

## 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  $\text{R} = \text{C}_2\text{F}_5$ ,  $\text{C}_3\text{F}_7$ ,  $\text{C}_4\text{F}_9$ ,  $\text{C}_6\text{F}_{13}$ ,  $\text{C}_8\text{F}_{17}$ , was prepared and characterized with MS, IR and  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  NMR spectroscopy. The studied species contained monomeric, bis-chelated  $[\text{Cu}(\text{dppb})_2]^+$  cations and uncoordinated  $\text{RCOO}^-$  anions. The Cu(I) coordination of the diphosphines resulted in slight high-frequency shifts of the  $^{31}\text{P}$  NMR resonances of the equivalent phosphorus atoms.

**Key words:** copper(I), diphosphines, perfluorinated carboxylates, MS,  $^{31}\text{P}$  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 BaCO<sub>3</sub> 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  $\text{Zn(II)}$ ;  $X = \text{Cl}, \text{NO}_3$ ] 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 (L<sub>1</sub>H<sub>2</sub>) and N-(ethyl-4-amino-1-piperidine carboxylate)-*p*-tolylglyoxime (L<sub>2</sub>H<sub>2</sub>) 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, <sup>1</sup>H-NMR and <sup>13</sup>C-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 L<sub>2</sub>H<sub>2</sub> 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- $\mu$ -methoxy bis[copper(II)(benzo[d]pyridazine-1(2H)-one) $_2$ ] $^{2+}$ with $\text{NO}_3$ or $\text{ClO}_4$ 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  $\text{ClO}_4$  and  $\text{L} = \text{benzo[d]pyridazine-1(2H)-one}$  (abbreviated  $\text{L}$ ). 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  $\text{Cu}_2\text{O}_2$  ring vibrations in 540–440  $\text{cm}^{-1}$  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 6–268 K range and a singlet-triplet energy gap of  $-145 \text{ cm}^{-1}$  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  $\alpha,\beta$ -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