

## **Impact of Copper Ions on Chemistry and Biology of Prion Protein**

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*(Received August 9th, 2006)*

The current state of art in the studies on  $\text{Cu}^{2+}$  ions interactions with mammalian and chicken prion protein (PrP) is discussed. The specificity of  $\text{Cu}^{2+}$  binding by tandem repeat domains of PrPs is actually well supported although the major contradictions still exist as far as the fifth binding site is concerned. The biological relevance of  $\text{Cu}^{2+}$  coordination to octarepeat region of mammalian PrP seems to be generally accepted although the binding of the fifth metal ion may be just a chemical property of PrP.

**Key words:** neurodegeneration, prion protein,  $\text{Cu}^{2+}$  complexes

## Synthesis and Characterization of 5,10,15,20-Tetra-(4-decanoyloxyphenyl)porphyrin and Transition Metal Complexes

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*(Received May 18th, 2006; revised manuscript September 27th, 2006)*

Transition metal complexes of 5,10,15,20-tetra-(4-decanoyloxyphenyl)porphyrin TDPPM [M = Mn, Fe, Co, Ni, Cu, Zn; TDPPH<sub>2</sub> = 5,10,15,20-tetra-(4-decanoyloxyphenyl)porphyrin] have been synthesized and characterized by UV-Vis, IR photoacoustic, <sup>1</sup>H NMR spectroscopy, elemental analyses, molar conductivity and differential scanning calorimetry (DSC). The ligand and its Zn complex have liquid crystalline behavior. According to the DSC thermogram the Zn complex exhibits a low phase transition temperature at -8.987°C and a wide mesophase range at 175°C.

**Key words:** porphyrin, transition metal complex, synthesis

## **Thermodynamic Stability of $\text{LaCrO}_3$ and $\text{CaZrO}_3$ Using a Solid-state Galvanic Cell Method**

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*(Received May 12th, 2006; revised manuscript October 16th, 2006)*

Thermodynamic stability of  $\text{CaZrO}_3$  with respect to  $\text{LaCrO}_3$  was investigated. The possible products of the reaction are  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{CaCr}_2\text{O}_4$ . The standard Gibbs free energy change for this reaction at  $T = 1273$  K was calculated. To this purpose the standard Gibbs free energy of formation (from oxides) of  $\text{LaCrO}_3$ ,  $\text{CaZrO}_3$ ,  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{CaCr}_2\text{O}_4$  were obtained from the measurements of electromotive force (EMF) of respective solid-state galvanic cells.  $\text{LaCrO}_3$  was confirmed to be able to react with  $\text{CaZrO}_3$  spontaneously. However, the solid solutions based on  $\text{LaCrO}_3$ , in which the activity of  $\text{LaCrO}_3$  at  $T = 1273$  K reached the values below 0.168, are thermodynamically stable with respect to  $\text{CaZrO}_3$ .

**Key words:** solid oxide fuel cells, solid galvanic cells, lanthanum chromite, calcium zirconate

## A Bimetallic Palladium(II) Catalyzed Synthesis of 1,2-Dibromo Compounds

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*(Received May 30th, 2006; revised manuscript September 7th, 2006)*

A bimetallic palladium(II) catalyst containing a triketone ligand and a bridging dinitrogen ligand oxidizes aromatic and cyclic aliphatic olefins in bromide-containing aqueous-THF to 1,2-dibromo compounds and bromohydrins. With aromatic olefins, the 1,2-dibromo products were obtained in a 70–80% yield and the bromohydrins in a 10–15% yield; this observation is opposite to that obtained in chloride containing medium where the chlorohydrin product predominates. The oxidation of 2,3-dihydrofuran gave *trans*-2,3-dibromotetrahydrofuran, 3-oxotetrahydrofuran, and 3-bromo-2-hydroxytetrahydrofuran in relative yields of 75%, 15%, and 10%, respectively. On the other hand, the oxidation of cyclopentene and cyclohexene affords only *trans*-1,2-dibromo products in about 90% yield. The stereochemistry is consistent with an anti-attack of bromide followed by decomposition involving attack of bromide from the coordination sphere of the Pd(II). The procedure outlined here is a convenient method for the one step synthesis of 1,2-dibromides.

**Key words:** palladium(II), catalysis, 1,2-dibromides, bromohydrin

**Lignans and Flavonoids from the Seeds of *Centaurea bornmuelleri* Hausskn. Ex. Bornm. and *Centaurea huber-morathii* Wagenitz.**

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(Received June 26th, 2006; revised manuscript September 8th, 2006)

The reversed-phase preparative HPLC purification of the methanol extracts of the seeds of two Turkish endemic species *Centaurea bornmuelleri* and *Centaurea huber-morathii* afforded several dibenzylbutyrolactone-type lignans and flavonoids. The lignans arctiin, matairesinol and matairesinoside, and the flavonoid, afzalin, were found in both species. While arctigenin and astragalin were only present in *C. bornmuelleri*, kaempferol was isolated from *huber-morathii*. A plant sterol, stigmast-4-en-3 $\beta$ -ol, was also isolated from the dichloromethane extract of *C. bornmuelleri*. The structures of the isolated compounds were determined by spectroscopic means. The chemotaxonomic significance of these compounds within the genus *Centaurea* has been discussed.

**Key words:** *Centaurea bornmuelleri*, *Centaurea huber-morathii*, Asteraceae, Compositae, lignan, flavonoid, chemotaxonomy

## **Is a Phase Transfer Catalyst Really Needed for *gem*-Dihalocyclopropanation of Alkenes with Haloforms in the Presence of Alkali Metal Hydroxide?**

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*(Received October 3rd, 2006)*

Chloroform, bromoform and dibromochloromethane react with alkenes in the presence of conc. aq. sodium hydroxide, without phase-transfer catalyst, giving *gem*-dihalocyclopropanes. The process is particularly useful for preparation of *gem*-bromochlorocyclopropanes which are formed in good yields and in high selectivity.

**Key words:** phase-transfer catalysis, uncatalysed reactions, dihalocarbenes

## Synthesis, Molecular and Crystal Structure of Two Tricyclic *N*-Aminoimides

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(Received July 28th, 2006; revised manuscript October 10th, 2006)

Two new *N*-aminoimides, 2-amino-4,7-epoxy-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)dione (**I**) and 2-amino-8-isopropyl-5-methyl-4,7-ethane-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (**II**), have been synthesized. Both compounds are *exo,cis* isomers. Crystals of (**I**) and (**II**) are noncentrosymmetric with two crystallographically independent molecules ( $Z' = 2$ ) in the asymmetric unit. The *N*-amine groups of the symmetry independent molecules differ in their environment, forming single or bifurcated N–H...O hydrogen bonds. Voluminous hydrocarbon parts evoke orthogonal electrostatic interactions between the imide ring and carbonyl or ether O atoms in (**II**) and (**I**), respectively, with C/N...O distances smaller than 3.2 Å (the shortest being of 2.9 Å).

**Key words:** *N*-aminoimide, crystal structure, 1*H*-isoindole-1,3(2*H*)-dione derivative, orthogonal electrostatic interaction

## **Interaction in Co–C System: Effect of Co Loading**

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*(Received July 12th, 2006)*

The interaction of 1 and 4 nm thick cobalt films with amorphous carbon support was investigated by transmission electron microscopy and electron diffraction. The samples were annealed in flowing hydrogen at 300–500°C. It was established that after heating at 350°C discrete particles or maze-like structure were formed in 1 nm and 4 nm thick films, respectively. The differences in the film morphology ensue from specific thermodynamic properties of the dispersed phase. In both systems formation of Co<sub>2</sub>C and Co<sub>3</sub>C carbides was detected after heating at 350 and 400°C. Decomposition of carbides took place following heating at 500°C.

**Key words:** Co thin films, electron microscopy, Co–C interaction, Co<sub>2</sub>C, Co<sub>3</sub>C

## **The Effect of Chlorine and Support Dissolution on Hydrogen Chemisorption on Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst**

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*(Received September 14th, 2006)*

Hydrogen chemisorption at 20–200°C was studied volumetrically on Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (4.6 and 10.8% of Ru) prepared from ruthenium chloride. The structure of the catalysts was determined by ICP-AES, BET, TEM and XRD methods. Large amount of Cl<sup>-</sup> was retained on the catalysts after H<sub>2</sub> reduction at 500°C. Ruthenium dispersion determined by the hydrogen chemisorption technique was found to be inaccurate due to the contamination of the ruthenium surface – during preparation of the catalysts – by chlorine from precursor and/or aluminum ions from the support. For the Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with high chlorine content, the mean particle sizes estimated from irreversible H<sub>2</sub> chemisorption at 100°C, were much greater than that obtained by TEM and XRD. The difference was much smaller for the catalysts subjected to washing procedure removing chlorine ions.

**Key words:** Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, hydrogen chemisorption, Ru metal dispersion

## **The Preparation of PVP/Tb(AA)<sub>3</sub>phen Luminescent Nanofibers by Electrospinning**

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*(Received September 16th, 2005; revised manuscript September 27th, 2006)*

Composite nanofiber films of poly(vinyl pyrrolidone) (PVP) containing Tb(AA)<sub>3</sub>phen were prepared by electrospinning technique. Transmission electron microscopy (TEM) and luminescence spectroscopy were used to characterize the composite nanofiber films. TEM observation showed that Tb(AA)<sub>3</sub>phen was dispersed homogeneously in composite nanofibers. Luminescence measurements indicated that Tb(AA)<sub>3</sub>phen showed superior emission lines and stronger intensities in the composite nanofibers than in pure Tb(AA)<sub>3</sub>phen powder. The lifetime of Tb(AA)<sub>3</sub>phen also lengthened when it was incorporated in the composite nanofibers.

**Key words:** PVP/Tb(AA)<sub>3</sub>phen nanofiber, electrospinning, luminescence

**Quantum Chemistry Studies on  
Bis(*p*-aminobenzoato)–lead(II) Complex  
[Pb(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>COO)<sub>2</sub>]**

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*(Received March 3rd, 2006; revised manuscript October 2nd, 2006)*

The title complex, bis(*p*-aminobenzoato)–lead(II) [Pb(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>COO)<sub>2</sub>], has been optimized at B3LYP/LANL2DZ level of theory and the calculated results show that the lead(II) ion adopts a four-coordinate geometry. The analyses of NPA and Mulliken atomic charge distributions indicate that during the process of the formation of this compound, both aminobenzoato ligands transfer their negative charges to the lead(II) ion. The lead atom and oxygen atoms form covalent bonds by using their 6*p* and 2*p* orbitals, respectively. The calculations of electronic spectra of the title complex show that there exist four absorption bands and the electronic transitions are mainly derived from the contributions of both an intraligand  $\pi \rightarrow \pi^*$  transition and ligand-to-metal charge transfer (LMCT) transitions. The thermodynamic properties of the studied compound at different temperatures have been calculated and the corresponding relations between the properties and temperatures have also been obtained. The calculation of the second order optical nonlinearity has been carried out, and the molecular hyperpolarizability of the title complex is  $7.61379 \times 10^{-30}$  esu.

**Key words:** aminobenzoato lead(II) complex, density functional theory, electronic spectra, thermodynamic property, the second order optical nonlinearity

## **Modification of the Acid-base and Catalytic Properties of CuCl<sub>2</sub>-KCl-LaCl<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> by MgAl<sub>2</sub>O<sub>4</sub> in Ethane Oxychlorination**

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*(Received October 4th, 2006)*

Effect of MgAl<sub>2</sub>O<sub>4</sub> on the structure, acidity as well as catalytic activity of CuCl<sub>2</sub>-KCl-LaCl<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst in ethane oxychlorination was studied. Impregnation of γ-Al<sub>2</sub>O<sub>3</sub> with Mg and Al nitrates formed magnesium aluminate spinel on the support. TPR results showed that Cu species were located on both γ-Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> phases. With modification of γ-Al<sub>2</sub>O<sub>3</sub> by MgAl<sub>2</sub>O<sub>4</sub>, the interaction between Cu species and support weakened and the surface active species CuCl<sub>2</sub> increased. Formation of MgAl<sub>2</sub>O<sub>4</sub> leads to a decrease of strong acid sites and an increase of weak acid sites. Much larger quantities of coke were deposited on the CuCl<sub>2</sub>-KCl-LaCl<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> than on the modified catalyst, which was attributed to its more strong acid sites. Based on these factors CuCl<sub>2</sub>-KCl-LaCl<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst exhibits better catalytic activity and stability than γ-Al<sub>2</sub>O<sub>3</sub> supported catalyst, and the highest vinyl chloride selectivity reached 46.8% and was still 40.6% after 210 h reaction.

**Key words:** oxychlorination, ethane, vinyl chloride, magnesium aluminate, spinel

## **Gyrolite Formation in CaO–SiO<sub>2</sub>·nH<sub>2</sub>O– $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O–H<sub>2</sub>O System under Hydrothermal Conditions**

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*(Received April 25th, 2006; revised manuscript October 17th, 2006)*

The influence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O additives on the gyrolite formation process in the CaO–SiO<sub>2</sub>·nH<sub>2</sub>O–H<sub>2</sub>O mixture has been examined. It has been proved that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is not recommended for the synthesis of gyrolite, because Al<sup>3+</sup> ions stimulate the formation of C-S-H(I) and 1.13 nm tobermorite (where C – CaO, S – SiO<sub>2</sub> and H – H<sub>2</sub>O). Na<sub>2</sub>O positively affects the formation of gyrolite: this compound is formed already after 8 hours of isothermal curing at 200°C. On the contrary, in the pure mixtures gyrolite formed after only 32 h at 200°C. In order to compare the cation exchange activity of synthesized gyrolite with (Al+Na)-substituted tobermorite, the ion exchange experiments were employed as a test reaction.

**Key words:** gyrolite, Z-phase, 1.13 nm tobermorite, pectolite, calcium-silicate-hydrate

## **Electrical Properties and Relaxation Behavior of TOPO Monolayers Formed at the Air/Water Interface**

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*(Received August 1st, 2006; revised manuscript October 26th, 2006)*

The properties of the Langmuir monolayer formed by tri-*n*-octylphosphine oxide (TOPO) have been analyzed. The investigations were based both on traditional (surface potential measurements) and more advanced (the relative reflectivity using Brewster angle microscopy BAM) experimental techniques and, for better analysis, the semiempirical computation using HyperChem programme has been done. Moreover, detailed characteristics of the relaxation behaviour of TOPO monolayers have been performed. It has been found that with the increase of the surface pressure ( $\pi$ ) the film thickness increases, and TOPO monolayer becomes denser; however its state does not change. Upon film compression, the reorientation of TOPO molecules occurs in this way that they become progressively more perpendicular to the surface until the collapse of the monolayer. The relaxation of TOPO monolayers formed both on water subphase as well as on NaCl solution of various concentrations were analyzed according to two-steps desorption mechanism. As it turned out, the stability of TOPO monolayer decreases with the surface pressure. At lower  $\pi$  the loss of the monolayer material is controlled both by dissolution and diffusion mechanism, while at higher surface pressure the monolayer relaxation is controlled by two dissolution steps of different rates and the monolayer does not achieve a steady-state. Moreover, the monolayer stability increases with ionic strength.

**Key words:** tri-*n*-octylphosphine oxide (TOPO), Langmuir monolayers, surface potential, relative reflectivity, relaxation phenomena

## **Charge Storage Properties of Hydrous Molybdenum Oxide Thin Films**

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*(Received July 4th, 2006; revised manuscript October 30th, 2006)*

Non-stoichiometric mixed-valent molybdenum oxide film was grown on a glassy carbon (GC) substrate by the electrodeposition method. The specific capacitance of this deposit was studied by cyclic voltammetry, chronopotentiometry and impedance spectroscopy. This non-stoichiometric hydrous oxide exhibits capacitive behaviour between  $-0.5$  and  $-1.0$  V (vs. Ag, AgCl|3 M KCl) in 0.1 M  $K_2SO_4$ . The specific capacitance of studied deposit achieves the value of  $160 \text{ F}\cdot\text{g}^{-1}$ .

**Key words:** molybdenum oxide, electrodeposition, impedance spectroscopy, pseudo-capacitance, supercapacitor

**King Is Naked: Comparison of *ab initio*  
and DFT Calculations of Magnetic Shielding  
of  $^{13}\text{C}$  Nuclei in Chloromethanes**

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*(Received September 21st, 2006)*

**Kinetic Effects of the Coordinated Oxalato Ligand  
on Electron Transfer Between a Tetraaza Macrocyclic  
Chromium(III) Complex and Hexacyanoferrate(III)  
Ion in Alkaline Media**

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*(Received June 28th, 2006; revised manuscript October 9th, 2006)*