

Thermal, Spectral and Magnetic Studies of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Mesaconic Acid

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Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) mesaconates were investigated and their quantitative composition and magnetic moments were determined. The IR spectra and powder diffractograms of the complexes prepared with general formula $M(C_5H_4O_4)_nH_2O$ (where $n = 3$ for Mn, Co, $n = 2$ for Ni, Cu and $n = 0$ for Zn) were recorded and their thermal decomposition in air was studied. During heating, the hydrated complexes are dehydrated in one (Ni, Co, Cu) or two (Mn) steps and next the anhydrous complexes of Mn(II) and Zn(II) decompose directly to oxides. The complex of Co(II) decomposes to oxide with intermediate formation of the free metal, whereas those of Ni(II) and Cu(II) complexes decompose to oxides with intermediate formation of mixture of free metal and its oxide. The effective magnetic moments for the paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain values 5.32, 4.77, 3.12 and 1.73 B.M., respectively.

Synthesis and Magnetic Properties of μ -Oxalato-Bridged Cu(II)–Fe(III)–Cu(II) Heterotrinnuclear Complexes

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Three new μ -oxalato-bridged copper(II)–iron(III)–copper(II) heterotrinnuclear complexes described by the overall formula $[\text{Cu}_2\text{Fe}(\text{ox})_3\text{L}_2]\text{ClO}_4$, where ox represents the oxalato dianions and L stands for 5-phenyl-1,10-phenanthroline (Ph-phen), 4,7-diphenyl-1,10-phenanthroline (Ph₂-phen) or 5-chloro-1,10-phenanthroline (Cl-phen), have been synthesized and characterized by elemental analyses, molar conductivity and magnetic moment (at room-temperature) measurements, IR and electronic spectral studies. It is proposed that these complexes have extended ox-bridged structures, consisting of two copper(II) and an iron(III) ions, in which the central iron(III) ion has an octahedral environment and the end capped two copper(II) ions have a square-planar environment. The variable-temperature susceptibilities of $[\text{Cu}_2\text{Fe}(\text{ox})_3(\text{Ph-phen})_2]\text{ClO}_4$ complex were measured and studied in the 4.2–300 K range. The least-squares fit of the experimental susceptibility based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, yielded $J = -9.89 \text{ cm}^{-1}$. The magnetic coupling parameter is consistent with an antiferromagnetic exchange interaction between the copper(II) and iron(III) ions through the oxalato-bridge in the complex.

Synthesis, Characterization and Magnetism of Fe(II)–Pd(II)–Fe(II) Heterotrinnuclear Complexes Bridged by Dioximato Groups

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Three new Fe(II)–Pd(II)–Fe(II) heterotrinnuclear complexes with dioximato-bridge have been synthesized and identified as $[\text{Fe}_2\text{Pd}(\alpha\text{-FD})_2(\text{Me}_2\text{-bpy})_4]\text{SO}_4$ (**1**), $[\text{Fe}_2\text{Pd}(\alpha\text{-FD})_2(\text{Me}_2\text{-phen})_4]\text{SO}_4$ (**2**) and $[\text{Fe}_2\text{Pd}(\alpha\text{-FD})_2(\text{Me-phen})_4]\text{SO}_4$ (**3**); where $(\alpha\text{-FD})^{2-}$ represents α -furildioximato; $\text{Me}_2\text{-bpy}$, $\text{Me}_2\text{-phen}$ and Me-phen denote 4,4'-dimethyl-2,2'-bipyridine; 2,9-dimethyl-1,10-phenanthroline ($\text{Me}_2\text{-phen}$) and 5-methyl-1,10-phenanthroline (Me-phen). Based on elemental analyses, molar conductance measurements, IR and electronic spectral studies, these complexes are proposed to have extended dioximato-bridged structures and to consist of two iron(II) ions and a palladium(II) ion, in which the central palladium(II) ion has a square-planar environment and the end capped two iron(II) ions have a distorted octahedral environment. The magnetic properties of complexes $[\text{Fe}_2\text{Pd}(\alpha\text{-FD})_2(\text{Me}_2\text{-bpy})_4]\text{SO}_4$ (**1**) and $[\text{Fe}_2\text{Pd}(\alpha\text{-FD})_2(\text{Me}_2\text{-phen})_4]\text{SO}_4$ (**2**) were investigated over the 4.2–300 K range and correspond to what is expected for an antiferromagnetic Fe(II)–Fe(II) pair with $S_{\text{Fe(II)}} = 2$ and $S_{\text{Pd(II)}} = 0$ (Pd^{2+} is a diamagnetic in a square-planar environment) local spins. The exchange integral (J) was evaluated as $J = -2.89$ for (**1**) and $J = -3.16$ for (**2**) based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$.

Synthesis and Magnetism of Copper(II)–Lanthanoid(III) Heterobinuclear Complexes with N,N'-Oxamidobis(propionato)cuprate(II) Ligand

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Eleven novel μ -oxamido-bridged copper(II)–lanthanoid(III) heterobinuclear complexes described by the overall formula $\text{Cu}(\text{obp})\text{Ln}(\text{Ph}_2\text{-phen})_2\text{ClO}_4$ ($\text{Ln} = \text{Y, La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb}$), where obp denotes N,N'-oxamidobis(propionato) and $\text{Ph}_2\text{-phen}$ represents 4,7-diphenyl-1,10-phenanthroline ($\text{Ph}_2\text{-phen}$), have been synthesized and characterized by elemental analyses, spectroscopic (IR, UV, ESR) studies, and molar conductivity measurements. The temperature dependence of the magnetic susceptibility of complex $\text{Cu}(\text{obp})\text{Gd}(\text{Ph}_2\text{-phen})_2\text{ClO}_4$ has been measured over the range 4.2–300 K and the magnetic properties were studied in detail, demonstrating the presence of a very weak ferromagnetic interaction between the adjacent Gd(III) and Cu(II) ions through the oxamido-bridge. Based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, the exchange integral (J) was evaluated as $+2.98 \text{ cm}^{-1}$. A plausible mechanism for the ferromagnetic coupling between Gd(III) and Cu(II) is discussed in terms of spin-polarization.

Voltammetric and Spectroscopic Behaviour of the Copper Adducts of Thiol and Thioether Ligands under Aerobic and Anaerobic Conditions

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Joint spectroscopic (ESR, electronic absorption and FT IR) and voltammetric (square-wave and cyclic voltammetry) techniques were employed to investigate the properties of copper adducts with cysteine, *N*-acetylcysteine and methionine under aerobic and anaerobic conditions. The metal oxidation state in the solid and solvated adducts adheres to the presence of oxygen, whereas ESR results ($g_{\parallel} = 2.245$, $g_{\perp} = 2.059$, $A_{\parallel} = 170$ Gauss) reveal tetragonally distorted octahedral copper(II) environment under aerobic circumstances. In presence of the thiol and thioether ligands under nitrogen voltammetric measurements evidence formation of copper(I) species.

Why Do Uranyl Salophene Ionophores Lose Phosphate Selectivity in Time? The ^1H NMR and UV/Vis Studies

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^1H NMR and UV/Vis studies on the interaction of uranyl complex of salophene (bis-salicylaldehyde-phenylenediimine) with nitrite, nitrate, sulphate, dihydrogenphosphate and fluoride anions are described. Only in the case of phosphate and fluoride ions an interaction was noticed. In the case of the former ion the changes in spectra were attributed to destruction of ionophore. The degradation of the ionophore is caused by the formation of uranyl phosphate, followed by hydrolysis of the Schiff base. Also the consecutive reaction might shift the hydrolysis equilibrium. NMR and UV/Vis studies aiming at the explanation of the mechanism of salophene decomposition are described.

Metal-Ion-Directed Synthesis of Homo- and Heteronuclear Dimetallic Schiff Base Podates. II.

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Homodinuclear complexes with magnesium(II), calcium(II), and barium(II) ions and heterodinuclear complexes with calcium(II) or cadmium(II) and lanthanide(III) ions containing Schiff base open-chain ligand terminated by one amine and one carbonyl group were prepared as a result of the partial Schiff base condensation reaction between 2,6-diacetylpyridine and 4-methyl-1,2-phenylenediamine in the presence of the appropriate ions acting as templates. The complexes were characterized by spectroscopic methods (IR, ¹H NMR, FAB-MS), thermogravimetric and elemental analyses.

**The Synthesis and Characterization of
1,2-Dihydroxyimino-3,6-di-aza-8,9-O-iso-butylidene
Nonane and Its Complexes with Ni(II), Cu(II), Zn(II)
and Cd(II)**

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1,2-Dihydroxyimino-3,6-di-aza-8,9-O-iso-butylidene nonane (H₂L) was synthesized starting from 1,2-O-iso-butylidene-4-aza-6-amino hexane (RNH₂) and antichloroglyoxime. Ni(II) and Cu(II) complexes of H₂L have a metal:ligand ratio of 1:2 and the ligand coordinates through two N atoms, as do most of the vic-dioximes. However, Zn(II) and Cd(II) complexes of H₂L have a metal:ligand ratio of 1:1 and one chloride ion and one water molecule are also coordinated to the metal ion. Structures of the ligand and its transition-metal complexes are proposed, according to elemental analyses, IR, ¹³C and ¹H NMR spectra, magnetic susceptibility measurements and thermogravimetric analyses (TGA).

Phase Equilibria in the System $\text{Nd}(\text{PO}_3)_3 - \text{KPO}_3$

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The system $\text{Nd}(\text{PO}_3)_3 - \text{KPO}_3$ has been investigated by differential thermal analysis (during heating), thermogravimetric analysis, mass spectrometry, Raman spectroscopy and X-ray powder diffraction and its phase diagram was proposed. It was discovered that initial metaphosphates react at a 1:1 molar ratio forming intermediate compound $\text{KNd}(\text{PO}_3)_4$. It was found that it melts incongruently at 854°C giving $\text{Nd}(\text{PO}_3)_3$ and a liquid rich in KPO_3 . Phosphate $\text{KNd}(\text{PO}_3)_4$ is stable down to room temperature and does not show any polymorphic transitions.

Nitration of Calixcrown 6 Influence on Extracting Abilities. Use of Cesium Salts for Detection of Crown Ether Macrocycles with the Electrospray Ionization Mass Spectrometry Technique

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Two organic synthetic reactions – mononitration and phosphorylation of crown-6 compounds were performed under Cs⁺ cation monitoring *via in situ* complexation using electrospray ionization mass spectrometry (ESI-MS). Formation of Cs⁺ complexes is a rapid analytical tool for characterization of complex reaction mixtures.

New Bradykinin Analogues Substituted in Positions 6 and 7 with Enantiomers of N-Methylphenylalanine

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Four new analogues of a previously designed bradykinin antagonist, D-Arg-Arg-Pro-Hyp-Gly-Thi-Ser-D-Phe-Thi-Arg, containing replacements in positions 6 and 7 with all possible combinations of enantiomers of N-methylphenylalanine (MePhe) were designed, synthesized and bioassayed. The presence of two consecutive MePhe residues in the sequence of the analogues caused great difficulties in the synthesis. The best results for the CO–N(CH₃) bond formation were obtained using O-(7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate/7-azabenzotriazol-1-ol (HATU/HOAt) as coupling reagent (Fmoc strategy). The antagonistic potency of these peptides was assessed by their ability to inhibit vasodepressor response to exogenous bradykinin in conscious rats. Our results showed that the modifications proposed resulted in a decrease in antagonistic activity. However, we demonstrated once again that the D-amino acid in position 7 of BK antagonists may be replaced by a suitable L-amino acid residue. Our results may be of value in the design of new B₂-antagonists.

**A New Diterpenoid, Taibairubescensin C,
from *Isodon rubescens***

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A new kaurenoid, taibairubescensin C (**1**), was isolated from the ethanol extract of the leaves and tender branches of *Isodon rubescens* (Hemsl.) Hara. Its structure was designated as 2 β ,6 α -diacetoxy-3 β ,11 β -dihydroxy-*ent*-kaur-16-en-15-one (**1**) on the basis of detailed spectroscopic analysis.

Synthesis of Isoxazolo[3,4-*d*]pyrimidines from 6-Chloropyrimidine-5-carbaldehydes

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4-Dialkylamino-6-chloro-2-methylthiopyrimidine-5-carbaldehydes with sodium azide in dimethylformamide underwent ring closure reaction to form the corresponding isoxazolo[3,4-*d*]pyrimidines.

The Synthesis and Structure of Diaza- and Tetraazacoronands

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A general method of the synthesis of simple azacoronands *via* the amidation reaction is presented. Several examples of the X-ray structure studies of the compounds obtained are given.

**A Theoretical Study on
(η^5 -C₅H₅)Fe(CO)(PPh₃)(C(O)CHMe)
Anion Structure and Stereoselectivity**

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Organometallic systems provide an exceptional tool in the stereoselective synthesis. The source of this selectivity, however, frequently remains a challenging question. In recent years, theoretical studies of mechanisms of organometallic and metalloprotein catalysis have received considerable attention. The density functional theory (DFT) methods have been shown to be very successful in these studies. Their application, however, is still limited by the performance of the present computers. As the result, a new class of methods, which employ quantum mechanical calculations combined with either semiempirical and/or molecular mechanics levels (QM/MM), has been developed. This stimulated development of a number of new semiempirical methods, which can handle metals. We present a comparison of a few of these new methods with the DFT level on the example of the acetyliron. In addition, the DFT calculations are used to shed some light on the mechanism of the stereospecific catalysis by acetyliron.

Electrical Double Layer at Zirconium Silicate/Electrolyte Solution Interface

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Parameters of the electrical double layer at zirconium silicate/aqueous sodium chloride interface were estimated from potentiometric titrations, background electrolyte ions adsorption and electrophoretic measurements data. Using numerical optimization the ionization and complexation constants of surface hydroxyl groups were determined. The best fit of calculations to the experimental data was achieved by assuming two kinds of surface hydroxyl groups that differ in acid-base properties.

**On the H_2NO ($^2\text{B}_1$) \rightarrow H_2 ($^1\Sigma_g$) + NO ($^2\Pi$) Mechanism.
A Combined Density Functional Theory and
Ab Initio Study**

by **A.F. Jalbout**

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The Theoretical Calculated Stability of Benzoyl Ions and Their Relative Intensities in the Electron Ionization Mass Spectra of Some 2,5-Disubstituted-1,3,4-oxadiazoles

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