Results of spectral UV-Vis absorption investigations on association of copper octacarboxyphthalocyanine, CuPcOC, are reported. Influence of pH on association is discussed. In pH < 5.5 only aggregates are present. Monomer appears above pH = 5.5 and at pH ≥ 6.2 only monomeric Pc forms exist. CuPcOC exhibits higher tendency towards association in phosphate buffer solutions than in redistilled water. In pH 5.9–6.0 monomers, dimers and trimers coexist in equilibrium in $1.0 \times 10^{-6} – 1.2 \times 10^{-5}$ mol/dm$^3$ concentration range at 25°C. The average assembling number $n = 3$ was determined for pH 5.6, 5.9 and 6.0 solutions. The spectrum of aggregate was calculated with two maxima at $\lambda_{max}$ approx. 600 nm and 630 nm attributed to trimer and dimer band, respectively. Decrease of pH causes an increase of cumulated association constant $K_n$. $K_n$ of order of $10^9$ (dm$^3$/mol)$^n$ was calculated for pH 6.0 and $10^{10}$ (dm$^3$/mol)$^n$ for pH 5.9. For pH 5.6 considerably higher $K_n$ was evaluated. A strong influence of pH on CuPcOC spectrum and equilibrium constants suggests that besides $\pi-\pi$ interactions hydrogen bonding between Pc molecules can also occur.

**Key words:** copper octacarboxyphthalocyanine, UV-Vis spectra, aggregation, buffered solutions
Investigation of Tetrahalogenoferrates(III) with Cations of Nitrogen-Containing Organic Bases.

X-ray Crystal Structure of 2,6-Dimethylpyridinium Tetrabromoferrate(III)

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The crystal and molecular structure of a new 2,6-dimethylpyridinium tetrabromoferrate(III), [2,6-LutH][FeBr₄] was determined. The iron(III) cation adopts a slightly distorted tetrahedral coordination with one angle smaller than tetrahedral, three almost equal to the tetrahedral ones and two larger. The bond valences were computed. The total valence of the iron atom is equal to 3.24. In the structure N(1)–H(1)--Br(3) hydrogen bond can be found.

Key words: Fe(III) complexes, tetrahalogenoferrate(III), crystal structure
Eco-friendly Synthesis of ZnO Nanorods in Water Using Acetylacetone as Template
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Nanocrystals of ZnO were prepared by microwave irradiation in water using Zn(II) acetate and acetylacetone (acac) as template. The ZnO obtained nanorods with hexagonal (wurtzite) structure were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), UV-vis absorption and FTIR spectroscopy.

Key words: ZnO, nanorods, microwave irradiation, acetylacetone
Synthesis and Characterization of Two Novel Mixed-Valent and Metal Oxo-Centered Trinuclear Complexes [Fe$_2$CoO(CHCl$_2$COO)$_6$(py)$_3$] and [Mn$_2$MnO(CHCl$_2$COO)$_6$(py)$_3$] by M. Yazdanbakhsh* and H. Tavakkoli

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Two novel μ$_3$-oxo trinuclear complexes, [Fe$_2$CoO(CHCl$_2$COO)$_6$(py)$_3$] (1) and [Mn$_2$MnO(CHCl$_2$COO)$_6$(py)$_3$] (2) have been synthesized and characterized by IR spectroscopy, elemental analysis, UV-Vis spectroscopy and atomic absorption spectroscopy. Complexes 1 and 2 are μ$_3$-oxo trinuclear compounds with the three metal atoms bridged by six dichloroacetates groups. M$_3$O and M$_4$O$_4$ units adopted D$_{3h}$ and D$_{4h}$ local symmetry, respectively, and are surrounded by six bridging dichloroacetates with C$_2$v local symmetry.

Key words: trinuclear complexes, bridging carboxylate, dichloroacetic acid, IR spectrum, UV-Vis spectrum
Synthesis, Characterization, in-vitro Biocidal and Nuclease Activity of Cu(II), Fe(II) and Fe(III) Complexes

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Complexes of Cu(II), Fe(II), and Fe(III) have been synthesized by reaction of their metal salts with bis(4-hydroxy-2oxo-2H-chromen-3-yl)-methane or bis(4-hydroxy-2oxo-2H-chromen-3-yl)-thiophene-2yl-methane or bis(4-hydroxy-2oxo-2H-chromen-3-yl)-pyridin-3yl-methane in molar ratio 1:2. They have been characterized using \(^1\)H-NMR, \(^{13}\)C-NMR, IR spectra, electronic spectra, magnetic measurements and elemental analyses and screened for their in-vitro antimicrobial activity against Bacillus cereus, Staphylococcus aureus, Escherichia coli, Bacillus subtilis, Salmonella typhi, and Serratia marcescens. The metal complexes exhibit moderate antimicrobial activity compared to parental compounds and standard drugs. In-vitro nuclease activity has been determined using agarose gel electrophoresis. The synthesized compounds show effective nuclease activity.

Key words: biocidal activity, DNA, nuclease activity, gel electrophoresis, IR and NMR spectra
Synthesis, Characterization and Electrochemistry of New Type Soluble Porphyrinate Containing 3-Phenylpropylthio Substituent

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Octakis(3-phenylpropylthio) porphyrinates MPz(SR)₈, where (M = Mg, H, Ni, Zn, Co) and R = C₈H₁₇, were synthesized starting with the corresponding unsaturated dicyanamide derivative. These new compounds have been investigated and characterized by UV, FT-IR, ¹H NMR, GC-MS and elemental analysis methods. As in the case of the unmetalated species, [H₂Pz], three reversible one-electron reductions and one reversible oxidation process (two for Co(II)Pz) were observed for all of the metal complexes. The \( E_{1/2} \) values are similar for the H₂Pz, Ni(II)Pz and Zn(II)Pz derivatives with negative shift due to the different effective charges of the central metal ion. Peak to peak separations and separation between the first reduction and first oxidation couples related with the HOMO-LUMO gap of the complexes are in harmony with the common porphyrinate complexes.

Key words: porphyrinate, electrochemistry, cobalt, nickel, zinc
Synthesis of 5,5-Bis(hydroxymethyl)-
N-hydroxyprrolidin-2-one Derivatives

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2,2-Disubstituted methyl 3-(5-nitro-1,3-dioxane-5-yl)propanoate derivatives were reduced with aluminum amalgam in a THF/water mixture to afford the corresponding methyl 3-(5-hydroxylamino-1,3-dioxane-5-yl)propanoates in high yields. Acetic anhydride acetylation of 3-(5-hydroxylamino-2,2-dimethyl-1,3-dioxane-5-yl)propanoate gave N-acetyl derivative in 91% yield. Heating of the γ-(hydroxylamino)esters in toluene furnished the mixture from which the corresponding N-hydroxyprrolidin-2-one derivatives were isolated in 38–56% yield. Unexpectedly, the cyclization appeared to be the critical step of synthesis of title pyrrolidin-2-ones.

Key words: γ-nitroesters, aluminum amalgam nitro group reduction, γ-hydroxylaminoesters, cyclic hydroxamic acids
Ambivalent Nucleophilicity of 1,4,5-Trisubstituted
Imidazole-2-thiones in Reactions with Dimethyl
Acetylenedicarboxylate and Phenylisocyanate

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The 1,4,5-trisubstituted 2,3-dihydro-1H-imidazole-2-thiones 1 react with electrophilic reagents via the S- or the N(3)-atom. The reaction with dimethyl acetylenedicarboxylate in methanol at room temperature occurs by the nucleophilic addition of the S-atom to give the corresponding 2-[(1H-imidazol-2-yl)sulfanyl]fumarates 4 in high yield. On the other hand, imidazole-2-thiones 1 react with phenylisocyanate in dichloromethane at room temperature to yield 2,3-dihydro-2-thioxo-1H-imidazole-1-carboxamides 5. The structures of both types of adducts were established by X-ray crystallography.

Key words: imidazole-2-thiones, addition reactions, acetylenedicarboxylates, isocyanates, X-ray crystallography
Selective Oxidation of Isobutane and Isobutene over Mo-Te Mixed Oxide Catalysts

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A series of TeMo$_x$ ($x = 3–6$) mixed oxides were prepared and investigated for the selective oxidation of isobutane and isobutene. Both the characterization results and the catalytic properties of the samples are quite different, depending on the composition of the calcined samples. Among them, TeMo$_3$ catalyst showed the best total selectivity to methacrolein and methacrylic acid (as high as 46%), and their yield reached 10.1% at 400°C in the selective oxidation of isobutane. However, TeMo$_4$ catalyst showed the best catalytic performance in the selective oxidation of isobutene, in which 73% selectivity to methacrolein and 9% selectivity to methacrylic acid can be obtained at 77.5% isobutene conversion at 440°C.

Key words: isobutane, isobutene, selective oxidation, methacrolein, methacrylic acid
Molar conductivities of dilute solutions of cesium bromide in binary mixtures of 2-butanol and water were measured in the temperature range from 288.15 to 308.15 K at 5 K intervals. The limiting molar conductivity ($\Lambda_\infty$) and the ion-pair formation constant ($K_A$) were determined by the Lee-Wheaton conductivity equation. Thermodynamic quantities, Gibbs energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) for the ion-association reaction were derived from the temperature dependence of $K_A$. The activation energy of the ionic movement ($\Delta H^\ddagger$) was derived from the temperature dependence of $\Lambda_\infty$. The obtained thermodynamic quantities, together with Walden product, were interpreted in terms of the ionic size as well as solvent basicity, structure and permittivity.

**Key words:** cesium bromide, 2-butanol + water mixtures, association to ion-pairs, thermodynamic quantities
Crystal Structure and Quantum Chemical Calculations on \(\alpha\)-Hydroxyacetophenone Phenylhydrazone

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\(\alpha\)-Hydroxyacetophenone phenylhydrazone has been synthesized and characterized by elemental analysis, IR and electronic spectroscopy. The X-ray crystal structure study shows that the compound contains two crystallographically independent molecules in the asymmetric unit and crystallizes in the monoclinic system, space group \(P2_1/c\), with \(M_r = 226.27\ (C_{14}H_{14}N_2O), a = 13.433(3), b = 10.738(2), c = 18.351(7) \ \text{Å}, \beta = 114.44(2)°, V = 2409.8(12) \ \text{Å}^3, Z = 8, D_T = 1.247 \ \text{Mg/m}^3, F(000) = 960, \mu (\text{Mo K}α) = 0.080 \ \text{mm}^{-1}, R = 0.0638, wR = 0.1535. \) Ab initio calculations of the structure, atomic charge distributions, natural bond orbital analysis and thermodynamic functions of the title compound were performed at HF/6-311G** and B3LYP/6-311G** levels of theory. Electronic absorption spectra were calculated by the time-dependent density functional theory (TD-DFT). Vibrational frequencies were predicted, assigned and compared with the experimental values. The calculation of the second order optical nonlinearity was carried out and the molecular hyperpolarizability of \(3.332 \times 10^{-30} \text{esu}\) was predicted.

Key words: crystal structure, quantum chemical calculation, vibrational frequencies, second order optical nonlinearity
Theoretical Study of Ionization Potential and Electron Affinity of Different Isomers of Pyridone

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The adiabatic (vertical) ionization potential (IP) and valence electron affinity (EA) of gaseous pyridone have been determined with HF method and three DFT methods: B3LYP, B3P86 and B3PW91 at 6-311++G(d,p) and 6-311++G(2d,2p) basis sets. IPs and EAs of pyridone in solutions have been calculated at the B3LYP/6-311++G(d,p) basis set. IPs and EAs of four isomers of pyridone are both positive values. The IPs in solutions are smaller than the results in the gaseous phase and decrease with the increase of dielectric permittivities in solutions. This finding indicates that the cationic states in solutions are more stable than those in the gaseous phase. All the EAs are negative in the gaseous phase, indicating that the anionic states are unstable with respect to the electron autodetachment, both adiabatically and vertically.

Key words: density functional theory, ionization potential, electron affinity, pyridone
Application of Chemometrics and Quantum Chemical Calculations to the Study of Complexation Equilibria Between 1,8-Bis(o-aminophenoxy)-3,6-dioxaoctane and Some Transition and Heavy Metal Ions in Acetonitrile Solution

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Evolutionary factor analysis (EFA) and rank annihilation factor analysis (RAFA) were applied to resolve the two-way equilibrium spectrophotometric data for the determination of stability constants of the complexes of 1,8-bis(o-aminophenoxy)-3,6-dioxaoctane (BOAPD) with Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Cd\textsuperscript{2+}, Pb\textsuperscript{2+} and Hg\textsuperscript{2+} ions. The number of component species was determined by factor analysis of the absorbance data and then a hard model between the analytical concentrations of the ligand and metal ions, the equilibrium concentrations of all species present and the corresponding equilibrium constants was written. By knowing the equilibrium constants, the equilibrium concentrations of the species will be calculated at each metal to ligand mole ratio. The values of equilibrium constants were varied iteratively and, at each iteration, the ligand’s information (i.e., the equilibrium concentration and spectral information) were annihilated from the original data matrix until the rank of the original data matrix was reduced by one. The results revealed that ligand forms ML complexes with Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Cd\textsuperscript{2+}, and Pb\textsuperscript{2+} and a ML\textsubscript{2} adduct with Hg\textsuperscript{2+} ion. The equilibrium constants, the concentration and spectrum profiles of each complexed species were then calculated. The residual standard deviation (RSD) of the residual matrix after bilinearization of the background matrix is regarded as the evaluation function.

Key words: EFA, RAFA, complexation equilibria, spectrophotometry, 1,8-bis(o-aminophenoxy)-3,6-dioxaoctane
Sensitizing of Semiconducting Photocatalysts by Cyanine Pigment with Two Conjugated Chromophores

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TiO$_2$ and CdS based heterostructures (HS) with biscyanine – cyanine pigment compriseding two conjugated chromophores as a sensitizer have been synthesized. Absorption spectra of HS have been analyzed and their photocatalytic activity (PA) in the reaction of methylene blue reduction was determined. Energy transformation and electron transferring processes induced by various spectral zones irradiation have also been described. It has been found that photocatalytic activity depends on the pigment concentration in HS. Interrelation between changes in PA and some important spectral parameters has also been determined.

**Key words:** titanium dioxide, cadmium sulphide, sensitizing, photocatalytic activity, cyanine pigment

Hydrogen underpotential deposition was studied by chronocoulometry with the initial potentials fixed by saturating the acid solution with hydrogen of defined partial pressure. Adsorption charges obtained from Anson plots enabled plotting adsorption isotherms in the range 0–400 mV vs. RHE. Lateral interaction parameters, $g$, calculated from the isotherms point out very strong repulsive interactions at very low coverages, most probably due to structure changes occurring upon desorption of bisulfate and, but less pronounced, for perchlorate anions. Since the $g$ parameter is roughly constant for 0.3 through 0.7, Frumkin type adsorption may be assumed in that range.

**Key words:** hydrogen underpotential deposition, hydrogen adsorption isotherm, platinum on glassy carbon, platinum on polyaniline
Water-Gas Shift Reaction over Magnetite Catalysts Obtained by the Templating Method with Activated Carbon as the Template

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Kinetics of Chromium(V) Formation from Some Tetraazamacrocyclic Chromium(III) Complexes in Alkaline Media

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