

## Synthesis and Structural Characterization of Self-Assembly Products Containing $[\text{Fe}(\text{CN})_6]^{4-}$ Building Blocks with Cationic $\{\text{R}_3\text{Sn}\}^+$ Fragments in the Absence or Presence of a Bidentate Uncharged Ligand $\{2\text{L}\}$

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Spontaneous self-assembly of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{R}_3\text{Sn}^+$  ions (R = Me, n-Bu or Ph) in the absence or presence of uncharged bidentate ligands (such as dioxane (diox), methylpyrazine (Mepyz), or 4,4'-bipyridine (bpy)) affords white precipitates. The products with the general composition  $[(\text{R}_3\text{Sn})_4\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O} \cdot 2\text{L}]$ ; 2L = diox, Mepyz or bpy, have been obtained as host-guest polymeric architecture. The new compounds have been compared with their hydrated systems  $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}]$ ; x = 2 or 4 and with the water-free  $[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6]$ . Results of extensive spectroscopic investigations (IR studies and X-ray powder diffractometry) suggest that the architecture of the novel host-guest systems involve three-dimensional networks, notably different from those of their parent system (containing four  $\text{H}_2\text{O}$  molecules). These compounds show no ion-exchange activity towards  $\text{NH}_4^+$  cations and are affected by moderate temperature. Also, these 3D-host-guest polymeric systems exhibit a high sensitivity to pH of the media.

## Synthesis, Spectral and Antiferromagnetic Interaction in Oxalato-Bridged Linear Trinuclear Oxovanadium(IV) Complexes

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Three new linear trinuclear oxovanadium(IV) complexes bridged by oxalato (ox) and end-capped with 2,2'-bipyridine (bpy); 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline (NO<sub>2</sub>phen); respectively, namely [(VO)<sub>3</sub>(ox)<sub>2</sub>(bpy)<sub>2</sub>]SO<sub>4</sub> (**1**), [(VO)<sub>3</sub>(ox)<sub>2</sub>(phen)<sub>2</sub>]SO<sub>4</sub> (**2**) and [(VO)<sub>3</sub>(ox)<sub>2</sub>(NO<sub>2</sub>phen)<sub>2</sub>]SO<sub>4</sub> (**3**), have been synthesized and characterized by elemental analyses, molar conductivity, magnetic measurements, IR, ESR and electronic spectral studies. It is proposed that these complexes have extended ox-bridged structures, consisting of three oxovanadium(IV) ions, each in a distorted square-pyramidal environment. Variable-temperature magnetic susceptibility measurements (4.2~300 K) of the complexes (**1**) and (**2**) revealed the occurrence of an intramolecular antiferromagnetic interaction between the oxovanadium(IV) ions through the oxalato-bridge within each molecule. The magnetic data have been also used to deduce the indicated structure. On the basis of spin Hamiltonian operator,  $\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3)$ , the magnetic analyses were carried out for the two trinuclear complexes and the spin-coupling constants (J) were evaluated as  $-9.85 \text{ cm}^{-1}$  for (**1**) and  $-10.16 \text{ cm}^{-1}$  for (**2**).

## **Phase Equilibria in the Ternary System $\text{Nd}_2\text{O}_3\text{--K}_2\text{O--P}_2\text{O}_5$ . The partial system $\text{NdPO}_4\text{--KPO}_3\text{--Nd}(\text{PO}_3)_3$**

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In the ternary system  $\text{Nd}_2\text{O}_3\text{--K}_2\text{O--P}_2\text{O}_5$  a partial system  $\text{NdPO}_4\text{--KPO}_3\text{--Nd}(\text{PO}_3)_3$  was investigated by thermoanalytical methods, X-ray powder diffraction and microscopy in reflected light and its phase diagram was proposed. In the system a double metaphosphate  $\text{KNd}(\text{PO}_3)_4$  appears. The compound forms in a side system  $\text{Nd}(\text{PO}_3)_3\text{--KPO}_3$ . It has been established that the  $\text{KNd}(\text{PO}_3)_4$  and  $\text{NdPO}_4$  form a section, which is a real system only in the subsolidus region. It is found, that a ternary peritectic ( $t_p \sim 885^\circ\text{C}$ ) and a ternary eutectic ( $t_E \sim 688^\circ\text{C}$ ) occur in the partial system  $\text{NdPO}_4\text{--KPO}_3\text{--Nd}(\text{PO}_3)_3$ .

**Photochemical Oxidation of 1,3-Dithianes with  
*tert*-Butyl Hydroperoxide (TBHP)**

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A variety of 1,3-dithianes deprotected to their corresponding carbonyl compounds in good to excellent yields in mild and efficient photo-oxidative method using *tert*-butyl hydroperoxide.

## **Trialkylsilyl Triflates – Practical Diastereoselective Catalysts in Conjugate Addition Reaction of Silyl Ketene Acetals and $\alpha,\beta$ -Unsaturated Ketones**

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Catalytic effect of trimethylsilyl triflate (TMSOTf) or *tert*-butyldimethylsilyl triflate (TBSOTf) in conjugate addition reaction of the respective trialkylsilyl derivatives of thioester enolates (silyl ketene acetals) **2a–2e** and  $\alpha,\beta$ -unsaturated ketones **1a–1c** has been studied. It was shown that silyl triflates are efficient catalysts with stereochemical profile similar to that of trityl hexachloroantimonate. The use of silyl triflates is particularly advantageous in tandem reactions involving conjugate addition as the first step.

## **Effect of Base and Acyl Chloride on Regioselectivity of Acylation of 8,8-Pentamethylene-2-methyl-7,9-dioxo-1-azaspiro[4.5]dec-1-ene 1-Oxide**

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Acylation of 2-methyl-7,9-dioxo-1-azaspiro[4.5]dec-1-ene 1-oxide (**5**) in the presence of pyridine gives 3-acyloxy-2-methyl-1-pyrroline derivatives **6** independently of kind of acid chloride, while treatment of **5** with benzoyl or *p*-nitrobenzoyl chloride and triethylamine affords mainly 2-benzoyloxymethyl-**8a** and 2-*p*-nitrobenzoyloxymethyl-1-pyrroline **8b**, respectively. Acetylation of **5** was base-independent.

## New Functionalized Derivatives of Sulfur- and Oxygen-Containing Hexacyclic Cage Compounds

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Several new sulfur- and oxygen-bridged hexacyclic cage compounds have been obtained via transannular cyclization of pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane-8,11-dione (**1**). Thus, cage-annulated thiapodands **9** and **10** were prepared via reaction of ditosylate **6** with 2-mercaptoethylamine (**7**) or 2-mercaptoethanol (**8**), respectively. Other ditosylate **11** was reacted with thiourea to afford the corresponding dimercapto podand **12**. An optically active podand (**R,R**)-**14** was prepared in similar fashion by reacting ditosylate **6** with (*R*)-2-amino-1-butanol (**R**)-(**13**). Functionalized 4-thiahexacyclo[5.4.1.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>.0<sup>8,11</sup>]dodecanes **17a–b** and **18a–b** were prepared via reactions of **1** with 2-chloro- (**15**) or 2-bromoethanol (**16**), respectively in the presence of H<sub>2</sub>S(g) and HCl(g). The corresponding reaction of **1** with 2 equivalents of **8** produced the corresponding bithioacetal **20**, which subsequently was changed into a spiro-cage-annulated dithiacrown ether **22**.

## Hydrogen Peroxide Oxidation of Naphthalene Derivatives Catalyzed by Poly(bis-1,2-diphenylene) Diselenide

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Oxidation of 1- and 2-substituted naphthalenes (**1**) with 30% hydrogen peroxide in the presence of poly(bis-1,2-diphenylene) diselenide (PPDS) has been investigated. Depending on the substrate used *trans*-2-carboxycinnamic acid (**2**), and its isomer, (1-oxo-1,3-dihydroisobenzofuran-1-yl)acetic acid (**3**) or 2-naphthoic acid (**4b**) was a major product. Oxidation of hydroxynaphthalenes **1b** and **1c** is a convenient way to obtain *trans*-2-carboxy cinnamic acid (**2**) in almost quantitative yield. The mechanism of the reaction is postulated.

**Creatinine and Creatinium Cation in Water Solution.  
Tautomerism and Quantitative Interpretation of the  
Solution Acidity Effect on  $^1\text{H}$ ,  $^{13}\text{C}$  and  
 $^{14}\text{N}$  NMR Chemical Shifts**

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$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR chemical shifts for creatinine in water solutions of various acidity have been measured. Analysis of these data enabled determination of the acidity constant of creatinium cation and the chemical shifts of the neutral and protonated forms of creatinine. Molecular energies and carbon and nitrogen magnetic shielding constants for various tautomeric structures of the investigated species have been calculated using the quantum chemistry method GIAO DFT B3LYP/6-311++G(2d,p). Compilation of the available experimental and theoretical results has provided additional information on the problem of tautomerism of this important biological molecule.

## **Synthesis of 2-Alkylbenzofurans *via* Acid-catalyzed Cyclization of 1,1-Dimethoxy-2-phenoxyalkanes**

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Treatment of 2-phenoxyalkanes **1a–e** with methanol at room temperature under homo- or heterogeneous acid-catalysis conditions leads to formation of diacetal as well as some quantities of appropriate 2-alkylbenzofurans. 2-Alkylbenzofurans **3a–e** were obtained in high yields *via* cyclization of the 1,1-dimethoxy-2-phenoxyalkanes **2a–e** under mild conditions over Amberlyst 15.

## **Synthesis of 8-*Epi*-9-*epi*-isolactarorufin, the First *trans* Fused Rings Isolactarane Sesquiterpene**

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8-*Epi*-9-*epi*-isolactarorufin, the first *trans* fused rings isolactarane sesquiterpene was synthesized. Its stereochemistry was determined by  $^1\text{H}$  NMR spectroscopy and X-ray analysis.

## **Oxidation of Hexacyanoferrate(II) by Peroxynitrite. A Mechanistic and Kinetic Study**

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A kinetic study of the oxidation of hexacyanoferrate(II) by peroxynitrite has been carried out, using a stopped-flow technique. The variation of the experimental rate constant over a wide concentration range of  $\text{Fe}(\text{CN})_6^{4-}$  has been investigated under different experimental conditions in terms of pH, ionic strength and temperature. A correlation between  $k_{\text{exp}}$  and the substrate concentration has been obtained and this shows first-order behavior in substrate at high concentrations of  $\text{Fe}(\text{CN})_6^{4-}$ . A reaction mechanism is proposed, in which the hexacyanoferrate(II) reacts in competitive pathways with the peroxynitrous acid (direct oxidation) and with  $\text{HO}\cdot$  and  $\cdot\text{NO}_2$  radicals formed in the homolysis of the peroxide bond of  $\text{HOONO}$  (indirect oxidation). Moreover, two individual constants,  $k_c$  (the formation constant of the germinated radical pair [ $\text{HO}\cdot \cdot\text{NO}_2$ ]) and  $k_7$  (direct oxidation constant), have been evaluated together with the thermodynamic parameters of these elementary steps.

## **Thermal Expansion Studies of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ . A New Refractory Material**

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The X-ray diffraction measurements of a  $\text{CaAl}_4\text{O}_7$  single crystal have been performed at seven temperatures above ambient, over a 300–773 K temperature range. The evolution of the lattice parameters was used to determine the second rank thermal expansion tensor of the crystal. The thermal expansion is minor and highly anisotropic. The principal thermal expansion coefficients are:  $7.91 \cdot 10^{-6}$ ,  $1.12 \cdot 10^{-5}$  and  $-3.48 \cdot 10^{-6} \text{ deg}^{-1}$ . The results are discussed in relation to the crystal structure.

## Analytical Functions for the Proton Transfer in the $\text{H}_3\text{O}_2^+$ Complex Immersed in a Solvent (Water, 1-Octanol)

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The analytical functions for the energy barrier of the proton transfer in  $\text{H}_3\text{O}_2^+$  complex have been fitted by nonlinear regression from *ab initio* quantum mechanical calculations for the complex in gas phase and solvent phase (water, 1-octanol) simulated using the PCM approach. The best fitted function describing the proton transfer energy for any distance  $R$  between  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  and for any proton position is of the form  $E(R, r) = E(R/2)\text{Erfc}(z)$ , where  $\text{Erfc}(z)$  is the complementary error function,  $z = [(r - 0.5R)/c]^2$ ,  $R$  is the  $\text{O}(\text{H}_3\text{O}^+) - \text{O}(\text{H}_2\text{O})$  distance,  $r$  is the space position of proton relative to  $R/2$  and  $c$  a constant determined by regression for each proton transfer at a given  $R$  distance. The fitted functions are:  $E(R/2) = [a + b/(R/2)]^2$  which is the highest potential energy value for the proton situated at  $R/2$  and  $c = a + b \ln(R/2)$ . The energy barriers for the solvent phase are higher than those for the gas phase, because of the solute–solvent interactions considered by PCM. The energy barrier for the 1-octanol phase is somewhat lower than that for water phase, most likely due to the amphipathic character of the 1-octanol. The energy potential values for the proton transfer in solvent can be expressed as a sum of two terms corresponding to the gas phase and to solvent effects contributions.

## **Kinetics of Methanol Decomposition on Cu/ZnO/ZrO<sub>2</sub> Catalysts**

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Interaction of methanol with Cu/ZnO/ZrO<sub>2</sub> (with different copper content) has been investigated by gravimetric and TPD methods. The TPD measurements of methanol adsorption on these catalysts show that it forms the complexes of two types. The first complex (I) decomposes at low temperature (453 K) yielding H<sub>2</sub> and CO<sub>2</sub> and second (II) decomposes at the temperature (573 K) giving CO and H<sub>2</sub>. In the process of the decomposition of the complex (I) takes part water which is adsorbed on the surface of the catalyst and the decomposition of the complexes (II) occurs without participation of adsorbed water. Gravimetric measurements of methanol adsorption show that Cu facilitates adsorption of methanol and that an increase of copper content leads to the changes in the kinetics of methanol adsorption and its decomposition. On the basis of gravimetric measurements a model of methanol adsorption and decomposition on Cu/ZnO/ZrO<sub>2</sub> catalyst has been proposed and the rate constants of methanol adsorption ( $k_a$ ) and decomposition with and without participation of water ( $k_1$  and  $k_2$ ) have been determined.

**Catalytic Ketonisation Over Oxide Catalysts. Part IX.  
Single Step Synthesis of Aliphatic Saturated and  
Unsaturated C<sub>11</sub> – C<sub>13</sub> Ketones from Carboxylic Acids**

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Metameric undecan-x-ones (x = 2–6), dodecan-y-ones (y = 2–5), tridecan-z-ones (z = 4–7) and two unsaturated aliphatic ketones were prepared by vapor phase ketonisation of the appropriate monocarboxylic acids in the presence of 20 wt% MnO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst under flow conditions. The ketones were obtained in yields between 48 and 89% in a multigram scale (80–250 g). Their physical and spectral data have been determined.

**Synthesis, Structure and Antibacterial Activities of Schiff  
Base Derived from PMBP with 2-Furfurylamine  
and Its Complexes**

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**Stability of Co(II), Ni(II) and Cu(II) Complexes with  
Methoxyacetic, Phenylacetic and Cyclohexylacetic Acids**

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**Peptide Bond Modification. I. Simple and Efficient  
Method of Boc-Gly $\Psi$ [CH(OH)CH<sub>2</sub>]Gly-OH Synthesis**

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**DNA Changes Dramatically Photoisomerization  
of Arylstilbazolium Ligands**

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