Stereoselection at the steady state is a process, which results from a complex interplay of reaction pathways that diverge and reconverge at various points. Therefore, it can be considered as a manipulation of stereocontrol mainly by reaction topography. The advantages of this process are at least twofold: First, stereoconvergence allows the system to exceed the yield of the initial stereoconvergent event, where stereomeric transition states compete. Second, a successive resolution of the reactive intermediates by chemoselective events allows the system to generate high stereomeric excess, practically without any stereoselective competition. While illustrated with radicals, the process may prove useful in other fields of chemistry.
Nickel(II) Dithiocarbamates with Bis(2-diphenylphosphinoethyl)phenylphosphine

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(Received July 21st, 2003; revised manuscript December 5th, 2003)

A Ni(II) dithiocarbamates with the tridentate P,P,P-ligand of composition [Ni(pe₂dtc)(triphosI)]X (triphosI = C₁₄H₁₃P₃ = bis(2-diphenylphosphinoethyl)phenylphosphine, pe₂dtc = dipentylidithiocarbamate, X = Cl, PF₆, ClO₄), [Ni(bz₂dtc)(triphosI)]X (bz₂dtc = dibenzyldithiocarbamate, X = Cl, PF₆) and [Ni(cetdtc)(triphosI)]X (cetdtc = cyclohexylethyldithiocarbamate, X = Cl, PF₆, BPh₄, ClO₄) have been synthesized and studied by thermal analysis, IR and UV/VIS spectroscopy, 3¹P{¹H}-NMR spectroscopy, magnetochemical and conductivity measurements.

All complexes are diamagnetic, 1:1 electrolytes. X-ray structural analysis was solved for the [Ni(pe₂dtc)(triphosI)]PF₆ and [Ni(bz₂dtc)(triphosI)]PF₆; the presence of NiS₂P₃ chromophore with penta-coordinated central nickel atom was confirmed.
Three new copper(II)–iron(II) heterodinuclear complexes bridged by the dianions of \textit{N,N'}-bis[2-(dimethylamino)ethyl]oxamido (dmoxae) and end-capped with 2,2'-bipyridine (bpy); 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline (NO2phen); namely \([\text{Cu}(\text{dmoxae})\text{Fe}(\text{bpy})\text{2}\text{]}\text{SO}_4 \) (1), \([\text{Cu}(\text{dmoxae})\text{Fe}(\text{phen})\text{2}\text{]}\text{SO}_4 \) (2) and \([\text{Cu}(\text{dmoxae})\text{Fe}(\text{NO2phen})\text{2}\text{]}\text{SO}_4 \) (3), have been synthesized and characterized. The three dinuclear complexes have not yet been isolated in crystalline form suitable for X-ray structure analysis, but based on elemental analyses, IR and electronic spectra studies, magnetic moments at room-temperature and molar conductivity measurements, these complexes are proposed to have an extended oxamido-bridged structure consisting of planar copper(II) and octahedral iron(II) ions. The \([\text{Cu}(\text{dmoxae})\text{Fe}(\text{bpy})\text{2}\text{]}\text{SO}_4 \) (1) and \([\text{Cu}(\text{dmoxae})\text{Fe}(\text{phen})\text{2}\text{]}\text{SO}_4 \) (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, \(\mathbf{H} = -2J \mathbf{S}_1 \cdot \mathbf{S}_2 - D \mathbf{S}_1 \cdot \mathbf{S}_2\), giving the exchange integrals \(J = -20.9 \text{ cm}^{-1}\) for (1) and \(J = -22.7 \text{ cm}^{-1}\) for (2). These results indicated that the spin coupling between the adjacent copper(II) and iron(II) ions through the oxamido-bridge in both complexes (1) and (2) is antiferromagnetic. The influence of methyl substituents in the amine groups of the bridging ligand and the relative stability of the chelate ring arrangement around the copper(II) on magnetic interactions between the metal ions of this kind of complexes is also discussed.
Synthesis, Characterization, Spectroscopic and Antimicrobial Activity Studies of Pyrimidine Dithiocarbamate Macrocyclic Complexes

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(Received November 3rd, 2003; revised manuscript January 20th, 2004)

The ligands disodium salts of thiobarbituric acid (Na₂L₁) and 5,5-diethylbarbituric acid (Na₂L₂) and their transition metal complexes of the type [M₂(L₁)₂] and [M₂(L₂)₂], where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), have been synthesized. The transition metal(II) complexes have been characterized by a range of techniques including IR, ¹H NMR, UV-visible spectroscopy, magnetic moment measurements, elemental analyses and molar conductance measurements. The spectroscopic studies indicate that the reaction of L₁ and L₂ with a divalent metal ions form binuclear dithiocarbamate macrocyclic complexes. The molar conductivity measurements suggest that all of the complexes are non-electrolytes. The magnetic moment values and electronic spectra reveal that the Ni(II) and Cu(II) complexes are square-planar, while Mn(II), Co(II) and Zn(II) complexes are tetrahedral. All of the compounds have been screened for antimicrobial activity against Staphylococcus aureus (gram-positive bacteria) and Escherichia coli (gram-negative bacteria). The results show that all the compounds inhibit the growth of bacteria. All the complexes showed better activity as compared with the ligands.
Synthesis, Characterization and Magnetic Properties of Copper(II)–Iron(III) Heterotetranuclear Complexes Bridged by Tris(oxalato)ferrate(III)

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(Received December 8th, 2003; revised manuscript January 26th, 2004)

The strategy of “complex as ligand” allowed us to synthesize three new μ-oxalato-bridged heterotetranuclear complexes identified as [Cu₃Fe(ox)₃(Me₂bpy)₃](ClO₄)₃ (1), [Cu₃Fe(ox)₃(Me₂phen)₃](ClO₄)₃ (2) and [Cu₃Fe(ox)₃(phen)₃](ClO₄)₃ (3), where ox represents the oxalato dianions; Me₂bpy, Me₂phen and phen stand for 4,4'-dimethyl-2,2'-bipyridine, 2,9-dimethyl-1,10-phenanthroline or 1,10-phenanthroline, respectively. These complexes are the first examples of [Cu³⁺Fe⁶⁺] species bridged by oxalato groups. Based on elemental analyses, molar conductivity and magnetic moment (at room-temperature) measurements, IR, ESR and electronic spectral studies, these complexes are proposed to have oxalato-bridged structure consisting of three copper(II) ions and an iron(III) ion, in which the iron(III) ion has an octahedral environment, and the three copper(II) ions have a square-planar environment. The complexes (1) and (2) were further characterized by variable-temperature magnetic susceptibility (4.2–300 K) measurements and the observed data were simulated by the equation based on the spin Hamiltonian operator, \( \hat{H} = -2 J (\vec{S}_{Cu1} \cdot \vec{S}_{Fe} + \vec{S}_{Cu2} \cdot \vec{S}_{Fe} + \vec{S}_{Cu3} \cdot \vec{S}_{Fe}) \), giving the exchange integrals \( J = -9.15 \text{ cm}^{-1} \) for (1) and \( J = -8.79 \text{ cm}^{-1} \) for (2). The results indicate the presence of an antiferromagnetic spin-exchange interaction between the copper(II) and iron(III) ions through the oxalato-bridge in both complexes (1) and (2).
Cobalt(II), Copper(II), Nickel(II), and Zinc(II)
Complexes of Naphthaldehyde Thiazolyl Hydrazones

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(Received November 6th, 2003; revised manuscript January 27th, 2004)

Two new Schiff base ligands containing 2,4-disubstituted thiazoles and cyclobutane rings, 2-hydroxy-1-naphthaldehyde \([4-(3\text{-methyl-3-mesitylcyclobutyl})-1,3\text{-thiazol}-2\text{-yl}]\) hydrazone (L\(1^{\text{H}}\)) and 1-(2-hydroxy-1-naphthyl)etanone \([4-(3\text{-methyl-3-mesitylcyclobutyl})-1,3\text{-thiazol}-2\text{-yl}]\) hydrazone (L\(2^{\text{H}}\)) and their mononuclear complexes with a 1:2 metal:ligand ratio have been prepared from chloride salts of Co(II), Cu(II), Ni(II) and Zn(II) in EtOH. The authenticity of new ligands and their complexes have been established by elemental analyses, infrared, \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra, and by magnetic susceptibility measurements. Thermal properties of the ligands and complexes have been studied by thermogravimetric analysis (TGA) technique. The novel complexes of transition metal ions contain two monoanionic, bidentate NO ligands. It was found that all the complexes are mononuclear.
Spectrochemical Properties of Noncubic Transition Metal Complexes in Solutions. XVI. Angular Overlap Treatments of \textit{cis}-Bis(2,2’-bipyridyl)oxalatechromium(III) Iodide in Aqueous Solution

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(Received November 18th, 2003; revised manuscript January 29th, 2004)

The electronic absorption spectrum of \textit{cis}-[Cr(ox)(bpy)\textsubscript{2}](bpy = 2,2’-bipyridyl; ox = oxalate ion) of aqueous (H\textsubscript{2}O) solution, has been measured at room temperature and interpreted using the angular overlap model (AOM), and assuming C\textsubscript{2v} as the effective symmetry. All the experimental transitions are derived from Gaussian analysis of the solution spectrum. The calculations of the ligand field parameters take into account all the transitions, which are required from the ligand field theory (except those energetically higher than the range of the measured spectrum). The coordination properties of the ligators and their bonding abilities have been discussed.

Spectrochemical Properties of Noncubic Transition Metal Complexes in Solutions. XVII. Angular Overlap Treatment of cis-Bis(2,2′-bipyridyl)malonatechromium(III) Iodide in Aqueous Solution

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(Received November 18th, 2003; revised manuscript January 29th, 2004)

A mixed ligands chromium(III) complex with bidentate ligands: 2,2′-bipyridyl (bpy) and malonic acid deprotonated (mal−, malonate ion), has been synthesized, investigated and characterized structurally and spectroscopically. Electronic spectra of this complex were recorded in an aqueous solution at room temperature. The ‘poor’ experimental contours were resolved into the component bands by Gaussian analysis. The spectra were interpreted using C2v symmetry. The resolved spectra have been treated using an angular overlap model (AOM). The effect of σ- and π-bonding of the bidentate ligands upon the chromium(III) ion in aqueous solution was described and discussed.
The Reactions of 2-(Bromoseleno)benzenesulfonyl Chloride with Primary Amines toward 2,2'-Diselenobis(benzenesulfonamides) and 1,3,2-Benzothiaselenazole 1,1-Dioxides: New Oxygen-Transfer Agents, Antimicrobials and Virucides

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(Received February 6th, 2004)

The reaction of title compound 6 with primary aliphatic or aromatic amines was investigated. The products were 2,2'-diselenobis(benzenesulfonamides) (4) accompanied in some cases by 1,3,2-benzothiaselenazole 1,1-dioxides (3). Exceptionally, when aniline was a reagent, 2-(sulfamoylphenyl)phenylselenenylanilide was produced. These results are interpreted in the light of the proposed mechanisms. The compounds 3 and 4 exhibited catalytic activity in hydroperoxide oxidation of cyclohexanone (12) and 1-naphthaldehyde N,N-dimethylhydrazone (17). Although they were inactive against patogenic bacteria and fungi an appreciable antiviral activity against HSV-1 and EMCV of the compounds 3b, 3c and 4b was observed.
Estimation of the Noncovalent Bond Dissociation Energies of the Gas-Phase Complexes of Macrocyclic Polyethers with Alkali Metal Cations Using an Electrospray Ionization/Triple Quadrupole Mass Spectrometer

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(Received January 20th, 2004; revised manuscript February 19th, 2004)

An attempt to use the commercial triple quadrupole mass spectrometer, equipped with an electrospray ion source, to estimate the noncovalent bond dissociation energies of gas-phase complexes of macrocyclic polyethers with metal cations has been made. It was found that, after standardization of the experimental conditions, the collision cell voltage required for decomposition of 50% of the selected complex ions (CE50%) is proportional to the binding energies with reasonable accuracy. Even better correlation was obtained after recalculation of the CE50% values to the center-of-mass frame (ECM50%). Measurements were made for 12-crown-4, 15-crown-5, 18-crown-6, and dibenzo-18-crown-6 complexes with alkali metal cations from Li⁺ to Cs⁺. These results indicate, that it is possible to estimate values of the binding energies after correct setting of the experimental conditions and using model compounds as the reference.
Electrochemical and Electrogravimetric Investigations of Prussian Blue on the Gold Electrode in the Presence of Thallium(I) Ions

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(Received January 6th, 2004)

Electrode processes of Prussian Blue (PB), deposited on the gold electrode, have been investigated in potassium and thallium salts solutions, using electrogravimetric and cyclic voltammetric methods. It is shown, that both electrode processes of PB (reduction of PB to Everitt’s salt and its oxidation to Berlin Yellow) undergo changes, when potassium ions are replaced by thallium(I) ones. In the presence of thallium, the formation of new redox system is observed, and Tl(I) acts as a counter-ion. The equilibrium constant of the reaction: \( K(I)PB + Tl(I) = Tl(I)PB + K(I) \) was estimated to be equal to \( K = (1.7 \pm 0.6) \times 10^4 \). At the same time almost 50% of the PB layer loses its electrochemical activity, whereas the remaining PB phase is electrochemically active. After transfer of the electrode to KNO\(_3\) solution, majority of inactivated layer recovers its previous activity. These findings are tentatively interpreted as a result of formation of two phases of PB with Tl(I): electrochemically active and inactive. Both phases are in equilibrium, and thallium ions could be replaced by potassium one. In the case of the Fe(CN)\(_6\)\(^{3-}\) electrode process (at more positive potentials), in the presence of Tl(I) irreversible deactivation occurs, since in KNO\(_3\) solution, no reactivation of the electrode process is observed.
Fluorescence and Circular Dichroism Studies on the Interaction of Bromocresol Purple with Bovine Serum Albumin

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(Received November 12th, 2003; revised manuscript January 29th, 2004)


The mechanism of interaction of bromocresol purple (BCP) with bovine serum albumin (BSA) has been investigated by spectrofluorometric and circular dichroism methods. Association constant for the BCP–BSA system showed that the interaction is non-covalent in nature and that there occurs only a partial occupation of a binding site. Binding studies in the presence of hydrophobic probe, 8-anilino-1-naphthalene sulphonate acid, sodium salt (ANS) showed that there is hydrophobic interaction between BCP and ANS and they may share common sites in BSA. Stern-Volmer analysis of fluorescence quenching data showed that the fraction of fluorophore (protein) accessible to the quencher (BCP), was close to unity, indicating thereby that both tryptophan residues of BSA are involved in dye-protein interaction. The rate constant for quenching, greater than $10^{10} \text{M}^{-1}\text{s}^{-1}$, indicated that the dye binding site is in close proximity to tryptophan residue of BSA. Thermodynamic parameters, obtained from data at different temperatures, showed that the binding of BCP to BSA involves hydrophobic bonds predominantly. Fluorescence intensity data in the presence of additives showed that hydrophobic interaction plays a prominent role. Significant decrease in concentration of free dye was observed for BCP in presence of paracetamol. Circular dichroism studies revealed the change in helicity of BSA, due to binding of BCP to BSA.
A Two-Dimensional Model of Reaction-Diffusion System as a Generator of Old Hebrew Letters

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(Received November 24th, 2003; revised manuscript February 9th, 2004)

Minimal models for many patterns observed in nature should be based on systems, in which only chemical reactions and diffusion transport occur (reaction-diffusion systems). In order to present a richness of patterns possible in such systems, we show here the asymptotic solutions to the nonlinear, partial, parabolic equations with zero flux boundary conditions in the form of patterns imitating all Old Hebrew letters (the Siloam inscription) obtained in two-dimensional systems. All letters are obtained in the same model, but sizes of the systems and initial conditions are different for each letter. The chemical model consists only of elementary reactions.
Photoinduced Oxidative Dehydrogenation of Benzylic Alcohols Using Mercury(II) Oxide

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(Received November 14th, 2003; revised manuscript December 12th, 2003)
Albery Model Applied to Fluorescence Decay of Alloxazines Adsorbed into Cellulose

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(Received March 5th, 2004)