

Synthesis and Characterization of Ionic Cu(I) Perfluorocarboxylate Compounds with 1,4-Bis(diphenylphosphino)butane

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A series of ionic Cu(I) perfluorocarboxylate compounds with 1,4-bis(diphenylphosphino)butane (dppb) of general formula $[\text{Cu}(\text{dppb})_2](\text{RCOO})$, where $\text{R} = \text{C}_2\text{F}_5$, C_3F_7 , C_4F_9 , C_6F_{13} , C_8F_{17} , was prepared and characterized with MS, IR and ^1H , ^{13}C , ^{19}F , ^{31}P NMR spectroscopy. The studied species contained monomeric, bis-chelated $[\text{Cu}(\text{dppb})_2]^+$ cations and uncoordinated RCOO^- anions. The Cu(I) coordination of the diphosphines resulted in slight high-frequency shifts of the ^{31}P NMR resonances of the equivalent phosphorus atoms.

Key words: copper(I), diphosphines, perfluorinated carboxylates, MS, ^{31}P NMR, coordination shifts

Synthesis and Characterization of Lanthanide(III) and Y(III) Complexes with 2-Hydroxy-3-methylbenzoic Acid

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The complexes of lanthanides(III) (La – Lu) and Y(III) with 2-hydroxy-3-methylbenzoic acid with a general formula $\text{Ln}(\text{C}_8\text{H}_7\text{O}_3)_3 \cdot n\text{H}_2\text{O}$, where $n = 3$ for La – Pr; $n = 4$ for Nd – Tm and Y, $n = 2$ for Yb – Lu were prepared and characterized by IR spectroscopy, X-ray diffraction patterns, thermogravimetric studies and solubility. Tri- and tetrahydrates form three isostructural groups; complexes of Yb and Lu are amorphous. The carboxylate groups in these complexes are symmetrical, bidentate chelating or bridging. When heated, hydrated complexes first loose molecules of water; then decompose to oxides of the respective metals. Solubility of these complexes in water at 293 K is of the order of $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$.

Key words: 2-hydroxy-3-methylbenzoates, 3-methylsalicylates, complexes of lanthanide(III), o-cresotic acid, thermal stability analysis, IR spectra, synthesis

**Spectroscopic and Thermal Studies of Magnesium(II),
Barium(II), Zinc(II), Copper(II), Lanthanum(III)
and Aluminium(III) Complexes with
3-Phenyl-1-methylpyrazolo[3,4-*b*]quinolino-6-carboxylic Acid**

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Magnesium(II), barium(II), zinc(II), copper(II), lanthanum(III) and aluminium(III) complexes with 3-phenyl-1-methylpyrazolo[3,4-*b*]quinolino-6-carboxylic acid (HPQ) were studied by IR and EPR methods, TG-DSC thermal analysis, powder X-ray method, absorption and fluorescence spectroscopy. The IR spectra suggest that the carboxylate ligand acts as mono- or bidentate species. EPR spectra indicate the dimerization of copper(II) complex. During thermal decomposition the hydrated complexes lose all the crystallization and coordination water molecules and decompose gradually to oxides, and to BaCO₃ in the case of barium(II) complex. The powder fluorescence spectra indicated the differences in emission of ligand and zinc(II), magnesium(II), aluminium(III) and copper(II) complexes.

Key words: EPR, IR, UV, fluorescence spectra; TG-DSC thermal analysis; chemosensors

Binuclear Octaazamacrocyclic Complexes of Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Derived from Tris(2-aminoethyl)amine and 1,3-Dibromopropane; Synthesis and Characterization

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A series of 20-membered binuclear octaazamacrocyclic complexes, $[M_2LX_2 X_2]$ [where $M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) ; $X = \text{Cl}, \text{NO}_3$] have been synthesized by metal ion controlled reaction between tris(2-aminoethyl)amine, tren and 1,3-dibromopropane in the presence of KOH in methanol. The proposed stoichiometry and the bonding in the macrocyclic moiety to metal ions alongwith the overall stereochemistry have been derived from the results of elemental analyses, conductivity data and the information revealed from FT-IR, $^1\text{H NMR}$, mass, UV-Visible, and EPR spectral studies. An octahedral geometry has been envisaged for Co(II), Ni(II) and Zn(II) complexes while a distortion in octahedral geometry has been noticed for Cu(II) complexes, where all four N-donor atom of tren moiety coordinate to metal ion and the rest two coordination sites have been occupied by two bridging anions.

Key words: tripodal ligand, binuclear, coordinated pendant arms, octaazamacrocyclic and 1,3-dibromopropane

Synthesis, Characterization and Redox Properties of Novel *vic*-Dioximes and Their Complexes with Nickel(II), Copper(II) and Cobalt(II)

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Two novel *vic*-dioxime, 1,2-dihydroxyimino-1-*p*-tolyl-3-aza-6-imidazole heptane (L₁H₂) and N-(ethyl-4-amino-1-piperidine carboxylate)-*p*-tolylglyoxime (L₂H₂) were prepared by the reaction of *anti-p*-tolylchloroglyoxime with 1-(3-aminopropyl)imidazole and ethyl-4-amino-1-piperidine carboxylate in absolute THF. Mononuclear complexes with a metal-ligand ratio of 1:2 were prepared using Co(II), Cu(II) and Ni(II) salts. The ligands and their Co(II), Cu(II) and Ni(II) complexes were characterized by elemental analyses, FT-IR, UV-Vis, ¹H-NMR and ¹³C-NMR and magnetic susceptibility measurements. The electrochemical behaviour of the complexes was investigated by cyclic voltammetry in dimethylsulfoxide. All metal complexes showed metal centered quasi reversible one-electron redox processes. However, metal complexes of the L₂H₂ ligand also exhibited ligand based irreversible redox waves.

Key words: *vic*-dioxime, copper(II), cobalt(II), nickel(II) complexes, synthesis, redox properties

Preparation, Spectroscopy and Magnetism of Di- μ -methoxy bis[copper(II)(benzo[d]pyridazine-1(2H)-one) $_2$] $^{2+}$ with NO_3 or ClO_4 as the Counter-ion

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The synthesis, spectroscopic and magnetic characterization of two new methoxo-bridged copper(II) complexes are described. Both compounds have the general formula $[\text{Cu}(\mu\text{-OCH}_3)(\text{L})_2]_2\text{X}_2$, in which $\text{X} = \text{NO}_3$ or ClO_4 and $\text{L} = \text{benzo[d]pyridazine-1(2H)-one}$ (abbreviated L). The title compounds all consist of dinuclear units with methoxo-bridging group. Both complexes have been synthesized in one-step reaction, and characterized by elemental analysis, FTIR and electronic spectra and by magnetic properties. The compounds exhibit antiferromagnetic interaction at room temperature. The UV-Vis spectra show three absorption bands, attributed to d-d transition of copper(II) ion, ligand \rightarrow metal charge transition and $\pi\rightarrow\pi^*$ or $n\rightarrow\pi^*$ transitions of ligand. The IR spectra indicate Cu_2O_2 ring vibrations in $540\text{--}440\text{ cm}^{-1}$ range. The magnetic properties of the $[\text{Cu}_2(\text{OCH}_3)_2(\text{L})_4](\text{NO}_3)_2$ has been investigated in the $6\text{--}268\text{ K}$ range and a singlet-triplet energy gap of -145 cm^{-1} was observed.

Key words: dinuclear copper(II) complexes, di-methoxo-bridged copper(II) complexes

Limbatolide F and G: Two New *trans*-Clerodane Diterpenoids from *Otostegia limbata*

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Two new *trans*-clerodane diterpenoids provisionally named as limbatolide F (**1**) and limbatolide G (**2**) were isolated from the chloroform extract of *Otostegia limbata*. Both compounds **1** and **2** have a unique feature of C-4/C-6 five membered α,β -unsaturated lactone. The structures of these new compounds as well as their relative configurations were determined by 1D and 2D NMR techniques including COSY, HMQC, HMBC, NOESY and NOE experiments.

Key words: *Otostegia limbata*, *trans*-clerodane, diterpenoids, Lamiaceae

Lactones 18. Synthesis of Bicyclic Lactones with Methyl-, Di- and Trimethyl Substituted Cyclohexane System

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Starting from racemic γ,δ -unsaturated esters (**1a–d**) twelve bicyclic γ -lactones with the cyclohexane system substituted with various number of methyl groups were synthesized. The esters mentioned were subjected to the alkaline hydrolysis and then to iodolactonization to furnish the corresponding iodolactones (**3a–d**). The reduction of these compounds with tributyltin hydride gave the saturated lactones (**4a–d**) whereas the dehydrohalogenation with DBU yielded their unsaturated analogues (**5a–d**). The structures of all lactones obtained were established by their spectral (¹H NMR, IR) data. For two of them the crystal structures were determined.

Key words: δ -iodo- γ -lactones, iodolactonization, DBU, antifeedants

Alkoxyethylaluminum Complexes with Cyclopentadienyl Ligand – Synthesis and Characterization

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A series of novel aluminum alkoxide derivatives, $[\text{Cp}(\text{Me})\text{Al}-\mu\text{-OR}]_2$, (where R = Me **1**, Et **2**, ^tBu **3**, ^tBuCH₂ **4**, ⁱPr **5**, ^tBu **6**) has been prepared by reacting Me(Cl)AlOR with CpNa. All the compounds were characterized by multinuclear NMR, elemental analysis and molecular weight determination cryoscopically in benzene.

Key words: aluminum, cyclopentadienyl, alkoxide, multinuclear NMR

Adenosine-N⁶-crown Ethers as a New Class of Ionophores

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Adenosine bearing 18-crown-6 and 15-crown-5 ether moiety was synthesized. Comparison of complexing ability towards alkali metal ions revealed strong potassium and sodium preference. Complex formation constants were estimated and thermodynamic parameters calculated.

Key words: crown ether, adenosine, selectivity

Nanosilica Partially Modified by Hexamethyldisilazane in Air

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Unmodified and modified nanosilicas containing different content of trimethylsilyl (TMS) groups grafted by interaction with various amounts of hexamethyldisilazane (HMDS) in a reactor contacting with air were studied using infrared spectroscopy, adsorption and potentiometric titration methods. Contribution of narrow gaps between spherical primary silica particles forming aggregates decreases with increasing TMS loading (θ_{TMS}), because of blocking of these gaps by grafted functionalities. Contribution of broader gaps corresponding to mesopores depends slightly on θ_{TMS} , and changes in contribution of macropores are rather random. IR spectra of modified samples depict changes in bands of the O–H stretching vibrations at 3750 and 3300 cm^{-1} (reduced with θ_{TMS}) and 3680 and 3500 cm^{-1} (changed nonlinearly with θ_{TMS}), since HMDS can interact with silanols and adsorbed water and affect the adsorbed amounts of water. Enhancement of the hydrophobic properties of the surface reduces the amounts of adsorbed water, and the IR band intensity at 3300 cm^{-1} diminishes. The adsorption of poly(vinyl pyrrolidone) on silicas decreases with θ_{TMS} in consequence of changes in the surface structure and the reduction of adsorption potential. The silylation diminishes the surface charge density and the electrostatic surface potential, and the point of zero charge shifts toward larger pH values with increasing θ_{TMS} value.

Key words: nanosilica, hexamethyldisilazane, partially hydrophobized silica, structural characteristics, adsorptive properties, infrared spectra, poly(vinyl pyrrolidone) adsorption, potentiometric titration, surface charge density

Analysis of the Absorption Spectrum of U^{3+} Doped YCl_3 Single Crystals

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Low-temperature emission and polarized absorption spectra of U^{3+} ions diluted in YCl_3 host single crystals have been recorded in the 4000–50000 cm^{-1} spectral range. The point symmetry of the doped U^{3+} ions has been assumed to be octahedral. 29 experimental crystal-field levels were fitted to seven parameters of a semi-empirical Hamiltonian representing the combined atomic, and one-electron crystal field operators, with a rms deviations of 49 cm^{-1} .

Key words: uranium(3+), $U^{3+}:YCl_3$ single crystals, absorption spectrum, crystal-field parameters

Kinetic Studies on the Quinolinium Dichromate Oxidation of Heteroacids

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Heterocyclic carboxylic acids reacted with quinolinium dichromate, in sulfuric acid, to yield the corresponding hydroxy-substituted acids. The kinetic results supported a mechanistic pathway proceeding *via* the rate-determining formation of the cyclic chromate ester.

Key words: kinetics, quinolinium dichromate, oxidation, heteroacids

n-Butane Conversion on Differently Pretreated Supported Palladium Catalysts

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Metal-support interactions in silica- and alumina-supported palladium catalysts have been re-investigated by using n-butane conversion as a test reaction. High temperature reduction at 600°C results in a considerable increase in the isomerization selectivity, *i.e.* a similar effect as in the case of previously studied reactions of 2,2-dimethylpropane and C₆-alkanes. Therefore, changes in the selectivity for isomerization and also in the activation energy can be regarded as useful diagnostic parameters towards determining whether or not palladium interacts with a support.

Key words: n-butane, catalytic conversion of, Pd/Al₂O₃, Pd/SiO₂, effect of catalyst pretreatment, isomerization selectivity

**Synthesis and Characterization of
2,3-Bis(hydroxyimino)piperazine and Its Ni(II), Co(II),
Cu(II) and U(VI)O₂ Complexes**

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