Direct Room-Temperature Synthesis of Ni(Hdmg)$_2$ Nanorods

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A simple and fast route based on microemulsion synthesis approach was developed to synthesis one-dimensional (1D) nanostructures of Ni(Hdmg)$_2$ (H$_2$dmg = dimethylglyoxime) using nickel chloride and H$_2$dmg as reactants. Scanning electron microscopy (SEM), transmission electron microscope (TEM), IR spectra and elemental analysis were adopted to characterize the as-prepared Ni(Hdmg)$_2$ nanostructures. The sizes of as-prepared nanorods can be adjusted easily and the formation mechanism was proposed tentatively. The successful synthesis of Ni(Hdmg)$_2$ nanorods provide a convenient avenue for tailoring nanocrystals of complexes containing organic groups that are sensitive to temperature.

Key words: nanostructures, microemulsion technique, complexes, dimethylglyoxime

Magnetic Properties of Novel One-Dimensional Ni(II) Chain and Binuclear Cu(II)–Ni(II) Complexes

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A novel one-dimensional chain with nickel(II) macrocyclic complex and extended terephthalato-bridged, namely, [Ni(L)(TPHA)]·8H$_2$O (**1**) (L = 1,3,6,9,11,14-hexaaza-tricyclo[12.2.1.1^{6,9}]octadecane, TPHA = terephthalate dianion) and a new binuclear Cu(II)–Ni(II) complex, [Cu(oxap)Ni(bpy)$_2$](ClO$_4$)$_2$·2H$_2$O (**2**) [oxap = N,N′-bis(2-aminopropyl)oxamido dianion, bpy = 2,2′-bipyridine] have been magnetically characterized by variable-temperature magnetic susceptibilities measurements. The fitting results of the magnetic data of all two complexes support exhibiting the occurrence of an antiferromagnetic coupling with J values of -1.25 cm^{-1} for **1** and -93.9 cm^{-1} for **2**, respectively.

Key words: complexes, terephthalato- and oxamido bridges, magnetic properties, macrocyclic complex

Catalytic Transfer Hydrogenation of Cycloalkanones on MgO. Vapour and Liquid Phase Modes of Reaction

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The reactivity of a series of cycloalkanones of the general formula $(CH_2)_nCO$, where n = 4, 5, 6, 7, 11 and 14 in the transfer hydrogenation reaction over magnesium oxide as the catalyst, either in vapour or liquid phase (VP or LP) has been studied. In the VP mode of reaction the activity of MgO treated with triethylamine, water, phenol or benzoic acid in the reduction of cyclopentanone by propan-2-ol has been determined. A strongly diminished or residual activity of MgO has been observed after the catalyst's treatment with phenol or benzoic acid, respectively. The occurrence of side reactions of cyclopentanone in the LP mode of reaction resulted in high conversions of the ketone (up to 91%), very low yields of cyclopentanol (I) (below 6%) and very high yields of 2-cyclopentyli-dene-cyclopentanone (II) (>80%).

Synthesis of Endothiopeptides by Using the 'Azirine/Oxazolone Method'

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The reaction of *tert*-butyl- or THP-protected mandelic thioacid (**7a** and **7b**) with *N*,*N*,2,2-tetramethyl-2*H*-azirin-3-amine (**2a**) gave the dipeptide analogues *t*Bu- and THP-Mns-Aibψ[CS]NMe$_2$ (**8a** and **8b**, resp.) with a C-terminal thioamide group. Treatment of **8a** with HCl gas in toluene led to 2-(1-*tert*-butoxybenzyl)-4,4-dimethyl-1,3-thiazole-5(4*H*)-one (**9**), which reacted with dimethylamine *via* ring opening to give *t*Bu-Mnsψ[CSNH]Aib-NMe$_2$ (**11a**), an isomer of **8a** with the thioamide group within the chain, *i.e.*, the product of a sulfur migration. In the case of **8b**, selective deprotection of the THP-hydroxy group was achieved by treatment with pyridinium *p*-toluenesulfonate (PPTS) in ethanol. Cyclization of the resulting Mns-Aibψ[CS]NMe$_2$ (**13**) yielded the 2-thioxomorpholin-5-one **10**. In a similar manner, Boc-Val-SH (**14**) reacted with azirine **2b** to give Boc-Val-Aibψ[CS]N(Me)Ph (**15a**), which was transformed to Fmoc-Val-Aibψ[CS]N(Me)Ph (**15b**) and further to Fmoc-Valψ[CSNH]Aib-N(Me)Ph (**16**) by treatment with ZnCl$_2$ in acetic acid. Coupling of two of these molecules *via* the 1,3-thiazol-5(4*H*)-one **17** yielded the endodithiopeptide Fmoc-Valψ[CSNH]Aib-Valψ[CSNH]Aib-N(Me)Ph (**19**).

Synthesis, Structure, and Pharmacological Screening of 2,7-Naphthyridine Derivatives

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An attempt to rearrange pyrrolo[3,4-*c*]pyridine-1,3-diones to the 2,7-naphthyridine ring under the conditions, described in only one report [1], gave compounds **7–9**, but did not yield the expected 2,7- or 2,6-naphthyridine isomers. Important for the synthesis of the naphthyridine ring from pyrrolo[3,4-*c*]pyridine was that, of the two possible isomers, only 2,7- not 2,6-naphthyridine was obtained. Ethyl (4-**R′**-1,3-dioxo-6-phenyl-1,3-dihydro-2*H*-pyrrolo[3,4-*c*]pyridin-2-yl)acetate (**5**, **6**, **10**) treated with sodium ethoxide was rearranged by the Claisen-Dieckmann reaction to ethyl 4-hydroxy-8-**R′**-1-oxo-6-phenyl-1,2-dihydro-2,7-naphthyridine-3-carboxylate (**13**, **14**), where **R′** = methyl or ethoxy. The structures of the new compounds were confirmed by elemental analysis and NMR and IR spectra. The structure of **14** was also determined by X-ray crystallography to prove the presence of 2,7-naphthyridine isomer. The *in vitro* anticancer activities of the final 2,7-naphthyridines were tested at the US NCI (Bethesda, MD). Compound **13** exhibited cytostatic activity *in vitro*.

Key words: pyrrolo[3,4-*c*]pyridines, 6-phenyl-2,7-naphthyridine-3-carboxylate derivatives, anticancer activity

Solvatochromism of Dyes. Part V. Apparent or Real Solvation Parameters?

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The UV/VIS spectroscopic behaviour of 7H-indolo[1,2-a]quinolinium perchlorates and their precursors, *i.e.* 1-phenyl-2-[2-(3-X-5-methoxy-4-hydroxyphenyl)ethenyl]-3,3-dimethyl-3H-indolium derivatives (X = Br, Cl, NO$_2$) in binary solvent mixtures is described. Based on the solvation equilibrium constants determined using the SA-SAB-SB model, a discussion of an influence of a band-shape parameter χ and a parameter for non-specific solute/solvent interactions β on the results obtained is presented. The evaluated real equilibrium solvation constants allow to describe properly the preference of solvation.

Key words: solvatochromic dyes, binary solvent mixtures, SA-SAB-SB model, solvation equilibrium constants, solvation preference, non-specific solute/solvent interactions

Synthesis of the Potential Mannosidase Inhibitor _via_ 1,3-Dipolar Cycloaddition Involving Cyclic Nitrone and Unsaturated Chiral γ-Lactone

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The 1,3-dipolar cycloaddition of cyclic nitrone derived from tartaric acid with (_S_)-5-hydroxymethyl-2(5_H_)-furanone leads to a single adduct which was transformed into 1,2,6,7-tetrahydroxy-2-hydroxymethyl-indolizidine _via_ reaction sequence involving protection of the hydroxymethyl group, reduction of the lactone moiety, protection of the resulting diol, and the _N–O_ hydrogenolysis followed by the intramolecular alkylation of the nitrogen atom.

Key words: nitrone, iminosugars, 1,3-dipolar cycloaddition

Efficient Catalytic Systems for Synthesis of 5,5″-Dibromo-2,2′:6′,2″-terpyridine and 5,5′-Dibromo-2,2′-bipyridine *via* Coupling of Dihalogenopyridines with 5-Bromo-2-trialkylstannylpyridines

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The results of the studies on the synthesis of 5,5′-dibromo-2,2′-bipyridine and 5,5″-dibromo-2,2′:6′,2″-terpyridine *via* coupling of 5-bromo-2-iodopyridine and 2,6-dihalogenopyridines with 5-bromo-2-trialkylstannylpyridines mediated by palladium catalysts have been presented. The catalytic activity of the Pd(II) and Pd(0) complexes (*e.g.* [PdCl$_2$(PPh$_3$)$_2$], [PdCl$_2$(COD)], [Pd(dba)$_2$]), and catalytic systems generated *in situ* from a stable precursor (*e.g.* [PdCl$_2$], [Pd(acac)$_2$]) and an external ligand (APh$_3$, where A = P, As, Sb; phosphines, phosphites) in the coupling of diiodopyridine with 5-bromo-2-tributylstannylpyridine was investigated. The most active system was that generated from [Pd(acac)$_2$] and P(OPh)$_3$, while the highest coupling selectivity was achieved with [Pd(acac)$_2$] and PPh$_3$. The catalytic activity of systems containing chelating ligands BINAP or dppf was slightly inferior. In all reactions the formation of 5,5′-dibromo-2,2′-bipyridine, the product of homocoupling of 5-bromo-2-tributylstannylpyridine, was observed. An increase of the L/Pd ratio for catalytic system generated from [Pd(acac)$_2$] and P(OPh)$_3$ resulted in improved selectivity of dbtpy formation (the yield of dbbpy, the product of homocoupling, decreased) and in an increased stability of the catalytic system (without decreasing the reaction rate even for Pd/L = 1:32). On the other hand, for the systems containing phosphines the increase of L/Pd above 4:1 for monodentate phosphines and above 2:1 for bidentate phosphines resulted in a fast decrease of the reaction rate. The coupling is faster for 2,6-diiodopyridine and slower for 2,6-dibromopyridine, while 2,6-dichloropyridine is nonreactive. The yield of coupling for trimethyl- and tributylstannyl derivatives is practically identical. Particularly advantageous solvents for the studied coupling reaction are xylene, toluene, and 1,2-diethoxyethane.

Key words: Stille coupling, palladium catalyst, dibromoterpyridine synthesis, dibromobipyridine synthesis

Synthesis, Crystal Structure, Characterization and
Ab Initio Calculations on a Dicycle Pyrazoline Derivative

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A dicycle pyrazoline derivative, 1-acetyl-5-(2-chlorophenyl)-3,4-(α-*o*-chlorotolylene-cyclohexano) pyrazoline, was synthesized and characterized by elemental analysis, IR, UV-Vis, fluorescence spectra and X-ray single crystal diffraction. Quantum chemical calculations were performed by using B3LYP and HF methods with 6-311G* basis set. Both methods can well simulate the molecular structure. Vibrational frequencies were predicted, assigned and compared with the experimental values, which suggest that both methods can only approximatively predict the vibrational frequencies. Electronic absorption spectra predicted by B3LYP/6-311G* method well corresponding with the experimental data and natural bond orbital analyses indicate that the absorption bands are mainly derived from the contribution of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. For the system studied here, HF/6-311G* method can not be used to obtain the electronic absorption spectra. On the basis of vibrational analysis, the thermodynamic properties of the title compound at different temperature have been calculated, revealing the correlations between $C_{p,m}^0$, S_m^0, H_m^0 and temperature.

Key words: crystal structure, vibrational frequency, electronic absorption spectra, fluorescence spectra, quantum chemical calculation

The Effects of Diluents on Sodium Ion Transport through Bulk Liquid Membrane with Crown Ether Carriers

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In this study, the effects of the different membrane diluents, carriers and variations in the concentrations of the carriers on the sodium ion transport were examined in bulk liquid membrane systems. The kinetic analysis of the sodium ion transport in the liquid membrane was performed through the implementation of two consecutive kinetic equations of first order irreversible reactions and the relevant kinetic parameters (k_1, k_{2a}, k_{2m}, R_{max}, t_{max}) were determined. Toluene, *n*-hexane, 1-octanol, chloroform and dichloromethane were used as membrane diluents, while 18crown6 (18C6), dicyclohexyl 18crown6 (DC18C6) and dibenzo 18crown6 (DB18C6) were used as carriers. The results reveal that the best sodium ion transport was realized when toluene-dichloromethane (90%–10%) was used as the membrane, and $1 \cdot 10^{-3}$ M DB18C6 was used as the carrier.

Key words: bulk liquid membrane, diluent's effect, crown ethers, sodium, kinetic analysis

Ab Initio Study of AuTe₂ Cluster

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The geometries of the lowest-lying isomers of small AuTe₂ cluster are determined through the MP2 method. The aspect of gold–telluride and telluride–telluride interaction, the electron correlation and relativistic effects on geometry and stability were investigated at the different theoretical levels of electron correlation. The results show that the electron correlation and relativistic effects are responsible not only for telluride–telluride attraction but also for additional gold–telluride interaction. Both effects are essential for determining the geometry and relative stability of coinage metal telluride compound AuTe₂ cluster.

Key words: metal telluride cluster, *ab initio*, electron correlation, relativistic effect

Preparation and Characterization of the Colloidal Ru/γ-Al$_2$O$_3$ Catalysts

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Highly dispersed ruthenium nanoparticles were prepared by a microwave-assisted polyol heating process and supported on γ-alumina. The structure of the Ru/γ-Al$_2$O$_3$ catalysts with different metal loadings was investigated using BET, XRD, TEM and HRTEM. The chemisorption of hydrogen and oxygen on the resultant supported metal materials was investigated as a means of determining the dispersion of the samples. Electron microscopy showed that the Ru nanoparticles were uniformly distributed on the alumina surface and their mean size slightly increased from 1.3 to 2.1 nm with Ru loading rising from 1.2 to 8.6 wt.%. For all samples, oxygen adsorption at RT was somewhat higher than at 0°C indicating some subsurface oxidation of small Ru nanoparticles. This process does not, however, affect significantly the Ru dispersion calculated from the O$_2$ uptakes at 0°C or at RT. Assuming a stoichiometry O/Ru$_s$ = 2, good agreement was obtained between the average Ru particle size calculated from O$_2$ and H$_2$ adsorption and TEM data. The formation of the surface oxide with stoichiometry close to RuO$_2$ on the surface of the Ru metal nanoparticles after O$_2$ uptake measurements was established, but no such phase was detected by HRTEM. Much lower value of O/Ru$_s$ < 1 was found, however, for the catalyst with the highest Ru loading. A large discrepancy between the results of O$_2$ adsorption and TEM for this sample was interpreted as an indication of partial encapsulation of the Ru particles with the support and/or that the metal surface was not reduced completely.

Key words: Ru nanoparticles, TEM, XRD, oxygen adsorption, hydrogen chemisorption, Ru/γ-Al$_2$O$_3$ catalyst

Influence of Vibration Changes on Jahn-Teller Distortion in $[Fe(H_2O)_6]^{2+}$ and $[Fe(NO)(H_2O)_5]^{2+}$

by H.T. Sun[1], Y.M. Li[2], Z.Z. Wang[1], C.F. Su[1], Z.Y. Zhou[1,2*] and K. Tang[1]

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Density functional theory (DFT) calculation and vibrational modes have been reported for the ferrous hexaaquo ions and ferrous cinqueaquo nitrosyl ions, using B3LYP gradient-corrected density functionals at standard 6-31+G(d) basis. The effect of hydrogen bonding in solvents has been influenced by polarizable continuum models (PCM). The optimized structures predict an abnormal FeO_6 octahedron for $[Fe(H_2O)_6]^{2+}$ reflecting a Jahn-Teller distortion with the H_2O molecules lying in the FeO_4 plane *in vacuo*. In $[Fe(NO)(H_2O)_5]^{2+}$, the Jahn-Teller distortion is more evident and the H_2O molecules are pushed from the FeO_4 plane. Then compared with the PCM methods, the Jahn-Teller distortion has been found to strengthen in the polarizable continuum model. Moreover, with the investigation of the vibrational mode and occupied orbital, we have found that the Jahn-Teller distortion has stronger influence on nitrosyl group than on H_2O molecules.

Key words: vibration, $[Fe(NO)(H_2O)_5]^{2+}$, $[Fe(H_2O)_6]^{2+}$, Jahn-Teller distortion

Effects of Short-chain Alcohols on the Phase Behavior, Solubilities and Solubilization Ability in Microemulsion Systems

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The effects of short-chain alcohols on the phase behavior, solubilities and solubilization ability in the microemulsion systems cetyltrimethyl ammonium bromide (CTAB) or cetylpyridinium bromide (CPB*)* or 1-hexadecyl-3-methylimidazolium bromide (C_{16}mimBr)/1-propanol or 1-butanol or 1-pentanol/*n*-octane/brine were investigated with the δ-γ fishlike phase diagram. The phase diagram was affected greatly by alcohols, and the magnitude of the middle phase region in the fish body is in the order 1-propanol >> 1-butanol > 1-pentanol. With the carbon chain length becoming shorter, more alcohol molecules are needed to balance the interfacial layer. Nearly all surfactants enter into the interfacial layer and little remains in aqueous or oleic phase. However, alcohols dissolve in the aqueous and oleic phases, besides they enter into the interfacial layer. The solubilization ability of the microemulsion system is mainly affected by the alcohols and the order is 1-pentanol > 1-butanol > 1-propanol.

Key words: phase behavior, solubility, solubilization, microemulsion, short-chain alcohol

Modified Ebulliometer for the Accurate Determination of Vapour-Liquid Equilibrium

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The modification of the Świętosławski ebulliometer for the accurate determination of vapour–liquid equilibrium at pressures between 5 and 300 kPa and temperatures from 300 to 500 K is described. The measurements can be performed with or without the determination of the composition (at very low and the whole range of concentrations) of the liquid and vapour phases at equilibrium. The accuracy of results obtained is limited only by the purity of the substances used and by the precision of weighing and introduction of the samples into the ebulliometer. The performance of the proposed modified ebulliometer has been checked on the five different in their nature pure substances: *n*-hexane, cyclohexane, acetone, methanol, water and one binary, very difficult for measurement mixture of acetone and methanol.

Crystal Structure of Potassium Samarium Octacyanomolybdate(IV) Decahydrate

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Nearly Monodisperse Nanoparticles of Prussian Blue Analogue Ni$_3$[Fe(CN)$_6$]$_2$·H$_2$O

by C.H. Li[1,2], J.T. Wang[1] and Q. Peng[2]**

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