Short Hydrogen Bonds in the Catalytic Mechanism of Alcohol and Lactate Dehydrogenases

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The survey of crystallographic data from the Protein Data Bank for 63 enzyme complexes with substrates indicates the presence of many short hydrogen bonds in the active site of alcohol (EC 1.1.1.1) and lactate (EC 1.1.1.27) dehydrogenases, which are formed between the substrate, or substrate analog, and the acid-base catalyst in enzyme. In the case of alcohol dehydrogenase enzymes, the short hydrogen bonds are clustering in the active site exactly at the bond-breaking position between the substrate and the acid-base catalyst in enzyme, with the frequency of 70–100\%. In lactate dehydrogenase enzymes, this frequency is much lower and amounts to 15–30\%. This result strongly suggests that the active site of alcohol dehydrogenases is designed to bind the substrate by short hydrogen bonds exactly at the bond-breaking position.

Key words: alcohol dehydrogenase, lactate dehydrogenase, short hydrogen bonds
Complexes of Mn(II), Cu(II) and Cd(II) with Bipyridine Isomers and Lactates

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The new mixed-ligand complexes containing bipyridine isomers and lactates with formulae Mn(2,4'-bpy)(lact)₂·2H₂O, Cu(2,4'-bpy)(lact)₂, Cd(2,4'-bpy)(lact)₂·2H₂O, Cd(4-bpy)(lact)₂·2H₂O (where: 2,4'-bpy = 2,4'-bipyridine, 4-bpy = 4,4'-bipyridine, lact = CH₃CH(OH)COO⁻) were obtained. These complexes and metal lactates Mn(lact)₂·2H₂O, Cu(lact)₂·2H₂O and Cd(lact)₂·H₂O were characterized by elemental analysis, IR, conductivity and magnetic measurements. The thermal behaviour of all compounds was studied by thermal analysis (TG, DTG, DTA) in air. A coupled TG/MS system was used to analyse the principal volatile products of thermolysis and fragmentation processes of Cu(II) compounds in air and argon.

Key words: bipyridine isomers, lactates, Mn(II), Cu(II) and Cd(II) complexes, IR spectra, conductivity, magnetic moment, thermal decomposition
Equilibria in Cobalt(II) – Amino Acid – Imidazole System under Oxygen-free Conditions. Part I. Studies on Mixed Ligand Systems with L-α-Alanine

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Glass electrode potentiometry and UV/Vis spectrophotometry experiments have been carried out in order to determine the equilibria in an oxygen-free Co(II)–Amac–Himid system in aqueous solution, where Amac = L-α-alanine and Himid = 1,3-diazole (imidazole). The presence of axial imidazole in the structure of the ternary complex was implicated by using a [Co(imid)]₃ polymer as starting material. Two proposed coordination modes of the mixed-ligand complex have been confirmed both by suitable experimental methods and by a fitting procedure (using EMF and absorbance data). One of these coordination modes is known as a model imitating the metal center in hemoglobin, whereas the other one has not been considered as yet.

Key words: cobalt(II), L-α-alanine, imidazole, oxygen-free ternary complexes
Coordination Chemistry of Nickel(II), Copper(II), and Cobalt(II) with MN₄ Core-Containing Two Novel vic-Dioximes Ligands. Synthesis, Spectroscopy and Redox Properties

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Two new vic-dioxime, N-(4-amino-1-benzyl piperidine)-anti-phenylglyoxime (L¹H₂) and N-(4-amino-1-benzyl piperidine)-anti-glyoxime (L²H₂) were prepared by the reaction of anti-phenylchloroglyoxime and anti-monochloroglyoxime with 4-amino-1-benzyl piperidine in absolute THF at –15°C. Mononuclear nickel(II), copper(II), and cobalt(II) complexes have a metal-ligand ratio of 1:2 in which the ligands coordinate through the two nitrogen atoms as do most vic-dioximes. The ligands and their Co(II), Cu(II), and Ni(II) complexes were characterized by elemental analyses, FT-IR, UV-vis, ¹H-NMR and ¹³C-NMR, magnetic susceptibility measurements, electrical conductivity measurements and cyclic voltammetry. The electrical conductivity of Ni(II), Co(II), and Cu(II) metal complexes were measured using Four-Point Probe analysis. The electro-chemical behavior of the Ni(II), Co(II), and Cu(II) complexes were investigated by cyclic voltammetry in DMSO.

Keywords: vic-dioxime, metal complexes, synthesis, redox properties, molar conductivity
Synthesis and Structural Studies on Oxovanadium(IV) Complexes with Polyaza Macrocyclic Ligands Derived from 1,4-Phenylenediamine, Formaldehyde and Primary Diamines

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A new series of N₄ donor macrocyclic oxovanadium(IV) complexes of type [VO(mac)]SO₄ (mac = macrocyclic ligands derived from 1,4-phenylenediamine, formaldehyde and various primary diamines) have been prepared by template method. Tentative structures of the complexes have been proposed on the basis of elemental analyses, electrical conductance, magnetic moment and spectral (IR, electronic and EPR) data. The X-band EPR spectra of all the complexes have been recorded at room temperature and at liquid nitrogen temperature. The room temperature EPR spectra do not show anisotropy because of rapid tumbling of molecules in solution. The spectral studies support square-pyramidal geometry for the oxovanadium(IV) complexes.

Key words: oxovanadium(IV), polyaza macrocycles, synthesis, structures
Speciation and Spectra of Bromokojatoiron(III) Complexes in Aqueous Solutions

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The formation of iron(III) complexes with chelating bromokojate anions \( L^- \) was investigated in aqueous solutions as a function of the pH and \( c(Fe^{3+}) : c(HL) \) molar ratio. Stability constants of the complexes \([FeL(H_2O)_4]^{2+}\), \([FeL(H_2O)_3(OH)]^+\), \([FeL_2(H_2O)_2]^+\), \([FeL_2(H_2O)(OH)]\) and \([FeL_2(OH)_2]^--\) were determined by the evaluation of UV-VIS spectral data. Based on the stability constants, distribution of the above complexes, \([Fe(H_2O)_6]^3+\), and \([Fe(H_2O)_5(OH)]^{2+}\) in solutions of various composition were calculated. The paper indicates a compatibility of the used data treatment and that not taking hydroxo complexes into account. Properties of the investigated bromokojic acid and its iron(III) complexes are compared to those required for therapeutic application as alternative iron chelators.

Key words: stability constants, speciation, iron(III) complexes, bromokojic acid
Synthesis, Characterization and Electrochemical Property of Dicyclohexyl-18-crown-6 Nickel(II) Bis(dithiolate) Complexes

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Two organic-inorganic hybrid dicyclohexyl-18-crown-6 nickel(II) bis(dithiolate) complexes, \([\text{K(DC18C6-B)}_2][\text{Ni(mnt)}_2]\) (1) and \([\text{K(DC18C6-A)}_2][\text{Ni(i-mnt)}_2]\) (2) (DC18C6-A = cis-syn-cis-dicyclohexyl-18-crown-6; DC18C6-B = cis-anti-cis-dicyclohexyl-18-crown-6; mnt = maleonitriledithiolate; i-mnt = isomaleonitriledithiolate), have been synthesized by the reactions of dicyclohexyl-18-crown-6 with NiCl\(_2\) and K\(_2\)(mnt) or K\(_2\)(i-mnt) respectively, and characterized by elemental analysis, FT-IR, UV-Vis spectroscopy and X-ray single crystal diffraction. They both crystallize triclinic, space group \(P\overline{1}\).

Complex 1 shows a neutral molecule composed of two \([\text{K(DC18C6-B)}_2]\)\(^{+}\) complex cations and one \([\text{Ni(mnt)}_2]\)\(^{-}\) complex anion via two K–N coordination bonds. In complex 2, the \([\text{K(DC18C6-A)}_2]\)\(^{+}\) complex cation and \([\text{Ni(i-mnt)}_2]\)\(^{-}\) complex anion afford a 1D chain-like structure by N–K–N interactions.

Key words: dicyclohexyl-18-crown-6, nickel bis(dithiolate) complex, synthesis and crystal structure
Phase Equilibria in the Oxide Nd$_2$O$_3$-K$_2$O-P$_2$O$_5$ System.
The Quasibinary System NdPO$_4$-K$_3$PO$_4$

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Phase diagram of NdPO$_4$–K$_3$PO$_4$ quasibinary system has been elaborated based on investigation by thermoanalytical methods, X-ray powder diffraction, IR spectroscopy and microscopy in reflected light. One binary orthophosphate of the formula K$_3$Nd(PO$_4$)$_2$ occurs in this system, and it melts incongruently at ~1415°C. The compound appears in two polymorphic modifications (transformation α→β-K$_3$Nd(PO$_4$)$_2$ proceeds at 1150–1175°C) and is stable down to room temperature.

Key words: phase diagram, thermal analysis (DTA; TG; DTG), X-ray powder diffraction, potassium-neodymium phosphates
tert-Butylimino-tris(dimethylamino)phosphorane as a Proton Acceptor in the System of Reaction of 1-Nitro-1-(4-nitrophenyl)alkanes in THF

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Unexpectedly the reaction of deprotonation of carbon acids with phosphazene bases occurred very slowly. The kinetic study of the proton transfer reactions between C-acids of the series of nitroalkanes with increasing bulk of R = H, Me, Et, i-Pr substituents as 4-nitrophenylnitromethane (1), 1-nitro-1-(4-nitrophenyl)ethane (2), 1-nitro-1-(4-nitrophenyl)propane (3), 2-methyl-1-nitro-1-(4-nitrophenyl)propane (4) and the tert-butylimino-tris(dimethylamino)phosphorane (5) named P1-t-Bu phosphazene is elaborated. The reactions have been studied in THF under pseudo-first-order conditions. The product of the proton transfer reaction with P1-t-Bu in THF appeared to be associated into ion pairs. The equilibrium constants range from >100000 to 11.8 decreasing along with growing bulk of alkyl substituent in the reacting C-acid. The second order rate constants (k2H) are rapidly declining: 9360, 2.31, 0.66, 0.09 dm3 mol–1 s–1 for 1, 2, 3, and 4 respectively, and could not be accounted for the small values of the enthalpies of activation ΔH°R = 6.1, 18.0, 20.7 and 11.1 kJ mol–1. The reactions show negative and relatively large values of the entropies of activation ΔS°R = –149.7, –176.5, –178.7, –227.8 J mol–1 deg–1. The primary deuterium kinetic isotope effects are large showing tendency of reverse relation towards steric hindrance of the reacting C-acids, kH/kD = 15.8, 13.6, 13.2 for 1, 2, and 3, respectively. The results have been discussed in terms of the influence of steric effects brought by the bulk of alkyl substituents in the C-acid and the base on formation of the transition state. Also the influence of traces of residual water present in the reaction system has been taken into consideration.

Key words: proton transfer, C-acids, phosphazene, rate constants, kinetic isotope effects
Density Functional Calculations on a Double Hydrogen Bonded Dimer of (p-Methoxyphenyl)thiosemicarbazide

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Density functional theory (DFT) calculations on a double hydrogen-bonded dimer of (p-methoxyphenyl)thiosemicarbazide were carried out at B3LYP/6-31G* level. The optimized geometry of the dimer closely resembles that in the crystal. The calculated results show that the total energy of the dimer is much lower than the sum of energies of the two monomers, and the average strength of the double hydrogen bond is about 21.92 kJ/mol. In order to probe the origin of the interactions in the dimer, natural bond orbital analyses have been performed. The thermodynamic properties of the title compound at different temperatures have also been calculated on the basis of vibrational analyses and the change of Gibbs free energy for dimerization of the two monomers. \( \Delta G_T = -18.40 \text{ kJ/mol} \) at 298.15 K and 0.1 MPa, which implies the spontaneous process of the dimer formation. The correlation graphs of \( S^0_m \), \( H^0_m \) and temperatures for the dimer are depicted.

Key words: hydrogen bonded dimer, density functional theory, natural bond orbital, thermodynamic properties
Insoluble Amphiphiles at the Air/Water Interface. The Characteristics of Alcohols Monolayers

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In this paper thorough characteristics of monolayers formed at the air/water interface by two alcohols namely hexadecanol and octadecanol has been presented. The experiments were based on surface pressure/area and surface potential measurements. The visualization of monolayers has been performed using Brewster Angle Microscopy. It has been found that both alcohols form at the air/water interface condensed monolayers with transition between liquid condensed (LC) and solid (S) state. From the experimental results the thickness of monolayers has been calculated and compared with theoretical value. These calculations allow drawing conclusion of the slope of the hydrocarbon tails of investigated alcohols in monolayers. From the surface potential measurements the conformation of the O–H bond and the orientation of dipole moments of both alcohols have been proposed. Moreover, the stability of monolayers formed by investigated alcohols has been studied and it has been found lower stability of hexadecanol monolayers in comparison with those formed by octadecanol.

Key words: insoluble monolayers, surface potential, Brewster Angle Microscopy, relative reflectivity

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The complex formation between iodine monochloride and aza-15-crown-5 (A15C5) has been studied spectrophotometrically in chloroform solution at 25\degree C. The results prove the formation of 2:3 and 3:4 stoichiometries between A15C5:ICl. In the case of 2:3 reaction, the simultaneous formation of I\textsubscript{3}Cl\textsubscript{2} and I\textsubscript{2} through two chemical equilibria is confirmed. The 3:4 reaction proceeds via consumption of I\textsubscript{2} and formation of I\textsubscript{3}\textsuperscript{+}. Several equations are suggested for the observations. The stability constants of 2:3 and 3:4 adducts were calculated by computer fitting of the absorbance-mole ratio data. The experiments were repeated at 40\degree C and results compared with those obtained at 25\degree C. The results indicate that the complexes are weaker at the higher temperature. The conductivity measurements are indicative of ion pairing in all cases. Finally, the solid 3:4 adduct was isolated and its IR spectrum compared with that of A15C5.

Key words: aza-15-crown-5, iodine monochloride, chloroform, spectrophotometry
Synthesis, Crystal Structure and Magnetism Study on a Two-Dimensional Cu(II) Coordination Polymer with 2,5-Dimethylpyrazine-1,4-dioxide as Bridging Ligand

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Preparation of Nano- and Macroscaled Porphyrin by a Simple Method

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