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The first surface-enhanced Raman scattering (SERS) spectra were reported in 1974. A few years after discovery SERS became a well established surface analytical technique, which is widely used to study electrochemical and catalytic processes under in situ conditions. Recently one can observe a large increase in the interest in SERS. It is due to two very important developments in the field of SERS spectroscopy, which have been made in the last decade. The first very important achievement is the observation of SERS spectra of single molecules. The second development, having an enormous potential for surface Raman spectroscopy, is the tip-enhanced Raman scattering (TERS): an AFM or STM tip made of the SERS active metal is used to increase the Raman scattering from molecules adsorbed at a surface located underneath the tip. In this approach, a very significant increase in the spatial resolution of SERS measurements is possible. This review is an attempt to provide an overview of the state of the art and further possibilities of these two recently developed SERS techniques.

Key words: SERS, SERRS, Single-Molecule Spectroscopy, Tip-Enhanced Raman Scattering
Prediction of the Retention Factor in Micellar Electrokinetic Chromatography Using Computational Descriptors and an Artificial Neural Network

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An artificial neural network (ANN) method is proposed to calculate retention factor of analytes using structural features computed using HyperChem software. The absolute average relative deviation (AARD) and individual deviation (ID) are calculated as accuracy criteria. The accuracy of the proposed method is compared with that of previously reported least square models. The proposed method was tested on eight experimental data sets and mean ± standard deviation of AARDs for ANN was 10.7±2.1 and those of previous models were 48.5±20.4 and 130.1±79.7, in which the mean differences were statistically significant (p < 0.001). The distribution of IDs sorted in three subgroups, i.e., ≤ 10, 10–30 and > 30%, shows the superiority of the ANN over the previous models.

Key words: retention factor, micellar electrokinetic chromatography, modeling, prediction, artificial neural network
Destructive Effects of Paper Conservation Procedure on the Writing Iron Gall Ink – Evidence from Transmetalation Reaction

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The influence of carboxylate-alumoxane protective coatings on the condition of writing paper inked with iron and copper gall inks has been investigated. All paper samples used in this study were coated with hexanato-alumoxane at room temperature changing the soaking time from 1 to 8 h. The influence of deconservation parameters (duration and temperature) on the stability of inks was also studied. Paper samples (untreated, coated and after deconservation) were examined by X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). Analytical characterization of paper samples showed no degradation of its cellulosic substrate during conservation. However, the destructive effect of alumoxane on the writing iron gall inks was determined.

Key words: paper, protective coatings, alumoxanes
Ability of 2,4D and 2,4DP Herbicides to Combine with Metal Ions of Biological Interest (Part 3): Manganese(II) Complexes

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The synthesis and properties of manganese(II) complexes with the commercial auxin herbicides: 2,4-dichlorophenoxyacetic acid (2,4D; C₈H₆O₃Cl₂) and 2-(2,4-dichlorophenoxy)-propionic acid (2,4DP; C₉H₇O₃Cl₂) are reported. On the basis of the results of elemental analysis and Mn(II) determination, the following molecular formulae were proposed for the obtained compounds: Mn(C₈H₆O₃Cl₂)₂·2H₂O (Mn-2,4D) and Mn(C₉H₇O₃Cl₂)₂·2H₂O (Mn-2,4DP). X-ray powder analysis was carried out. The water solubility of the synthesized complexes at room temperature was determined. The IR spectra, conductivity data (in methanol and dimethylformamide), variable temperature magnetic susceptibility and the way of Mn-herbicide coordination are discussed. Thermal decomposition of these complexes in air was studied by TG, DTG, DTA and TG/MS methods with simultaneous analysis of the solid and gaseous products of pyrolysis.

Key words: 2,4-dichlorophenoxyacetic acid, 2-(2,4-dichlorophenoxy)-propionic acid, manganese(II) complexes, IR spectra, magnetic properties, conductivity, solubility, TG, DTA and TG/MS data
Metal-Ion-Directed Synthesis of the New Macrocyclic and Acyclic Homo- and Heterodinuclear Schiff Base Complexes Derived from Putrescine

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The template reaction of 2,6-diacetylpyridine with putrescine, a biogenic diamine, in the presence of lanthanum(III) and zinc(II) ions produces homo- and heteronuclear complexes of 22-membered macrocyclic ligand with an N₆ set of donor atoms as a result of the [2+2] Schiff base cyclocondensation. Complexes containing Schiff base acyclic ligands terminated by two carbonyl groups or one carbonyl and one amine group as products of the partial metal-promoted condensation have been also isolated. They might be regarded as possible intermediates in the formation of the macrocyclic complexes. The complexes have been characterized by spectral data (IR, ¹H NMR, ESI-MS) and elemental analyses.

Key words: dinuclear complexes, Schiff base macrocycles, Schiff base acyclic complexes, lanthanum, zinc; template synthesis
Nickel can be dissolved at temperature 323 K in binary organic mixtures containing dimethyl sulfoxide and one of halogeno aliphatic derivatives: 1,2-dibromoethane or tribromomethane, 1,1,2,2-tetrabromoethane, tetrabromomethane and hexachloroethane. As a result of dissolution of metallic nickel in binary organic system the octahedral nickel(II) complexes were obtained. Products of the dissolution of metallic nickel were characterized by UV-Vis and IR spectroscopy, MS spectrometry, thermal decomposition and analytical methods.

**Key words:** nickel oxidation, nickel complexes, UV-Vis spectroscopy, IR spectroscopy, S, O ligands, mass spectrometry
Synthesis, Characterization and Antimicrobial Activities of Some Metal Complexes with \(N\text{'-(2-Chloro-benzoyl)thiourea Ligands: The Crystal Structure of fac-[CoL_3] and cis-[PdL_2]}

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We report the synthesis, structural characterization and antimicrobial activities of \(N,N\text{-dimethyl-N'-(2-chloro-benzoyl)thiourea (L_1H) and N-pyrrolidine-N'-(2-chloro-benzoyl)thiourea (L_2H)}\) and their \(\text{Ni(II), Cu(II), Zn(II), Pt(II), Pd(II) and Co(III)}\) complexes. The structure of the prepared compounds was investigated by using elemental analyses, IR, \(^1\text{H-NMR, UV-Vis, mass spectra and magnetic susceptibility. The prepared compounds were screened for their in vitro antibacterial and antifungal activities. All compounds showed antimicrobial activity, however, the antibacterial efficacy is better than antifungal activity. Molecular structures of Co(L_1\(^3\)); and Pd(L_1\(^2\)); were determined by single crystal X-ray diffraction methods. The ligands coordinate to Ni(II), Cu(II), Zn(II), Pt(II) and Pd(II) in a bidentate manner yielding essentially neutral complexes of the type ML_2. The coordination polyhedra around the Co(III) ion are distorted octahedra.

Key words: thioureas, synthesis, X-ray structure, antimicrobial activities, benzoylthiourea complexes

Synthesis and Spectral Studies on 16-Membered Diamidediimine Tetraazamacrocyclic Complexes, $[\text{MLCl}]\text{Cl} \ [\text{M} = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)} \ \text{and} \ \text{Zn(II)}]$

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A series of 16-membered diamidediimine tetraazamacrocyclic complexes of the type $[\text{MLCl}]\text{Cl} \ [\text{M} = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)} \ \text{and} \ \text{Zn(II)}]$ bearing amide groups have been synthesized by the template condensation of o-aminobenzoic acid with phthalaldehyde and 1,2-diaminoethane in the presence of transition metal ions. The stoichiometry of proposed macrocyclic complexes has been ascertained on the basis of results of elemental analyses and conductivity measurements. The mode of bonding of macrocyclic moiety and the overall geometry around metal ion have been confirmed by IR, 1H-NMR, reflectance and UV-Vis studies. A pseudo-octahedral geometry has been suggested for all the complexes in DMSO, while a pentacoordination around metal ions has been noticed in reflectance spectra of Fe(II), Co(II), Ni(II) and Cu(II) complexes.

Key words: tetraazamacrocycle, diamidediimine, template condensation, amide bands, spectral studies
Mixed-ligand Ni(II) and Zn(II) Complexes with Bipyridine Isomers and Bromoacetates

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New mixed-ligand complexes of the following stoichiometric formulae: Ni(2-bpy)(CBr₂HCOO)₂ · 5H₂O, Ni(4-bpy)(CBrH₂COO)₂ · 2H₂O, Ni(4-bpy)(CBr₂HCOO)₂ · 2H₂O, Ni(2,4'-bpy)(CBr₂HCOO)₂ · 2H₂O, Ni(2,4'-bpy)(CBr₂HCOO)₂ · 4H₂O, Zn(2-bpy)(CBrH₂COO)₂ · H₂O and Zn(4-bpy)(CBr₂HCOO)₂ · 2H₂O (where: 2,2'-bipyridine = 2-bpy, 4,4'-bipyridine = 4-bpy and 2,4'-bipyridine = 2,4'-bpy) were isolated in pure state. The IR and VIS spectra, molar conductivity, magnetic moments are discussed. Thermal behaviours of complexes were studied by means of DTA, DTG, TG techniques under static air conditions. During heating the complexes decompose via different intermediate products. The final product of nickel(II) complexes pyrolysis was NiO; in the case of zinc(II) complexes total mass loss was observed.

Key words: bipyridine isomers, Ni(II) and Zn(II) mixed-ligand complexes, IR and VIS spectra, thermal decomposition
Optical Properties of Some 4-Aryl-1H-pyrazolo[3,4-b]quinolines

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Series of 6-substituted 4-(4'-tolyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]quinolines (1) and 4-(4'-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazolo[3,4-b]quinolines (2) were synthesized and their solution absorption and emission spectra in 10 solvents were recorded. Positions and intensity of the emission and longest wavelength absorption band as well as the quantum yield of emission and its lifetime were analysed in terms of the corresponding identity criteria involving a given parameter $i$ from series (1) against the same parameters from the series (2). Mostly only tendencies to the linearity were observed in terms of the correlation coefficient.

\textbf{Key words:} absorption spectra, emission lifetime, emission quantum yield, emission spectra, luminophores, solvent effect, substituent effects
Synthesis of 8-Chloro-5,5-dioxo[1,2,4]triazolo[4,3-b][1,4,2]benzodithiazine Derivatives with Potential Anticancer and Anti-HIV-1 Activities

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A series of $N'-(6$-chloro-1,1-dioxo-1,4,2-benzodithiazin-3-yl)carbohydrazides (6–17) was obtained by the reaction of 6-chloro-3-methylthio-1,1-dioxo-1,4,2-benzodithiazines (1–4) with carbohydrazides (5a–f) in boiling toluene. Cyclocondensation reactions of the compounds 6–17 in thionyl chloride gave the appropriate 8-chloro-5,5-dioxo[1,2,4]triazolo[4,3-b][1,4,2]benzodithiazines (18–29) in good yields. The in vitro antitumor activity of compounds 18, 21–26, and anti-HIV-1 activity of compounds 19, 20, 23 and 27 were tested at the US National Cancer Institute (Bethesda). Screening data indicated that the only 8-chloro-3,7-dimethyl-5,5-dioxo[1,2,4]triazolo[4,3-b][1,4,2]benzodithiazine (23) exhibited significant activities against 56 human tumor cell lines (GI$_{50}$ = 2.8–29.1 μM) and a moderate anti-HIV-1 activity (EC$_{50}$ = 64.8 μM; IC$_{50}$ = 141 μM).

Key words: 8-chloro-5,5-dioxo[1,2,4]triazolo[4,3-b][1,4,2]benzodithiazines, synthesis, antitumor and anti-HIV-1 activities
The Structure of Levorin A₃, a Minor Component of Levorin Complex

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The structure of aromatic heptaene macrolide Levorin A₃ was established on the basis of MS and NMR studies with DQF-COSY and ROESY experiments. The relative configuration of Levorin A₃ chiral centers was assigned as: 9R*,11S*,13S*,15R*,17S*,18R*,19S*,21R*,36S*,37R*,38S*,40S* and 41S*. The geometry of the heptaene chromophore was defined as: 22E, 24E, 26Z, 28Z, 30E, 32E and 34E.

Key words: polyene macrolide, antibiotic, NMR, stereochemistry
The Structure of Nystatin A2
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The structure of nystatin A2 was established on the basis of NMR studies which contained
DQF-COSY, ROESY, HSQC and HMBC experiments.

Key words: polyene macrolide, antibiotic, NMR, stereochemistry
Stereoselective Synthesis of (1→6)-α-Linked Di- and Trisaccharides, Derivatives of 2-Deoxysugars

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We present herein the totally stereoselective synthesis of (1→6)-α-linked di- and trisaccharides by addition of thioglucosides to D-glucals.

Key words: glycals, thioglycosides, glycosidation, block synthesis of oligosaccharides
Platinum(IV) Inhibition during Hexacyanoferrate(III) Oxidation of Reducing Sugars

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The kinetics of oxidation of reducing sugars viz glucose, fructose, lactose and maltose by alkaline hexacyanoferrate(III) in the presence of platinum(IV) has been studied. The kinetic data support the formation of [platinum(IV)–sugar] complexes and their resistance to react with hexacyanoferrate(III). A spectrophotometric evidence for the formation of 1:1 and 1:2 complexes between platinum(IV) and reducing sugar has also been obtained.

Key words: hexacyanoferrate(III), chloroplatinic acid, kinetics, oxidation, reducing sugars
Ammonia Oxidation over Cobalt-Type Catalysts.
Effect of La and Ce Loading

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