

## **Anthracenedione Analogues – Synthesis and Biological Activity**

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This article concerns synthesis and biological activity of anthracenedione analogues which are considered as prodrugs.

**Key words:** anthracyclines, anthracenedione, anthraquinone analogues, synthesis, biological activity, antineoplastic agent

## Bond-valence Approach to the Semicoordination in Seven-Coordinated Copper(II) Complexes with 4-Aminopyridine: Crystal and Molecular Structure of Bis(4-aminopyridine)di(acetato)(aqua)copper(II)

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The structure of  $[\text{Cu}(\text{CH}_3\text{COO})_2(4\text{-aminopyridine})_2(\text{H}_2\text{O})]$  was X-ray studied. Heptacoordinated copper atoms of  $[\text{Cu}(\text{CH}_3\text{COO})_2(4\text{-aminopyridine})_2(\text{H}_2\text{O})]$  complex are consistent with bond valence sum model based on orbital metal-ligand interaction. Equatorial plane of deformed tetragonal bipyramid as copper coordination polyhedron is formed by atoms O of carboxylato ligands and water molecule. Two N atoms of 4-aminopyridine molecules occupy the axial sites. Each copper atom is semicoordinated by two atoms O from two carboxylato chelates. The lengths of two semicoordinated Cu...O bonds are 3.041(2) Å (twice). Seven-coordinated copper atom of the studied compound and  $\text{Cu}(\text{oxalato})(\text{H}_2\text{O})(4\text{-aminopyridine})_2$  is consistent with the bond valence sum model.

**Key words:** copper(II) complex, semicoordination, crystal and molecular structure

## Synthesis and Magnetic Studies of Copper(II)–Lanthanide(III) Heterobinuclear Complexes Bridged by N,N'-Bis[3-(dimethylamino)propyl]oxamido

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Ten new copper(II)–lanthanide(III) heterobinuclear complexes bridged by N,N'-bis[3-(dimethylamino)propyl]oxamido dianions (dmoxpn) and end-capped with 2,2'-bipyridine (bpy), namely,  $\text{Cu}(\text{dmoxpn})\text{Ln}(\text{bpy})_2(\text{NO}_3)_3$  (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb), have been synthesized and characterized by elemental analyses, molar conductivity measurements, and spectroscopic (IR, UV, ESR) studies. The  $\text{Cu}(\text{dmoxpn})\text{Gd}(\text{bpy})_2(\text{NO}_3)_3$  complex was further characterized by variable-temperature magnetic susceptibility (4.2–300 K) measurements and the magnetic data have been also used to deduce the indicated heterobinuclear structure. The results derived from least-squares fit of the experimental data have confirmed that the adjacent copper(II) and gadolinium(III) ions through the oxamido-bridge in the complex are ferromagnetically coupled with the exchange integral  $J_{\text{Cu-Gd}} = +8.59 \text{ cm}^{-1}$ . A plausible mechanism for the ferromagnetic coupling between gadolinium(III) and copper(II) is discussed in terms of spin-polarization.

**Key words:**  $\mu$ -oxamido-bridge, copper(II), lanthanide(III), heterobinuclear complexes, ferromagnetic coupling, synthesis

## **Ligand-Field Analysis of Low-Spin N,N'-Propylenebis(naphthyldiiminate)nickel(II) in Ethanol Solution**

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Titled complex denoted as  $[\text{Ni}(\text{nappn})]\cdot 0.5\text{H}_2\text{O}$ , where  $\text{H}_2\text{nappn}$  is tetradentate Schiff base: 1,3-bis(naphthylideneimine)propane, has been characterized by elemental analysis, molar conductivity, ultraviolet (UV) and visible (Vis) spectroscopy. The known X-ray structure of this complex shows that Ni atom adopts square-planar coordination. Combined multi-technique experiments have been applied to establish the structure of complex in solution. The molar conductivity value indicates non-electrolytic properties of solution studied. The spectroscopic measurements were used to study the coordination properties of donor-atoms and their bonding abilities. All the experimental transition energies are derived from Gaussian analysis of the solution spectrum. The d-d transition energies were used to derive the angular overlap model (AOM) and crystal-field model (CFM) parameters for the studied complex in  $D_{4h}$  symmetry. The first full ligand-field interpretation of the low-spin Schiff base nickel(II) complex in solution has been presented.

**Key words:** nickel(II) complex, Schiff base: 1,3-bis(naphthylideneimine)propane, solutions, electronic spectra, Angular Overlap Model, ligand-field parameters

## **New Dinuclear Nonaazadentate Schiff Base Podates of Rare Earth(III) Ions**

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As a result of [1+2] Schiff base condensation in the template reaction between 2,6-diacetylpyridine and 3,7-diazanonane-1,9-diamine in the presence of rare earth(III) ions ( $M = Y^{3+}, La^{3+}, Pr^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}$ ), new dinuclear architectures containing a ligand with  $N_9$  set of donor atoms with terminal amine groups have been formed. The complexes have been characterized by the spectroscopic and thermogravimetric data and microanalyses.

**Key words:** dinuclear complexes, lanthanides(III), Schiff base podates, template synthesis, yttrium

## Reversal of Diastereoselectivity of Mesitronitrile Oxide 1,3-Dipolar Cycloadditions with Penta-1,4-diene-3-ol by Mg(II)

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1,3-Dipolar cycloadditions of mesitronitrile oxide (**4**) to penta-1,4-diene-3-ol (**5**) proceed regioselectively irrespective of the presence or absence of the Mg(II) additive. Addition of Grignard reagent reverses the diastereoselectivity of the cycloaddition. The reaction of mesitronitrile oxide with magnesium alkoxide of penta-1,4-diene-3-ol (**5**) proceeded with exclusive diastereoselectivity giving the *syn* **6b** and **7c** isomer of the resulting isoxazolines.

**Key words:** cycloaddition, diastereoselection, nitrile oxides, isoxazolines, Lewis acids

## **Efficient Synthesis of Macrocyclic Dilactam Crown Ethers by Fast Addition Method**

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A simple and convenient method for preparing macrocyclic dilactam crown ethers containing  $N_2O_5$ ,  $N_3O_3$ ,  $N_3O_4$ ,  $N_3O_5$  and  $N_2O_{10}$  donor atoms with 18–32 membered rings was developed. These compounds were obtained in the macrocyclization step under vigorous stirring conditions as well as fast addition of reactants. This step does not require external cyclization factors such as high dilution approach, template effect or nitrogen protection and provides the expected dilactams in high yields, ranging from 65–95%. The course of the reaction is assumed to depend on the occurrence of self assembly phenomena which are stimulated by a logic concentration in a selected solvent and the yields are improved by application of high speed stirring and fast addition of reactants.

**Key words:** dilactam crown ethers, fast addition method, high dilution technique, macrocyclization, self assembly

## Preparation of New Phenol-based Acyclic Ligands with Double Set of Coordination Sites

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A convenient four-step preparation of the two compartmental ligands 1,6-bis(2-pyridyl)-2,5-bis(2-hydroxy-3-hydroxymethyl-5-chlorobenzyl)-2,5-diazaheptane **3a** and 1,7-bis(2-pyridyl)-2,6-bis(2-hydroxy-3-hydroxymethyl-5-chlorobenzyl)-2,6-diazaheptane **3b** starting from 4-chlorophenol **4** is reported. Compound **4** was converted to triol **5** which was then protected to 2,2-dimethyl-6-chloro-8-(hydroxymethyl)benzo-1,3-dioxin **6** with 2-methoxy propene. Compound **6** was chlorinated to 2,2-dimethyl-6-chloro-8-(chloromethyl)benzo-1,3-dioxin **7** and then reacted with 1,6-bis(2-pyridyl)-2,5-diazaheptane or 1,7-bis(2-pyridyl)-2,6-diazaheptane in the presence of Na<sub>2</sub>CO<sub>3</sub> in dioxane. Subsequent acid hydrolysis gave **3a** and **3b**, respectively. The total yields were 38%.

**Key words:** acyclic ligand, phenol-based ligand, compartmental ligand



## Synthesis and Biological Activities of Nine 1,2,3,5-Tetrahydroimidazo[2,1-*b*]quinazoline Derivatives

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A series of variously substituted 1,2,3,5-tetrahydroimidazo[2,1-*b*]quinazoline derivatives **3–4** and **6–7** were prepared by the reactions of 2-chloro-4,5-dihydroimidazole (**1**) with the appropriate 2-aminophenyl ketones **2** and **5**. The structures of the new compounds obtained were determined by elemental analysis as well as IR and NMR spectroscopic data. Biological activities of the compounds **3** and **6** was examined on P<sub>2</sub> membrane preparations obtained from rat whole brains and rat tail artery. Among the compounds tested, 5-methylidene-1,2,3,5-tetrahydroimidazo[2,1-*b*]quinazoline (**6a**) showed high and moderate binding affinities to I<sub>2</sub> imidazoline ( $K_i = 5.2$  nM) and  $\alpha_2$ -adrenergic ( $K_i = 149$  nM) receptors, respectively.

**Key words:** 5-hydroxy- or 5-methylidene-1,2,3,5-tetrahydroimidazo[2,1-*b*]quinazoline derivatives, synthesis, I<sub>2</sub> imidazoline and  $\alpha_2$ -adrenergic receptors binding affinities, circulatory activity

## **Octasilsesquioxanes as Hybrid Nanocomposite Platforms. II. Synthesis, Characterization and Properties of Some Alkyl-functionalized Silsesquioxanes**

by **E.O. Dare**<sup>1</sup>, **G.A. Olatunji**<sup>2</sup> and **D.S. Ogunniyi**<sup>2</sup>

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The syntheses of octaalkylsilsesquioxanes **3**, **4**, **5** and **6** have been achieved by the platinum-catalyzed hydrosilylation of octahydrogensilsesquioxane **2** with  $\omega$ -halo-alkenes and other unsaturated substrates. These compounds were characterized by spectroscopic techniques and elemental analysis. Thermogravimetric analyses of **3** and **4** shows that they are reasonably stable thermally, and may act as building blocks to ceramics, nanometer ball bearing at around 400°C and photoresist materials.

**Key words:** hydrosilylation, octaalkylsilsesquioxanes, sol-gel process, nanocomposite, organic-inorganic hybrid material, building blocks, thermogravimetric analysis

## **New Routes to Functionalized Polyhedral Oligomeric Silsesquioxanes *via* Friedel-Crafts Alkylation and Dichlorocarbene Addition to Octavinylsilsesquioxane**

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Selective functionalization of  $(\text{CH}_2=\text{CH})_8\text{Si}_8\text{O}_{12}$  **1** by the addition of dichlorocarbene to vinyl double bonds giving  $(\text{C}_3\text{H}_3)_8\text{Si}_8\text{O}_{12}$  **2** or  $(\text{C}_2\text{H}_3)_4(\text{C}_3\text{H}_3\text{Cl}_2)_4\text{Si}_8\text{O}_{12}$  **3** respectively is described. The dichlorocarbene was generated from  $\text{CHCl}_3$  in phase transfer catalytic system (PTC). Furthermore,  $(\text{PhCH}_2\text{CH}_2)_8\text{Si}_8\text{O}_{12}$  **4** has been synthesized by Friedel-Crafts alkylation reaction of benzene with **1** using  $\text{AlCl}_3$  as catalyst.

**Key words:** octavinylsilsesquioxane, dichlorocarbene, phase transfer catalysis, functionalized silsesquioxane, dichlorocyclopropane, Friedel-Crafts alkylation

## Transformation of *O*-Amidinyhydroxylamine into Benzothiazoles *via* Iminocarbonyl Sulfenamides

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The reaction of *O*-amidinyhydroxylamine **3** with aryl isothiocyanates leads to the formation of benzothiazole derivatives **5a–c**. The proposed mechanism of the reaction involves initial formation of iminocarbonyl sulfenamides **A** which, in turn, undergo spontaneous sulfurization of aromatic ring with loss of amine **7**. The later compound reacts with excess aryl isothiocyanate to give 1,3-diazaspiro[4,5]decane-2-thione **6**.

**Key words:** *O*-amidinyhydroxylamine, (benzothiazol-2-yl)imidazolidin-2-ones, 1,3-diazaspiro[4,5]decane-2-thione, synthesis, X-ray crystallography

## **Preparation, Characterization of MCM-49 and Catalytic Performance of Pd/MCM-49 Catalysts in One-step Synthesis of MIBK from Acetone**

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Highly crystalline and pure MCM-49 was hydrothermally synthesized by a dynamic method, and it was used as supports to prepare Pd/MCM-49 catalysts by ion-exchange method. The physicochemical properties of the samples were characterized by XRD, TEM, TG-DTG and ICP. MCM-49 synthesized was markedly different from those in previous reports, showing much smaller crystals. One-step synthesis of methyl isobutyl ketone from acetone was investigated over Pd/MCM-49. These catalysts showed a high reactivity and selectivity to MIBK, reaching a conversion of 35.6% and a selectivity of 85% to MIBK. Stable MIBK yields were obtained during 60 h of time on stream.

**Key words:** Pd/MCM-49, acetone, methyl isobutyl ketone, one-step synthesis

## **The Study of the Micropolarity of the Interfaces in Iridescent Solutions of Tetradecyldimethylaminoxid**

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We have studied the micropolarity of the interfaces in iridescent solutions of tetradecyldimethylaminoxid ( $C_{14}$ DMAO) on increasing the mean distance between the bilayers. The values of the effective dielectric constant have been determined both on and under the surface of the bilayers, *i.e.* on the bulk water side, and on the micelle hydrocarbon interior side, respectively. For the surface region and micelle interior, hexaldehyde and pyrene were used as the polarity probes, respectively. Interpretation of the obtained results indicates that the micropolarity of the interfaces depends on the thickness of the bilayers, and does not depend on the mean distance between the lamellar layers.

**Key words:** iridescent phases, micropolarity, fluid interfaces, surfactant bilayers, UV/vis spectroscopy

## **Regularities in Complex Asymptotic Oscillations in the Belousov-Zhabotinsky Reaction at Various Residence Times and Inflow Malonic Acid Concentration**

by **M. Rachwalska<sup>1</sup>** and **A.L. Kawczyński<sup>2</sup>**

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Simple and complex oscillations have been observed in an asymptotic regime of the Belousov-Zhabotinsky (BZ) system of bromate-malonic acid-ferroin in a continuously stirred tank reactor (CSTR). Changes of the residence time and the influx concentration of malonic acid induce the appearance of regularities in complex patterns which resemble the period adding bifurcation. All experimental results can be reproduced by a simple model suggested earlier for qualitative description of asymptotic and transient oscillations observed in the BZ system.

**Key words:** complex chemical oscillations, the Belousov-Zhabotinsky reaction, period adding bifurcations

## **The Characterization of Modified Higher Aliphatic Alcohols – Synthesis Catalysts by EPR and XPS Methods**

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A series of copper-zinc catalysts for aliphatic alcohols synthesis with a varying amount of additives was prepared by thermal decomposition of metal citrates. The results of catalytic experiments, made in a laboratory high-pressure reactor, showed a good stability and almost constant activity and selectivity during 4 months. In this paper the catalyst before (A) and after (B) reaction is characterized by EPR and X-ray photoelectron spectroscopies. For catalyst A the copper species were identified as isolated  $\text{Cu}^{2+}$  ions in a dynamic Jahn-Teller configuration. For the sample B the EPR spectrum is complex and its features are corresponding to: clustered  $\text{Cu}^{2+}$  species with dipole-dipole interaction;  $\text{Fe}^{3+}$  ions in rhombically distorted symmetry;  $\text{O}_2$  centres.

**Key words:** EPR, X-ray photoelectron spectroscopy, Cu based catalyst