Syntheses and Structure of Ni(III) Complexes with 1-Toluene-3,4-dithiole. Bond-Valence Approach to the Oxidation State of the Central Atom

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The complex compounds of the formula (R)[Ni³⁺(tdt)₂], R = Met₄N (I), Et₄N (II), Pr₄N (III), MePh₃P (IV), Ph₄P (V); tdt = 1-toluene-3,4-dithiole have been synthesized. The crystal structures of the compounds III and IV were determined by X-rays studies. Bond valence as a function of inter-nuclear distance for Ni–S bonds was estimated. On the basis of physico-chemical measurements and bond-valence sum model, the formal oxidation state III of Ni atoms for both structures was proposed.
Isothermal Section of Phase Diagram of Lu–Ge–In Ternary System at 870 K


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The isothermal section of the Lu–Ge–In phase diagram at 870 K over the whole concentration range has been constructed using X-ray phase analysis. Only LuGe_{1-x}In_x (x = 0.035) compound (CrB-structure type, space group Cmcm, a = 4.1582(1), b = 10.4616(4), c = 3.8664(1) Å) is formed in the ternary system. The Lu5Ge3 compound dissolves up to 10 at. % of indium along the isoconcentration of lutetium 62.5 at. %.

Syntheses and Crystal Structures of Zinc(II) Complexes with Two Kinds of Benzoate Derivatives

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Two novel zinc(II) complexes of $[\text{Zn}(L_1)_2(\text{phen})] \cdot 5\text{H}_2\text{O}$ 1 ($L_1$ = 4-aminobenzoic acid, phen = 1,10-phenanthroline) and $[\text{Zn}(L_2)_2(\text{en})]$ 2 ($L_2$ = 4-methoxybenzoic acid, en = ethylenediamine) have been prepared and characterized by X-ray single crystal structural analysis. Complex 1 crystallizes in the tetragonal system, space group $I4_1/a$. The zinc atom of the central $\text{ZnO}_3\text{N}_2$ system is pentahedrally coordinated by two N atoms of phen and three O atoms of 4-aminobenzoic acid. Complex 2 belongs to orthorhombic system, space group $Pbcn$. The zinc atom of the central $\text{ZnO}_2\text{N}_2$ system lies on a twofold symmetry axis and is tetrahedrally coordinated by two N atoms of en and two O atoms of 4-methoxybenzoic acid.
Angular Overlap Treatment of cis-Dichlorobis(1,10-phenanthroline)chromium(III) Chloride Dihydrate in Aqueous Solution

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Low-symmetry mixed-ligands cis-[CrCl2(phen)2]Cl complex (phen = 1,10-phenanthroline) has been characterized spectroscopically. Electronic spectrum of aqueous solution of this complex has been measured at room temperature and interpreted using the angular overlap model (AOM), and assuming C2v symmetry. All the experimental transition energies are derived from Gaussian analysis of the solution spectrum. The calculations of the ligand-field parameters take into account all the transitions, which are required in the ligand-field theory (except those energetically higher than the range of the measured spectrum).
Novel Ferromagnetic Coupling Dicopper(II), Antiferromagnetic Dicobalt(II) and Dimanganese(II) Complexes with 3-Nitro-phthalato as Bridging Ligand: Synthesis, Spectrum and Magnetism

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Novel copper(II), cobalt(II) and manganese(II) binuclear complexes have been synthesized, namely \[ \text{[Cu}_2(3-\text{NO}_2-\text{phth})(\text{phen})_4](\text{ClO}_4)_2 \] and \[ \text{[M}_2(3-\text{NO}_2-\text{phth})(\text{phen})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \], where M = Co or Mn, phen = 1,10-phenanthroline and 3-NO\(_2\)-phth denotes 3-nitro-phthalate dianion. Magnetic susceptibility measurements between 4.2–300 K (or 77–300 K) demonstrate a ferromagnetic interaction between two copper(II) ions in the Cu–Cu complex, and a weak antiferromagnetic interaction between the metal ions in Co–Co and Mn–Mn complexes. Based on spin Hamiltonian operator, \[ H = -2J\mathbf{S}_1\mathbf{S}_2 \] \( (\mathbf{S}_1 = \mathbf{S}_2 = 1/2, \mathbf{S}_1 = \mathbf{S}_2 = 3/2 \) or \( \mathbf{S}_1 = \mathbf{S}_2 = 5/2 \)), J is found to be equal to +5.26 cm\(^{-1}\), -1.72 cm\(^{-1}\) and -0.62 cm\(^{-1}\) for the Cu–Cu, Co–Co and Mn–Mn complexes, respectively.
New Analogues of *Cucurbita maxima* Trypsin Inhibitor III (CMTI-III) Substituted with D-Arg or D-Lys in Position 5 (P₁)

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Two new analogues of trypsin inhibitor CMTI-III substituted with D-Arg or D-Lys in position 5 (P₁) were synthesized by the solid-phase method. The first analogue ([D-Arg⁵]CMTI-III) displayed association equilibrium constants (Kₐ) with bovine β-trypsin by about three orders of magnitude lower than did wild CMTI-III. The second analogue ([D-Lys⁵]CMTI-III) displayed Kₐ by about four orders of magnitude lower than [Lys⁵]CMTI-III. The configuration of basic amino acid residue (Arg or Lys) in the reactive site (position P₁) of CMTI-III and its analogues played an important role for the stabilization of the inhibitors active structure.
Composition of Tautomeric Mixtures Studied by Nitrogen Chemical Shifts and \textit{Ab Initio} Molecular Orbital Calculations

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Some nitrogen and carbon chemical shifts and \textit{ab initio} Gauge Invariant Atomic Orbitals – Coupled-Perturbed Hartree-Fock (GIAO-CPHF) calculations are reported for benzotriazole \textit{1}, 5-nitrobenzimidazole \textit{2}, 5-nitrobenzotriazole \textit{3}, 4-nitrobenzotriazole \textit{4}, and N-methyl derivatives of compounds \textit{1–3}. A good correlation is found between the calculated and observed \textsuperscript{13}C and \textsuperscript{15}N chemical shifts. Two methods were employed for calculation of equilibrium constants. The prototropic equilibria exhibited by the system studied are found to be controlled by enthalpy rather than entropy.

Hydroperoxide Oxidation of Azomethines and Alkylarenes Catalyzed by Ebselen

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2-Phenyl-1,2-benzisoselenazol-3(2H)-one (ebselen), known as glutathione peroxidase mimic, is found as an efficient catalyst for hydrogen peroxide and tert-butyl hydroperoxide oxidation of the azomethine group in azines, aldoximes, and methyl or methylene group in alkylarenes. Depending on the substrate used and the reaction conditions, the major products are aldehydes, ketones, carboxylic acids or their derivatives. It is postulated that ebselen is involved in the free-radical oxidation mechanism.
Novel Porphyrin Ribose Derivatives; Synthesis and Physicochemical Characterization

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Four new mono-ribosyl derivatives (5, 6, 9, and 11) and one four-ribosyl derivative (12) were synthesized. Complexes of a few of these compounds with metals were also synthesized. All compounds were characterized by spectroscopic methods.
Reaction of 2,2,4,4-Tetramethyl-3-thioxocyclobutanone with Dimethyl Diazomalonate Catalyzed by Rh$_2$(OAc)$_4$

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The reaction of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (1) with dimethyl diazomalonate in the presence of Rh$_2$(OAc)$_4$ in toluene at 50°C yielded a mixture of three products 10, 11, and 12. Thiocarbonyl ylide 8 is believed to be the common intermediate. The formation of 10 is rationalized by the 1,3-dipolar electrocyclization of 8 to give spirocyclic thirane 9, which spontaneously eliminated sulfur. On the other hand, the 1,5-dipolar electrocyclization of 8 led to 1,3-oxathiole 11, which is converted into lactone 12 by hydrolysis.
Reactions of 5-(2-Dimethylamino-6-methyl-4-pyrimidinylsulfanyl)methyl)-1,3,4-oxadiazole-2-thione with Carbon Electrophiles

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From 2,4-dichloro-6-methylpyrimidine (1) via esters 2 and 3, (2-dimethylamino-6-methyl-4-pyrimidinylsulfanyl)acethydrazide (4) was synthesized. The latter under treatment either with carbon disulfide in the presence of a base or with potassium O-ethylxanthate in ethanol yielded 5-(2-dimethylamino-6-methyl-4-pyrimidinylsulfanyl)methyl)-1,3,4-oxadiazole-2-thione (5). Alkylation of 5 afforded S-alkyl derivatives 6a,b, whereas aminomethylation, acylation or cyanoethylation gave N(3)-substituted derivatives 7–9. Compounds were tested for their anti-inflammatory activity.
Conduction Microcalorimetry and $^{13}$C NMR Spectroscopic Studies on the Complexing Ability of D-erythro-L-manno-D-gluco-dodecitol with Selected Lanthanide Salts in Water Solutions

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Complexing ability of D-erythro-L-manno-D-gluco-dodecitol (1) with lanthanides salts: La(NO$_3$)$_3$·6H$_2$O and PrCl$_3$·6H$_2$O in water by conduction microcalorimetry and $^{13}$C NMR spectroscopy was studied. It was compared to the complexing ability of known D-galactitol (2), D-mannitol (3), and D-glucitol (4) under the same conditions.
Influence of Intermolecular Interactions on Nuclear Magnetic Shielding Constants of OCS

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The gauge-included atomic orbital (GIAO) method has been applied within the coupled Hartree-Fock (CHF) approximation to compute $^{13}$C, $^{17}$O and $^{33}$S NMR chemical shifts for solid OCS. Increasing clusters of OCS molecules taken out of crystal lattice have been used in an additive approximation to estimate the effect of intermolecular interactions on shielding of the carbon, oxygen and sulphur nuclei. There is a very good agreement achieved for NMR chemical shifts between the results of calculations and experimental measurements obtained for $^{13}$C and also some discrepancies for $^{17}$O and $^{33}$S nuclei, probably due to deficiency of ab-initio calculations (lack of electron correlation). The results reveal that the $^{33}$S NMR signal of OCS is strongly dependent on intermolecular interactions.
A Comparison of Basicities of Substituted Pyridines
and Pyridine N-Oxides

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The basicity of pyridine and its derivatives, as representatives of monocyclic heterocyclic 
N-bases, has been compared with that of pyridine N-oxide and its derivatives representing 
the class of heterocyclic monocyclic oxygen-containing bases. The basicities have been 
compared both in the gas phase and in solution. To do this, correlated were both calculated 
(at RHF, MP2 levels and using SCRF and PCM methods) energy parameters, ΔEprot and 
ΔGprot, with experimental pKₐ values for a particular class of the bases, as well as theore-
tical and experimental characteristics of the two classes of compounds studied. Results of 
the correlations paved the way to discussion of the effect of the medium on basicity of 
both classes of compounds, as well as enabled to compare the basicities of these very 
important classes of organic bases in a quantitative way.
An Optimal Characterization of Structure by Means of Several Molecular Connectivity and Complexity Indices

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An improved numerical procedure is presented in order to enhance the possibilities of fitting polynomial equations to predict log P data within the realm of the QSAR/QSPR theory. The use of real exponents instead of restricting to integer ones for the variables in the mathematical equations gives better results and a minor number of independent variables are needed to achieve a given accuracy degree. Some possible future extensions of the method are pointed out.
Determination of Stability Constants of Complexes of Selected Amide Ionophores with Alkali Metal Cations

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Properties of four amide-type ionophores towards binding of alkali metal cations (K⁺, Na⁺, Li⁺) have been established by determining the respective complex stability constants with the use of the liquid membrane ion-selective electrodes (ISEs).
Electrochemical Behavior of Pt - Au Alloys

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The electrochemical behavior of the Pt - Au alloys in the whole composition range has been studied by cyclic voltammetry. The alloys were prepared by electrochemical deposition and the bulk compositions were determined by EDAX analysis. The surface areas of the electrodes were calculated from charges needed for oxidation of hydrogen adsorbed on platinum and reduction of gold or platinum oxide monolayer. These data were used for the estimation of the surface composition. The results were compared with data obtained from double layer capacity measurements. The surface area and platinum concentration on the surface, calculated from charges needed for platinum oxide reduction, are overestimated, because the charge needed for platinum oxide reduction corresponds to more than a one monolayer.

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Interaction of the Components in Ti–{Si, Ge}–Bi Systems at 670 K

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