

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

by V. Leskovac<sup>1</sup>, S. Trivić<sup>2</sup> and M. Popović<sup>1</sup>

<sup>1</sup>*Faculty of Technology Novi Sad and* <sup>2</sup>*Faculty of Science Novi Sad, University of Novi Sad, 21000 Novi Sad, Serbia*

*(Received June 19th, 2006; revised manuscript September 4th, 2006)*

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

by D. Czakis-Sulikowska, A. Malinowska and K. Kafarska

*Institute of General and Ecological Chemistry, Technical University of Łódź,  
Żeromskiego 116, 90-924 Łódź, Poland*

*(Received June 1st, 2006; revised manuscript July 27th, 2006)*

The new mixed-ligand complexes containing bipyridine isomers and lactates with formulae  $\text{Mn}(2,4'\text{-bpy})_2(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(2,4'\text{-bpy})_2(\text{lact})_2$ ,  $\text{Cd}(2,4'\text{-bpy})_2(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cd}(4\text{-bpy})(\text{lact})_2 \cdot 2\text{H}_2\text{O}$  (where: 2,4'-bpy = 2,4'-bipyridine, 4-bpy = 4,4'-bipyridine, lact =  $\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$ ) were obtained. These complexes and metal lactates  $\text{Mn}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{lact})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cd}(\text{lact})_2 \cdot \text{H}_2\text{O}$  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- $\alpha$ -Alanine**

by M. Woźniczka<sup>1</sup>, M. Pająk<sup>1</sup>, A. Vogt<sup>2</sup> and A. Kufelnicki<sup>1</sup>

<sup>1</sup>*Laboratory of Physical and Biocoordination Chemistry, Faculty of Pharmacy, Medical University of Łódź, 1 Muszyński Str., 90-151 Łódź, Poland*

<sup>2</sup>*Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie Str., 50-383 Wrocław, Poland*

*(Received January 18th, 2006; revised manuscript July 28th, 2006)*

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- $\alpha$ -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)<sub>2</sub>]<sub>n</sub> 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- $\alpha$ -alanine, imidazole, oxygen-free ternary complexes

## Coordination Chemistry of Nickel(II), Copper(II), and Cobalt(II) with $MN_4$ Core-Containing Two Novel *vic*-Dioximes Ligands. Synthesis, Spectroscopy and Redox Properties

by A. Kilic<sup>1</sup>, E. Tas<sup>1</sup>, B. Gumgum<sup>2</sup> and I. Yilmaz<sup>3</sup>

<sup>1</sup>Department of Chemistry, Harran University, Sanliurfa 63510, Turkey

<sup>2</sup>Department of Chemistry, Dicle University, Diyarbakir 21280, Turkey

<sup>3</sup>Department of Chemistry, Technical University of Istanbul, 34469, Istanbul, Turkey

(Received February 8th, 2006; revised manuscript August 7th, 2006)

Two new *vic*-dioxime, N-(4-amino-1-benzyl piperidine)-*anti*-phenylglyoxime ( $L_1H_2$ ) and N-(4-amino-1-benzyl piperidine)-*anti*-glyoxime ( $L_2H_2$ ) were prepared by the reaction of *anti*-phenylchloroglyoxime and *anti*-monochloroglyoxime with 4-amino-1-benzyl piperidine in absolute THF at  $-15^\circ\text{C}$ . 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,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ , 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 electrochemical behavior of the Ni(II), Co(II), and Cu(II) complexes were investigated by cyclic voltammetry in DMSO.

**Key words:** *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**

by **J.K. Pandey, O.P. Pandey and S.K. Sengupta**

*Chemistry Department, DDU Gorakhpur University, Gorakhpur - 273009, India*

*(Received June 12th, 2006; revised manuscript August 23rd, 2006)*

A new series of N<sub>4</sub> donor macrocyclic oxovanadium(IV) complexes of type [VO(mac)]SO<sub>4</sub> (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

by J. Šima<sup>1</sup>, R. Šípoš<sup>1</sup>, M. Izakovič<sup>1</sup>, D. Valigura<sup>1</sup> and P. Tarapčík<sup>2</sup>

<sup>1</sup>*Department of Inorganic Chemistry, <sup>2</sup>Department of Analytical Chemistry,  
Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia*

*(Received April 11th, 2006; revised manuscript September 19th, 2006)*

The formation of iron(III) complexes with chelating bromokojate anions  $L^-$  was investigated in aqueous solutions as a function of the pH and  $c(Fe^{3+}) : \alpha(HL)$  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

by Y.-M. Sun<sup>1,2</sup>, F.-Y. Dong<sup>1,2</sup>, J.-M. Dou<sup>1</sup>, D.-C. Li<sup>1</sup>, X.-K. Gao<sup>1</sup>  
and D.-Q. Wang<sup>1</sup>

<sup>1</sup>Department of Chemistry, Liaocheng University, Liaocheng, 252059, P. R. China

<sup>2</sup>Department of Plant Protection, Laiyang Agricultural College, Qingdao, 266109, P. R. China

(Received September 12th, 2005; revised manuscript September 26th, 2005)

Two organic-inorganic hybrid dicyclohexyl-18-crown-6 nickel(II) bis(dithiolate) complexes,  $[\text{K}(\text{DC18C6-B})]_2[\text{Ni}(\text{mnt})_2]$  (**1**) and  $[\text{K}(\text{DC18C6-A})]_2[\text{Ni}(\text{i-mnt})_2]$  (**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  $\text{NiCl}_2$  and  $\text{K}_2(\text{mnt})$  or  $\text{K}_2(\text{i-mnt})$  respectively, and characterized by elemental analysis, FT-IR, UV-Vis spectroscopy and X-ray single crystal diffraction. They both crystallize triclinic, space group  $P\bar{1}$ . Complex **1** shows a neutral molecule composed of two  $[\text{K}(\text{DC18C6-B})]^+$  complex cations and one  $[\text{Ni}(\text{mnt})_2]^{2-}$  complex anion *via* two K–N coordination bonds. In complex **2**, the  $[\text{K}(\text{DC18C6-A})]^+$  complex cation and  $[\text{Ni}(\text{i-mnt})_2]^{2-}$  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 $\text{Nd}_2\text{O}_3\text{-K}_2\text{O-P}_2\text{O}_5$ System. The Quasibinary System $\text{NdPO}_4\text{-K}_3\text{PO}_4$**

by **T. Znamierowska and D. Mizer**

*Department of Inorganic Chemistry, Faculty of Engineering and Economics, Wrocław University of Economics, Komandorska 118/120, 53-345 Wrocław, Poland (e-mail: znamier@credit.ae.wroc.pl)*

*(Received June 16th, 2006; revised manuscript October 10th, 2006)*

Phase diagram of  $\text{NdPO}_4\text{-K}_3\text{PO}_4$  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  $\text{K}_3\text{Nd}(\text{PO}_4)_2$  occurs in this system, and it melts incongruently at  $\sim 1415^\circ\text{C}$ . The compound appears in two polymorphic modifications (transformation  $\alpha/\beta\text{-K}_3\text{Nd}(\text{PO}_4)_2$  proceeds at  $1150\text{--}1175^\circ\text{C}$ ) 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**

by **Ż. Wisłocka, I. Nowak and A. Jarczewski**

*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*

*(Received April 24th, 2006; revised manuscript July 27th, 2006)*

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 P<sub>1</sub>-*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 P<sub>1</sub>-*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 ( $k_{2H}$ ) are rapidly declining: 9360, 2.31, 0.66, 0.09 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for **1**, **2**, **3**, and **4** respectively, and could not be accounted for the small values of the enthalpies of activation  $\Delta H_H^\ddagger = 6.1, 18.0, 20.7$  and 11.1 kJ mol<sup>-1</sup>. The reactions show negative and relatively large values of the entropies of activation  $\Delta S_H^\ddagger = -149.7, -176.5, -178.7, -227.8$  J mol<sup>-1</sup> deg<sup>-1</sup>. The primary deuterium kinetic isotope effects are large showing tendency of reverse relation towards steric hindrance of the reacting C-acids,  $k_H/k_D = 15.8, 13.6, 13.2$  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

by P.S. Zhao<sup>1</sup>, R.Q. Li<sup>1</sup>, L.L. Zhang<sup>1</sup> and F.F. Jian<sup>2</sup>

<sup>1</sup>Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials  
Huaiyin Teachers College, Huaian, Jiangsu, 223300, China

<sup>2</sup>New Materials & Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao Shandong 266042, China

(Received March 20th, 2006; revised manuscript July 20th, 2006)

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.  $\Delta G_T = -18.40$  kJ/mol at 298.15 K and 0.1 MPa, which implies the spontaneous process of the dimer formation. The correlation graphs of  $S_m^0$ ,  $H_m^0$  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**

by **P. Wydro**<sup>1</sup>, **K. Hąc-Wydro**<sup>2</sup> and **M. Paluch**<sup>1</sup>

<sup>1</sup>*Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry,  
Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland*

<sup>2</sup>*Department of General Chemistry, Faculty of Chemistry, Jagiellonian University,  
Ingardena 3, 30-060 Kraków, Poland*

*(Received June 7th, 2006; revised manuscript August 1st, 2006)*

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

## **Spectrophotometric Study of the Interaction of Iodine Monochloride with Aza-15-crown-5 in Chloroform Solution**

by **A. Semnani**<sup>1</sup>, **H.R. Pouretedal**<sup>2</sup>, **M.H. Keshavarz**<sup>2</sup> and **Ali R. Firooz**<sup>1</sup>

<sup>1</sup>*Faculty of Science, Shahrekord University, Shahrekord, Iran*

<sup>2</sup>*Faculty of Science, Malek-ashtar University of Technology, Shahin-shahr, P. O. Box 8314-115, Iran*

*(Received December 21st, 2005; revised manuscript September 18th, 2006)*

The complex formation between iodine monochloride and aza-15-crown-5 (A15C5) has been studied spectrophotometrically in chloroform solution at 25°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  $\text{ICl}_2^-$  and  $\text{I}_2$  through two chemical equilibria is confirmed. The 3:4 reaction proceeds *via* consumption of  $\text{I}_2$  and formation of  $\text{I}_3^-$ . 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°C and results compared with those obtained at 25°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**

by J.-M. Shi, X. Zhang, C.-J. Wu and L.-D. Liu

*Department of Chemistry, Shandong Normal University, Jinan 250014, P. R. China*

*(Received May 8th, 2006; revised manuscript August 17th, 2006)*

**Preparation of Nano- and Macroscaled  
Porphyrin by a Simple Method**

by **W. Liu**<sup>1,2</sup>

<sup>1</sup>*College of Materials Science and Engineering, Shandong University of Technology, Zibo 255049, China*

<sup>2</sup>*College of Chemistry, Jilin University, Changchun, 130023, China*

*(Received May 18th, 2006; revised manuscript September 27th, 2006)*