

Complexes of Benzenboronic Acid and Triphenylboroxin with Amines

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Benzenboronic acid reacts with aliphatic amines to give a stable 1:1 complex formed by triphenylboroxin with an amine molecule. The structure of the complex of triphenylboroxin with n-butylamine (1) has been determined by X-rays. Several complexes with other amines have been characterized spectroscopically. The equilibrium in the system depends on the amine and the solvent nature.

Key words: benzenboronic acid, triphenylboroxin, complexes with amines

New Neutral Schiff Base and Its Metal Complexes Derived from Mannich Base, N-(1-Morpholinobenzyl)acetamide

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New neutral Schiff base complexes of Cu(II), Co(II), Ni(II) and Zn(II) derived from 4-aminoantipyrine and N-(1-morpholinobenzyl)acetamide (Mannich base) have been synthesized. The structural features of the complexes have been confirmed by microanalytical data, IR, UV-Vis., NMR, EPR, and CV techniques. Electronic absorption spectra of the complexes indicate an octahedral geometry around the metal ion. Their magnetic susceptibility measurements and low conductance data provide evidence for the monomeric and neutral natures of the complexes respectively. The electrochemical behaviour, the anodic and cathodic potential and the number of electrons transferred were calculated using cyclic voltammogram. The X-band EPR spectrum of copper complex in DMSO at 300 K and 77 K was recorded and its salient features are reported. The antimicrobial activity of the ligand and its complexes has been extensively studied on microorganisms such as *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruginosa* and the fungi *Aspergillus niger* and *Rhizoctonia bataicola* by well-diffusion technique using DMF as solvent. It has been found that all the complexes have higher activity than the free ligand and the standard.

Key words: 4-aminoantipyrine, N-(1-morpholinobenzyl)acetamide, Schiff base complexes, antimicrobial activity

Metal Directed Synthesis of Hexaazamacrocyclic Complexes of Co(II), Ni(II), Cu(II) and Zn(II) and Their Physico-Chemical Studies

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A series of 18-membered N₆ macrocyclic complexes was synthesized by template condensation of α, α' -dibromo-*o*-xylene and 2,6-diaminopyridine. The proposed stoichiometry and nature of the macrocyclic complexes have been confirmed on the basis of elemental analyses and conductivity data, respectively. The bonding in these complexes has been elucidated from the IR, and ¹H-NMR spectral studies, while the overall geometry has been deduced from the UV-visible, magnetic measurements and EPR spectra.

Key words: 2,6-diaminopyridine, α, α' -dibromo-*o*-xylene, hexaazamacrocyclic complexes, spectral studies, template condensation

Synthesis, Structural Characterization, Cyclic Voltammetric and Antibacterial Studies of Tetraaza 13-Membered Macrocyclic Copper(II), Nickel(II), Cobalt(II) and Zinc(II) Complexes Derived from the Schiff Base 3-Salicylidene-2,4-di(imino-4'-antipyrinyl)pentane and *o*-Phenylenediamine

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A tetraaza macrocyclic Schiff base (L), synthesized from the Schiff base 3-salicylidene-2,4-di(imino-4'-antipyrinyl)pentane (3SDAP) and *o*-phenylenediamine, acts as a tetradentate ligand to form cationic solid complexes with Cu(II), Ni(II), Co(II) and Zn(II) metal salts in ethanol. All the synthesized complexes were characterized by microanalytical data, magnetic susceptibility measurements, IR, UV-Vis, ¹H-NMR, ¹³C-NMR, ESR and mass spectral techniques. The IR and UV-Vis spectral data and magnetic susceptibility values of the complexes suggest that the [CuL]Cl₂, [NiL]Cl₂, [CoL]Cl₂ and [ZnL]Cl₂ complexes exhibit square-planar geometry. The electrolytic behaviour and monomeric nature of the chelates were confirmed from their molar conductance data and magnetic susceptibility values respectively. Cyclic voltammetric data of copper complex in DMSO reveal that the unusual oxidation states such as Cu(I) and Cu(0) are stabilized by the ligand system. The cyclic voltammogram of the nickel(II) complex was also recorded in DMSO solution and the salient features are reported. The X-band ESR spectra of the copper complex in DMSO solution at 300 K and 77 K were recorded and their spin Hamiltonian parameters were calculated. The *in vitro* biological screening effects of the investigated compounds were tested against some microorganisms. The metal complexes have higher activity than the free ligand and the standard.

Key words: 4-aminoantipyrine, macrocyclic Schiff base, ESR spectra, antibacterial studies

Some Properties of Sodium Tungsten Bronzes as a Function of Sodium Concentration

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Sodium tungsten bronzes, Na_xWO_3 have been prepared ranging in composition from $x = 0.25$ to 0.85 by solid state reaction at 850°C in argon atmosphere. X-ray diffraction and IR absorption spectra were used to characterize the structure of the product samples. It was found two distinct phases in the range from $x = 0.25$ to 0.85 , tetragonal and cubic structure. The reflectance measurements in the range from 300 to 780 nm have been performed by diffuse reflection method. The reflectivity increased with sodium concentration and it was found above 70% for the sample with higher sodium content ($x = 0.85$). The electrical conductivity (σ) has been measured as a function of sodium concentration and temperature from 300 to 550 K. The conductivity was found to increase with increasing sodium concentration and decrease with temperature for the prepared samples.

Key words: sodium tungsten bronzes, X-ray, IR, electrical conductivity, optical reflectance

Study of Complex Formation Between 18-Crown-6 with Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} Cations in Some Binary Mixed Non-aqueous Solvents Using the Conductometric Method

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The complexation reactions between Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} metal cations with 18-crown-6 (18C6) were studied in methanol (MeOH)–dimethylformamide (DMF) and ethylacetate (EtOAc)–dimethylformamide (DMF) binary mixtures at different temperatures using the conductometric method. The conductance data show that the stoichiometry of the complexes in all cases is 1:1 (ML). The values of thermodynamic parameters (ΔH_c^0 , ΔS_c^0) for 18C6– Cu^{2+} , 18C6– Zn^{2+} , 18C6– Cd^{2+} and 18C6– Pb^{2+} complexes in MeOH–DMF and EtOAc–DMF binary systems were obtained from temperature dependence of stability constants. The results show that the thermodynamics of complexation reactions is affected by the nature and composition of the mixed solvents and in most cases, the complexes are enthalpy stabilized but entropy destabilized. The stability constants K_f of all complexes increase with increasing the concentration of solvent with lower donicity (based on Gutmann donicity scale) in the binary mixed solvents. In most cases, a non-linear behaviour was observed for variation of $\log K_f$ of the complexes with the composition of the mixed solvents. The selectivity order of 18C6 for these metal cations in all solvent systems used in this study is: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$.

Key words: 18-crown-6, Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} cations, methanol – dimethylformamide, ethylacetate – dimethylformamide binary mixtures, conductometry

The Bonds Analysis of Hexamethylenetetramine

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Natural Bond Orbital (NBO) method was used for the investigation of the hexamethylenetetramine (hmt). The nature of bonds and electronic properties of the titled compound were analysed by means of quantum mechanical calculations on the structural molecular geometries from neutron diffraction measurements carried out in seven, different temperatures. Calculations were performed using density functional theory method (B3LYP) with 6-31++G(d,p) basis set. The values of total and stabilization energy, orbital populations, vibrational frequencies, dipole moments are discussed. As expected, the total hmt energy value decreases as the temperature decreases. The most profitable energy value was obtained for the lowest hmt measurement temperature, which implies that the significant and favourable reduction of thermal motion took place. The geometric parameters of hmt molecule are similar in all structures, the only normality is the shortening and hence enhancing of C–N bond with the temperature increasing. The NBO analysis of donor-acceptor interactions resulted in decreasing of localized n_N , σ_{CH} orbital occupancy, increasing of σ_{CN}^* occupancy and stabilization energy associated with following delocalizations: $n_N \rightarrow \sigma_{CN}^*$ and $\sigma_{CH} \rightarrow \sigma_{CN}^*$. The results indicated that there exist very slight interactions between this nitrogen pair and the C–H antibonding orbitals of nearest neighbouring hmt molecule when the sets of hmt molecules are considered.

Key words: hexamethylenetetramine, hmt, Natural Bond Orbital analysis

Preparation of 2-Nitro-5,10,15,20-tetraphenylporphyrin Zinc(II) Complex – *post scriptum* to Electrophilic Nitration of Porphyrins at the β -Pyrrolic Position

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The selective nitration of *meso*-tetraphenylporphyrin zinc(II) complex is described. The reaction of the above porphyrinate, with 25% or 50% HNO₃ at room temperature, results in the formation of the corresponding mono β -nitroporphyrin derivative (30–40%), accompanied by small amounts of 2,7-dinitro-*meso*-tetraphenylporphyrin zinc(II) complex. Increasing the nitric acid concentration to 50%, with a prolonged reaction time to 2 h, resulted in an increased yield of the β,β -dinitrated porphyrinates (up to 40%).

Key words: *meso*-tetraphenylporphyrin zinc(II) and derivatives, β -nitroporphyrins, electrophilic aromatic substitution

Chalcones from the Seeds of *Psoralea corylifolia*

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Psorachalcone A, a new chalcone was isolated from the seeds of *Psoralea corylifolia* and assigned the structure (2E)-1-[2,4-dihydroxy-3-(2-hydroxy-3-methylbut-3-en-1-yl)phenyl]-3-(4-hydroxyphenyl)prop-2-en-1-one **1** by spectroscopic analysis including HR-ESI-MS and 2D-NMR. In addition, known chalcones corylifol B **2**, isobavachalcone **3**, bavachalcone **4** and bavachromene **5** were also isolated from these species.

Key words: *Psoralea corylifolia*, chalcone, psorachalcone A

Quantum Chemical Study on Chiral Recognition Modes Between Esters of α -Hydroxycarboxylic Acids and Amino Acids

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Chiral recognition between methyl ester of (R)-lactic acid and (R)- or (S)-alanine has been studied by means of quantum chemistry. The interacting systems *in vacuo* have been studied up to B3LYP/6-311++G(3df,3pd)//B3LYP/6-31+G(d) and MP2/6-31+G(d) levels, while aqueous solution effects have been included *via* solvation model SM5.4 calculations. The obtained results shed new light on chiral recognition between homochiral and heterochiral α -hydroxy carboxylic acid esters and amino acids. Energy of binding by about 3 kJ/mol favors associations between homochiral (R + R) molecules of methyl ester of lactic acid and alanine then associations between heterochiral (R + S) molecules. In the heterochiral complex alanine accommodates significantly larger deformation than in the homochiral association.

Key words: chiral recognition, α -hydroxyacids, amino acids

Trifluoromethylation of Carbonyl Compounds with Trifluoromethyltrimethylsilane (Ruppert Reagent) Promoted by Triphenyldifluorostannates

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Nucleophilic trifluoromethylation of aromatic aldehydes and ketones with trifluoromethyltrimethylsilane is initiated with $\text{KF}/n\text{-Bu}_3\text{MeN}^+\text{HSO}_4^-/\text{Ph}_3\text{SnF}$ cocatalytic system in CH_2Cl_2 or with $\text{K}[\text{Ph}_3\text{SnF}_2]$ in DMF.

Key words: organofluorine compounds, tin, hypervalent compounds, phase-transfer catalysis, fluorides

Spectroscopic Characterization, Crystal and Molecular Structure of $[\text{ReBr}_2\text{N}(\text{PPh}_3)_2]$

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Rhenium nitrido-complex $[\text{ReNBr}_2(\text{PPh}_3)_2]$ has been characterized by X-ray diffraction, IR and UV-Vis spectroscopies. The geometry optimization was carried out with the DFT method using B3LYP functional. The electronic spectrum was calculated with the TDDFT method.

Key words: rhenium complexes, nitrido-complexes, X-ray structure, molecular orbital calculations

Adsorption and Desorption States of Deuterium on Sintered Thin Gold Films

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Interaction of atomic deuterium, thermally generated on hot tungsten filament with thin Au polycrystalline film was studied. The surface topography, preferential crystallographic orientation and real area of the films were determined on the basis of AFM, XRD and BET data. The experiments with deuterium were carried out measuring the change of the adsorbent resistance ΔR during D atoms adsorption under isothermal conditions (78 or 87 K). It has been found that the rate of adsorption occurs according to Eley-Rideal (ER) model. One adsorption state exists, characterized by sticking probability $S_0 = 0.25$ and ER recombination probability $\gamma = 0.22$. Measurements of the resistance changes ΔR of thin gold films with deuterium deposit caused by an increase of temperature were applied to study desorption phenomena. Differentiation of ΔR against temperature T in the course of thermal desorption reveals the existence of two desorption states with maxima of desorption rates around 120 and 170 K. We suggest that the first one corresponds to desorption of (D-D) ad-dimers, and the second one to associative desorption due to recombination of D ad-atoms. Thus the adsorption and desorption states of atomic deuterium on thin gold films differ.

Key words: atomic deuterium adsorption, thin gold films, sticking probability, recombination probability

Phase Studies on the Quasi-Binary Thallium(I) Telluride – Lead(II) Telluride System

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The phase diagram for the system $\text{Tl}_2\text{Te} - \text{PbTe}$ has been delineated from the results of phase studies by common thermal analysis. The diagram has been compared with two other diagrams published earlier for the same system, obtained by differential thermal analysis, and with that found for the analogous system $\text{Tl}_2\text{Te} - \text{SnTe}$.

Key words: thallium telluride binary system, phase diagram, thermal analysis

Density Functional Theory Study of the Hydrogen Bonding Interaction of 1:1 Complexes of Alaninamide with Water

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The hydrogen bonding of 1:1 complexes formed between alaninamide and water have been investigated using DFT and MP2 methods at varied basis set levels from 6-311g to 6-311++g(d,p). Five reasonable geometries are considered with the global minimum being a cyclic double-hydrogen bonded structure. The optimized geometric parameters and interaction energies for various isomers at different levels are estimated. The IR intensities and vibrational frequency shifts are reported. The solvent effects on the geometries of the complex have also been investigated using SCRF calculations at the B3LYP/6-311++g(d,p) level. The results indicate that polarity of the solvent has significantly influenced the structures and the relative stabilities of different isomers.

Key words: density functional theory, hydrogen bonding, solvent effect

Studies on the Distribution of Mefenamic Acid in Two-Phase Systems: Aromatic Solvent – Water

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The detailed description of equilibria of mefenamic acid in the aqueous solutions and in the two-phase systems: aromatic solvent – water was made. Isoelectric point, pH_I , dissociation constants of the protonated form, K_{a1} , and the neutral form, K_{a2} , in the aqueous solutions were determined. On the basis of the spectrophotometric investigations the values of the distribution ratio, D , of mefenamic acid were obtained. Employing the results of the potentiometric titration in the two-phase systems, organic solvent – water, and using models of singular and multistep equilibrium the values of the partition constants, K_D , and dimerization constants, K_d , were calculated. The significant influence of the polarity of the applied organic solvents and of pH of the aqueous phase on the percentage of the particular forms of mefenamic acid in the two-phase systems were proved.

Key words: mefenamic acid, liquid–liquid distribution, two-phase systems equilibria

**Unusual Baeyer-Villiger Oxidation of
23-Oxosarsasapogenin Acetate**

by **I. Jastrzębska and J.W. Morzycki**

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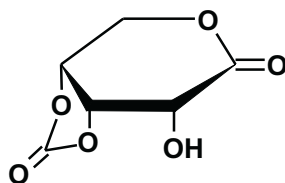
Corrigendum to “New Complexes of Ribose Derivatives”

[*Polish Journal of Chemistry* 2005, **79** (2), 323]

by I. Pintér

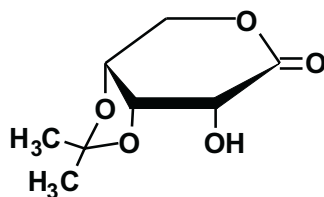
ERCOM Ltd., Budapest, U-1525 P.O. Box 17, Hungary

On page 325 structure 4:



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The author apologises for the error.