

**Schiff Base Metal Complexes of Chromium(III),  
Manganese(III), Iron(III), Oxovanadium(IV),  
Zirconium(IV) and Dioxouranium(VI)**

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The Schiff base 2,5-dihydroxyacetophenone isonicotinoyl hydrazone ( $H_2L$ ) has been synthesized by condensation of 2,5-dihydroxyacetophenone with isonicotinoyl hydrazide in ethanol. Metal complexes of the Schiff base were prepared from salts of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and  $UO_2(VI)$ . Characterization of the ligand and its metal complexes were carried out by elemental analysis, molar conductivity, magnetic susceptibility measurements, IR,  $^1H$  NMR, electronic and thermogravimetric analysis in air. The Schiff base behaves as flexidentate ligand and commonly coordinates through the oxygen atom of the deprotonated phenolic group and the nitrogen atom of azomethine group. The thermal data have been analyzed for the kinetic parameters by Broido and Horowitz-Metzger methods. All the compounds were also screened for their antimicrobial activity by agar cup-plate method against various organisms and the results have been compared.

## Synthesis and Magnetic Analysis of $\mu$ -Oxamido-Bridged Copper(II)–Iron(II) Heterodinuclear Complexes

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Five new copper(II)–iron(II) heterodinuclear complexes bridged by the dianion of N,N'-bis[3-(dimethylamino)propyl]oxamido (dmoxpn) and end-capped with 2,2'-bipyridine (bpy); 1,10-phenanthroline (phen); 5-nitro-1,10-phenanthroline (NO<sub>2</sub>-phen); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen); namely [Cu(dmxpn)FeL<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (L = bpy, phen, NO<sub>2</sub>-phen, Cl-phen, Br-phen), have been synthesized and characterized. Based on elemental analyses, magnetic moments (at room temperature), molar conductivity measurements, and spectroscopic studies, extended oxamido-bridged structures consisting of a copper(II) ion and an iron(II) ion, which have a square-planar environment and an octahedral environment, respectively, are proposed for these complexes. The [Cu(dmxpn)Fe(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**) and [Cu(dmxpn)Fe(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**2**) complexes have been further characterized by variable temperature magnetic susceptibility (4.2–300 K) and the observed data were least-squares fitted to the susceptibility equation derived from the spin Hamiltonian including single-ion zero-field interaction for the iron(II) ion,  $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 - D\hat{S}_{Z1}^2$ , giving the exchange integrals  $J = -15.9 \text{ cm}^{-1}$  for (**1**) and  $J = -17.5 \text{ cm}^{-1}$  for (**2**). These results indicated that the spin coupling between the adjacent copper(II) and iron(II) ions through oxamido-bridge in both complexes (**1**) and (**2**) is antiferromagnetic. The influence of methyl (-CH<sub>3</sub>) substituents in the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

## **Synthesis and Characterization of New Thiocyanato Bridged Complexes with the General Formula $[\text{ML}_n]_3[\text{Cr}(\text{NCS})_6]_2 \cdot m\text{H}_2\text{O}$ , where $\text{M} = \text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Co}(\text{II})$ ; $\text{L} = \text{Various Substituted Imidazoles}$**

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New thiocyanato bridged complexes of the type  $[\text{CuL}_4]_3[\text{Cr}(\text{NCS})_6]_2 \cdot m\text{H}_2\text{O}$  [ $\text{L} = 1\text{-methylimidazole (1-Meim), 2-methylimidazole (2-Meim), 1,2-dimethylimidazole (1,2-Me}_2\text{im)}$ ] and  $[\text{M}(1\text{-Meim})_6]_n[\{\text{M}(1\text{-Meim})_4\text{Cr}(\text{NCS})_6\}_{2n}] \cdot m\text{H}_2\text{O}$  ( $\text{M} = \text{Ni}(\text{II}), \text{Co}(\text{II})$ ) were prepared by the reaction of  $[\text{Cr}(\text{NCS})_6]^{3-}$  with the appropriate  $[\text{ML}_n]^{2+}$  complex in an aqueous solution and characterized by elemental and thermal analysis, IR, UV-VIS, EPR and temperature variable magnetic susceptibility. The presence of NCS bridges between  $\text{M}(\text{II})\text{--Cr}(\text{III})$  centres is evident from IR spectra. The electronic spectra correlate with proposal of different composition of  $\text{Cu}_3\text{Cr}_2$  and  $\text{M}_3\text{Cr}_2$  ( $\text{M} = \text{Ni}, \text{Co}$ ) systems. The parameters determined from temperature dependence on magnetic susceptibility (80–300 K) indicate weak or negligible antiferromagnetic interaction for obtained  $\text{Cu}(\text{II})\text{--Cr}(\text{III})$ ,  $\text{Ni}(\text{II})\text{--Cr}(\text{III})$  and  $\text{Co}(\text{II})\text{--Cr}(\text{III})$  systems. Thermal decomposition after dehydration is multistage and yields  $\text{CuO} + \text{CuCrO}_2$  and  $\text{M}^{\text{II}}\text{O} + \text{M}^{\text{II}}\text{Cr}_2\text{O}_4$  as final products, respectively.

## Synthesis of N-Unsubstituted 1,3-Thiazolidines by [2+3]-Cycloaddition of an Azomethine Ylide with Thiocarbonyl Compounds

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1,3-Dipolar cycloadditions of azomethine ylides with thiocarbonyl compounds have been used for the preparation of N-unsubstituted 1,3-thiazolidines. The reactive 1-phenyl-*N*-(trimethylsilyl)azomethine ylide (**1c**) was generated *in situ* by treatment of *N*-(benzylidene)[(trimethylsilyl)methyl]amine (**6**) with trimethylsilyl triflate and CsF in HMPA. All cycloadditions proceeded non-regioselectively, which led to mixtures of 4-phenyl- and 2-phenyl-substituted 1,3-thiazolidines.

## Stability of 1-Phenacylpyridinium and 1-(2-Hydroxy-2-phenylvinyl)pyridinium Cations

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1-Phenacylpyridinium cation,  $C_5H_5N^+-CH_2COC_6H_4R-p$ , is the only tautomeric form detected in DMSO solution. This shows that the vicinity of the strong electron-acceptor pyridinium group has a minor effect on acidity of the methylene protons in 1-phenacylpyridinium salts. It was found that substitution in the benzene ring does not affect the tautomeric equilibrium. Although 1-(2-hydroxy-2-phenylvinyl)pyridinium cation is stabilized by conjugation, the *ab initio* calculated energies confirm the higher stability of the keto form (electron-acceptor substituents slightly increase stability of the enol form). It was found that 1-(2-hydroxy-2-phenylvinyl)pyridinium cation is not planar. Calculations show that electrostatic attraction between the onium nitrogen and hydroxy oxygen atoms takes place in this cation.

## **New Ionic Liquids with Alkoxyethyl Hydrophobic Groups**

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Air and water stable new ionic liquids with alkoxyethyl hydrophobic substituents and alkyl group on C(2) in imidazolium cation have been prepared and characterized. 14 tetrafluoroborate salts and 8 hexafluorophosphate salts are liquids at r.t. The properties of obtained salts are reported. The variation of substituents on the imidazolium cation have led to useful trends in the melting point and density and have a significant influence on the thermal stability.

## **Characterization of Small Azocrown Ether Stereoisomers**

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The stable *E*- and *Z*-isomers of 10-membered azocrown ether have been isolated and studied by X-ray, <sup>1</sup>H NMR and UV-Vis methods. Their structures in a solid state indicate the stretched conformation for *trans*-isomer and unstressed for *cis*-isomer. The concerted effect of azo-group  $\pi$ -conjugation with benzene residue and steric strain of molecular conformation results in the observed stability of isomers.

## **Stereoselective Synthesis of Alkyl $\alpha$ -D-Glucopyranosides**

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Glycosylation of  $\beta$ -D-glucosyl *N*-allyl thiocarbamates with alcohols using bromine as activator proceeded under mild conditions in a highly stereoselective fashion to afford the corresponding  $\alpha$ -glucosides in high yields. Hindered tertiary alcohols can be also used as glycosyl donors.

## Amidation-Sulfonation of Selected Unsaturated Monoterpenes

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Amidation-sulfonation of (+)-camphene (**1**), (–)- $\beta$ - and (–)- $\alpha$ -pinene (**3,4**), (+)-limonene (**5**), (+)-2-carene (**16**), and (+)-carvone (**21**) with a mixture of 25% oleum and aceto- or propionitrile is described. Camphene (**1**) gave racemic *exo*-2-amidobornanesulfonic acids (**8,9**), whereas **3** and **4** produced optically active *p*-mentheneamidosulfonic acids (**10–15**). Under the same reaction conditions 1,4-addition to (+)-2-carene (**16**) leading to (1*R*,4*R*)-(–)-4-(1-acetylamino-1-methylethyl)-1-methyl-cyclohex-2-enesulfonic acid (**17**) was observed. Mixtures of diastereomeric structural terpene analogues of N-acetyltaurine were obtained from **5** and **21**. Mechanisms of the investigated reactions are proposed.

## Solvent Deuterium Isotope Effect in the Acid Catalyzed Decarboxylation of Phenylpropionic Acid in 85% D<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O

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A comparative study of the solvent deuterium isotope effect in the decarboxylation of phenylpropionic acid (PPA) in 85% perdeuteriated orthophosphoric acid, D<sub>3</sub>PO<sub>4</sub>/D<sub>2</sub>O, has been carried out and the ratio of the decarboxylation rate constants,  $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$  equal  $1.88 \pm 0.07$ , interpreted as caused by different dissociation constants,  $K_{\text{h}}/K_{\text{a}}$ , of normal and perdeuteriated phosphoric acids in H<sub>2</sub>O and in D<sub>2</sub>O respectively, and by the deuterium discriminations in the subsequent steps of hydrogen transfer from the solvent H<sub>3</sub>O<sup>+</sup>/D<sub>3</sub>O<sup>+</sup> to triple bond of PPA and finally by proton transfer from  $\pi$ -complex to nearest C <sub>$\alpha$</sub> -carbon and sp<sup>2</sup>(C <sub>$\alpha$</sub> -H) covalent bond formation. The detachment of carbon dioxide from PPA (decarboxylation step) is the fast process taking place or directly after the rate determining T.S. formation or stepwise by hydration of the vinyl cation and formation of the benzoylactic acid intermediate compound, which then decarboxylates in the kinetically insignificant step. The discussion is supplemented by calculating the  $k(\text{H}_2\text{O})/k(\text{D}_2\text{O})$  ratios for decarboxylation scheme involving protonation of the triple bond in the rate determining step and for the reaction scheme involving fast isotope equilibrium between protonated water and protonated triple bond, followed by the rate determining transfer of proton from  $\pi$ -complex to the usual sp<sup>2</sup>(C-H) covalent bond. A good agreement between experimental solvent D<sub>2</sub>O I.E. and values calculated for reaction scheme involving proton transfer in the r.d.s. (what follows also from the <sup>13</sup>C K.I.E. determinations in decarboxylation of PPA in H<sub>3</sub>PO<sub>4</sub>/H<sub>2</sub>O and D<sub>3</sub>PO<sub>4</sub>/D<sub>2</sub>O solvents) was found.

## **Free Energy Contribution Due to the Specific Solvation of Anions. A Comparison of “Pure” Acidity Solvent Scales**

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Four “pure” acidity solvent parameters (*i.e.* assumed to be free from non-specific solvation) proposed in the literature on quite different basis: E of Koppel and Palm [1],  $E^N$  of Krygowski *et al.* [2],  $\alpha$  of Taft and Kamlet [3,4] and SA of Catalán and Díaz [5] gave the same contribution of the specific solvation of chloride ion to its standard molar free energy of transfer between a given solvent and water, as expected for “pure” scales.

<sup>2+</sup>  
**Complexation Study of UO<sub>2</sub> Ion with 18-Crown-6,  
Dicyclohexyl-18-crown-6 and Dibenzo-18-crown-6  
in Binary Nitromethane-Acetonitrile Mixtures  
by a Competitive NMR Technique  
Using <sup>7</sup>Li Nucleus as a Probe**

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Lithium-7 NMR measurements were used to determine the stability of 1:1 Li<sup>+</sup> complexes with 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in various binary nitromethane-acetonitrile mixtures. A competitive <sup>7</sup>Li NMR technique was also employed to probe the complexation of UO<sub>2</sub><sup>2+</sup> ion with these crown ethers in the mixed solvents used. In all solvent mixtures, the stability of the resulting 1:1 complexes was found to decrease in the order DC18C6 > 18C6 > DB18C6. There is an inverse relationship between the complex stability and the amount of acetonitrile in the mixed solvents.

## Effect of the Electrode Material on the Electrochemical Reduction of Some 2,5-Dihydro-1,3,4-thiadiazoles

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During cyclic voltammetric studies of the 2,5-dihydro-1,3,4-thiadiazoles ( $\Delta^3$ -1,3,4-thiadiazolines) (**1a–e**) on HMDE in  $0.1 \times 10^{-3}$  mol/dm<sup>3</sup> LiClO<sub>4</sub> acetonitrile and aqueous-acetonitrile or aqueous-ethanol Britton-Robinson's buffer solutions in second polarization cycle, besides peaks equivalent to polarographic waves, an additional new system of peaks was observed. The corresponding analogous system of additional peaks has not been observed during the reduction of these substances on electrodes of other materials, as *i.e.*, platinum, gold or glassy carbon. This study showed that it results from the oxidation and reduction of organo-mercury compounds, formed in reaction of the electrode material (Hg) with an adsorbed product of 2,5-dihydro-1,3,4-thiadiazoles reduction.

## Differences between $\Delta H$ and $\Delta S$ Values of the 1:2 Complexes of Camphor Enantiomers with $\alpha$ -Cyclodextrin Determined by NMR Titrations and by Other Techniques

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$\Delta H_{12}$  and  $\Delta S_{12}$  values for the 1:2 complexes of camphor enantiomers with  $\alpha$ -cyclodextrin by NMR titrations, carried out from 25 to 48°C, yielded  $-16.0 \pm 0.2$  kcal/mol and  $28.3 \pm 0.3$  e.u. for **1a@2** and  $-9.8 \pm 0.2$  kcal/mol and  $9.1 \pm 0.2$  e.u. for **1b@2**. A comparison of the values obtained by other groups, using isothermal titration calorimetry and reversed-phase liquid chromatography, showed considerable differences except the  $\Delta H_{12}$  and  $\Delta S_{12}$  for **1a@2**, obtained by NMR and ITC methods. The reason of the differences, involving RPLC, are not discussed in view of internal inconsistencies of this method. On the other hand, the disagreement between the ITC and NMR results seems to be due to the difference in solvents ( $H_2O$  and  $D_2O$ , respectively) used in both methods, which causes deuteration of all 36 OH groups of the host cyclodextrins. Interestingly, the deuteration causes a lowering of the absolute values of  $\Delta H_{12}$  and  $\Delta S_{12}$  for **1b@2**, while the corresponding values of the complex with the second enantiomer are either unchanged or undergo only small changes upon the complexation.