

## Hydrothermal Synthesis, Crystal Structure and Properties of a New Cyanide-containing Supramolecular Compound

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Under hydrothermal conditions, reaction of  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{NiCl}_2$  and dien results in the formation of a cyanide-containing heterometallic compound  $[\text{Ni}(\text{dien})_2][\text{Fe}(\text{CN})_4]$  **1**. The structure consists of one octahedral  $[\text{Ni}(\text{dien})_2]^{2+}$  cation, square  $[\text{Fe}(\text{CN})_4]^{2-}$  anion, which are held together by N–H $\cdots$ N hydrogen bond to form one-dimensional supramolecular chains. Its magnetic property was measured from 5 to 300 K, showing very weak ferromagnetic interactions. This compound in DMF solutions has a strong third-order non-linear optical (NLO) behavior with absorption coefficient and refractive index  $\alpha_2 = 2.10 \times 10^{-11} \text{ m w}^{-1}$ ,  $n_2 = -2.05 \times 10^{-18} \text{ m}^2 \text{ w}^{-1}$ , respectively, and third-order NLO susceptibility  $\chi^{(3)} 2.73 \times 10^{-10}$  esu.

## **Spectroscopic Studies of Charge-Transfer Complexation of Octathia-24-crown-8 with Iodine in Chloroform Solution**

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The charge-transfer complexation between octathia-24-crown-8 (OT24C8) and iodine in chloroform solution was studied spectrometrically at various temperatures. The molar absorptivities and formation constants of the resulting 1:1 complex were determined. The formation of the OT24C8-I<sub>2</sub> complex was also confirmed by <sup>1</sup>H NMR spectrometry. The enthalpy and entropy of the charge-transfer complexation were determined from the temperature dependence of the formation constant, as  $\Delta H^\circ = -31.0 \pm 0.5 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = -84 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$ .

## **Ability of 2,4D and 2,4DP Herbicides to Combine with Metal Ions of Biological Interest (Part 1): Copper(II) Complexes**

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Copper(II) complexes with the commercial auxin herbicides 2,4-dichlorophenoxyacetic acid (2,4D;  $C_8H_6O_3Cl_2$ ) and 2-(2,4-dichlorophenoxy)-propionic acid (2,4DP;  $C_9H_8O_3Cl_2$ ) were prepared and characterized. On the basis of the results of elemental analysis and Cu(II) determination, the following molecular formulae were proposed for the obtained compounds:  $Cu(C_8H_5O_3Cl_2)_2 \cdot 4H_2O$  (**Cu-2,4D**) and  $Cu(C_9H_7O_3Cl_2)_2 \cdot H_2O$  (**Cu-2,4DP**). Water solubility of synthesized complexes at room temperature was determined. The complexes have been characterized by IR, VIS and EPR spectroscopy, conductivity (in methanol and dimethylformamide), magnetic measurements and X-ray diffraction analysis. Thermal decomposition of these compounds in air was studied by TG, DTG, DTA and TG/MS methods with simultaneous analysis of the solid and gaseous products.

## **The Role of Synthesis Parameters in Preparation of Cu,Cr-Layered Double Hydroxides**

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A series of Cu,Cr-layered double hydroxides of Cu/Cr ratio equal 2 has been synthesized by co-precipitation at a constant pH, using different preparative conditions. The investigated synthesis parameters included: ageing time, speed of reactants addition, temperature of co-precipitation and pH of synthesis. The dominant product of the synthesis was the nitrate form of Cu,Cr-LDH, containing *ca.* 10 mol% of carbonate. Modifications of experimental conditions affected chiefly the samples crystallinity. The most obvious effects were associated with changing of pH of the co-precipitation, the most acidic conditions providing a material of the best crystallinity. At the medium synthesis temperature (55°C), a slow addition of the reactants and a long ageing were favourable, but a significant shortening of the ageing time caused only minor deterioration of the sample crystallinity. The latter finding is of practical importance for an upscaling of the process.

## **Studies on Schiff Base Complexes of $\beta$ -Diketones/ $\beta$ -Ketoesters with 2,4-Dinitrophenylhydrazone and Their Antimicrobial Activities**

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2,4-Dinitrophenylhydrazone derivatives of Cu(II), Co(II) and Ni(II) complexes have been synthesized. The structural features of the complexes have been confirmed by microanalytical data, IR, UV-Vis, EPR, CV, TGA and powder XRD techniques. The electronic absorption spectra and magnetic susceptibility indicate a square-planar geometry for copper and tetrahedral for cobalt and nickel complexes. The neutral nature of the complexes is characterized by their low molar conductance. The cyclic voltammogram of copper complex in DMSO solution shows a quasi-reversible peak. The EPR spectrum of copper complex in DMSO at 300 K and 77 K was recorded and its salient features are reported. The antimicrobial activity of the complexes has been extensively studied on microorganisms such as *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruginosa* and the fungi *Aspergillus niger* and *Rhizoctonia bataicola* by well-diffusion technique using pyridine as solvent. The values of zone of inhibition were found out at 37°C for a period of 24 h. It has been found that all the product complexes have a higher activity than the parent complexes and the standard.

## **Synthesis and Structure of Two Thiocarboxypyrazolic Acid Derivatives**

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Two thiocarboxypyrazolic acid amide derivatives were obtained unintentionally in a reaction of thiosemicarbazone with 2-acetylbutyrolactone, and structures of the final products have been determined by X-ray diffraction. Due to conjugation of the thioamide group with the planar pyrazolic ring, the molecule is flat, except 2-hydroxyethyl chain, accidentally adopting similar conformation in the two studied molecules. Also similar is the packing, despite different hydrogen bonding schemes, resulting from the different number of donoric H atoms and the presence of an additional water molecule in the second compound. The mechanism of the reaction is suggested.

## **Reactions of Complexation of Co(II), Ni(II), Cu(II), Cd(II) and Hg(II) Ions with Adenosine 5'-Diphosphate**

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The reaction of complexation has been studied in the systems of the ions: Co(II), Ni(II), Cu(II), Cd(II) and Hg(II) with adenosine 5'-diphosphate. The composition and stability constants of the complexes formed have been determined by the potentiometric method. The presence of the species type: MHL,  $ML_x$ , and MLOH has been confirmed and their mode of coordination has been identified on the basis of the spectral data. In the acidic solution, the coordination dichotomy N(1)/N(7) has been found in all systems studied. At pH above 7, the dichotomy does not occur in the systems with Cu(II), while in the systems with Hg(II) only phosphate groups are involved in metallation. In the synthesized solid complexes of Cd(II) with *AMP* or *ADP*, the metal ion is bound by the donor nitrogen atom N(1), and in the complexes with *ATP* by the nitrogen atom N(7) of the nucleotide. Moreover, in the species with adenosine di- and triphosphate, the oxygen atoms of the phosphate groups are engaged in the complexation, while in the species Cd(AMP), similarly as in the liquid phase, the phosphate group is not involved in metallation.

**New Reactions of Thiocyanatobismuthates(III) with Organic Compounds. II. Reactions of Tetrathiocyanatobismuthates(III) with Monocarboxylic Acids Salts Containing an Aromatic Ring**

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Our previous work [1] presented the reactions of caesium tetrathiocyanatobismuthate(III) with the solutions of sodium salts in aliphatic monocarboxylic acids. In this study the still unreported reactions of  $\text{Cs}[\text{Bi}(\text{SCN})_4]$  with solutions of sodium benzoate, salicylate and anthranilate, and those of  $\text{Rb}[\text{Bi}(\text{SCN})_4]$  with sodium salicylate solution are treated. The chemical, XRD, IR and thermal analyses of the reaction products were carried out. The composition of the product depends on the type of the ligand. In the case of benzoate in the solid phase, only one complex compound,  $\text{Cs}_2\text{Na}[\text{Bi}(\text{SCN})_6]$  is formed, whereas the salicylate and anthranilate form two complex bismuth compounds,  $\text{Cs}_2\text{Na}[\text{Bi}(\text{SCN})_6]$  and  $\text{BiX}_3$  (X – a salicylate or anthranilate anion) or  $\text{BiX}_3 \cdot \text{NaX}$ .

**An Anionic Moiety,  $MCl_4^{2-}$  (M = copper, zinc, cadmium and mercury) Stabilized by Bis(diethylenetriamine)copper(II) Cation**

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Bimetallic complexes of the type  $[Cu(dien)_2][MCl_4]$ , where M = Cu(II), Zn(II), Cd(II) and Hg(II), were prepared by reacting bis(diethylenetriamine)copper(II) dichloride with copper, zinc, cadmium and mercury dichlorides in ethanol. They have been characterized by elemental analyses, IR, electronic and EPR spectra, magnetic moment, TGA and conductivity measurements. Electrical conductivity of all the complexes indicated them to be 1:1 electrolyte in DMF and that the copper(II) ion is paramagnetic, maintaining its octahedral geometry, while metal ions in the anionic moiety of the complexes achieve their usual tetrahedral environment. An augmented magnetic moment has been observed in the  $[Cu(dien)_2][CuCl_4]$  complex, which is attributed to the ferromagnetic effect. From the EPR spectra, the Cu–Cu distance ( $r_{jk}$ ) has been found to be larger in  $[Cu(dien)_2][CdCl_4]$  than in  $[Cu(dien)_2][CuCl_4]$ . The TGA of  $[Cu(dien)_2][CuCl_4]$  showed the decomposition of various fragments between 226 to 1000°C.

## **Thermal, Spectral, Magnetic and Biological Studies of Thiosemicarbazones Complexes with Metal Ions: Cu(II), Co(II), Ni(II), Fe(III), Cd(II), Zn(II), Mn(II) and UO<sub>2</sub>(VI)**

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Thiosemicarbazones ligands, isatin-3-thiosemicarbazone (HIT) and N-acetylisatin-3-thiosemicarbazone (HAIT), which have tridentate ONN coordinating sites were prepared. The complexes of both ligands with Cu(II), Co(II), Ni(II), Fe(III), Cd(II), Zn(II), Mn(II) and UO<sub>2</sub>(VI) ions were isolated. The ligands and their metal complexes were characterized by elemental analyses, IR, UV-Vis and mass spectra, also by conductance, magnetic moment and TG-DSC measurements. All the transition metal complexes have octahedral configurations, except Cu-complexes, which were found to have the square-planar geometry and the UO<sub>2</sub>(VI) complexes which have coordination number 8 and may acquire the distorted dodecahedral geometry. Thermal studies explored the possibility of obtaining new complexes. Inversion from octahedral to square-planar configuration occurred upon heating the parent Ni-HAIT complex to form the corresponding pyrolytic product. The antifungal activity against the tested organisms showed that some metal complexes enhanced the activity with respect to the parent ligands.

## Urease Inhibiting Guaianolides from *Amberboa ramosa*

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New sesquiterpene lactones have been isolated from the chloroform-soluble fraction of *Amberboa ramosa* and assigned two structures 4 $\beta$ -(chloromethyl)-3 $\beta$ ,4 $\alpha$ -dihydroxy,8 $\alpha$ -[(s)-2-carboxypropionyloxy]-1 $\alpha$ H,5 $\alpha$ H,6 $\beta$ H,7 $\alpha$ H-guaia-10(14),11(13)-dien-6,12-olide (**1**) and 4 $\beta$ -(chloromethyl)-3 $\beta$ ,4 $\alpha$ -dihydroxy,8 $\alpha$ -[(s)-3-hydroxy-2-methylpropionyloxy]-1 $\alpha$ H,5 $\alpha$ H,6 $\beta$ H,7 $\alpha$ H-guaia-10(14),11(13)-dien-6,12-olide (**2**), respectively. In addition 5-hydroxy-6-methyl-7-methoxyflavone (**3**), 6,2',5'-trihydroxy-3,5,7-trimethoxyflavone (**4**) and 5-hydroxy-3,7,8,2'-tetramethoxyflavone (**5**) have also been reported for the first time from this species. Compounds **1** and **2** displayed promising inhibitory potential against enzyme urease in a concentration-dependent fashion.

## **Cholesteryl Derivatives of Tetra-phenylporphyrins**

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Several tetra-phenylporphyrin mono-derivatives of cholesterol were obtained, along with one di- and one tetra-cholesterol derivatives. These compounds are strongly hydrophobic and are well soluble in nonpolar solvents. Owing to the cholesterol substituent, they can be used in various systems, where this feature is of importance; for example in preparing liposomes, in incorporating in other lipid bilayers and micelles. The large cholesterol substituent does not alter characteristic spectral features of tetra-phenylporphyrin.

## Polycyclic [2+3]-Cycloadducts from the Thermal Decomposition of Bis(2,5-dihydro-1,3,4-thiadiazoles) in the Presence of *N*-Methylmaleimide

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Thermal decomposition of a mixture of the two stereoisomeric bis(2,5-dihydro-1,3,4-thiadiazoles) *cis*- and *trans*-**2**, which was prepared by treatment of 2,2,4,4-tetramethylcyclobutane-1,3-dithione with excess of diazomethane in the presence of two equivalents of *N*-methylmaleimide, led to a mixture of three 1:2 cycloadducts of type **4**. The structures of these thiocarbonyl methanide-adducts have been established by X-ray crystallography. In the presence of only one equivalent of *N*-methylmaleimide, a complex mixture of the three 1:2 adducts of type **4**, the known dispirocyclic bis-thiiranes *cis*- and *trans*-**3**, and a 1:1 adduct **6**, containing one thiirane ring and one fragment resulting from a [2+3]-cycloaddition of a thiocarbonyl methanide, was formed. The structure of the latter has again been proven by X-ray crystallography.

## **Facile Synthesis of 2-Substituted Quinazolinones**

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Anthranilic acid reacts with aromatic nitriles in the presence of potassium *tert*-butoxide to form 2-arylsubstituted quinazolinones in good yields.

## **Synthesis of Thio Derivatives of Phenobarbital and Its N-Methyl Derivatives**

**by A. Stasiewicz-Urban, M. Kubaszek, M. Żylewski, M. Cegła and J. Bojarski**

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Differently substituted thio derivatives of phenobarbital and its N-mono- and N,N'-dimethyl derivatives were obtained by thionation of respective substrates with Lawesson's reagent. The structure of the products not described in the literature was confirmed by spectral and elemental analyses. The spectral properties allow to differentiate between positional isomers of the products.

## **Synthesis of New Diaryl and Dialkyl Diselenides as Potential Virucides and Antimicrobials**

by **J. Palus**<sup>1</sup>, **M. Chojnacka**<sup>1</sup>, **E. Piasecki**<sup>2</sup>, **E. Zbońska**<sup>1</sup> and **J. Młochowski**<sup>1</sup>

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The synthesis of three new groups of alkyl and aryl diselenides: 2,2'-diselenobisbenzamides, 4,4'-diselenobisbutyramides and 2,2'-di(selenomethyl)bisbenzamides designed as potential virucides and bacteriocides was elaborated. It was based on acylation of free amino group in monoprotected diamines or 4'-aminobenzo-15-crown-5 with corresponding diselenobiscarboxylic acids or their chlorides.

## **An Expedient Transformation of Alcohols into *N*-Boc-Amines**

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*t*-Butyl methyl iminodicarbonate (**3**) can be easily alkylated with primary or secondary alcohols under Mitsunobu conditions (DIAD, TPP) to give the corresponding *N*-alkyl iminodicarbonates. Partial deprotection of the latter with methanolic potassium hydroxide affords *N*-Boc-amines (**5**) in good yields.

## **Acidity of the N<sup>+</sup>CH<sub>2</sub> Protons in N-Phenacyl-R-pyridinium Bromides**

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UV-Vis, FTIR, <sup>1</sup>H and <sup>13</sup>C NMR and MS spectra of 19 N-phenacyl-R-pyridinium bromides and their ylides were measured and analysed. In crystals the investigated salts appear as keto-tautomer, but in water solutions in a keto-enol tautomeric equilibrium. In most salts, the N<sup>+</sup>CH<sub>2</sub> hydrogens, undergo fast hydrogen-deuterium exchange in neutral D<sub>2</sub>O at room temperature, which confirms the presence of some amount of enolic tautomers in aqueous solutions. The intensity of the ylide bands in the 385–480 nm region is substituent and time dependent and reflects the rates of their formation and decomposition. The ylides with electron-withdrawing substituents form and decompose much faster than those with electron-donating ones.

## ***In-situ* Generated Functionalized Benzimidazol-2-ylidene-palladium Catalyst for Suzuki Reaction**

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From readily available starting materials functionalized 1,3-dialkylbenzimidazolium salts (**1a–g**) have been prepared and characterized by conventional spectroscopic methods and elemental analysis. The *in situ* prepared three component system Pd(OAc)<sub>2</sub>/1,3-dialkylbenzimidazolium halides (**1a–g**) and Cs<sub>2</sub>CO<sub>3</sub> catalyses Suzuki cross-coupling of aryl chloride substrates. These concepts for making catalysts *in situ* open the way for the discovery of many new catalysts *via* the interaction of commercially available metal complexes and suitable electron releasing ligands.

## Properties of Langmuir Monolayers from Perfluorohexyl-*n*-alkanes

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A series of semifluorinated *n*-alkanes (SFAs), of the general formula:  $F(CF_2)_m(CH_2)_nH$ , (in short FmHn), where  $m = 6$  and  $n = 16–20$ , have been synthesized and employed for Langmuir monolayer characterization. Surface pressure and electric surface potential measurements were obtained under a variety of experimental conditions. The Langmuir monolayer experiments have been complemented with Brewster angle microscopy results, which enabled both a direct visualization of the monolayers structure and the estimation of their thicknesses at different stages of compression. Our results show, that these “non-classical” film-forming materials, which are completely hydrophobic in nature and do not possess any polar group in their structure, are capable of monolayer formation at the air/water interface. The negative sign of the measured surface potential,  $\Delta V$ , proves that SFA molecules are oriented at the air/water interface with their perfluorinated parts directed towards the air, independently on the length of hydrogenated moiety. The change of electric surface potential achieves the minimum value of *ca.*  $-0.75$  V for all the investigated SFA. The minimum effective dipole moment is achieved for a molecule oriented at the angle of about  $35^\circ$  to the surface normal. The relative intensity measurements allow one to conclude, that film molecules are oriented vertically in respect to the surface normal at the vicinity of collapse.

## Spectroscopy and Photophysics of 6,8-Dimethylalloxazine. Experimental and Theoretical Study

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Photophysics of 6,8-dimethylalloxazine was studied experimentally in function of solvent properties and theoretically by using time-dependent density functional theory (TD-DFT) calculations. The absorption spectrum of 6,8-dimethylalloxazine in the near-UV region shows one broad maximum at approximately 350 nm (*ca.* 28600 cm<sup>-1</sup>), which is a superposition of the two lowest-energy bands, and a fluorescence emission band varying from about 462 nm (21600 cm<sup>-1</sup>) in dioxane and acetonitrile to 475 nm (21000 cm<sup>-1</sup>) in methanol solution. In aprotic solvents neither band shows a significant dependence on the solvent polarity. The fluorescence lifetime increases in protic relative to aprotic solvents, and increases with increasing solvent polarity, due to reduction of the non-radiative rate constant. TD-DFT calculations provide details of the electronic structure of the molecule in its excited states and allow the interpretation of the observed photophysics in terms of the proximity effect.

## **Voltammetric Behavior of the Nitro Radical Anion Generated Electrochemically from Furazolidone at Glassy Carbon Electrode**

by **L. Fotouhi and L. Kiapasha**

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The electrochemical behavior of the nitro radical anion resulted from the reduction of furazolidone has been studied in mixed aqueous-dimethylformamide (DMF) solvent at glassy carbon electrode (GCE) by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Furazolidone is reduced in two cathodic steps in the low concentration of DMF and acidic media, giving hydroxylamine and amine derivatives *via* reduction by four and two electrons, respectively. The addition of DMF to the basic buffer solution enables the presence of two different reduction processes to be established. The first cathodic peak is related to a 1e-reversible reduction process corresponding to the formation of nitro anion radical ( $\text{RNO}_2^-$ ) and the more negative peak is due to the formation of hydroxylamine *via* a 3e-irreversible reduction process. The cyclic voltammetry technique has been employed to the study of  $\text{RNO}_2/\text{RNO}_2^-$  couple. The reversibility of radical anion is investigated by the ratio of anodic to cathodic current,  $I_{a1}/I_{c1}$ , by increasing DMF content and pH. The influence of scan rate on the  $I_{a1}/I_{c1}$  ratio shows an  $\text{EC}_i$  mechanism, in which this subsequent chemical reaction corresponds to protonation reaction of  $\text{RNO}_2^-$  that is initiated electrochemically. The effect of cationic and anionic surfactants has been reported on the electrochemical behavior of furazolidone.

## **A Model of Formic Acid Pyrolysis in the Gas Phase Based on Harmonic Mode Analysis**

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Mechanism of the thermal decomposition of formic acid in the gas-phase catalyzed by water or water dimer is proposed by vibrational mode analysis. The barrier heights for both dehydration and decarboxylation reactions are revealed to be significantly lower than previously reported values, implying the importance of the catalytic effect of H<sub>2</sub>O and (H<sub>2</sub>O)<sub>2</sub> at the B3LYP/6-311G(d,p) level. The relationships of the intermediates, transition states and products are elucidated by the vibrational mode and vibrational frequencies. We used different methods to calculate the energy of all the species in order to further elucidate our calculations.

## **Adsorption of Hydrogen on Unsupported and Supported Nickel**

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The interaction of hydrogen with Ni powder and supported nickel catalysts was studied by temperature-programmed desorption (TPD) method. The measurements of hydrogen desorption were started at about 100 K, which resulted in formation of extended spectra of hydrogen chemisorbed on nickel. Preliminary examinations of the spectra indicate that at low temperature considerable quantity of hydrogen is located in subsurface region of nickel. Quantitative analysis of the spectra recorded for Ni powder showed that at low temperature the stoichiometry of hydrogen chemisorption on nickel, *i.e.* H/Ni<sub>s</sub> ratio, is close to 1.8. The studies of hydrogen adsorption on supported nickel catalysts indicate that commonly applied measurements of hydrogen adsorption at room temperature are justified for characterization of Ni/Al<sub>2</sub>O<sub>3</sub>, but appear inappropriate for Ni/SiO<sub>2</sub>.

## **Morphology Study of Co/SiO<sub>2</sub> Model Catalyst by Electron Microscopy. Effect of Oxidation-Reduction Treatment**

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Effect of pretreatment in air (500–1000°C) of Co/SiO<sub>2</sub> model catalysts on morphology of Co phase formed upon reduction at 700°C in H<sub>2</sub> for 4 h has been investigated by electron microscopy. The model catalysts were thin cobalt films (1 and 4 nm thick) on an amorphous layer of SiO<sub>2</sub>. It is concluded that the morphology of formed Co particles depends on Co loading, state of the surface support and Co-silica interaction in the oxidized state. The size distribution of Co particles and Co dispersion in samples subjected to various pretreatment are discussed. The highest dispersion of Co was observed for samples (4 nm thick) preheated at 800°C.

**Changes in Aromaticity in the Ring  
of Monosubstituted Benzene Derivatives**

by **T.M. Krygowski and B.T. Stepień**

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**Aromaticity Properties of Kojic Acid and Maltol  
Complexes with Oxovanadium(IV) Ion**

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**Methane Conversion in Dielectric-Barrier Discharge  
in the Presence of Quartz Packing**

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## **Equation of State for $\text{ErFe}_2$ from Quantum Calculations**

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**Temperature Programmed Oxidation of  
Carbonaceous Deposits Left after Thermodesorption of  
Organic Bases from Pd/Al<sub>2</sub>O<sub>3</sub> Catalysts**

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