

## **Calixarene Assemblies**

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Selected examples of calixarene dimers and oligomers are presented, along with calixarene assemblies with other molecules, including those containing fullerene units.

## Copper(II) Complexes of 4-Azocyanoacetamidoaniline Antipyrine and 4-Azocyanoacetamido-*m*-toluidine Antipyrine

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The synthesis and characterization of copper(II) complexes with 4-azocyanoacetamidoaniline antipyrine (HL<sup>1</sup>) and 4-azocyanoacetamido-*m*-toluidine antipyrine (HL<sup>2</sup>) are reported. Elemental analyses, molar conductivities, magnetic moments and spectral (IR, electronic and ESR) studies have been used. The elemental analyses and IR spectra show that the ligands behave as neutral or monobasic bidentate ones, either in the ketoazo or enolazo form. The IR spectra also show that, in the chlorocomplexes (1 and 4), the cyano group is changed to amide (—CO—NH<sub>2</sub>). Stereochemical structures for the complexes are proposed.

## **Methyl Transfer from Methylcobalt(III) Phthalocyanine to Bromide and Iodide Ions in Sulfolane**

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Rates of methyl transfer from methylcobalt(III) phthalocyanine ( $\text{MeCo}^{\text{III}}\text{Pc}$ ) to bromide and iodide nucleophiles in sulfolane were measured in the temperature range 20–40°C. In contrast to iodide, bromide ion forms an unreactive complex  $\text{MeCo}^{\text{III}}\text{PcBr}^-$ , formation constant for which was determined. Rates of reaction between  $\text{Co}^{\text{I}}\text{Pc}^-$  and methyl iodide were also measured. Identity rate constant for methyl transfer between two  $\text{Co}^{\text{I}}\text{Pc}^-$  nucleophiles of  $51 \text{ M}^{-1} \text{ s}^{-1}$  at 25°C was obtained using the Marcus equation. This identity rate is the largest out of many determined in this solvent.

## **Copper(II) Pyridine-2,6-dicarboxylates. Coordination and Distortion Isomers of [Cu(pydca)(H<sub>2</sub>O)<sub>2</sub>]**

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Copper(II) pyridine-2,6-dicarboxylate dihydrate and its ronicol (ron), nicotinamide (nia) and caffeine (caf) complexes were prepared and their spectral, magnetic as well as their bio-activities were studied. X-ray analysis of [Cu(pydca)(H<sub>2</sub>O)<sub>2</sub>] (pydca = pyridine-2,6-dicarboxylate) shows, that the complex exists in two isomeric forms: monoclinic and triclinic and it is an example of the coordination isomerism. Triclinic forms also exists in two isomeric forms, differing mostly by degree of distortion and being an example of the distortion isomerism. On the basis of spectral and magnetic properties for Cu(pydca)L (L = ron, nia or caf) a square-pyramidal coordination of the copper(II) ion can be proposed. Highest bio-activity shows [Cu(pydca)(H<sub>2</sub>O)<sub>2</sub>].

## **Semiempirical Calculations in a Search for a Mechanism of 2-Methyl-4-phenylquinoline Formation from 4,4-Diphenyl-3-buten-2-one Oxime Acetate**

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The known thermal non-catalytic formation of 2-methyl-4-phenylquinoline from 4,4-diphenyl-3-buten-2-one oxime acetate was analyzed by semiempirical MNDO, AM1 and PM3 methods of calculation, assuming the process consists of three steps: thermal disrotatory electrocyclicization of the oxime acetate, inversion of the cyclic intermediate on the nitrogen atom and elimination of acetic acid from the inverted intermediate according to E<sub>i</sub> mechanism. It appears from PM3 calculations, which led to better results than MNDO or AM1, that the disrotatory electrocyclicization is the rate-determining step for the whole synthesis.

## Reactions of Thioesters with Organic Azides – A Novel Access to Imidates and Thioimidates

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The reaction of O-methyl thiocarboxylates **8a, b** with organic azides at 110°C yielded the corresponding imidates of type **9**, which were easily hydrolyzed to give amides **10**. The formation of **9** can be rationalized by a 1,3-dipolar cycloaddition of the azide with the C=S group, followed by the “twofold extrusion” of N<sub>2</sub> and S. The analogous reaction with methyl dithiobenzoate (**11**) led to thioimidates **13**. On heating, the latter were transformed into thioamides **12**.

## **Synthesis of the Potent Antitumor Saponin OSW-1 Aglycone**

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A simple synthesis of the saponin OSW-1 aglycone is described. A key step of the synthesis is the reaction of a recently reported steroidal  $17\alpha$ -hydroxy-22,16-lactone with *isoamyllithium*. The relative reactivity of the hydroxy groups in the  $16\beta$ -,  $17\alpha$ -, and 22-positions was examined.

## **Crown Ethers with Azo or Azoxy Unit and Sulfur Atom(s) in 16-Membered Macrocycle**

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16-membered crown ethers bearing oxygen and sulfur atom(s) and an azo or azoxy group in the macrocycle have been synthesized by reductive macrocyclization of respective dinitropodands. Behavior of the compounds as ionophores in ion-selective membrane electrodes has been studied. The structure of 16-membered azothiacrown ether has been solved by X-ray analysis.

## Electrokinetic Properties of Nafion 117 in NaCl + KCl Solutions

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The applicability of the extended Nernst-Planck equation with the homogeneous distribution of ions and the capillary model (the Boltzmann distribution of ions) to the description of electrokinetic phenomena in the system Nafion 117|0.1 M mixture of NaCl and KCl has been discussed. It has been found that only the capillary model can reasonably describe those phenomena, simultaneously preserving the Onsager reciprocity relation. The extended Nernst-Planck equation gives unsatisfactory results by either strongly breaking the reciprocity relation or, assuming the reciprocity relation ( $\alpha_i$  must be 1), leading to large discrepancies between the hydrodynamic permeability and the electrical conductivity. The interpretation of  $\alpha_i$  in terms of the capillary model has been given.  $\alpha_i < 1$  for counterions and  $\alpha_i > 1$  for coions result from the radial concentration profiles of those ions and of the convective velocity. The dependence of  $\alpha_i$  on the kind of acting force has been proved.

## **Kinetic Studies on Perborate Oxidation in Non-aqueous Media. Oxidation of Diphenylamine**

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Solution of perborate in glacial acetic acid generates peracetic acid on aging and the peracetic acid oxidation of diphenylamine is fast. Hydrogen peroxide in glacial acetic acid does not yield peracetic acid on standing; also, the hydrogen peroxide oxidation rate is only two-third of perborate. The aging effect was overcome by dissolving perborate in 1,2-diols. The oxidation in 1,2-diols-acetic acid is zero order in the oxidizing agent, whereas the same oxidation with fresh solution of perborate in acetic acid is first order with respect to the oxidizing agent. However, the rate of the former and the specific rate of the latter show first order dependence on  $[\text{perborate}]_0$ . The reactions proceed *via* two paths, one is first order and the other is zero order in diphenylamine. In 1,2-diols-acetic acid, the perborate oxidation is slower than hydrogen peroxide. The reaction mechanism is discussed and the rate laws derived.

## **Hydrogen Evolution Reaction at Indium Electrode in Molten Ethylammonium Tetrafluoroborate**

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The hydrogen evolution reaction (HER) has been studied at indium electrode in pure molten ethylammonium tetrafluoroborate ( $\text{EtNH}_3\text{BF}_4$ ). Measurements were carried out from 424 to 474 K. The a.c. impedance and potentiostatic polarization techniques were used. The exchange current density of the HER, its overall apparent activation energy, the cathodic transfer coefficient and the double layer capacitance have been determined. It has been postulated that the amine molecules do not adsorb on the indium electrode surface in the potential range applied and do not inhibit the HER.

## **A Theoretical Study of the *cis-syn* Cytosine-containing Pyrimidine Dimers in the Gas Phase and a Water Cluster and a Tautomer-Bypass Mechanism for the Origin of UV-induced Mutations**

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A quantum mechanical study of *cis-syn* cyclobutane cytosine-containing photodimers including the normal and rare tautomeric forms of bases has been performed using the *ab initio* method at HF/6-31G(d,p), MP2(fc)//HF/6-31G(d,p) and MP2(fc)/6-31G(d,p) levels. It is predicted that in the gas phase all photodimers containing the rare imino form of cytosine are more stable than those containing its normal form. The Monte Carlo study of the hydration for cytosine-consisting dimers showed that the dimer containing the imino form of cytosine is stabilized by water cluster more than that containing its amino forms. As a result, the imino form of cytosine in the cytosine-containing dimer directs the incorporation of adenine in the complementary strand during replicative bypass. Data obtained point to the cytosine tautomerism as a possible mechanism for the origin of UV-induced mutation.

## **Diffusion Coefficients of Deuterium in Palladium Deuteride during Ab- and Desorption in High Pressures of Gaseous Deuterium at 298 K**

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Exerting pressure jumps of several kbar in gaseous deuterium in the range of 5–28 kbar, surrounding a palladium deuteride wire, the diffusion coefficients of deuterium in the solid phase were evaluated by following the time course of the electrical resistance. Absorption of deuterium is characterized by a smaller diffusion coefficient than its desorption. Both represent a decreasing function with the increase of deuterium pressure. The difference of the ab- and desorption kinetics is explained by the influence of the elastic energy on the energetics of the occupation of metallic interstitials by deuterium particles. Comparisons with previous measurements are given.

**Catalytic Hydrogen Transfer over Magnesia. XVI.  
Liquid Phase Reduction of Cycloalkanones by 2-Octanol**

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**Synthesis and Crystal Structure of Copper(II) Complex  
with Bis(2-aminoethyl)sulfide and Thiocyanate as Ligands**

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**Synthesis, Crystal Structure and Magnetism of  
 $\mu$ -Thiocyanato Bridged Complex:  
[Ni<sub>2</sub>(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>(NCS)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>**

by J.M. Shi<sup>1</sup>, C.Y. Shu<sup>1</sup>, W.T. Yu<sup>2</sup>, L.J. Sun<sup>1</sup>, C.J. Wu<sup>1</sup> and J.J. Lu<sup>1</sup>

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## **Crystal Structure of $\text{Nd}_2\text{Ni}_2\text{Pb}$ and $\text{Nd}_5\text{NiPb}_3$ Compounds**

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## **Phase Diagram of Y–Rh–Ga System at 870 K**

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**Complexes of Hg(II) with Carboxylic Acids  
in Water and Water-Methanol Solutions**

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