present. Although there is a large number of available techniques for oil spill cleanup none of them provides a satisfactory solution to the problem. If the weather conditions at the site of the spill are good and the spill is attacked before it spreads over a large area, the combined use of containment and recovery methods can have adequate results. If oil treatment methods are used to fight the oil, the side effects can often be more harmful to the environment than the oil itself. Finally the bioremediation methods although still at an early stage are promising. In conclusion, probably the best way to fight oil spills is to have good contingency planning that allows fast reaction before the spill spreads.

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A QUESTIONNAIRE FOR HYGIENE AND SAFETY AT THE LABORATORIES OF THE DEPARTMENT OF CHEMISTRY IN THE UNIVERSITY OF ATHENS

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During the last ten years in Greece, considerable emphasis has been placed on occupational health and safety legislature, both on the national and the European Union level. The pur-pose of this study was to derive some preliminary indications concerning the implementation of the above mentioned legislature and the hygiene and safety condition at the laboratories of the Department of Chemistry.

A questionnaire was given to 23 students and faculty members It consisted of 47 questions which fell under the seven categories: awareness of the health and safety laws; existence of accident prevention means in the laboratories; use of hoods and personal safety equipment; storage, transportation and disposal of toxic materials; education on health and safety issues; personal questions on age, sex etc.; general questions and/or comments.

Approximately one fifth of the subjects was aware of the existence of the above mentioned legislature. A slightly higher percentage said that specific measured mentioned in these laws have already been implemented in the department.

Almost everybody reported the presence of fire alarms, gas detectors and fire hydrants in the laboratories. Only two thirds though mentioned the existence of first aid kits and less than one quarter said there are water sprinklers, emergency exits and sorbing materials for fighting spills of toxic chemicals.

Everybody in the labs and almost always uses lab coats. Fewer people, a little more than three quarters, wear goggles and gloves. Moreover, occasional usage is the rule rather than the exception this time. Only one out of ten subjects mentioned the usage or even the presence of respirators in the labs. Finally, although more than 90% of the subjects believe that the hoods work efficiently less half actually use them when working with volatile toxic chemicals.

Specially arranged areas for storage of toxic materials do exist in the department but nearly half of the subjects reported the need for more space. During transportation of toxic chemicals most people in the department take special precautions only occasionally, whereas almost half of the answers mentioned a lack of special stands for gas tanks. Additionally, nearly 50% re-ported that there are warning labels on toxic material containers. Almost all subjects where able to "decipher" the pictures on these labels but less than half knew what the R and S codes on the labels stand for. Finally, nearly three quarters reported that toxic substances are simply poured down the sink instead of being collected for recycling or proper disposal.

Only a small percentage, around 15% said that health and safety handouts are available to the students and that seminars or classes are offered. Finally 23 accidents were reported, most of which had to do with some sort of fire, burns or foreign objects in the eyes.

Overall, the results of the study indicated that although some steps have been accomplished, there is still much ground to be covered.

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Oxygen Free Radicals and Diseases of the Respiratory System. Studies of the Synergistic Action of Asbestos Fibers and Aqueous Cigarette Tar by Electron Spin Resonance

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Oxygen free radicals can be formed in the respiratory system by exposure to environmental pollutants, such as fibrous dusts, ozon, nitrogen oxides, tobacco smoke etc. These pollutants react with lipids in the membrane of the cells or can pass in the alveolar duct bifurcations were they are deposited. Clearance is difficult of the entrapped fibers in lung tissues. Formation of oxygen free radicals, especially hydroxyl radical (HO•) and superoxide anion ($O_2^{\cdot -}$),has been observed in aqueous solution in the presence of hydrogen peroxide or simply oxygen of air, which is bioavailable. Oxygen free radicals and reactive oxygen species(ROS) increased DNA damage in experimental systems. Scavengers of hydroxyl radicals, like DMSO, mannitol and sodium benzoate, decreased both the formation of hydroxyl radicals and strand breaks of DNA in mixtures exposed to asbestos and cigarette tar extracts.
In 1992 Kamp, Graceffa, Pryor and Weitzman published the most important review on the subject of the synergy of asbestos fibers and cigarette tar in the generation of oxygen free radicals and ROS.But the quantitative aspects of the cooperative action of the two carcinogenic agents was missing. In the Lab of Organic Chemistry,we studied the formation of the hydroxyl radicals by using spin trapping techniques(with DMPO which is a water soluble spin trap and Sodium formate as an indirect trap of the hydroxyl radical) and Electron Paramagnetic Resonance(EPR). When asbestos fibers (fresh after grinding) and aqueous cigarette tar extract (fresh after extraction) are mixed, the hydroxyl radical concentration increases 3-5 times, compared to the separate formation by asbestos only or cigarette tar. The addition of the EDTA (an iron chelating agent) in the mixture increases substantially the formation of hydroxyl radicals. Separation of iron from the fibers by EDTA also showed continued generation of hydroxyl radicals. As it was indicated by other studies, iron ion in the fibers play an important role by Fenton reaction in the catalysis of the formation of radicals. Grinding of the fibers increases the generation of fresh surfaces which are not oxidized. Crocidolite is more reactive than chrysotile, which can be explained by the higher iron content of the fibers. These studies can explained the synergistic or cooperative action of both carcinogens. Also, these results can provide a valuable explaination to the epidemiologic results, which showed that asbestos workers who were at the same time smokers have ten time higher risk to develop lung cancer and 80 times higher risk from persons with no exposure at all to both agents.

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NONS - NOTIFICATION OF NEW SUBSTANCES EUROPEAN INSPECTION PROJECT THE ROLE OF CHEMIST

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ABSTRACT

Recently the European Union in the framework of Dir. 92/32/EEC, which has already been implemented into the Greek Legislation, has initiated on the "new" substances the NONS European Inspection Project, which started on May 1995 and is scheduled to be finished by June 1996. The aim is to develop a uniform procedure for carrying out company inspections in all Member-States, in order to protect successfully man and environment.

According to the provisions of the Legislation, people who put "new" substances in the European Union market are obliged to inform the National Competent Authorities on the danger which the substance may present for men and the environment.

The General Chemical State Laboratory which is the Greek Competent Authority, participates in this project and the Division of Environment coordinates the national project.

The role of the chemist, either the inspector or the company officer or the independent consultant is of crucial importance, during the performance of the inspection.

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CHEMISTRY AND QUALITY OF LIFE

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A general outlook is given on catalytic processes which have replaced conventional polluting processes during the last decades. Present directions for the study of new environmentally friendly processes are also discussed. The use of organometallic chemistry appears of fundamental importance to work out procedures with low ambiental impact. The quality of life throughout the world will increasingly depend on organometallic processes and particularly on catalysis.

Group VIII metals and especially palladium are well suited to obtain highly selective reactions under mild conditions. Examples of recent achievements are given. These works were not aimed at solving specific problems, but only at establishing general methodologies, which may prove quite useful when the need arises of carrying out organic reactions selectively and catalytically with one-pot procedures and under mild conditions.

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PHOTODEGRADATION OF ORGANIC POLLUTANTS WITH POLYOXOMETALLATES. FUTURE PROSPECTS.

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Pollution is an ever increasing problem for the industrial word. To remedy this problem the scientific community acts in two directions:
(a) To find new non polluting catalytic manufacturing processes (green technology) and (b) To find methods to clean the environment.
Various methods have been employed for the degratation of pollutants [1]. Those that involve electromagnetic radiation are: (a) Treatment with 60Co-γ-radiation, (b) UV light, (c) UV light in presence of H_2O_2, or O_3 and (d) UV and near visible light in presence of TiO_2. Methods (a), (c) and (d) lead, more or less, to decomposition to CO_2 and H_2O.
We present a new method for the complete photodegradation of organic pollutants to CO_2 and H_2O with near visible and UV light, in presence of polyoxotungstates (POM) as photocatalysts. As is known, POM are redox catalysts that find diversified applications in important industrial processes. Photolysis of POM at the O-M CT bands (near visible and UV light) enhances their redox ability rendering these species powerful oxidizing reagents. These properties have been exploited in selective and non selective oxidation of organic compounds [2]. The mechanism of photodegradation involves mainly OH radicals produced by reaction of the excited POM with H_2O. The data concerning the mineralization of two characteristic pollutants o-chlorophenol and p-cresol is described [3].

REFERENCES

1. O. Legrini, E. Oliveros and A. M. Brown, *Chem. Rev., 93* (1993) 671.
2. E. Papaconstantinou, *Chem. Soc. Rev., 18* (1989) 1.
3. A. Mylonas, Ph.D. Thesis, *National Technical University of Athens - NCSR Demokritos*, 1995.

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ENVIRONMENTAL MANAGEMENT SYSTEMS A BROAD INTERPRETATION OF QUALITY

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CYPRUS ORGANIZATION OF STANDARDS
AND CONTROL OF QUALITY

ABSTRACT

During the last few decades, the target to face environmental problems has been considered of high importance and this reflects on the priorities set by the world society. Environmental Management Systems represent a framework for an efficient organization of any activity, taking into main consideration environmental issues related to design, production and distribution. Nowadays, quality includes also the environmental issue.

An integral assessment of products and processes should be based on a technical, economic and ecological evaluation. Therefore an evaluation of raw materials, energy, water and other natural resources used as well as the environmental impact during production, transport and distribution tion, use/consumption, disposal or reuse/ recycling have to be taken into account when planning for a particular product, service or activity.

In order to assess a procedure (production or service) some tools have been developed. Environmental Management Systems (e.g.BS 7750) provide the means to ensure that the effects of the activities, products and services of an organization corform to a declared environmental policy. On the other hand, the Eco-Management and Audit System of the European Union includes some additional provisions for auditing and symbols for sites operating under the scheme.

The Life Cycle Assessment (LCA) represents a useful tool for the ecological evaluation of materials and products. The procedure includes Life Cycle Inventory, Life Cycle Impact Analysis and Life Cycle Improvement Analysis.

Local conditions play a dominant role, since factors like the availability of raw materials, energy and other resources vary greatly from country to country. Therefore LCA can be of significance to small developing countries only after a suitable adjustment of all aspects involved.

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CARCINOGENIC CHEMICAL SUBSTANCES IN THE WORKING AND THE AMBIENT ENVIRONMENT. CLASSIFICATION ,RISK ASSESSMENT AND REGULATORY POLICIES

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In the last decades, cancer incidence and mortality are increasing and now neoplasms are the second most important cause of death in the developed countries after cardiovascular diseases. It has been established long time ago that extrinsic or environmental factors are the main causes of cancer in humans. Smoking, diet, alcohol consumption and reproductive or sexual behaviour are responsible for the majority of cancers. Also, exposure to chemical carcinogens in the work places and in the ambient environment cause a substantial number of occupational and environmental cancers. In the last decade many regulatory policies were implemented in developed countries restricting or banning carcinogens. Classification and risk assessment of carcinogens by national and international agencies and research institutes have improved substantially. Our knowledge as to the mechanisms of carcinogenesis and the type of exposure which are causing the higher risk to humans has been in an advance stage.

International Agency for Research on Cancer (Lyon) is a research institution of the World Health Organization dealing with the problems of criteria and evaluation of carcinogenic risks of chemicals, mixtures, occupations and industrial processes. IARC's Monographs on the Evaluation of Carcinogenic Risks to Humans (1970-1995) have become valuable data on carcinogens. Other institutions which are dealing with carcinogens are the Environmental Protection Agency (EPA) and the National Toxicology Program (NTP) in the USA. Also, the Health and Safety Executive (Great Britain), the Swedish Board of Occupational Safety and Health (SBOSH), the Deutsche Forschungsgemeinschaft (DFG), the National Institute of Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administartion(OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) in the USA, evaluate carcinogenic risks from chemicals and set regulations for exposure limits of toxic, carcinogenic and mutagenic chemicals. There are many new Directives from the European Union dealing with carcinogens at work and in the ambient environment.

Epidemiologic studies, risk assessment, research on the actual mechanisms in vitro and in vivo and regulations of chemical carcinogens are very complicated scientifc issues. There are many controversies in testing and risk assessment methodology. But despite the difficulties, there is enough progress in setting priorities and starting preventative measures to decrease risks to humans from environmental carcinogens.

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STUDY ON CHEMICAL COMPOSITION OF THE MEMBRANE AND PROSPERTIES OF THE COLD - AND SALT- TOLERANT BACTERIUM , *LISTERIA MONOCYTOGENES* . , RESPONSIBLE FOR SERIOUS FOODBORNE DISEASE

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ABSTRACT

Listeriosis from food contaminated with Listeria (cheese , meat , vegetables) can cause septicemia , meningitis and death. Listeria is resistant to high salinity and cold . Food handling practices can therefore promote its growth. Cold adaptation may involve unique properties of membrane lipids. Extraction of Listeria total lipids yielded 7±1 mg / ml wet cells. 64% of total lipids were polar lipiids that contained 9% phosphorus and fractionated into 14 components. 88% of polar lipids (eight components) contained phosphorus , among these was one major component (34% of polar lipids) . The fatty acid profile of polar and neutral lipids was variable, e.g., polar contained 15: anteiso (50%) and 17: anteiso (25%) fatty acid species .

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MEDITERRANEAN DIET: THE CONTRIBUTION OF FOOD CHEMISTRY IN THE PREVENTION OF ATHEROMATOSIS GENERATION AND OF HEART DISEASES

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ABSTRACT

Mediterranean Diet, although relatively high in fats and especially in olive oil, results in lower mortality rate due to hematosis disorders. In addition, relatively high fat intake and low mortality have been observed in Japan. We strongly believe that Platelet-Activating Factor (PAF) is implicated in atheromatosis generation since we detected PAF which is produced during LDL oxidation and causes *in situ* inflammation. PAF action results in endothelium destruction and gap formation, as well as in the proliferation of smooth muscle cells in which several cells such as foam cells and platelets adhere. In addition, other blood constituents such as lipids also adhere in the above complex, generating the atheromatic plaque. This mechanism is also supported by *in vivo* experiments performed by other investigators, in which atheromatosis generation was not detected in the experimental animals fed by cholesterol-rich food along with specific inhibitors of PAF. The above findings show that specific PAF inhibitors may protect from atheromatosis generation. Based on this assumption, we investigated the possible existence of PAF inhibitors in Mediterranean Foods. We detected in olive oil, honey and wax, milk and yoghurt, in fishes and plants, lipid compounds which inhibit PAF actions. The existence of the above lipids may explain the defensive role of Mediterranean Foods in atheromatosis generation.

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OPTIMUM NUTRITION (ON) FOR PREVENTION OF DISEASE AS RECOMMENDED BY THE MAASTRICHT TREATY

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The Maastricht Treaty, title X, article 129, decrees: "Community Action shall be directed towards the prevention of diseases, in particular the major health scourges". ON has been shown by a great body of research to be one of the best means of preventing especially degenerative disease. As our food is now depleted ON aims at maximising individual health potential and uses, apart from good diet, natural products and vitamins and minerals ~ 10 to 50 times the chancily determined Recommended Daily Allowances (RDAs) which only stop dire malnutrition. The difference between effective and too high dose is for these nutrients very much greater than that for drugs so that ON is very safe. It is now possible to prevent cancer towards 80% with good life-style and groups of anti-oxidant supplements. Mortality of breast cancer is f.i . inversely proportional to Selenium intake. There is a database of over 3000 references on cancer-nutrition in Bristol, England, available on Tel. 01272 743 216. A Vit E intake of 400-1200 IUs a day over 4 to 10 years can reduce risk of degenerate heart disease by 20 to 75 times, a still strangely unknown fact. (R.A.Passwater, "Prevention " 1976). Fat deposits in arteries can be eliminated with 2-5 g of Vit C and the aminoacid L-Lysine (Research, The Pauling Institute, Pasadena, California). Coenzyme Q10 trebles heart attack survival. Pycnogenol from pine bark, a ca 1000 times stronger free-radical scavenger than Vit C, preserves collagen, prevents wrinkles and varicose vein problems. As 85 % of mental disease cases can be socially rehabilitated with mainly supplements, this type of illness can often be prevented by ON. There is a very well proven link Crime- Nutrition, and crime can be halved and many criminals rehabilitated with anti-allergenic, low sugar diet and nutrients, chiefly Zinc, Chromium and Manganese. Suicides in prisons can be totally prevented.

It is thus extremely important that the European Commission which is now planning new legislation concerning nutrients, hopefully unlike that planned in 1992, realizes that free access to supplements of prevention strength is necessary to implement The Maastricht Treaty decree. EC-legislation must also f.i. reflect the great Se-Vit C- and D-needs in north Europe as compared to the Mediterrenean countries, blessed with more sun and minerals.

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THERMAL DEGRADATION OF APPLE TEXTURE

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ABSTRACT

Instrumental Texture Pofile analysis can be used in studying thermal degradation of apple texture. Heating time and temperature were significantly affected the change of textural parameters. Two first-order kinetic mechanisms were needed to descibe apple softening, which were different during short and long heating times. During the first few minutes of heating, the change of TPA parameters can be described by an apparent first-order kinetic model. Rate constants were variety dependent and were different for Red and Golden Delicious apples. Activation energy varied between 24.2 and 92.6 kJ/mole, while z values were 25-99°C and Q_{10} coefficient between 1.26 and 2.50.

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ISOLATION AND STUDY OF PHOSPHONOLIPIDS FROM MUSSELS
(GENUS : Mytilus , SPECIES : galloprovincialis)

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ABSTRACT

The accurate role of phosphonolipids (PnLipids) remains to be determined. Possible roles are that the PnLipids may contribute to the protection of cellular integrity and survival of aquatic organisms [Mollusca (gasteropoda , bivalvia), Cnidaria] containing them at high percentages. We are interested in chemical composition of foods as mussel, regarding the PnLipids .

Extraction of Mytilus galloprovincialis total lipids yielded 2,53gr/ 196,2 gr of wet tissue. 44,7% of total lipids were polar lipids which contained 44.795 microgram phosphorus . Total lipids fractionated by column chromatography and 2-dimension High Performance Thin Layer Chromatography to the next main components : Phosphatidylethanolamine , 33,5 % ; Phosphatidylcholine , 44,3 % ; and two more components which were considered to belong to Sphingophosphonolipid class , the major one 11,5% and the minor one 2,5-3,5 % . The Thin Layer Chromatography Rf values on several solvent systems measured and structural studies for their identification were mentioned.

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DETECTION OF PROTEIN IN GREEK OLIVE OIL

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ABSTRACT

Five different greek olive oil samples (Gargalianoi, Naupaktos, Heraklio, ELAIS, ELANTHI-filtered) have been examined for the presence of proteins and the oxidative enzymes, LOX, PPO and POD. SDS-PAGE and silver staining of the gels have shown the existence of proteins only in the first four samples. This electrophoretic image has become fainter after storage of the olive oil for several months. LOX-like activity has been detected in all samples. PPO-like activity has been found in the first four samples and POD-like activity only in the fourth one.

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A RHEOLOGICAL STUDY ON THE APPLICATION OF CARBOHYDRATES-PROTEINS TO THE DEVELOPMENT OF VERY LOW FAT SPREADS

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ABSTRACT

Several commercial edible dispersions (butter, margarine and low fat spreads) have been analysed in order to develop a background understanding of the viscoelastic properties, phase behaviour and oral evaluation of these systems.

Parameters have been derived from compression testing, dynamic oscillation and creep compliance experiments. Butter and margarine have a defined plastic rheology and attempts have been made to imitate it with their fat and water continuous substitutes. The ratio of plastic to maximum stress (σ_p/σ_m) of butter and margarine is substantially higher (0.96-1.0) than the ratio of inflectional to maximum stress (σ_i/σ_m) of commercial low fat spreads with a strong, gel-like character (up to 0.83). In other cases, commercial embodiments with reduced amounts of structural components have stress-strain profiles resembling those of viscous solutions instead of a plastic product. The maximum strain (ε_{max}) for butter and plastic spreads usually occurs over a narrow range of true strain units (from 0.24 to 0.26).

Strain sweeps on dynamic oscillation, the concentration dependence of storage and loss moduli (G' and G" respectively) and above all the melting profiles are useful probes for assessing the firmness and spreadability of a product. In creep compliance experiments the minimum instantaneous deformation required for the product to exhibit substantially no recovery of shape is a useful characteristic of its viscoelastic properties. Butter requires lower initial strain to exhibit negligible recovery of shape after the removal of stress, than do commercial low fat spreads with a pronounced elastic component. Application of a temperature ramp to butter results in a drastic decline of G' with the network melting out completely at 33°C due to the contribution of fat crystals. This illustrative evidence is entirely different from the behaviour patterns in spreads where a slower two-step characteristic melting profile is obtained at much higher temperatures than in the mouth (37°C).

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WATER-ETHANOL SEPARATION BY ADSORPTION ON STARCHY MATERIALS: EFFECT OF ADSORBENT PARTICLE SIZE

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ABSTRACT

Inverse gas chromatography was used to study the adsorption of water and ethanol on two fractions of corn meal with two different particle size compositions (80-100 and 100-120 mesh), in the temperature range 50-90^oC. Values for the separation factor (s) and the thermodynamic parameters, namely the Gibbs free energy (ΔG^os) and enthalpy (ΔH^os) of adsorption, were calculated from the chromatographic retention data. The results showed that water was adsorbed more strongly than ethanol by both materials, at all temperatures. In addition, it was found that lower temperatures were more favourable for the adsorption of both solutes. Adsorption was stronger for corn meal of 100-120 mesh particle size. The highest value for the separation factor was obtained for corn meal of 100-120 mesh particle size as well, at the lowest temperature used (50^oC).

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ENZYMIC HYDROLYSIS OF STARCH IN AQUEOUS TWO PHASE SYSTEMS

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ABSTRACT

Aqueous two phase systems have been widely used in many biochemical preparations and recently in the field of industry.

Aqueous two phase systems are formed by mixing either two water soluble polymers or one polymer and a salt.

In this study, different polymers and mainly PEG-Dextran at various concentrations of the polymers were investigated for use in enzymic hydrolysis of starch.

Enzymic hydrolysis of starch with a combination of amylase and glucoamylase was studied in polyethylene glycol (PEG) 5%-Dextran 3% aqueous two phase system under various conditions of temperature and agitation.

All experiments were conducted in laboratory flasks with a total volume of 10 ml. The course of the reaction was estimated by measurements of glucose production with the chromatometric method of phenol-sulfuric acid and by HPLC with an Aminex HPX-87C column. The best results in terms of glucose production were obtained with agitation at 55°C.

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PULLULAN PRODUCTION FROM OLIVE OIL MILL EFFLUENT ('KATSIGAROS')

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ABSTRACT

'Pullulan' is an extracellular maltotriose Polysaccharide polymer of evident industrial interest. 'Katsigaros', a major pollutant of the environment, is produced in enormous quantities in olive oil producer countries. This waste, containing various amounts of water-soluble sugars, was used for 'Pullulan' production by cultivation of the yeast-like fungus *Aurebasidium pullulans*.

The temperature effects on the cellular forms (hyphae, blastospores, chlamydospores, swollen cells) and 'Pullulan' synthesis by *A. pullulans* (strain AP2) which we have isolated from carob tree leaves, were studied. Preliminary experiments showed that this fungus shows a complex life-cycle (hyphae, chlamydospores etc) under several culture conditions. 'Pullulan' production appeared to be dependent on the already mentioned cellular forms. Chlamydospores and swollen cells were found to be dominating with increasing incubation temperature resulting in a higher 'Pullulan' synthesis and a lower production of biomass and protein content. A marked increase in carbohydrate content and changes in the chemical composition of the cell walls, should be taken place. This is possibly due to the response of the fungus to stress which can be brought about by temperature increase of incubation. Under these unfavorable conditions, *A. pullulans* produces more 'Pullulan' than other polysaccharides, which are precipitated by ethanol. In this way, the microorganism may deal any adverse for its growth conditions better. The reduction of the biomass protein content under higher than 30°C temperatures should be due to the other cellular forms (chlamydospores and swollen cells) prevailing, which are richer in protective constituents than the hyphae. The answer to the question of what temperature of incubation would be better for 'Katsigaros' valorization, should be given after construction of an appropriate econometric model.

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ASPERGILLUS FLAVUS's OCCURANCE IN GREEK FOOD OF PLANT ORIGIN

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Aflatoxins are toxic secondary metabolits produced by molds like *A.flavus*, that often contaminate agricultural products. At the present study we investigate the occurence of *A.flavus* in some commodities of Greek origin such as cereals, nuts, dry fruits and in some samples of coffee. It was found that 93% of the samples were contaminated by microorganisms but only 37% exceeded the limit of 100 cfu/g. Contamination was larger in commodities without packaging. The presence of *A.flavus* depended on the composition of the food; that is samples rich in lipids such as nuts and cereals were more susceptible to contamination than the others. Some samples in which *A.flavus* was detected were examined for the presence of Af B_2 and Af G_2. A modified analytical method was used (recovery 60%, detection limit 2 ng). Aflatoxins were extracted with ($MeOH+H_2O$), purified in seppack C_{18} and quantitated by TLC with visual estimation. Results were negative.

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THE INFLUNCE OF FINING AGENTS ON WINES OF VARIETIES XINOMAVRO AND SAVATIANO

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Abstract

The fining of wines is a very important enological technique, as besides wine fining and stabilization, it influences organoleptic characters.

In this paper changes in organoleptic characters as well as in chemical composition and more specifically chromatic characteristics of two wines fined with seven fining agents, were studied. One red wine from the variety Xinomavro and one white wine from the variety Savatiano. The fining agents used are: Bentonite, gelatine, egg albumen, casein, PVPP, active coal and arabic gum.

Fining Agents	Xinomavro	Savatiano
Bentonite	Good fining ability. Enrichment of wines with some inorganic cations	
Gelatine	Medium fining ability	
Egg Albumen	Medium fining ability and improvement of the organoleptic characters	
Casein	Medium fining ability	Good fining ability
PVPP	Good fining ability	
Active Coal	Good discoloring ability	
Arabic Gum	Medium fining ability	

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EVALUATION OF QUALITY AND SAFETY OF VARIOUS TYPES OF COFFEE ACCORDING TO THE PRESENCE OF MICROORGANISMS IN DIFFERENT PACKAGES

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This report examines the safety of coffee types in seven different packages. It was found that ground roasted Greek coffee is more contaminated by microorganisms than instant coffee. But freshly roasted Greek coffee without being packaged is less contaminated than ground roasted coffee in plastic and alumina packages. In addition instant coffee in a glass jar was found safer than the instant coffee in metalic and paper packaging. Contamination is also related with the size of coffee granules that is, the bigger the size the less contamination. *A.flavus* was found in several samples in spite of packaging and of the type of coffee. Determination of Aflatoxins B_2 and G_2 was done in some coffee samples using TLC and HPLC. But many natural occuring substances contained in coffee interfere in the determination of Aflatoxins so results were difficult to be interpretated. It is suggested that the extraction and cleaning steps need to be modified.

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RESULTS ON MICROBIOLOGICAL QUALITY CONTROL OF FOODS AND MEALS SAMPLING FROM 4 HOSPITALS OF ATHENS DURING THE YEARS 1990 - 1993.

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ABSTRACT

This work concerns the microbiological quality control of raw foods and prepared meals served in 4 hospitals of the region of Athens during the years 1990 - 1993. The foods were tested for the most common kids of microbs, namely : total aerobic, Escherichia coli and coliforms, other enterobacter and Staphylococci.

The percentage of examinations found in the not acceptable range were: 11% in diary products, 19% in salads, 8% in meat and meat products, 10% in poultry and none in fish. The above situation was improved, by following the proper rules of storing, as compared to the previous years and preparation of foods, and keeping cleanliness.

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WATER SORPTION AND PERMEABILITY OF BIODEGRADABLE PACKAGING FILMS

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ABSTRACT

The water vapour transmission rate (WVTR, method ASTM-E96-90) was determined and the sorption isotherms of a series of biodegradable films (Zellglass, Biocell, Mater Bi, Fluntera, EMS and Novon) were constructed at 30°C. The WVTR of Mater Bi, Novon and EMS ranged between 22-35 g/m^2.day values similar to conventional synthetic plastics films such as LDPE and PET. The WVTR for Zellglass, Biocell and Fluntera ranged between 131-140 g/m^2/day corresponding to intermediate degree of protection of the packaged foodstuff to moisture. The sorption isotherms of the experimental films showed very low moisture uptake (~0.02g/100g) at low a_w values and low moisture uptakes (0.1-0.25 g/100g) at high a_w values, similar to those of conventional LDPE to film. Based on the above preliminary results the above biodegradable films may be used in food packaging applications which do not require a high barrier to moisture.

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EFFECT OF STORAGE CONDITIONS ON THE TOTAL QUALITY OF SAFFRON

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ABSTRACT

The effect of temperature and water activity on the stability of saffron was investigated. The coloring power and bitter taste of saffron were better preserved at low temperatures and low water activities. A better development and keepability of the aromatic characteristics of saffron was observed at low water activities and higher temperatures.

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SHELF-LIFE STUDY OF CITRUS JUICES

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ABSTRACT

Citrus juices and the related beverages, like all other fruit juices, are susceptible to microbiological as well as to various chemical degradations. Among the most significant reasons of chemical degradation is the development of off-flavors, the product discoloration (caramelization, nonenzymic browning) and furthermore, the loss of important nutrients, i.e. vitamins.

Among the factors that affect the "shelf life" of citrus juice's products are the processing conditions, the quantity of oxygen that is included, the type of container, the storage temperature and the specific type of the product. As far as changes are concerned that lead to the formation of off-flavors, they may be divided into two major categories : a) loss of the original caracteristic flavor and b) development of new foreign flavors usually accompanied by off-colors that are not found in fresh juices.

For all the above reasons, the "shelf-life" study of citrus products must be included in the standard controls not only for eliminating the results affecting the marketability of the final product but also, for being in accordance with the new Nutritional Labeling and Education Act which imposes that the contents of vitamins and minerals must be shown on the label of the product.

The basic controls that are included in a "shelf-life" study and which must be regularly repeated at least during one year, are vitamins control, color stability control, determination of sugar and aminoacid concentrations and the determination of the natural essential oil as well as of the "off-flavors" formed.

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CHEMISTRY AND QUALITY OF LIFE: A PHILOSOPHICAL APPROACH

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At the end of the 20th century the standard of life has been raised for a major part of humanity to a level, that in past times would have seemed utopian. The contribution of chemistry to this task is of unique importance, since the development of new drugs, working materials or dyes was only possible with its aid. This story of success is accompanied, however, since the beginnings of the chemical industry by problems and conflicts that arise from undesired secondary effects of chemical processes. These secondary effects become today some times a serious menace for the foundations of human life, so that chemistry is often the target of criticism and sees itself in the dock of public opinion.

So nowadays chemistry has become the object of a public discourse, to that obviously the chemists participate only as simple members. The results of this discourse depend, however, in a great degree on the epistemological point of view of the participants and on the clarity and stringency of their arguments and conclusions. The contribution of philosophical reflection hereto consists in providing sharp definitions of the fundamental terms needed in this discourse and by indicating which epistemological position is the most suitable for its success.

Following a terminological distinction made by JANICH 1995 the terms "sustenance" and "quality of life" are methodically introduced, so that ensuring the first is precondition for ensuring the second. "Ensuring sustenance" means "providing the means for the support of life" and "ensuring the quality of life" means that measures are taken against discomforts that arise from the methods and processes utilised for achieving the first aim. Due to the fact that the definition of "comfort" and "discomfort" depends mainly on the cultural context it is very difficult to establish universally accepted criteria for the means that "ensure the quality of life".

At this point the choice of the appropriate epistemological position is of great importance for the understanding of the motives in a discourse about quality of life and in helping to establish some rational criteria for it. The today prevailing Naturalism tries "to incorporate in his description the culture as a part of nature, because in his opinion even man as upholder of civilisation and the world that is changed by civilising means were always nature and obeyed in that sense natural laws" (JANICH 1992: 13). In spite of its *prima facie* attractiveness Naturalism leads to an impasse because it condemns its followers to passivity even against the consequences of their own actions, since they are understood as obeying the adamant laws of nature or as relying on "micro structures". The only consequence remaining for a naturalist who discovers that his actions have undesirable side effects is to cease any further engagement in his object.

The epistemological alternative to Naturalism is Culturalism, that "places the human actions in the focus of the description of reality and regards nature as an object of human praxis" (JANICH ibid.). The culturalistic approach to the problems concerned with chemistry and quality of life is the philosophical expression of the responsibility of mankind not only for the correct performance of human actions but also for the establishment of rational and universally worthy aims. The discourse about the quality of life is then not a discourse about how we are forced to live but about how we wish to live with respect not only to the immediate life sustaining needs but also with respect to the cultural needs of mankind.

Literature:

JANICH 1992: P. Janich. *Grenzen der Naturwissenschaft*, Munich 1992.

JANICH 1995: P. Janich. Chemie und Kultur, in: H. Abele (ed.) *Chemie und Lebensqualität, Forum Engelberg 1994*, in press.

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PHOTOFRAGMENTATION OF ORGANIC AND ORGANOSILICON COMPOUNDS. AN ESR AND LASER PULSE PHOTOLYSIS STUDY

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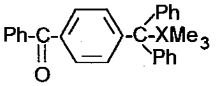
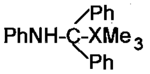
Much of the current research activity in photochemistry is focusing in understanding the factors that govern the energy transfer in polychromophoric systems. In this context we have studied the photochemical activity (homolysis/heterolysis) of a distal bond (C-C or C-Si) in organic or organometallic chromophoric systems (1,2) using ESR Spectroscopy and nanosecond laser pulse photolysis.

Compounds 1α,2α undergo a very efficient photodesilylation to the radicals 3,4 respectively ($\Phi \approx 0.9$) by irradiation in common organic solvents with UV light ($\lambda > 290$nm). The radicals 3,4 were identified using ESR spectroscopy and the final products by GC-MS.

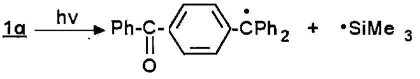


1α X=Si
1β X=C



$PhNH\text{-}C(Ph)_2\text{-}XMe_3$

2α X=Si
2β X=C



(1)

3

$$2\alpha \xrightarrow{h\nu} PhNH\text{-}\dot{C}Ph_2 + \bullet SiMe_3 \qquad (2)$$

4

The carbon analogues 1β,2β do not lead under the same conditions to a C-C bond cleavage, despite the fact that their bond dissociation energies (C-Si and C-C) are similar.

Compounds 1α,β were also studied with ns laser pulse photolysis at 248nm (KF* eximer laser) and 308nm (XeCl*) and the spectra of the produced transients were recorded. 1α gives 0.5 ns after the generating laser pulse the radical 3, while 1β leads in 1μs to the formation of a long lived benzophenone-like triplet state ($^3BP^*$) and later to the same radical 3, a fact that probably indicates that the homolysis results from the $^3BP^*$.

The anilino compound 2α leads to the formation of the radical 4 and to minor amounts of the 4a,4b-dihydro-fluorenyl radical, through a biphotonic process.

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ENHANCED EMISSIONS FROM ACTIVE NITROGEN AND OXYGEN

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ABSTRACT

Enhanced emissions from active nitrogen and oxygen were observed without a catalyst and at higher pressures than those reported previously.

Enhanced emission of the first positive band system of nitrogen was observed from various vibrational levels of the N_2 ($B\ ^3\Pi_g$) state in a mixture of active nitrogen and oxygen without a catalyst and at higher pressures than those reported in previous research. Arguments are presented to identify the species responsible as well as implications to previous research of this phenomenon of homogeneous excitation to N_2 ($B\ ^3\Pi_g$) induced by excited O_2.

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NON LINEAR OPTICAL PROPERTIES OF FLEXIBLE MOLECULAR CLAIM. COMPUTATIONAL METHODS OF H_2S_{12}.

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ABSTRACT

The structures of the global energy minimum and of five relative energy minima of the polysulfide H_2S_{12} were determined using the GMMX and MNDO programmes. The total energy E, the dipole moment μ, the polarisability α, the first hyperpolarisability β_μ and the second hyperpolarisability γ were compouted using the MNDO method. The global energy minimum structure, which is a helix, haw a second hyperpolarisability which is 28% higher in comparison with the γ value of the next conformer (Figure 1, II).

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THERMODYNAMIC PROPERTY AND PHASE EQUILIBRIUM (VAPOR-LIQUID AND LIQUID-LIQUID) PREDICTIONS OF CFC AND HCFC MIXTURES WITH HYDROCARBONS AND HYDROGEN FLUORIDE

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ABSTRACT

The Associated-Perturbed-Anisotropic-Chain-Theory (APACT) is used to predict the vapor pressure and saturated liquid density of pure CFCs, HCFCs, hydrocarbons and hydrogen fluoride (HF) from low temperature up to near the critical temperature of the components. The same equation is used to predict the vapor - liquid and the liquid - liquid equilibria of binary and ternary mixtures containing these components. Theoretical predictions are in good agreement with the experimental data and therefore the model can be used in case that no experimental data are available. In addition, the model predicts partially miscibility between HF - R12 and HF - R22 that needs to be verified experimentally. Finally, calculations are shown from two cubic equations of state, the Peng-Robinson and the Soave-Redlich-Kwong, for comparison. APACT is superior than these two equations for most of the mixtures examined in this work.

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CHEMICAL SYNERGISTIC EFFECTS OF AIR POLLUTANTS, ACTING ON SOLID SURFACES

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The deposition velocity and the reaction probability of air pollutants on the surfaces of cultural heritage can be measured in the presence of synergistic effects due to gaseous chemical reactions and adopting non-linear adsorption isotherms of the pollutants. The experimental set-up is that of the Reversed-Flow Gas Chromatography technique and the mathematical analysis is based on the equation

$$H^{1/M} = A_1\exp(B_1 t) + A_2\exp(B_2 t) + A_3\exp(B_3 t)$$

where H is the height of the sample peaks obtained by repeatedly reversing the flow direction of the carrier gas for short periods (10-60s) at time t, and M the response factor of the detector.

The physical meaning of the exponential coefficients of time B_1, B_2 and B_3 lead to the calculation of the local equilibrium parameter k, the desorption rate constant k_{-1}, the first-order rate constant of the surface reaction k_2, the deposition velocity V_d and the reaction probability γ of the pollutants with solid surface.

The equations derived have been applied to the deposition of propene on marble powder, at two temperatures, and in the presence of gaseous nitrogen dioxide.

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THE EFFECT OF ADSORBED TOLUENE ON THE SURFACE PROPERTIES OF CALCIUM HYDROXIDE

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ABSTRACT

The surface properties of commercial grade calcium hydroxide were studied by nitrogen adsorption isotherm analysis using a Micromeritics ASAP 2000 automated instrument, FTIR spectroscopy (transmission and diffuse reflectance) on a Shimadzu 8000 spectrophotometer and TGA analysis on a Shimadzu thermogravimetric analyzer, before and after toluene adsorption.

Experimental results show that the surface texture of calcium hydroxide is little affected despite the relatively high amounts of adsorbed toluene and that the organic molecules are strongly bonded on the solid. However, if toluene treatment preceded by heat treatment in vacuum, the penetretion of the organic molecule into the bulk is achieved, resulting in a very stable complex.

It is suggested that the high internal surface of the thermaly treated calcium carbonate is accessible to toluene molecules, possibly because openings are slit-shaped, affording access to the flat-shaped molecules.

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DIFFUSION COEFFICIENTS IN LIQUIDS BY HPLC AND THE RESPECTIVE CALIBRATION FACTORS

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When an analyte can be chromatographed on a HPLC column using a suitable solvent, the diffusion coefficient of this analyte into the solvent can easily and accurately be determined, together with the calibration factor of the detector for this analyte. The experimental arrangement is based on a slight modification of the HPLC valve so that analyte is introduced into the chromatographic column via a short diffusion column filled with the solvent. The new method is theoretically developed and the required mathematical relations have been derived. As an example, the diffusion coefficient of liquid benzene in chloroform, together with its calibration factor, are measured, under various experimental conditions, and the values found compare very well with that calculated by Wilke-Chang formula. Diffusivities and calibration factors of ions in aqueous liquid systems can also be determined by the new method.

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X-RAY CRYSTALLOGRAPHIC ANALYSIS OF THE GLYCOGEN PHOSPHORYLASE b-2-DEOXY-GLC-6-P COMPLEX.

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ABSTRACT

Kinetic and crystallographic studies have characterized the effect of 2-deoxy-glucose-6-phosphate on the catalytic and structural properties of glycogen phosphorylase b. Previous work has shown that 2-deoxy-glucose-6-phosphate does not exhibit co-operativity in inhibiting the phosphorylase b reaction[1]. 2-Deoxy-glucose-6-phosphate acts competitively with both the activator AMP and the substrate glucose-1-phosphate, with K_i values of 0.53 mM and 1.23 mM respectively. The binding of glucose-6-phosphate in the T state crystals of phosphorylase b is accompanied by substancial conformational changes[2]. The glucose-6-phosphate molecule is situated at the subunit-subunit interface and participates in hydrogen bonds to both subunits, leading to the suggestion of a possible route for the mediation of homotropic and heterotropic interactions. The binding of 2-deoxy-Glc-6-phosphate to T state glycogen phosphorylase b in the crystal, has been investigated and the complex phosphorylase b-2-deoxy-glucose-6-phosphate refined to give a crystallographic R factor of 17.3%, for data between 8 and 2.3 Å[3]. 2-Deoxy-glucose-6-phosphate binds at the allosteric site as the α anomer and adopts a different conformation compared to glucose-6-phosphate. The two conformations differ by 160° in the torsion angle about the C5-C6 bond. The contacts from the phosphate group are essentially identical to those made by the phosphate of glucose-6-phosphate but the 2-deoxy-glucosyl moiety binds in a quite different orientation compared to the glucosyl of glucose-6-phosphate. The structure of the 2-deoxy-glucose-6-phosphate complex helps to explain the biochemical properties of the inhibitor.

REFERENCES

[1] Bailey, I.A., Williams, S.R., Radda, G.K. & Gadian, D.G. (1981). Activity of phosphorylase in total global ischaemia in the rat heart. A phosphorus-31 nuclear-magnetic-resonance study. *Biochem. J.* **196**, 171-178.

[2] Johnson, L.N., Martin, J.L., Acharya, K.R., Barford, D. & Oikonomakos, N.G. (1993). The refined crystal structure of the glycogen phosphorylase-glucose 6-phosphate complex. *J. Mol. Biol.* **232**, 253-267.

[3] Oikonomakos, N.G., Zographos, S.E., Johnson, L.N. , Papageorgiou, A.C. & Acharya, K.R. (1995). The Binding of 2-Deoxy-Glucose-6-Phosphate to Glycogen Phosphorylase b : Kinetic and Crystallographic Studies. *J. Mol. Biol.* **253**, 114-131.

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EXPERIMENTAL AND MATHEMATICAL METHODOLOGY FOR THE DESCRIPTION OF THE DYNAMICAL BEHAVIOUR OF A SYSTEM CLOSE TO THE BIFURCATION POINT

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The behaviour of dynamical systems can be a static, periodic, quasi-periodic or even chaotic. The modelling of dynamical systems is often very difficult due to the complex dynamical behaviour and the bifurcations observed by varying a bifurcation parameter. The microscopic processes giving rise to dynamical behaviour are rarely known, causing an additional difficulty to the modelling of such systems.

In the present work we propose a systematic methodology for the construction of model differential equations describing the bifurcation of dynamical systems from experimental observations,

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x} + \mathbf{P}(\mathbf{x}), \qquad \mathbf{x} \in \mathbf{R}^d, \tag{1}$$

where $\mathbf{x}$ is the vector of the dynamical variables of the system, $\mathbf{A}$ is a $d \times d$ matrix with constant coefficients and $\mathbf{P}(\mathbf{x})$ is a non-linear vector function. By recording steady state curves and time series, performing perturbation experiments on the steady states, reconstructing the attractors and calculating the Lyapunov and power spectra, a possible linear part of the model equations can be constructed. The non linear terms of the model equations can be calculated from the proposed linear part $\mathbf{A}$ of Eq.(1) by solving the following system of differential equations,

$$\mathbf{DP}(\mathbf{x}) \cdot \mathbf{A}^* \cdot \mathbf{x} = \mathbf{A}^* \cdot \mathbf{P}(\mathbf{x}), \tag{2}$$

where $\mathbf{DP}(\mathbf{x})$ is a $d \times d$ matrix with elements $\frac{\partial P_i(\mathbf{x})}{\partial x_j}$, $i, j = 1, 2, ..., d$, and $\mathbf{A}^*$ the complex conjugate of the matrix $\mathbf{A}$. The matrix $\mathbf{P}(\mathbf{x})$ satisfies the boundary conditions $\mathbf{P}(\mathbf{0}) = \mathbf{0}$ and $\mathbf{DP}(\mathbf{0}) = \mathbf{0}$.

The resulting equations are expected to reproduce the dynamical behaviour and the stability of the system close to a bifurcation point. The present methodology can be applied to experimental systems when :

1. The steady state curves can be recorded by varying a bifurcation parameter.
2. The steady states can be perturbed.
3. The time evolution of the response function can be recorded for long time in order to calculate the power spectrum and the Lyapunov exponents.

For these systems it is possible to construct the matrix **A**, to solve Eq.(2) and so Eq(1) will describe the system close to the bifurcation point.

The method have been applied to the electrochemical system Fe/2M H_2SO_4. The system of differential equations constructed by the proposed method reproduce qualitatively the experimental bifurcation sequences and the geometry of the chaotic attractor. Additionally, the experimental and theoretical bifurcation diagrams show a qualitative similarity.

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EXPERIMENTAL BIFURCATION ANALYSIS OF THE ELECTROCHEMICAL STEADY-STATE AND OSCILLATORY BEHAVIOUR OF THE Fe/14.8 M H_3PO_4 SYSTEM

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ABSTRACT

In this study, the bifurcation analysis of the electrochemical steady-state and oscillatory behaviour of the Fe/14.8 M H_3PO_4 system is carried out by using as control parameters the applied potential (E), the Fe-disc rotation speed (ω) and the external resistance (R_{ex}), which was inserted between the ground and the Fe electrode. The critical values of the bifurcation parameters for which the system leaves the stable limiting current (SS1) and passive (SS2) regions to attain the oscillatory region (OSC), and vice versa, are determined along with the types of the local bifurcations occurring close to these critical values. The determination of these local bifurcations was based on the absence of hysteresis for both the SS1⇔OSC and OSC⇔SS2 transitions and the variation of the oscillation amplitude and period with the distance $|E-E_{bif}|$ from the bifurcation potential E_{bif}. It is found that close to the SS1⇔OSC transition, the oscillation amplitude varies linearly with $|E-E_{bif}|^{0.5}$, whereas close to the OSC⇔SS2 transition, the oscillation period varies exponentially with $|E-E_{bif}|$. These findings are consistent with the diagnostic criteria supporting a supercritical Hopf bifurcation (SUPH) for the former transition and a saddle-node of infinite period bifurcation (SNIPER) for the latter one.

The IR-drop as a primary factor that induces oscillations is discussed. The R_{ex} induces only periodic, whereas ω induces quasiperiodic and complex oscillations in agreement with the results obtained by varying the $C_{H_3PO_4}$. This result indicates that the complex behaviour of the system can only be explained if the coupling of mass-transport and electrode processes should be combined with an IR-drop mechanism. A theoretical model proposed to describe the dynamical behaviour of the Fe/14.8 M H_3PO_4 system must reproduce the SUPH and SNIPER bifurcations for the transitions SS1⇔OSC and OSC⇔SS2, respectively.

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Computer Aided Two-Parameter Sensitivity Analysis of Isotherms Application in Sorption of Cyanides by Activated Carbon

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ABSTRACT

Parameter-values of a sorption isotherm depend on the way they have been estimated (i.e. on the regression model used). To ensure comparability and compatibility of these values, a method of determination of intersection of joint confidence regions is suggested, to locate a domain of common validity of parameters of the same semi-linear isotherm estimated through different non-linear and linearized regression models, by means of least squares. A computer-aided implementation of this method is presented in the case of sorption of cyanides by activated carbon following the Freundlich isotherm. The method is easily extended to cover multiparameter non-linear isotherms.

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CHEMICAL DYNAMICS OF THE DIMERIZATION REACTION OF OX RADICALS (X = Br, Cl)

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ABSTRACT

Preliminary studies of the chemical dynamics of the dimerization reaction of BrO are reported, based on the LEPS approximation of the potential energy surface. Comparison of the theoretical rate constant to the experimental results show satisfactory description of the mechanism of the reaction

The dimerization of BrO radical was found experimentally to take place through the following channels

$BrO(^2\Pi) + BrO(^2\Pi) \rightarrow BrOO(^2A'') + Br(^2P) \rightarrow 2Br(^2P) + O_2\,(^3\Sigma_g^-)$ ΔE= -30.53 kJ/mol (a)

$BrO(^2\Pi) + BrO(^2\Pi) \rightarrow Br_2\,(^1\Sigma_g^+) + O_2\,(^3\Sigma_g^-)$ ΔE=-222.63 kJ/mol (b)

Channel (a) is the dominant one with a ratio of k_{2a} to the total dimerization rate constant, k_2, of about 0.85 at 298 K and 0.68 at 220 K. Also, a negative temperature dependence has been observed for the overall rate coefficient.

The potential energy surface has been constructed based on the extended LEPS form for a four-atom system, by empirically adjusting the Sato parameters. For a linear transision state geometry it predicts an energy well at the entrance valley followed by a low energy barrier with respect to the reaction products, which may account for the negative temperature dependence observed experimentally. For the trapejoidal transition state configuration which favours channel (b), a low energy barrier is predicted at the entrance valley of the reaction. This explains the smaller contribution of channel (b) to the overall reaction rate constant.

Further extended calculations are underway to elucidate the mechanism of the reaction and the mode of partitioning of the total energy available into the reaction products.

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LASER-RAMAN SPECTROSCOPY OF α,ω-DISUBSTITUTED n-ALKANES

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ABSTRACT

Studies of low-frequency Raman spectra of crystalline n-alkanes[1,2] have led to an understanding of their whole molecule vibrational modes, particularly the Longitudinal Acoustic Mode (LAM) which derives from bond angle and bond length distortion of the trans planar chains. The most informative and widely studied of these modes is the single-node longitudinal acoustic (or accordion) mode (LAM-1), since its frequency is approximately proportional to the reciprocal of the ordered chain length from which it originates irrespectively of the chain packing in the crystal.

A well recognised difficulty is the perturbation of the LAMs vibrations by end effects, i.e. end groups (including chain folds) through their inertial masses or interlayer (or interlamellar) forces[3].

The present work yields results of α,ω disubstituted n-alkanes[4,5]as:

$Br^-Me_3N^+\text{-}(CH_2)_{20}\text{-}N^+Me_3Br^-$, $Br^-Et_3N^+\text{-}(CH_2)_{20}\text{-}N^+Et_3Br^-$, $H_2O_3P\text{-}O\text{-}(CH_2)_{12}\text{-}O\text{-}PO_3H_2$ and $H_2O_3P\text{-}O\text{-}(CH_2)_{16}\text{-}O\text{-}PO_3H_2$

Raman spectra have been taken at high frequency region (200-4000cm^{-1}) as well as at low freqency region (5-200cm^{-1}), and at temperature range 100K-293K.

We have examined the effect of end groups on the LAM-1 frequencies. Calculations have been carried out, using the linear chain model of Minoni and Zerbi[6]. The model allows for the fact that the molecules are packed into layer crystals, and treats the case of the infinite one-dimensional crystal with an oligomeric repeat unit. If the alkyl block is treated as a point mass the required parameters are the force constants between chain groups (f_c) and between end groups (f) and the masses of chain groups (m_c) and end groups (m). The phase angle (θ) of the longitudinal vibration centred on the oligomer is be given by the equation:

$$(2\pi v)^2 = (2f_c/m_c)(1-\cos\theta)$$

Calculations were carried out with values of fc=460 Nm^{-1} (based on the elastic modulus of carbon chain) and f=3 Nm^{-1} (van der Waals forces)[7].

The experimental values are in fairly agreement with the calculations.

REFERENCES

1. S. Mizushima and T.Shimanouchi, *J.Am.Chem.Soc.*, **71**, 1320 (1949)
2. H.G. Olf and B. Fanconi, *J.Chem.Phys.*, **59**, 534, (1973)
3. K. Viras, *Macromol.Symp.*, **94**,121 (1995)
4. A. Kokkinia, *Ph.D. Thesis University of Athens* (1994)
5. A.Kokkinia, K.M. Paleos and D. Dais, *Mol.Cryst. Liq. Cryst.*, **186**,239 (1990)
6. G. Minoni and G. Zerbi, *J.Phys. Chem.*, **86**, 4791 (1982)
7. K. Viras, C. Campbell, T.A. King and C. Booth, *J. Phys.Chem.*, **93**,3479 (1989)

Chimika Chronika, New Series, 26,254 (1997)

THE CRYSTAL STRUCTURE OF THE 1:1 COMPLEX OF THE (2,3,6-TRI-*O*-METHYL)α-CYCLODEXTRIN WITH 1,7DIOXASPIRO[5,5]UNDECANE

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ABSTRACT

In a systematic investigation of inclusion complexes of pheromones in cyclodextrins or their methylated derivatives, we have solved the structure of the complex of 1,7-dioxaspiro[5,5]undecane, the main component of the pheromone of *dacus oleae,* with (2,3,6-tri-*O*-methyl)α-Cyclodextrin (TMαCD). A racemic mixture of the pheromone was used in the preparation. The structure (space group $C222_1$, **a**=24.002, **b**=14.8120, **c**=21.792A) was refined to a final R=0.0828. The approximate six-fold axis of the TMαCD molecule coincides with the two-fold crystal axis **a**, therefore half of the host molecule is in the asymmetric unit. The guest sits on the two-fold crystallographic axis in the middle of the host cavity, disordered over two positions with occupation factors 0.5. The sites of the two enantiomeric pheromone molecules in the TMαCD cavity have been found by fitting the R and S molecular models on the difference electron density maps using Molecular Graphics. Subsequent refinement of the models gave occupation factors 0.5 and 0.0 for the R and S enantiomers respectively. This clearly indicates that only the R enantiomer is included, thus TMαCD shows enantioselectivity towars the (R)-1,7dioxaspiro [5,5]undecane. The structure shows that only one of the two rings of the guest molecule is inside the host at the secondary methoxy region, its two oxygen atoms interacting with two methyl groups of the host.

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STRUCTURE OF THE COMPLEXES OF β-CYCLODEXTRIN WITH Z-7-TETRADECENAL AND Z-7 TETRADECENOIC ACID

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ABSTRACT

Z-7-tetradecenal is the main component of the pheromone of the olive pest *Prays Oleae.* Part of our efforts to find efficient formulations for the slow release of the pheromone in order to control ecologically the insect, was the structure determination of the inclusion complexes βCD/Z-7-tetradecenal and βCD/Z-7-tetradecenoic acid which were solved to final R=0.096 and R= 0.109 respectively. The βCD molecules form dimers which align themselves along the **c** axis to form a channel. The difference electron density Fourier maps, when the guest is not included, show strong electron density inside the CD cavity, along the 7-fold βCD axis. In both complexes two molecules of βCD include one guest molecule in a disordered fashion over two positions thus, the host:guest ratio is 2:1. However, for the βCD/Z-7-tetradecenal complex the host:guest ratio when the complex is freshly prepared is 1:1, as determined by NMR. Furthermore, studies of the release rate of Z-7-tetradecenal from the complex show that about 50% of the active pheromone is protected by βCD, whereas the other 50% is easily released and oxidized. Therefore, It seems that a number of pheromone molecules are not included in the βCD cavity. The crystallographic evidence supports the above: There is a continuous electron density along the length of the dimer in the crystal lattice outside the cavity. This has the right length to be attributed to a disordered molecule of Z-7-tetradecenal.

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IMPEDANCE OF INCLUSION COMPLEXES OF β-CYCLODEXTRIN

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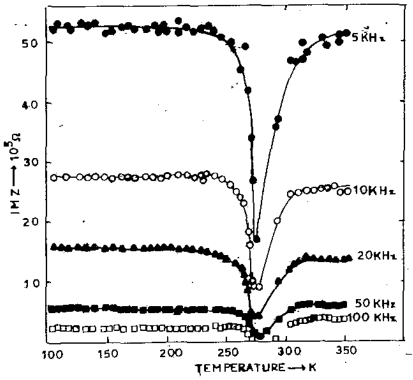
ABSTRACT

The Impedance of the polycrystaline complex of β-cyclodextrin with the 4-tert-bytyltoluene was investigated with a dynamic signal analyser coupled to a computer controlled system.The Real(ReZ) and Imaginary(ImZ) parts of impedance were taken over frequency and temperature ranges of 0-100KHz and 100-350K respectively. Around 270K a transition appears for every frequency. This can be interpreted as the result of orientation of polar molecules, i.e. water molecules, under the influence of the applied field. In the low frequencie range the alignement of dipoles is sufficiently fast to follow the changes of the applied electic field. However, in the higher frequencies it is impossible to follow those changes and the dipols remain inert. The result is manifested in the observed difference in phase between the polarization of the medium and the applied field. As a consequence, there is a tranfer of energy from the field to the medium.



Chimika Chronika, New Series, 26, 257 (1997)

INHIBITORS OF GLYCOGEN PHOSPHORYLASE b AS POTENTIAL ANTIDIABETIC DRUGS : KINETIC AND CRYSTALLOGRAPHIC STUDIES.

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ABSTRACT

Hyperglycaemia in the non-insulin-dependent form of the desease diabetes mellitus (Type II diabetes) patients results from diminished insulin release and/or insulin resistance that leads to impaired glucose uptake and impaired suppression of hepatic glucose output[1] where the glucose is produced by gluconeogenesis and glycogen metabolism. Glucose is a physiological regulator of hepatic glycogen metabolism and induces sequentially the inactivation of glycogen phosphorylase and the activation of glycogen synthase[2]. Structural studies with glycogen phosphorylase have led to the design of a series of glucose analogue inhibitors that can act as powerful regulators of liver glycogen metabolism. The best compound to date is an epimeric spirohydantoin of glucopyranose and exhibits a K_i that is 3 orders of magnitude lower than that of glucose. This is the first example of specific enzyme inhibition by a spyrohydantoin at the anomeric position of a sugar[3].

REFERENCES

[1] De Fronzo, R. A., *Diabetes*, 1988, 37, 667-687.

[2] Bollen, M., Stalmans, W.,*Crit. Rev. Biochem.Mol. Biol.*, 1992, 27, 227-281.

[3] Bichard, C. J. F., Mitchell, E. P., Wormald, M. R., Watson, K. A., Johnson, L. N., Zographos, S. E., Koutra, D. D., Oikonomakos, N. G., Fleet, G. W. J., *Tetrahedron Lett.*, 1995, **36**, 2145-2148.

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APPLICATION OF CYCLODEXTRINS AS RELEASE RATE REGULATORS FOR THE VOLATILE SEX PHEROMONE COMPONENTS OF *BACTROCERA OLEAE*

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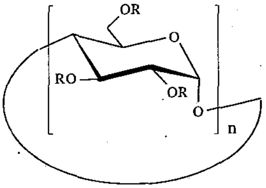
ABSTRACT

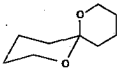
Cycloderxtrins (CDs) are cyclic oligosaccharides which form inclusion complexes with the four major components (**1** - **4**) of the sex pheromone of the olive fruit fly *Bactrocera oleae,* resulting in much reduced volatility of these substances.



n = 6, 7, 8

R = H: α-, β-, γ-CD

R = Me: TMα-, TMβ-, TMγ-CD



1

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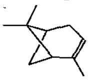

2

4

These volatile constituents are released from *saturated* aqueous solutions of the complexes with constant and controlled rate. This is due to the equilibrium between free and complexed states, governed by the dissociation constant K_D. The guests are continuously released from the saturated solution and the concentration of the CD increases until it reaches its solubility S_{CD}. Then the concentration of the guest also remains constant, $[G] = K_{sp}/S_{CD}$, thus and its release rate. The values of K_D, S_{CD}, and the K_{sp} were calculated for each of the above CDs with the four guest molecules.

$$\begin{tikzcd} CDG \arrow[r, shift left, "K_D"] \arrow[d, shift left] & CD + G \uparrow \arrow[l, shift left] \arrow[d, shift left, "S_{CD}"] \\ CDG_S \arrow[u, shift left, "S"] & CD_S \arrow[u, shift left] \end{tikzcd}$$

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EXCESS THERMODYNAMIC FUNCTIONS AND INTERACTIONS IN BINARY MIXTURES OF ALKYL ACETATES WITH P-CHLOROTOLUENE AT 293.15 K

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ABSTRACT

Thermodynamic interactions of binary mixtures of P-Chlorotoluene with Methyl (MA),Ethyl (EA) and Propyl (PA) acetates have been studied in terms of a number of excess functions from the measured mixtures properties as density,viscosity and refractive index at 293.15 K.

For all mixtures, the values of excess volumes,V^E are negative, which generally decrease with increasing size of methyl group. The interactions in these mixtures may be classified as weak dipole-induced dipole type forces resulting from the polarization of ester molecules by the dipoles of P-Chlorotoluene.This effect can be superimposed upon the dipole-dipole interactions and thus lead to a slight increase in the attraction, giving negative V^E.However in the case of mixture of MA + P-Chlorotoluene volume contractions are comparatively smaller and the value is -0.05.

The mixtures of esters with P-Chlorotoluene show the trend in excess viscosity values,n^E,as MA<EA<PA,with negative values of n^E for the mixture of MA + P-Chlorotoluene whereas for the mixture of PA + P-Choiotoiuene n^E is positive.In the case of EA + P-Chlorotoluene the values of n^E show a sigmoidal behaviour,with a reversal point around x =0.6.

The values of excess Gibbs free energy of activation of flow,ΔG^{*E} for all mixtures are positive in the following order : MA>EA>PA ,with maxima occuring around the middle of the composition scale.Interactions among dipole-induced dipole of polar molar of P-Chlorotoluene with less polar molecules of esters lead to the rupture of the molecular order as evidenced by the positive ΔG^{*E}.

The excess refraction values R^E,are negative for the mixtures of MA and EA with P-Chiorotoluene with minima at x =0.5.For the mixture of PA + P-Chlorotoluene the R^E values are very close to zero and this can be attributed to their small differences in molar volumes (for PA V =115.0372 cm^3 Mol^{-1};for P-Chlorotoluene V =118.3748 cm^3 Mol^{-1}).

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PHYSICOCHEMICAL STUDY OF MIXED MICELLE SYSTEMS

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ABSTRACT

Bolaform surfactants refer to molecules consisting of an alkyl chain (or a more complex moiety) terminated at both ends by a polar (ionic,zwitterionic or nonionic) group[1].They exhibit a number of properties (larger c.m.c values, smaller micelle size etc) which differentiate them from surfactants with one polar group[2-6] .Therefore, it is intriguing to investigate how the formation of micelles is influenced by the presence of a bolaform surfactant in a mixed system.

In the present study, the behaviour of the mixed surfactant system consisted of the bolaform molecule $(CH_3)N(CH_2)_{10}N(CH_3)Br_2$ ($DMBr_2$) and the conventional surfactant $CH_3(CH_2)_9SO_3Na$ (DSNa) has been investigated by means of electrical conductivity at different temperatures as a function of the concentration.

In the examined concentration range, the change of the specific conductivity κ=f (C), of the solutions containing the pure $DMBr_2$, does not show any break point which would be characteristic for the existence of the critical micelle concentration (c.m.c) in the above area, whereas the value of the c.m.c for the solutions of DSNa was received by the bibliography[7] . The obtained data suggest changes of the micellar composition in the mixed surfactant solution for different molar ratios of the dicationic bolaform and the anionic surfactant. Moreover, in the 1:1 ratio, that is mixing of equimolar quantities (case B), the formation of the molecules $DM\text{-}DS_2$ and NaBr takes place. In the 1:2 ratio (case A) except the formation of the the above stated molecules, the excess of DSNa is present. In the ratios 2:1 and 4:1 (cases C,D) excess of $DMBr_2$ is present instead of DSNa. Finally, in the situations where the ionic species $DM\text{-}DS_2$ and $DMBr_2$ coexist, the concentration of $DM\text{-}DS_2$ remains constant in all series I, II, III, having the values of 0.05, 0.20, 0.50 M respectively. (In the first solution of each series the concentration of $DMBr_2$ is equal to zero implying mixing of equimolar quantities of $DMBr_2$ and DSNa).

The surfactant activation energy for conduction ΔE for the mixed system is expressed by the relation $\kappa=\kappa_o \exp(-\Delta E/RT)$, (where κ_o : the constant of the particular system) and is determined in all systems by the plot of κ=f (1/T). In the case of equimolar solutions, it remains constant and it is smaller than the one observed in anionic-nonionic systems[8] .

REFERENCES

1.Brody,O.V.,and Fuoss, R.M., J. Phys. Chem., **60**,156(1956)
2.Menger,F.M., and Wrenn, S., J. Phys. Chem., **78**,1387,(1974)
3.Zana, R., "Mixed Surfactant Systems", Holland, P.M., and Rubingh,D.N. ed., chap.19, p.292, Amer.Chem.Society, 1992
4.Meguro, K., Ikeda, K., Otsuji, A., Taya, M., Yasuda, M., and Esumi, K., J.Colloid and Interface Sci.,**118**,372(1987)
5. Zana R., Yiv, S., and Kale, K., M.,J.Colloid and Interface Sci ., **77**,456(1980)
6. Zana R., Muto, Y., Esumi, K., and Meguro, K., J Colloid and Interface Sci., **123**, 502(1988)
7.Mukerjee P., Mysels KJ : "Critical micelle concentrations of aqueous surfactant systems" NSRDS- NBS36, Nat. Bur. Stand, Washington, 1970
8.Ogino K., Tsubaki N., Abe M., J. Colloid and Interface Sci., **98**, (1984)

Chimika Chronika, New Series, 26, 261 (1997)

MIXED MICELLIZATION PHENOMENA AT THE Hg-ELECTROLYTE SOLUTION INTERFACE

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ABSTRACT

The formation and properties of mixed micellar films on the Hg electrode in the presence of sodium dodecylsulfate (SDS) - cetyltrimethylammonium bromide (CTAB), SDS - Tween 80® and CTAB - Tween 80® in electrolyte solutions are studied by means of differential capacitance measurements. The experimental data are analysed and discussed on the basis of previous theoretical treatments. It is found that in the first system the interfacial behaviour is strongly determined by the ratio c_{SDS}/c_{CTAB}. For values of this ratio between ca 0.1 and 10 the two surfactants form immiscible bulk solutions. For values of this ratio higher than 500 or lower than 0.005 the system behaves like solutions of pure SDS and CTAB, respectively. When this ratio takes values from ca 10 to 50 the electrode surface is covered with a film of mixed micelles from -0.2 V(SCE) up to -1.6 V(SCE). When the ratio c_{SDS}/c_{CTAB} ranges from ca 0.01 to 0.05, the electrode surface is covered with a bilayer of micelles composed exclusively of CTA^+ from -0.2 V(SCE) up to -1.2 V(SCE). Negatively to this potential, this bilayer collapses to a compact layer due to its penetration of dodecylsulfate anions. In the second system and in electrolyte solutions rich in SDS, the electrode is covered with micelles of pure dodecylsulfate anions from the capacitance peak at positive potentials up to the first capacitance peak at negative potentials. Negatively to this peak the electrode surface is covered by mixed micelles rich in tween 80®. In electrolyte solutions rich in tween 80®, the capacitance peak in far negative potentials shifts to more positive potentials with the increace of SDS in bulk solution, in agreement with theoritical studies. Finally, in the third system the electrode is covered with a mixed micellar film throughout the range of potential we studied. The composition of this film depends on bulk concentrations and possibly on the potential.

Chimika Chronika, New Series, 26, 262 (1997)

STUDY OF THE ELCTRODEPOSITION OF SILVER FROM NITRATE SOLUTIONS IN BINARY WATER/DIOXANE SOLVENT SYSTEMS IN THE PRESENCE OF TARTARIC ACID

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ABSTRACT

Silver electrodeposition from $AgNO_3$ solutions never gives compact, smooth plates unless an organic additive such as tartaric acid (H_2T) is used as growth inhibitior. However depending on the bulk pH, tartaric acid may exist either as a undissociated molecule H_2T or as dissociated entities like HT^- or T^{2-}. We have shown previously that the inhibiting effect of H_2T clearly depends on the degree of dissociation of this acid. Because of this behaviour, it was decided to examine the influence of tartaric acid on the electrodeposition of silver from $AgNO_3$ solutions in binary Water/Dioxane solvent systems (10-30%v/v), where the addition of the organic solvent enables us to change the degree of dissociation of H_2T.

This work showed that in each series of electrolyte deposits (i.e. in each series of deposits obtained from solutions with constant solvent composition) the parameter controlling the growth inhibition was the activity, α_{HT^-}, of tartaric monanions. It was also concluded that the amount, Δp, of the organic substance incorporated into the deposits is a function of α_{HT^-}.

On the other hand, it was found that $\Delta p/p$ (p being the theoretical weight of the deposit predicted from the Faraday's law) also depends on the solvent composition and increases as the dioxane content increases.

The parameter $\Delta p/p$ affects most of the structural features of Ag deposits, e.g. their grain size, the superficial roughness and even the polycristalline structure expressed by the preferential orientation of the crystallographic axe [110].

Chimika Chronika, New Series, 26, 263 (1997)

PHYSICAL BEHAVIOUR OF SOME FUSED SALT+SOLVENT BRIDGING SYSTEMS. DENSITY, MOLAR VOLUME, THERMAL EXPANSION AND VISCOSITY CHANGES OF (Ag,Tl)NO_3+DIMETHYLSULFOXIDE+WATER SYSTEMS AT SEVERAL TEMPERATURES

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ABSTRACT

Viscosities and densities of the system $(Ag_{0.5},Tl_{0.5})NO_3$+DMSO+ H_2O were determined in the temperature range $376.15 \leq T / K \leq 394.15$ K with the mole fraction of the mixed melt, x_s, ranging between 0 and 0.9. This system, formed by the eutectic mixture of $AgNO_3$ and $TlNO_3$ (eutectic point equal to 83 °C, $AgNO_3/TlNO_3$ mole ratio equal to 1.062) and an equimolar mixture of dimethylsulfoxide with water, is liquid over the specified temperature and composition range.

Parameters such as the molar volume, the volume coefficient of thermal expansion, the rheochor and the activation entropy and enthalpy in the Eyring's equation were determined. An attempt has been made to express these properties by means of single equations, wherein the temperature and composition effects are involved.

In all temperatures studied, it was found that the values of the excess molar volume V^E of the mixtures are negative, and the corresponding curves V^E=f(x_s) at each temperature present a pronounced minimum at $x_s \approx 0.40$. Taking into account that solute-solvent interactions increase density and decrease molar volume; the negative values of V^E have been attributed to this behaviour.

The study of the activation enthalpy of viscous flow $\Delta H^{\neq}$ as a function of x_s showed that the number of holes, in the process of viscous flow, increases when the equimolar solvent mixture of DMSO and H_2O is progressively added to the melt.

The behaviour of the system studied here is compared with that of the corresponding $(Ag_{0.5}, Tl_{0.5})NO_3$+DMSO systems, previously investigated. The results indicate that the partial replacement of DMSO with water decreases the cation-dipole interactions.

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ELECTRODEPOSITION OF POLYANILINE AT IRON SURFACES FOR THE FORMATION OF PROTECTIVE COATINGS AGAINST CORROSION

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ABSTRACT

The anodic electropolymerization of aniline in oxalic acid solutions at an iron electrode is studied. The framework of this project is to coat Fe with an electron conducting polymer in order to replace the electrodissolution of the metal by another electrochemical reaction taking place on the top of the film. Cyclic voltammetry between -0.6 ÷ 1.5 V is used for the electrodeposition of polyaniline (PA) on Fe from 0.1 M $C_6H_5NH_2$ + x M $(COOH)_2$. The use of oxalic acid as a supporting electrolyte was based on the large potential range where the Fe/x M $(COOH)_2$ system exchibits passivity. The passive surface of iron resembles that of noble metals and the polymerization proceeds more easily. The polymerization of aniline starts with the electroxidation of aniline at 1.4 V but continues with a catalytic mechanism based on the electroxidation of PA. The PA coatings appear to be deposited over the passive iron oxide film but the potential region where iron oxalate film is formed must be scanned in order the reversible electroactivity (redox couple $E_a = 0.28$ V, $E_c = 0.3$ V, 2nd cycle) of PA to be seen. The ability of the PA coatings to protect iron surface against corrosion is examined in 0.5 M sulfuric acid solution. The I-E polarization curves of the Fe electrodes coated with PA show a remarkable decrease (about 80%) of the electrodissolution currents in both the active and the limiting current regions. In addition, the passive region is extended towards lesser positive potentials by almost 0.15 V. These good protective features of the PA coatings are useful from a technological point of view and could be further improved in terms of adhesion at Fe surface or microporosity.

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TEST OF THEORETICAL MODELS USED IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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ABSTRACT

Two models, which adopt the adsorption and the partitioning mechanisms for the retention in reversed-phase liquid chromatography, are tested against the experimental data of a great number of organic solutes. The model of the adsorption mechanism has been developed in our laboratory and assumes the adsorption of solutes at the edges of the carbon chains of the chromatographic column. In contrast, the model of the partitioning mechanism has been developed by K. Dill and his co-workers and assumes the partitioning of the solute molecules within the carbon chains. These two models are tested by comparing the theoretically predicted variation of the retention time upon the concentration of the organic modifier in the mobile phase with experimental data obtained using isopropanol as modifier in aqueous phosphate buffer solutions (pH=2.5) and 20 organic solutes of the category of catecholamines, indolamines and their derivatives. It is shown that the basic equations of these models describe satisfactorily the experimental data only if we disregard the physical constraints which are involved in the treatment of these models. In contrast, if we take into account these constraints, then both models fail completely to describe the retention mechanism, pointing out the necessity for further theoretical studies.

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EFFECT OF ORGANIC MODIFIER CONTENT IN REVERSED-PHASE LIQUID CHROMATOGRAPHY

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ABSTRACT

The effects of variations in organic modifier concentration on the retention behaviour of several monoamine transmitters and some metabolites and precursors were studied in an octadecyl silica reversed-phase system. Mixtures of either methanol or isopropanol with aqueous buffer solutions were used as mobile phase. Using isopropanol as the organic modifier better data for retention and peak width were obtained for all solutes studied than in the case of methanol. These retention data were fitted to three models, a reciprocal, a quadratic and a linear one, describing the effects of organic modifier concentration on retention in reversed-phase liquid chromatography.

The quadratic model proved to work most satisfactorily. Because of its accuracy, simplicity and good numerical behaviour, it could be used as a basis for predicting separation as a function of solvent strength. This model requires only three initial HPLC runs, where the organic modifier content is varied in order to locate the optimal mobile phase composition. The nonlinear retention behavior of these solutes is not surprising. The introduction of isopropanol to the pure aqueous mobile phase is accompanied by the extraction of the isopropanol by the alkyl chains of the stationary phase. The uptake of isopropanol by the bonded phase changes the nature of the surface of the stationary phase. This change of the stationary phase is more pronounced during the initial introduction of isopropanol to the mobile phase. Therefore, the retention of chromatographic solutes would not be a simple linear function.

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STUDY OF PHYSICOCHEMICAL PARAMETERS FOR EVALUATION OF SORBENTS FOR SAMPLING OF VOLATILE ORGANIC COMPOUNDS IN AIR

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ABSTRACT

The breakthrough volumes (BTV) of 11 volatile organic compounds (VOC) have been determined, using the direct and indirect method. The chemical structure of the VOC has been related to the calculated BTV values. In addition, the evaluation of performance of sorbent has been based on the following physicochemical parameters: enthalpy of sorption, distribution coefficient, sorption capacity, which have been calculated using B.T.V. values and Langmuir equation for the sorbent-analyte system.

Keywords: physicochemical parameters, breakthrough volumes, sorbents, sampling, volatile organic compounds, enthalpy of sorption, sorption capacity

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GOETHITE, A MESOPOROUS SOLID

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ABSTRACT

The present study examines the surface properties of synthetic goethite (α-FeOOH), which may be used as a cationic exchanger for the clean-up of waters from heavy metals by adsorption mechanisms. FTIR/DRIFTS spectroscopy and nitrogen adsorption isotherm measurements were carried out after degassing the samples at various temperatures.

According to isothermal N_2 adsorption results, all solids were found to be mesoporous. This was supported by the type IV shape of the isotherms. There was no appreciable change in the BET surface area but a decrease in the micropore area and a small increase in both total volume and average pore diameter. It is suggested that on heating, there is first elimination of molecular water, and then dehydroxylation, leading to elimination of narrow pores and their merger into mesopores, thus leading to an increase in their diameter. Heating to higher temperatures leads to a collapse of the structure resulting in lowering of the BET surface area accompanied by an opening of the structure, as evidenced by an increase in particle size. At lower temperatures, it appears that the observed changes are due to changes in the aggregate structure whilst the particle size remains constant. This would explain changes in pore volume and diameter without significant changes in BET surface area. Similar BET surface areas, but with different pore diameters were given by samples prepared under various preparative conditions, suggesting that the sample consists of loose aggregates. It is this aggregation rather than the particle size which are influenced by changes in treatment.

Spectroscopic and thermogravimetric (TGA) analysis support the change of the goethite structure occuring around 473K. It can, thus, be said that experimental results show that orthorhombic α-FeOOH undergoes a structural change to a corrundum α-Fe_2O_3-like structure at elevated temperatures, thus altering its surface and consequently its cationic exchanging properties.

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AN ANOMALOUS ADSORPTION OF ZSM-5 ZEOLITES

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ABSTRACT

The last twenty years have seen a growing interest for zeolite use in the chemical industry and its potentials to protect ecosystems. These microporous aluminosilicates with uniform pore dimensions convey a molecular sieving effect and possess ion-exchange properties. Their ability to develop internal acidity combined with their high thermal stability make them desirable catalysts. The MFI-type ZSM-5 zeolites, exhibiting a three-dimensional porous structure enclosed by two different 10-membered oxygen rings, may be synthesised in a controllable manner so that crystals may be formed suitable for certain catalytic applications. Recently, "template-free" systems have been used which require no organic material present for synthesis and are, thus, more environmentally friendly.

In this work, the surface properties of synthetic template-free Na-ZSM-5 microporous zeolites were studied by isothermal N_2 adsorption measurements and FTIR/DRIFTS spectroscopy. An anomalous adsorption type I isotherm exhibiting a descending curvature towards high pressures was obtained for one of the samples of high $NaOH/SiO_2$ degassed at 300K. This was attributed to the change in Al distribution and formation of defects effected by the increase in -OH. Aluminium ions affect the crystallization process by controlling the degree of hydration it possesses. Increasing the hydroxide concentration and, thus, the pH of the system, stepwise hydration of Al^{3+} to $Al(OH)^{2+}$...$Al(OH)_4^-$ occurs, leading to polymeric species and altering the Al distribution in the sample. Directly related to the pH is the creation of internal defects. In high pH, polycondensation of the silicate species does not occur which gives rise to $\equiv Si\text{-}O^-$ groups and Si/Al-atom vacancies.

Although microporous solids have high BET surface areas, this specific sample gave relatively low BET surface and micropore areas. This can be due to the presence of Na^+, a reagent in the reaction mixture, which is postulated to act as a template and a structure-directing agent, interacting with H_2O molecules to form clathrate structures. These act as a pore fillers lowering the surface values and stabilising the structure. On subsequent measurements upon the same sample, a uniform decline of the surface data, related to reorganisation of the claththrate H_2O molecules in the zeolitic voids, was observed. Heating to higher temperatures leads to removal of molecular water causing a rise to BET surface and micropore areas which fall into the expected levels.

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SORPTION OF NEODYMIUM ONTO NATURAL MICROPOROUS MATELIAS

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ABSTRACT

An attempt was made to estimate the retardation ability and the possible applications of Neodymium sorption on three earth materials, such as Montmorillonite, Kaolinite from Melos island, Aegean Sea and Zeoliferous rocks from Thrace, Greece. Montmorillonite was chosen as a representative of swelling clays, as well as its use as backfilling material for high level radioactive waste repositories. Kaolinite was studied as a representative material of non swelling clays. Experimental data reveal Langmuir type sorption on Zeolite and Montmorillonite, while a Freundlich type on Kaolinite. Montmorillonite presents the higher sorption ability in comparison with the other studied materials.

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MEASUREMENTS, MECHANISMS AND MODELS OF HOMOGENEOUS AND HETEROGENEOUS PHYSICOCHEMICAL PROCESSES IN THE ATMOSPHERE, STUDIED BY REVERSED-FLOW GAS CHROMATOGRAPHY

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Laboratory kinetic experiments can be performed under conditions of concentration, temperature, pressure, humidity etc. very close to those prevailing in the atmosphere, and in the presence of heterogeneous sinks, by the Reversed-Flow Gas Chromatography (RF-GC) technique. It is an absolute rate constant technique, but the system is neither a static nor a flow one. It is a diffusion controlled system, by means of which rate constants and reaction orders with respect to time n_t of unimolecular and bimolecular chemical reactions of atmospheric species with other substances, can be measured. In the presence of heterogeneous sinks, the following physicochemical parameters are determined under non-steady-state conditions: The local adsorption parameter k of the analyte A under study, and the experimental isotherm; the desorption rate constant of A from the solid surface k_{-1} ; the rate constant k_2 of a possible first-order or pseudo-first-order surface reaction of the adsorbed analyte; the deposition velocity V_d and the reaction probability γ of A on the heterogeneous sink.

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PHYSICOCHEMICAL INVESTIGATION OF THE SO_2 OXIDATION OVER MOLTEN SALTS CATALYSTS

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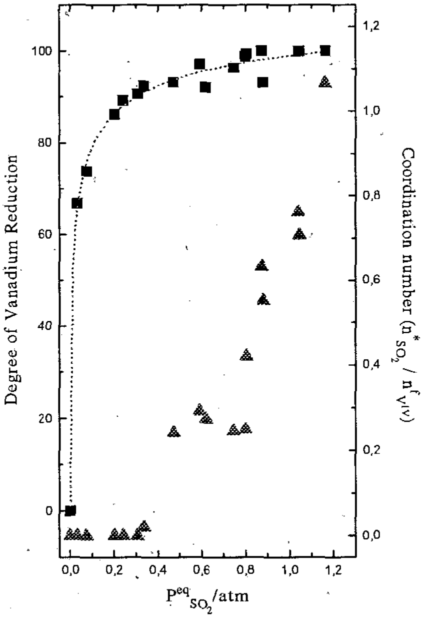
ABSTRACT



The molten salt-gas system $M_2S_2O_7/V_2O_5$-$SO_2/O_2/SO_3/N_2$ (M=Na, K, Cs), at 400-600°C is considered a realistic model of the working industrial catalysts for sulphuric acid production and flue gas cleaning. At normal operating conditions the catalytically active phase is a melt basically consisting of vanadium complexes dissolved in potassium pyrosulphate formed on the pore of the surface of the solid inactive silica support. The SO_2 oxidation takes place as a homogeneous reaction in the liquid phase. To date no definite conclusion has been made for the SO_2 oxidation mechanism on a molecular level. The present work describes our recent spectroscopic (UV/Vis, Raman) investigations on the possible coordination of SO_2 to V(V)- and V(IV)- complexes in the melt. In accordance with the figure no stable V(V) complex coordinated to SO_2 seems to be formed while V(IV) can coordinate SO_2 at higher partial pressures of SO_2. The measurements can so far be explained by the equilibria:

$$V_2O_5 + 2S_2O_7^{2-} \rightleftharpoons (VO)_2O(SO_4)_4^{2-}$$

$$(VO)_2O(SO_4)_4^{2-} + SO_2 \rightleftharpoons 2VO(SO_4)_2^{2-} + SO_3$$

$$VO(SO_4)_2^{2-} + SO_2 \rightleftharpoons VO(SO_4)_2(SO_2)^{2-}$$

The above conclussions may add important information to the process mechanism.

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RAMAN SPECTROSCOPIC STUDY OF THE DISSOLUTION OF WCl_6 IN LiCl-KCl EUTECTIC MELT

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ABSTRACT

Raman spectroscopy indicates that the dissolution of Tungsten hexachloride in the LiCl/KCl eutectic melt at 450°C produces the octahedral ion $[WCl_6]^-$ (385 cm $^{-1}$). This production may be attributed to the chemical reduction of W(VI) by the free chloride ion in the melt (r.1) which can be further supported by the evolution of Cl_2 in the vapor phase. The two-phase separation and the rather dark coloration, are typical features of this melt. Addition of excess of W metal results to a further reduction of W(VI) and W(V) to W(IV) (r.2) and the formation of the octahedral ion $[WCl_6]^{2-}$ (344 cm $^{-1}$). The vanishing of the vapor phase above the melt together with the change of the color of the upper layer from deep orange into light green, strongly demonstrate the end of reduction. In the metal containing system, the linear oxo-bridged complex ion $[W_2OCl_{10}]^{4-}$ (223 cm $^{-1}$), product of a minute amount of oxide impurity, was also detected, as a result of Resonance Raman effect. The following reactions have been established :

$WCl_6 + Cl^- \rightarrow [WCl_6]^- + 1/2\ Cl_2 \uparrow$ (r.1)

$4[WCl_6]^- + W + 6Cl^- \rightarrow 5[WCl_6]^{2-}$ (r.2)

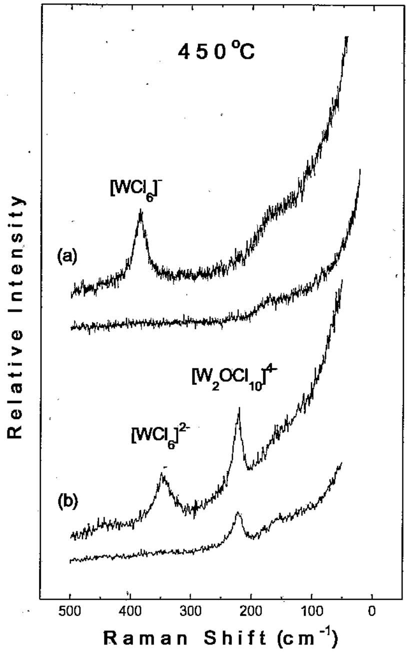

Fig. (a) LiCl/KCl(eut)-WCl_6 and (b) LiCl/KCl(eut)-WCl_6-W

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RAMAN SPECTROSCOPIC STUDY OF LANTHANIDE CHLORIDE - ALUMINUM CHLORIDE BINARY SYSTEMS IN THE VAPOR, LIQUID AND GLASSY STATE

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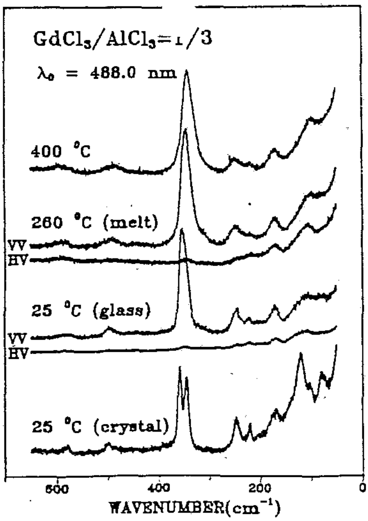
ABSTRACT

Raman spectra of molten $LnCl_3$-$AlCl_3$ (Ln=La, Nd, Gd, Ho) mixtures are obtained in the temperature range 230-400 °C. A study of the concentration dependence of the Raman spectra shows the formation of stable liquids with compositions La/Al=Nd/Al=1/4 and Gd/Al=Ho/Al=1/3 and main participating units "$AlCl_4$" and "Al_2Cl_7". The band observed for all the systems at the region 230-255 cm^{-1} is assigned to Ln-Cl stretching mode. Rapid cooling of these mixtures in water or liquid nitrogen, results in formation of glasses, whose Raman spectra are similar with the spectra of liquids as shown e.g. in the figure for the Gd-Al-Cl system, suggesting that the local structures of the liquids are maintained in the glassy state. The spectra are interpreted i) in terms of 9-fold coordination around La, Nd involving edge- or face-coordinated $AlCl_4$ tetrahedra and bridging or non-bridging Al_2Cl_7 units and ii) in terms of 8-fold coordination around Gd, Ho. Raman spectra of $GdAl_3Cl_{12}$ and $HoAl_3Cl_{12}$ crystals, formed in the mixtures with compositions Gd/Al=Ho/Al=1/3, exhibit (apart from band sharpening) the same features with the corresponding liquid and glass spectra. Instead of the broad "$AlCl_4$" band present at 350 cm^{-1} in the liquid/glassy state, a doublet is observed in the crystal spectra, attributed to bridging and terminal Al-Cl modes within the $AlCl_4$ tetrahedra. Finally, laser excitation of the $LnCl_3(s)$-$AlCl_3(g)$ vapor mixtures (Ln=Nd, Pr, Dy, Ho) gives rise to resonance fluorescence due to f-f transitions of Ln^{3+} in $LnCl_3(AlCl_3)_x$ vapor complexes. Laser induced fluorescence from excited states in the visible region has been studied by using different excitation lines.



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LIGHT SCATTERING FROM MOLTEN ALKALI HALIDES (CsX, LiX (X=F, Cl))

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ABSTRACT

In recent years, theoretical and molecular dynamics simulations studies have been used to calculate light scattering spectra of simple molten NaCl, LiCl and LiF. The simulated spectra of NaCl and LiCl were in good agreement with the experimental data. In the present work we have undertaken a systematically and extensive study of light scattering (Raman) at temperatures up to 850 ^{o}C of the following melts: LiCl, CsCl, LiF and binary mixtures of LiCl-CsCl.

Reduced isotropic and anisotropic Raman relative intensities have been measured at different compositions and temperatures. Typical reduced spectra measured for the LiCl-CsCl eutectic mixture are shown in Fig. 1. The band maxima in the reduced spectra are different in the isotropic and anisotropic represantations and are associated to different polarization-induced interactions.

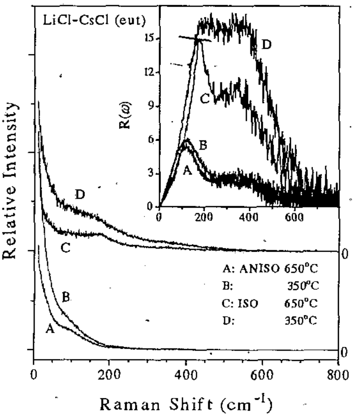

Fig. 1: Temperature dependence of the measured and reduced (inset) Raman spectra of the LiCl-CsCl eutectic mixture.

The strong isotropic light scattering of the LiX melts arises from contributions of the short range overlap interactions. The spectral differences between the LiF and LiCl are attributed to the structural peculiarities imposed by the relative sizes of the X^- and Li^+ ions. On the other hand, dipole-induced-dipole (DID) interactions contribute to the anisotropic scattering of molten CsCl. In the LiCl-CsCl mixtures the drastic increase of the isotropic scattering intensity with increasing temperature is associated mainly with the Li-Cl short range overlap interactions and the "symmetry" of the local structrures around the anion.

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THE REACTION ^{37}Cl (η,γ) ^{38}Cl IN MIXTURES OF CARBON TETRACHLORIDE AND TERTIARY BUTYL ALCOHOL

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N.C.S.R. 'DEMOKRITOS'

ABSTRACT

An investigation on the reaction ^{37}Cl (η,γ) ^{38}Cl in mixtures of CCl_4 and tertiary alcohols, shows that the obtained results depend on the tendency of breaking of the -COH group in CO and H.

If σ_i is the cross section for a mole of component i, $fi = x_i \sigma_i$, Y_i the organic yield of the pure component i, then, the measured Y% is $Y = \Sigma f_i Y_i$. For components A and B $Y = f_A Y_A + f_B Y_B = x_A \sigma_A Y_A + x_B \sigma_B Y_B$.

If S is the ratio σ_A/σ_B, we have

$$(Y_B-Y)/x_A = Y(S-1) + (Y_B-SY_A) \quad (1)$$

The plot of Y_B-Y/x_A versus Y must then be a straight line. Yet in mixtures of CCl_4 with aliphatic alcohols the plot obtained was a curve.

This is explained by assuming that the recoil chlorine atom, slowing down in a liquid reaches thermal energies in a region with a high local concentration of radicals, the "hot" zone where it can produce labelled organic molecules. After leaving the "hot" zone, the radical diffuses through the mixture. In mixtures rich in CCl_4, the diffusing Cl radical can meet a perchloromethyl radical and reform CCl_4 in the exothermic reaction.

$$CCl_3 + Cl' \rightarrow CCl_4$$

So, there exists now a second zone (besides the "hot" one) where labelled molecules can be produced and the straight line curves gradually. If in the mixtures of CCl_4 and other aliphatic compouds, we find a straight line, this is due to the fact that the organic yield drops much more abruplty in the mixtures of CCl_4 with alcohols, than in mixtures of CCl_4 with other aliphatic compounds, as the x of CCl_4 diminishes. From the plots obtained one could assume that the organic yield due to diffusion becomes large enough to be observed at 0.3 x_A. If at this point, Y is large, a very small margin is left till Y_B (the yield of pure CCl_4) is reached and the reaction due to diffusion will hardly be observable. This explains also the results obtained in mixtures of CCl_4 with secondary and tertiary alcohols.

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NMR DETERMINATIONS OF ENANTIOMERIC PURITY. USE OF CYCLODEXTRINS AS CHIRAL SHIFT REAGENTS

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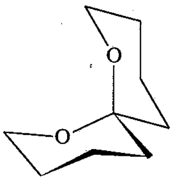
ABSTRACT

The applicability of cyclodextrins (CDs) as chiral solvating agents in solution NMR spectroscopy is briefly reviewed. The dynamic process which takes place in solution upon complex formation between CDs and enantiomeric mixtures results in changes of the observed signals, due to the formation of diastereoisomrs. The enantiomeric composition of an unknown mixture and, depending on the case, the preferential binding of the CD to one of the enantiomers can be determined. Research examples from our laboratory show some interesting applications. Thus, CDs can be effectively used in discriminating enantiomers of very apolar molecules in aqueous solution, such as the enantiomers in racemic α-pinene, by ^{1}H NMR spectroscopy. The association of a particular CD can be enantioselective toward one of the enantiomers and this enantioselectivity can be quantified for a variety of cyclodextrins. The same apply for 1,7-dioxaspiro[5.5]undecane, the enantiomeric constitution of which can be determined by ^{13}C NMR. In this case, complete isolation of the *R*-enantiomer has been achieved with permethylated α-CD, and this result has been verified with chiral GC and x-ray crystallography.



R- 1,7-dioxaspiro[5.5]undecane

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^{13}C CP/MAS NMR STUDIES OF HEMOPROTEIN MODELS WITH AND WITHOUT AN AXIAL HINDERED BASE: ^{13}C SHIELDING TENSORS AND COMPARISON WITH HEMOPROTEINS AND X-RAY STRUCTURAL DATA

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Abstract

^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectra of several carbonmonoxide (93-99% ^{13}C enriched) hemoprotein models with 1,2-dimethylimidazole (1,2-diMeIm) and 1-methylimidazole (1-MeIm) as axial ligands are reported. This enables the ^{13}CO spinning sideband manifold to be measured and hence the principal components of the ^{13}CO chemical shift tensor to be obtained. Negative polar interactions in the binding pocket of the cap porphyrin model and inhibition of Fe $\rightarrow$CO back-donation result in a reduction in shielding anisotropy; on the contrary, positive distal polar interactions result in an increase in the shielding anisotropy and asymmetry parameter in some models. It appears that the axial hindered base 1,2-dimethylimidazole has little direct effect on the local geometry at the CO site, despite higher rates of CO desorption being observed for such complexes. This suggests that the mechanism by which steric interactions are released for the 1,2-diMeIm complexes compared to 1-MeIm complexes does not involve a significant increase in bending of the Fe-C-O unit. The asymmetry of the shielding tensor of all the heme model compounds studied is smaller than that found for horse myoglobin and rabbit hemoglobin.

himika Chronika, New Series, 26, 279 (1997)

STUDIES OF BOUND WATER MOLECULES TO BIOLOGICAL MACROMOLECULES BY THE USE OF MULTINUCLEAR, TWO- DIMENSIONAL AND THREE-DIMENSIONAL NMR IN SOLUTION AND SOLID STATE

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ABSTRACT

In this communication recent developments in the use of multinuclear, two-dimensional and three-dimensional homonuclear and heteronuclear NMR to the direct study of bound water molecules to biological macromolecules are summarized. Particular emphasis will be given to the use of: (A) ^{17}O nuclear shielding constants; (B) Two - dimensional heteronuclear intermolecular nuclear Overhauser effect spectroscopy (HOESY); (C) Two - dimensional homonuclear intermolecular multiple quantum coherence spectroscopy; (E) ^{1}H-X (nucleus) cross polarization MAS NMR of hydrated solids.

Chimika Chronika, New Series, 26, 280 (1997)

NMR STUDY OF COMPLEXES OF OXOTECHNETIUM(V) AND OXORHENIUM(V) WITH AMINODITHIOLS

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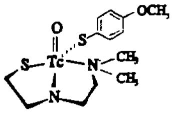
ABSRTACT

The complete assignment of the ^{1}H and ^{13}C resonances of oxotechnetium (1-4) and oxorhenium (5, 6) complexes is reported. These complexes are designed as potential brain imaging agents.

Chemical shift assignments were based on ^{1}H - ^{1}H correlation (COSY), ^{13}C - ^{1}H correlation (HETCOR) and 2D nOe (NOESY) data. In complexes 1 - 4 all protons and carbons have distinct resonances due to the asymmetry of the complexes and the anisotropic environment around the Tc=O core. Protons facing toward the Tc=O core (*endo*) appear deshielded relative to their geminals facing away (exo). In the isomeric complexes 5 and 6 chemical shifts depend also on the orientation of the free chain on nitrogen (*syn* or *anti* relative to the Re=O core). The ^{1}H spectrum of the free chain is characteristic of its orientation and allows the identification of each isomer by inspection.



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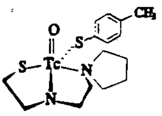

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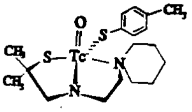

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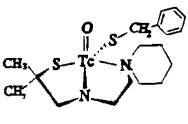

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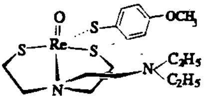

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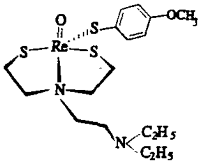

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Chimika Chronika, New Series, 26, 281 (1997)

COMPLEXES OF 2-(a-HYDROXYBENZYL) THIAMINE MONOPHOSPHATE AND 2-(a-HYDROXYETHYL) THIAMINE PYROPHOSPHATE WITH Hg^{2+} , Cd^{2+} AND Zn^{2+}

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ABSTRACT

In this communication we report on the interaction of 2-(a-hydroxybenzyl)thiamine monophosphate (HBTmp) and 2-(a-hydroxyetyl)thiamine pyrophosphate (HEtpp) with metal ions such as Hg(II),Cd(II),Zn(II). Complexes of the formulae $MLCl_2$, ML_2Cl_2 , ML_2Cl_4 , $MLCl_3$, $M_2L_2Cl_4$ (L=ligand) were isolated depending on pH. The complexes were characterised using various techniques such as ^{1}H-, ^{13}C- , ^{31}P- , ^{13}C-CP MAS , ^{31}P-CP MAS -NMR , IR , elemental analysis etc. The N_1' site of the pyrimidine moiety is the main binding site with the metalls, although phosphate coordination was also observed in some cases.

Chimika Chronika, New Series, 26, 282 (1997)

^{13}C NUCLEAR MAGNETIC RELAXATION STUDY OF POLY(VILYL CHLORIDE) IN DILUTE SOLUTIONS. DECLINATION OF LOCAL MOTIONS FROM KRAMERS' THEORY.

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ABSTRACT

In the present study is tested the applicability of Kramers' theory on the local dynamics of the industrially important polymer, polyvinyl chloride (PVC). The Kramers' theory predicts that in the high friction limit, and in the absence of specific solvent-polymer interactions, the rate of local dynamics should scale linearly with the solvent viscosity. Nevertheless, the applicability of Kramers' equation, as an accurate description of solvent-polymer coupling, has been questioned in a number of investigations. In these experiments, nonlinear dependencies of the rates of chain local processes on the solvent viscosity were observed. Chain local dynamics of PVC have been investigated previously in dibutyl phthalate (DBP) and 1,1,2,2-tetrachloroethane (TCE-d_2) solvents. In this study, solvent effects on polymer dynamics have explained in terms of the solvent thermodynamic quality. However, this treatment may not be so accurate, and the results could be better explained in terms of the solvent-polymer interactions. To distinguish between the two viewpoints, further relaxation experiments in other solvents should be performed. ^{13}C NMR measurements of the local dynamics of PVC in dilute solutions as a function of temperature and magnetic field are reported here. Three more solvents (Chloroform-d ($CDCl_3$), dioxane-d_8, and dimethylsulfoxide-d_6 (DMSO)) in addition to DBP and TCE-d_2 are utilized covering a sufficient viscosity range. Chain local motions for PVC in deutero 1,1,2,2-tetrachloroethane-d_2 and dibutyl phthalate solutions have been described successfully by using a model developed by Dejean-Lauprete-Monnerie (DLM). The same bimodal model is used in the present study to describe the local dynamics of PVC in chloroform, dioxane, and dimethylsulfoxide solvents. This model describes the backbone reorientation in terms of two independent kinds of motion: (1) a diffusional process along the chain, which occurs via conformational transitions described by two correlation times τ_0 and τ_1, for isolated, single-bond conformational transitions and for cooperative transitions, respectively, (2) bond librations, i.e. wobbling in a cone motion of the backbone internuclear C-H vectors. The librational motion is associated with a correlation time, τ_2, whereas the extent of the libration about the rest position of the C-H bond (the axis of the cone) is determined by the cone half-angle θ. Our findings are consistent with a nonlinear relationship observed between the local dynamics of PVC and solvent viscosity. The correlation time describing chain local dynamics of PVC is scaled by $\eta^{0.60}$ whether the viscosity is varied by changing temperature or solvent.

Chimika Chronika, New Series, 26, 283 (1997)

INTERACTIONS OF BIOLOGICALLY ACTIVE MOLECULES WITH MEMBRANES USING ^{31}P-NMR SPECTROSCOPY

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We have studied the effects of VPI-68 in model DPPC bilayers and erythrocyte ghost membranes using ^{31}P-NMR spectroscopy. VPI-68 has been shown to exert antineoplastic properties (IC_{70}=5.6 μg/ml) in four out of six xenografts of human cancers. Its mechanism of action is still unknown but it is believed to act on the membrane level. Therefore, it does not exert any genotoxic effects. The derived results from ^{31}P-NMR spectroscopy were combined with those of Differential Scanning Calorimetry (DSC). The DSC results have shown that VPI- 68 affects only marginally the main phase transition of DPPC while it abolishes the small endotherm pretransition event. We felt that the abolishment of the pretransition temperature might reflect its action on head groups of DPPC phospholipids. ^{31}P-NMR spectroscopy strengthened that assumption by showing that the molecule affects the headgroup of the DPPC bilayers and decreases its cooperativity. This probably explains the absence of pretransition in DSC experiment. In DSC and ^{31}P-NMR spectroscopy experiments with red blood cell erythrocyte ghosts VPI- 68 affected the phase transition properties and the head group of phospholipids.

Chimika Chronika, New Series, 26, 284 (1997)

A ^{1}H, ^{13}C AND ^{183}W NMR SPECTRAL STUDY OF THE GEOMETRICAL ISOMERS AND THE MECHANISM OF THE ISOMERISATION IN TRIGONAL PRISMATIC TUNGSTEN AND MOLYBDENUM TRIS-DITHIOLENES

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ABSTRACT

Tungsten and molybdenum tris-1,2-dithiolenes is proved by NMR spectral methods to exist in a trigonal prismatic configuration in solution. This is proved by the ^{1}H, ^{13}C and ^{1}H-{^{183}W} HMQC spectra at -40°C. The acquisition of the HMQC spectrum is possible because there is a coupling between the dithiolenic hydrogen and tungsten. The complexes exist in two isomers, the *cis* and the *trans*.

The *trans* isomer prevails, because it is “abnormal”, has a higher entropy, compared to the *cis*. The *trans:cis* ratio calculated by theory is 3, which agrees with the experimentally measured value. No dependence of the equilibrium constant to the temperature is observed, in agreement with the theoretical approach.

The two isomers are in a rapid equilibrium between them, more rapid than is normal for six coordinate complexes. The motion seems to freeze in the NMR timescale at about -40°C, in the solvents used. The mechanism for the isomerisation involves an intramolecular rearrangement. The possibilities of associative or dissociative paths are improbable because of the independence of the rate on the solvent.

The mechanism proposed involves the twist of only one ligand around the metal-centre of carbon-carbon double bond axis. This twist has a trigonal prismatic intermediate with the ligands being at great distances between them, and is thus energetically favourable. Mechanisms analogous to those proposed for octahedral complexes are sterically hindered and thus improbable in our case.

A theoretical calculation on the twist mechanism (EHMO method) yields results that agree with the experimentally measured values for the activation energy.

Chimika Chronika, New Series, 26, 285 (1997)

CHARACTERIZATION OF $[Cr(n^6\text{-}C_6HMe_5)(CO)_3]$ WITH ^{13}C SOLID-STATE NMR AND X-RAY CRYSTALLOGRAPHY.

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ABSTRACT

The dynamic behavior in the solid state of $[Cr(n^6\text{-}C_6HMe_5)(CO)_3]$ has been investigated by ^{13}C CP MAS NMR spectra of variable-temperature. The NMR results have shown unambiguosly that there is rapid exchange between the CO groups at room temperature in the solid state.

Chemical shift anisotropy measurements at 296 and 155K have indicated that the angle between the C-O bond and the axis of rotation is 127±0.2. The activation energy barrier for the process was estimated to be 31±4kJmol^{-1}, which is significantly lower than that observed in related complexes.

Structural characterization of this complex has been carried out at 293 and 150K. The rapid exchange of the CO groups at room temperature makes the molecule to seem like $[Cr(n^6\text{-}C_6Me_6)(CO)_3]$, while at 150K, where this rotation does not exceed, the crystal data for the $[Cr(n^6\text{-}C_6HMe_5)(CO)_3]$ has been taken. Crystal data: space group Pbca, orthorombic, a=13.229(1)A, b=13.308(1)A, and c=14.998(2)A, $\alpha=\beta=\gamma=90^{o}$, z =8, V=2660,3(5)A^3, d =1,420g/cm^3.

Chimika Chronika, New Series, 26, 286 (1997)

QUANTITATIVE ^{13}C NMR DETERMINATION OF THE MOST IMPORTANT FATTY ACIDS OF TRIGLYCERIDES FROM OLIVE OIL

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A new method for the quantitative determination of the most important olive oil fatty acids based on ^{13}C - NMR spectroscopy, has been developed. This method, compared to the classic method that uses Gas Chromatography does not involve any sample preparation (e.g. hydrolysis and esterification) and it provides an additional information: the positional distribution of the fatty acids on the glycerol backbone.

The inverse gate sequence is used in order to record the ^{13}C spectral intensities, of the carbonylic and ethylenic regions quantitatively. The data processing includes a peak deconvolution step in order to obtain the individual area of each peak. These individual areas (S_i) are reflecting the concentration of each fatty acid (in mole %) through normalisation over the sum of the areas of all peaks in the carbonylic region:

$$\text{mol\%}\ i = \frac{S_i}{\sum_{i=1}^{n} S_i}$$

The ethylenic region is used for quantitative calculation of the unsaturated fatty acids because it suffers to a less extent from peak overlap.

However, the precision of this method is lower than the GC method due to peak overlap especially in the carbonyl region. Nevertheless, the collection of the positional distribution data can provide valuable information on the authenticity and geographical origin of the olive oil sample. These two objectives are under investigation in a EU project involving a large scale sampling from the most important oil producing regions of Greece.

Chimika Chronika, New Series, 26, 287 (1997)

^{1}H NMR STUDY OF THE SYNTHETIC PEPTIDE CORRESPONDING TO THE SEQUENCE 35-54 OF THE INTERLEUCIN-2 RECEPTOR (β CHAIN).

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#Pharmaceutical Departement, University of Patras, 261 10 Patras

ABSTRACT

The ^{1}H NMR resonances of the synthetic peptide corresponding to the sequence 35-54 of the Interleukin-2 Receptor β-chain (IL-2Rβ) were sequentially assigned in water and dimethylsulfoxide solutions. In both solvents the main conformation is that of the extended chain. Of the possible isomers arising from the presence of two prolines in positions 5 and 18 , the trans,trans is predominant as denoted by NOE cross peaks of the type αδ and αδ' d(i,i+1).

Chimika Chronika, New Series, 26, 288 (1997)

^{31}P NMR STUDIES OF NADPH BOUND TO HYDRATED L.casei DIHYDROFOLATE REDUCTASE IN THE SOLID

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ABSTRACT

^{31}P NMR spectra on solid lyophilized and low level hydrated samples of NADPH bound to Lactobacillus casei dihydrofolate reductase (DHFR) have been recorded using the techniques of cross polarization, magic angle spinning and high power proton decoupling. The presence of both the dianionic and monoionic states of the 2′-phosphate group have been determined. In experiments examining progressively hydrated samples, the observed signals become increasingly narrower probably because the microenviroments of the ^{31}P nuclei become more homogeneous upon sample hydration. Magnetization transfer from the "solvent" water molecules to protons close to individual sites on NADPH results in the complete suppression of the two pyrophosphate signals while the 2′-phosphate phosphorous signal remains. This indicates the presence of mobile water molecules in the vicinity of the 2′-phosphate nucleus.

Chimika Chronika, New Series, 26, 289 (1997)

USE OF ^{13}C SHIELDING TENSORS TO INVESTIGATE THE STRUCTURE OF THE Fe-^{13}C-O GROUP IN RABBIT HEMOGLOBIN IN THE SOLID STATE

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ABSTRACT

The first high-resolution solid-state ^{13}C NMR results on ^{13}CO in rabbit hemoglobin in the solid state are presented. A selective excitation pulse sequence was used in order to reduce the problem of peaks overlapping with those arising from the natural ^{13}C abundance hemoglobin molecule. The results indicate only a composite ^{13}C resonance for both α and β subunits and that there is a large increase in asymmetry of the ^{13}C shielding tensor in ^{13}CO-rabbit hemoglobin compared to heme model compounds containing the close to linear Fe-C-O moiety.

Chimika Chronika, New Series, 26, 290 (1997)

HYDRATION STUDIES OF CIS/ TRANS AMIDES BY THE USE OF TWO-DIMENSIONAL HETERONUCLEAR ^{13}C, ^{1}H OVERHAUSER EFFECT NMR SPECTROSCOPY (HOESY ^{13}C,^{1}H)

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ABSTRACT

Two-dimensional heteronuclear ^{13}C, ^{1}H Overhauser effect spectroscopy (2D ^{13}C, ^{1}H HOESY) can provide a valuable probe for investigating hydration of the carbonyl carbons of amide and peptide groups. The present communication describes the first application of an intermolecular carbon-13-proton-^{1}H HOESY 2D experiment to study solvation differences of *cis* and *trans* isomers of amides (*tert*-butylformamide, TBF).

Chimika Chronika, New Series, 26, 291 (1997)

STUDY OF SOLVATION PHENOMENA IN AMIDES AND ACETONE BY THE USE OF ^{17}O NMR SHIELDING CONSTANTS; COMPARISON WITH SEMIEMPIRICAL CALCULATIONS

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ABSTRACT

The effects of solvents on the ^{17}O shielding constants of acetone and the amides N-methylformamide (NMF) and dimethylformamide (DMF) have been investigated. Very good linear correlation between $\delta(^{17}O)$ of amides and $\delta(^{17}O)$ of acetone was found for different solvents which have varying dielectric constants and solvation abilities. The resulting correlation demonstrates that $\delta(^{17}O)$ for amides and carbonyl compounds appear to be reflecting a similar type of electronic perturbation despite the higher polarizability of the amide oxygen. Sum-over-states (SOS) calculations, within the solvaton model, significantly underestimate changes in ^{17}O shielding upon the dielectric constant of the medium while finite perturbation theory (FPT) calculations give good agreement with the experiment.

Chimika Chronika, New Series, 26, 292 (1997)

^{17}O AND ^{1}H- ^{15}N HMQC NMR STUDIES OF AMIDES; EVIDENCE OF AN OUT-OF-PLANE (TORSION ANGLE) DEFORMATION OF THE AMIDE BOND

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ABSTRACT

^{17}O and ^{1}H-^{15}N heteronuclear multiple quantum coherence NMR studies of linear amides demonstrate the occurence of an out-of-plane (torsion angle) deformation of the amide bond and pyramidicity at the amide nitrogen for the sterically hindered trans-isomer of N-tert-butylformamide. Solvent accessibility, steric hindrance and, thus, torsion angle deformation is shown to be strongly solvent dependent.

Chimika Chronika, New Series, 26, 293 (1997)

SYNTHESIS AND BIOLOGICAL ACTIVITY OF 1,2- DIHYDRO-1,2-DISUBSTITUTED ACRONYCINE DERIVATIVES, A SERIES OF NOVEL AND HIGHLY ACTIVE ANTITUMOR AGENTS.

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The alkaloid acronycine (**1**), isolated from several species of *Rutaceae*, exhibits a broad antitumor activity.[1,2] Unfortunately, its clinical trials had a limited success,[3] mainly due to its extremely low water solubility. The search for more soluble and more active derivatives has previously led to the preparation of quaternary salts, to the synthesis of structural analogs modified at the side chain in 6-position or at the carbonyl group and to the preparation of various isosters.[1] Comparately, modifications at the dimethylpyran ring have been less explored and previous works in that field are limited to the preparation of dihydro, nitro and bromo derivatives.

We describe here the synthesis of 68 acronycine derivatives modified at the dimethylpyran ring, and their biological evaluation, both *in vitro* and *in vivo*, towards a wide range of experimental murine (L1210 and P 388 leukemias, B 16 melanoma) and human (HT 29 and C 38 colon cancers) tumors. Their cytotoxic and antitumor properties were compared with those of acronycine itself. The alcohols resulting from H_2O_2 addition on the double bond of the pyran ring and the corresponding mono- and di-esters are the most active compounds. *Cis*-1,2-diacetoxy-1,2-dihydroacronycine (**26**) was selected for further evaluation on the basis of its high level of activity.

1- M. Suffness and G. Cordell (1985) in : *The Alkaloids*, (A. Brossi, ed.), Vol. **25**, pp. 38-48, Academic Press, New York.
2- R. T. Dorr, J. D. Liddil, D. D. Von Hoff, M. Soble, and C. K. Osborne (1989), *Cancer Research*, **49**, 340.
3- J. H. Scarffe, A. R. Beaumont, and D. Crowther (1983), *Cancer Treatment Reports*, **67**, 93.

Chimika Chronika, New Series, 26, 294 (1997)

NMR STUDIES OF THE HYDRATION STATE OF AMINOACIDS IN AQUEOUS SOLUTION BY THE USE OF ^{14}N NMR SPECTROSCOPY

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ABSTRACT

^{14}N NMR was utilized to investigate the change in resonance linewidths, $\Delta\nu_{1/2}$, versus pH values of several aminoacids, with and without composite proton decoupling. The $\Delta\nu_{1/2}$ values, which were obtained with the decoupling method, versus molecular weights of aminoacids at pH values 6 and 0.5 indicate an increase in the hydration state of aminoacids in aqueous solution at pH 0.5 compared to pH 6. The change of the nuclear quadrupolar coupling constant is rather small.

Chimika Chronika, New Series, 26, 295 (1997)

EVALUATION OF WINE ASTRINGENCY BY MEANS OF THE CHEMILUMINESCENT SYSTEM OF TANNIN - KIO_4

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Six wine samples of Greek origin were first analysed for their tannin content by means of the chemiluminescent system of tannin - KIO_4. Sample solutions were prepared by dissolution of a certain quantity of hydroxylammonium chloride (signal enhancer) in wine, so that the final solutions were 7.0 mM in NH_2OH. These solutions were then injected into a flow injection system that allowed them to react with a buffered solution of KIO_4 in front of the detector (photomultiplier tube). The signal corresponding to the power of the light emitted was recorded and the samples were ranked according to their relative tannin content.

After the wine samples had also been ranked by means of an organoleptic evaluation performed by seventeen people chosen at random, the extent of the agreement between the two ranks was checked by way of the Spearman rank correlation coefficient method and the null hypothesis of no correlation was rejected at the $p = 0.0693$ level.

The method under study proved to be a very good means for the evaluation of wine astringency and, above all, it was very rapid, requiring little sample preparation (mixing with the enhancer). Due to its simplicity and rapidity, it could easily be used for the monitoring of fermentation and especially wine ageing.

Chimika Chronika, New Series, 26, 296 (1997)

NEW TECHNOLOGIES IN THE ANALYSIS OF FOOD AND BEVERAGES. SNIF-NMR® (SITE NATURAL ISOTOPE FRACTIONATION - NUCLEAR MAGNETIC RESONANCE) : AUTHENTICITY OF THE PRODUCTS.

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ABSTRACT

The concept of authenticity of a particular food or beverage is defined as a conformity to a standard. A product is non-authentic because inferior ingredients are used to cut production costs and increase profits. Wide-scale adulteration in the area of wines, alcoholic drinks, fruit juices, flavors, has recently been brought out to the use of new advanced isotopic analytical methods (MS, NMR). Among these methods isotopic mass spectrometry (^{13}C, ^{14}C, ^{2}H) occupy a prime position. Unfortunately, it is now known that these methods can be often countered by adulterators by addition of isotopically enriched compouds (in the case of flavors) and they show also limitations related to the recognition of the botanical origin of a product (in the case of wines, fruit juices, ...). The SNIF-NMR® method which provides isotopic ratios for each molecular position within a molecule can be an uncounterfeitable 'fingerprint' of natural molecules bringing new information inaccessible by other methods, on the botanical or synthetic origin of a molecule, on the geoclimatic environment of the biosynthesis and on the technological conditions of the elaboration of the product. The SNIF-NMR® method has been applied to ethanol (wines, alcoholic drinks, fruit juices), vanillin, anethole and more recently to a wide range of other natural molecules. Today, given this remarquable technological progress, by putting together a good package of analytical methods, traditional and isotopic, we are able to detect all the economically interesting forms of adulteration.

Chimika Chronika, New Series, 26, 297 (1997)

STUDY OF THE PPh_3 - $P(OPh)_3$ MIXED COMPLEXES OF TETRATHIOMOLYBDATODIRHODIUM WITH ELECTRONIC AND ^{31}P NMR SPECTROSCOPIC TECHNIQUES

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ABSTRACT

The formation of mixed PPh_3-$P(OPh)_3$ rhodium(I) tetrathiomolybdato-complexes was studied by electronic and ^{31}P NMR spectroscopic techniques. The $[\{(P(OPh)_3)_2Rh\}_2(\mu\text{-}MoS_4)]$ was found to be the major species for total $P(OPh)_3$ to PPh_3 molar ratios higher than *ca.* 2.1. An unusual long range effect between chemically different phosphorus nuclei, six bonds apart each other, transmitted through the tetrathiomolybdato-bridging ligand is observed. The chemical shifts and coupling constants of the mixed complexes follow monotonous behaviour, suggesting the possibility of predictable chemical activity upon introduction of the appropriate phosphorus ligands.

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AZAROMATICS IN LIGHT ENERGY STORAGE SYSTEMS

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Exposure of de-aerated azaromatic solutions in amide or phosphate solvents, even to the diffuse light of the laboratory, results in photolysis the same being true for γ-irradiation of said solutions in a ^{60}Co source. Subsequent addition of sodium hydride or singlet oxygen to the reaction mixture gives rise to chemiluminescence (CL). We consider this sequence to be a light storage system in the sense that light is both absorbed and reclaimed

In our experiments in N,N-dimethylformamide and triethylphosphate, photolysis results in substituted dihydroazaromatics via a free radical mechanism and proton transfer from solvent. The same product was identified and in γ-radiolysis experiments with radiation doses up to 1200 Gy in high yields. Optimum azaromatic concentration is 10^{-4} M, while the presence of atmospheric oxygen is deleterious to the photochemical or radiochemical reaction. Addition of sodium hydride to the spent reaction mixtures resulted in CL with a quantum yield of ca. 10^{-3} in DMF or ca. 10^{-5} einstein . mol^{-1} in triethylphosphate. Replacement of NaH by other strong bases such as t-buOK, MeONa resulted in quantum yields lower, yet of the same order of magnitude.

In conclusion, the present system, in addition to its light storage properties, it also posesses the following characteristics (a) The novel substituted dihydroazaromatic derivatives formed are chemiluminescent with quantum yields comparable to those of the classical CL compounds such as luminol and lucigenin. (b) In contrast to most CL reactions requiring oxygen and an oxidant this reaction proceeds in de-aerated media and in the case where NaH is employed, it proceeds in a strongly reductive environment. The oxygen required here for "azaromatic-ketone" formation comes from the solvent. (c) Plots of azaromatic absorption vs γ-irradiation dose as well as plots of CL intensity- time integrals vs γ-irradiation dose indicate that both types of plots can be employed as γ-radiation dosemeters.

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STUDY OF THE RELATIONSHIP BETWEEN SEPARATION NUMBER AND HEIGHT EQUIVALENT TO A THEORETICAL PLATE IN A SERIALLY COUPLED CAPILLARY CONUMNS GAS CHROMATOGRAPHIC SYSTEM

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ABSTRACT

Serially coupled open tubular column chromatography has been recently proposed as an alternative technique for tedious chromatographic separations of environmental sampes. A combination of the characteristics of the stationary phases coupled in series helps to tune the overall selectivity of the system leading to a base-to-base resolution of complex mixtures of volatile organic compounds. The selectivity can be tuned by proper selection of the temperature and/or the flow rates of the columns. Separation number (TZ) and Height Equivalent to a Theoretical Plate (HETP) have been considered as indicative parameters of the separation power of a chromatographic system. In this paper, the relationship between these parameters is studied and the effects of temperature and pressure on them are discussed, using a system of two columns coupled in series.

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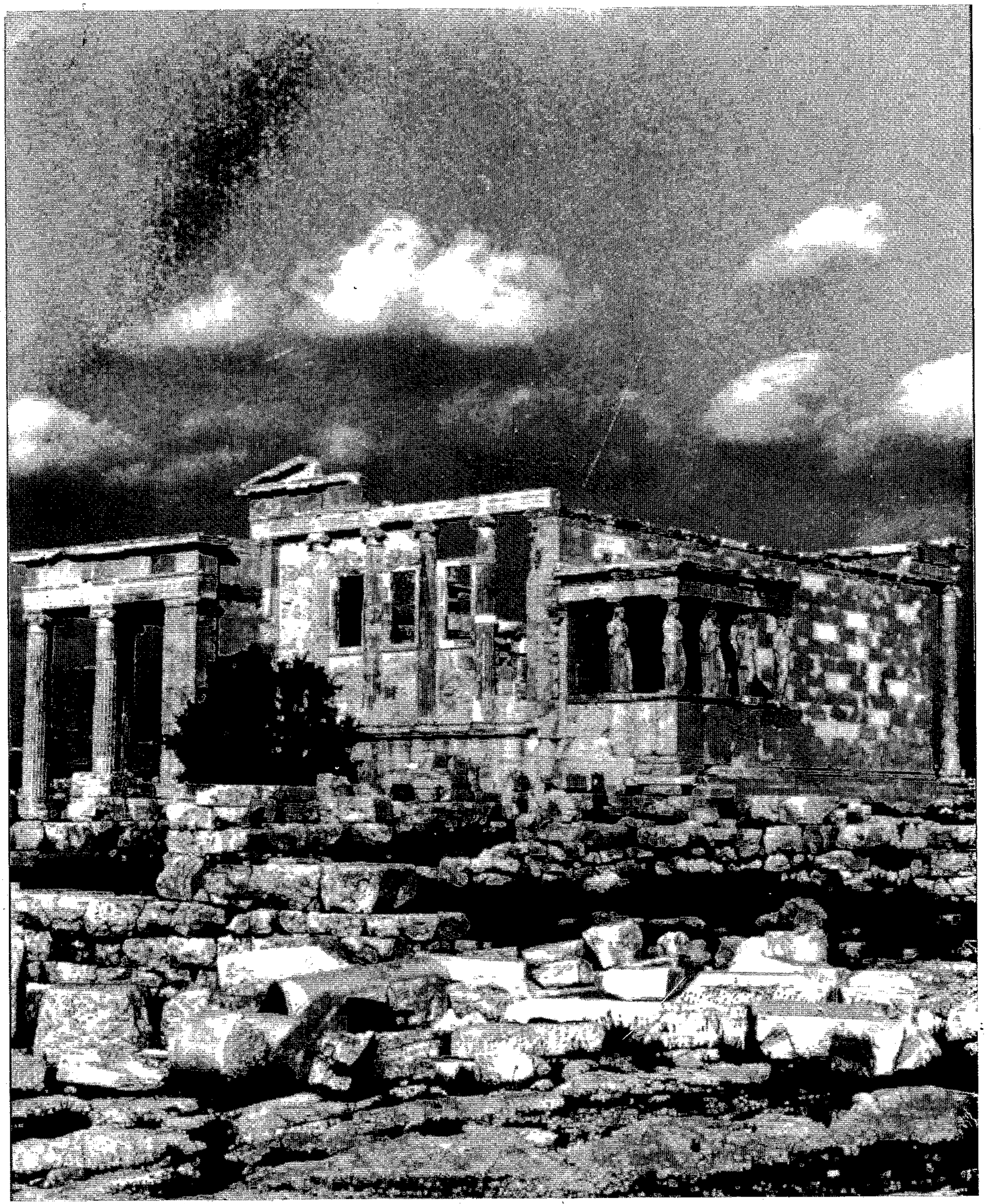

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