Polish J. Chem., **81**, 2031–2038 (2007) **INORGANIC CHEMISTRY**

Crystal Structure of Terbium Potassium Octacyanotungstate(IV) Heptahydrate

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The crystal structure of $TbKW(CN)_8 \cdot 7H_2O$ has been solved from X-ray single crystal diffraction data. The compound crystallizes in the triclinic system, space group *P*-1, lattice parameters a = 7.6713(7), b = 9.2686(8), c = 14.5523(14) Å, α = 80.506(11), β = 87.580(11), γ = 77.751(10)°, V = 997.27(16) Å^3, Z = 2, D_x = 2.385 g cm^{-3}, $R1$ = 0.0240 and $wR2$ = 0.0525 for 3623 independent reflections. The coordination polyhedra of the tungsten atoms are intermediate between $[W(CN)_8]$ tetragonal antiprisms and bicapped trigonal prisms (rectangular faces are centered) and of the terbium atoms $[TbN_4(H_2O)_4]$ tetragonal antiprisms. Part of the cyanogroups act as bridging units, connecting $[W(CN)_8]$ and $[TbN_4(H_2O)_4]$ structural units into "slab-like" structure. These slabs are connected *via* potassium ion to form 3-dimensional structure. The formula of the coordination polymer can be written as $\{[Tb(H_2O)_4][K(H_2O)][W(CN)_8]\}_n \cdot 2nH_2O$.

Key words: crystal structure, coordination cyanide, tungsten(IV) complex

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Synthesis, Characterization and Biopotency of Some Metal(II) β-Ketoiminates and Their Mixed-ligand Complexes

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VO(IV), Co(II) and Cu(II) complexes of β-ketoimine [$C_6H_5COH{:}CH(CH_3)C{:}N(C_6H_4)Cl$] and their mixed-ligand complexes with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) have been synthesized and characterized by elemental analysis, magnetic susceptibility, conductance, infrared and electronic spectral measurements. The ligand is bidentate, coordinating *via* the imine N and enolic O atoms. The magnetic moments and electronic spectra measurements corroborate a tetrahedral and square planar geometry for Ni(II) and Cu(II) complexes, the VO(IV) complex is five-coordinate square pyramidal while the Co(II) complex and the mixed-ligand complexes are six-coordinate, octahedral. The compounds are magnetically dilute and none is an electrolyte**.** The antimicrobial properties of these compounds against *S. aureus, Bacillus subtilis, Bacillus cereus, Proteus sp, Klebsiella sp, Pseudomonas sp,* and *Salmonella spp* are found to be generally good. The compounds, [$VO(L)_2$], [$VO(L)_2$(phen)] and [$Co(L)_2$(bipy)] have comparable activity to Ciprofloxacin, a broad spectrum antibiotic. The minimum inhibitory concentrations (MICs) of the sensitive compounds are between 3.0 and 9.0 mg/mL.

Key words: antimicrobial, β-ketoimine, ciprofloxacin, mixed-ligand complexes

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The Synthesis and Morphology of Tl_xS_y Layers Deposited on the Surface of Polyethylene Films from Solution

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Thallium sulfide layers will be formed on the surface of low-density polyethylene (PE) if the PE layer is sulphured in a solution of higher polythionic acid $H_2S_{33}O_6$, and then immersed in the alkaline solution of thallium(I) sulfate. Sulphur concentration increases on PE surface with the increase of the sulphurization time. The amount of thallium in the Tl_xS_y layers depends on a sulphur concentration sorbed-diffused into PE. Three phases TlS, Tl_2S and Tl_2S_2 were identified by X-ray diffraction analysis in thallium sulfide layers. Scanning Electron (SEM) and Atomic Force (AFM) microscopies were used to characterize surface morphology of thallium sulfide layers. The films deposited on the PE surface have a non-homogeneous structure and consist of separated islands. The process of their growth on PE surface starts from nucleation sites creating islands of TlS with diameter in tenths of microns which increase up to 9 μm during 1 h deposition.

Key words: high polythionic acid, sulphurization, thallium sulfide layer

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Studies on DNA Cleavage and Antimicrobial Screening of Transition Metal(II) Complexes Derived from Tetradentate Schiff Base

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A new series of transition metal complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), VO(IV), Hg(II) and Cd(II) have been synthesized from the Schiff base (H_2L) derived from 4-aminoantipyrine, 3-hydroxy-4-nitrobenzaldehyde and 2-aminophenol. The structural features have been arrived from their elemental analyses, magnetic susceptibility, molar conductance, mass, IR, UV-Vis, ^{1}H NMR and ESR spectral studies. The data show that the complexes have composition of ML type. The UV-Vis, magnetic susceptibility and ESR spectral data of the complexes suggest a square planar geometry around the central metal ion except VO(IV) complex which has square-pyramidal geometry. The redox behavior of copper and vanadyl complexes has been studied by cyclic voltammetry. The minimum inhibitory concentration (MIC) values of the investigated compounds indicate that the complexes have higher antimicrobial activity than the free ligand. The nuclease activity of the above metal complexes shows that only copper and nickel complexes cleave DNA through redox chemistry.

Key words: Schiff base, 4-aminoantipyrine, CT-DNA, nuclease activity

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Synthesis of New Thia-Derivative Salens, Their Complexes with Copper(II) and Analytical Application for Potentiometric Sensors

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Three new salen derivative ligands (L1, L2 and L3), containing mixed-ligand donor sets of NSNO, have been synthesized. The thermodynamics of complexation reaction between new synthesized salens and copper(II) ion in acetonitrile solution was studied by conductometric method. Formation constants of the resulting 1:1 complex was determined from the conductance-mole ratio data. The results have shown that the new salens, as a neutral chelating agent formed selective and stable complex with Cu(II) ion. Thus, the L1 new salen compound was used as neutral ion carrier in the construction of a Cu^{2+}-PVC membrane electrode. The influence of some experimental parameters such as membrane composition, nature and amount of plasticizer, additive and concentration of internal solution on the potential response of the Cu^{2+}-sensor were investigated. The electrode exhibits a Nernstian response for Cu^{2+}-over wide concentration range ($5.0\cdot10^{-6}$–$1.0\cdot10^{-1}$ M) with a slope 29.7±0.5 mV/decade and detection limit $1.0\cdot10^{-6}$ M. It could be used in a pH range of 4.0–8.0. The electrode shows excellent discriminating ability towards Cu^{2+} ion with regard to several alkali and alkaline earth metal ions. It has a fast response time of about 20 s. The proposed sensor as an indicator electrode was used successfully in the potentiometric titration of Cu^{2+}-ions with EDTA.

Key words: salen–Cu^{2+} complex, thermodynamics, potentiometric sensor, conductometry

Polish J. Chem., **81**, 2081–2087 (2007)

Synthesis and Spectral Studies of Mixed Ligand Complexes of Co(II) with 5-Nitrosalicylaldehyde and β-Diketones, Hydroxyaryl Aldehydes or Ketones

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Mixed ligand complexes of Co^{II} of the type $[CoLL'(H_2O)_2]$ (where HL = 5-nitrosalicylaldehyde, HL′ = salicylaldehyde, 2-hydroxyacetophenone, 2-hydroxypropiophenone, 2-hydroxybenzophenone, 2-hydroxy-1-naphthaldehyde, pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione) have been synthesized and characterized by elemental analyses, TLC, conductances, magnetic moments, IR, electronic and FAB mass spectra.

Key words: mixed ligand complexes, cobalt(II) complexes, IR spectra, electronic spectra, FAB mass spectra

Polish J. Chem., **81**, 2089–2096 (2007) **ORGANIC CHEMISTRY**

^{1}H NMR, ^{13}C NMR and Computational Study of the Structure of Salicylaldehyde Anion in Solution

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^{1}H NMR and ^{13}C NMR spectra of salicylaldehyde potassium salt in DMF-d_7 solution with addition of kryptofix 222 were measured. Quantitative comparison of carbon chemical shifts with shielding constants calculated for *syn* and *anti* conformers of salicylaldehyde anion [GIAO DFT B3LYP/6-311G(2d,p) PCM] revealed that in the applied conditions the *anti* form prevailed. Similar correlation performed for salicylaldehyde lithium salt indicated that in this case the *syn* conformer dominated. Analysis of experimental and calculated $J(^{1}H,^{13}C)$ and $J(^{1}H,^{1}H)$ values supported above conclusions.

Key words: salicylaldehyde salts, NMR, DFT study

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Synthesis of *N*-Arylamino(ferrocenyl)methylphosphinic Acids and Their Cholesteryl Esters

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The synthesis of *N*-arylamino(ferrocenyl)methylphosphinic acids by the action of hypophosphorous acid on an azomethine bond of ferrocenyl *N*-aryl Schiff bases is described. Ferrocenyl aminophosphinic acids obtained in this way have been converted into their cholesteryl esters by their reaction with cholesterol in the presence of DCC.

Key words: ferrocenecarbaldehyde, Schiff bases, aminophosphinic acids, ferrocene moiety, cholesterol, cholesteryl aminophosphonites

Polish J. Chem., **81**, 2103–2114 (2007)

Synthesis and Structure of Mono- and Disubstituted Derivatives of 4,5-Dihydro-1*H*-1,2,4-triazol-5-one

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In the reaction of hydrazide of 1,2,4-triazol-1-acetic acid with isocyanates the semicarbazide derivatives were obtained (**Ia–Ii**). Depending on the chemical nature of the starting isocyanate, cyclization of **Ia–Ii** in alkaline medium led to formation of three groups of derivatives of 4,5-dihydro-1*H*-1,2,4-triazol-5-one (**IIa–IIi**). Alkyl and aryl substituents of semicarbazides formed 3,4-disubstituted compounds (**IIa–IIf**), the ethoxycarbonyl group promoted formation of 3-substituted compound **IIg**, while compounds **IIh** and **IIi** are 4-substituted triazol-5-ones resulting from benzoyl and benzenesulfonyl isocyanates. Molecular structures of three products (**IIb, IIc, IId**) were confirmed by the X-ray structure analysis. Different substituents at the *N*4 atom (ethyl in **IIb,** cyclohexyl in **IIc** and 1-naphthyl in **IId**) influence the molecular association pattern in the crystal structure.

Key words: 1,2,4-triazol-5-one derivatives, semicarbazide cyclization, X-ray structure analysis

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D-Glucosamine Derivatives as Ligands in Highly Enantioselective Palladium-catalyzed Allylic Alkylations

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The rigid derivative of D-glucosamine bearing single diphenylphosphino benzoic acid moiety was synthesized and applied as the ligand for the enantioselective allylic alkylations. Best results were obtained for 1,3-diphenylpropenyl acetate (up to 96% *ee*).

Key words: D-glucosamine, allylic alkylation, palladium, enantioselectivity

Polish J. Chem., **81**, 2121–2131 (2007)

Tetrazole Analogues of Aspartic, Glutamic and α-Aminoadipic Acids and Their Derivatives with Tetrazole Ring in Side Chains Useful for Solid-Phase Peptide Synthesis

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Tetrazole analogues of Fmoc-aspartic, -glutamic and -α-aminoadipic acids with acidic tetrazolyl group in side chains suitable for solid-phase peptide synthesis were obtained. Moreover, the appropriate derivatives of aspartic and glutamic acids containing tetrazole ring methylated in position N1 or N2 were synthesized as well.

Key words: tetrazole analogues of aspartic, glutamic and α-aminoadipic acids; isosters of carboxylic acids, esters and amides

Polish J. Chem., **81**, 2133–2142 (2007)

Synthesis of (3-Amino-7-chloro-8-methyl-1,1-dioxo-4*H*-1,5,2-benzo[*f*]dithiazepin-4-ylidene)acetic Acid Derivatives as Potential Antitumor Agents

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Several 3-amino-7-chloro-8-methyl-1,1-dioxo-4*H*-1,5,2-benzo[*f*]dithiazepin-4-ylidene)acetic acid derivatives (**2**, **4–15**) have been synthesized. The *in vitro* antitumor activity of the compounds **8**, **10–12** and **14–15** have been evaluated in the US National Cancer Institute. Screening data indicated that compounds **10**, **11** and **14** exhibited high activity against 1–28 human tumor cell lines (GI_{50} < 0.01 to 3.0 μM). [3-(Benzo-2,1,3-thiadiazol-4-ylamino)-7-chloro-8-methyl-1,1-dioxo-4*H*-1,5,2-benzo[f]dithiazepin-4--ylidene]acetic acid **11** is the prominent one due to remarkable activity and selectivity toward CNS cancer SF-295 cell line of (GI_{50} < 0.01 μM; TGI = 0.05 μM) and BT-549 cell line of breast cancer (GI_{50} < 0.01 μM; TGI = 0.09 μM).

Key words: (1,1-dioxo-4*H*-1,5,2-benzo[*f*]dithiazepines, sulfonamides, antitumor activity

Polish J. Chem., **81**, 2143–2149 (2007)

1-(2,4-Dinitrophenyl)-5-nitrouracil a Versatile Reagent for the Synthesis of N^1-Modified Uracil Derivatives

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1-(2,4-Dinitrophenyl)-5-nitrouracil has been used as a substrate in reactions with a number of compounds possessing primary amino groups such as: amino alcohols, aminodiols, esters of amino acids and benzylamines. As a result of regioselective course of performed reactions the series of 5-nitro-1-substituted uracils were obtained. All newly synthesized compounds were subjected to primary bioactivity assays as inhibitors against *Mycobacterium tuberculosis*; two of them exhibited inhibition ability.

Key words: 5-nitrouracil, aminodiols, *ANRORC* reaction, acyclic nucleosides, amino acids methyl esters, tuberculosis inhibition

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The Attempts of the Cyano Group Reduction in 1-Cyanoethyl 5-Substituted Uracil Derivatives

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A variety of reductants for the reduction of 1-cyanoethyl-5-substituted uracil derivatives has been examined. Commonly used reductants, borane dimethyl sulphide complex, ammonium formate and sodium borohydride were applied. For the most investigated 5-substituted uracil derivatives the reduction with sodium borohydride has shown the highest efficiency when nickel(II) chloride as a catalyst has been applied. The reactions were performed in methanol at decreased temperature in the presence of di-*tert*-butyl carbonate as a "trapping" agent. The *Boc*-protected 1-(3-aminopropyl)pyrimidine-2,4(1*H*,3*H*)-diones were synthesized in moderate to high yields.

Key words: reduction of cyano group, 5-substituted uracils, nickel chloride as co-catalyst, sodium borohydride

Polish J. Chem., **81**, 2157–2169 (2007) **PHYSICAL CHEMISTRY**

The Miscibility of Sodium Dodecyl Sulfonate with Anionic, Nonionic and Cationic Surfactants in Mixed Monolayers and Micelles

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The surface properties of sodium dodecyl sulfonate (*SDSn*), dodecyl-β-D-glucoside (*DG*), dodecyltrihydroxyethylammonium bromide (*DTEAB*) and sodium dodecyl sulfate (*SDS*) and their mixtures: *SDSn/SDS*, *SDSn/DG* and *SDSn*/*DTEAB* were studied. The miscibility and the composition of the mixed monolayers and micelles as well as the interactions between their components were analyzed with the Motomura theory. It was found that among the investigated mixed systems the best surface properties reveal the anionic-cationic mixtures. Moreover, the investigated systems mix nonideally both in the monolayers and micelles. The magnitude of the deviations from ideal behaviour increases in the order: *anionic/anionic* < *anionic/nonionic* << *anionic/cationic*. Both the mixed monolayers and micelles formed from *SDSn/SDS* and *SDSn/DG* mixtures are richer, as compared to the mixed solutions, in the more surface-active component, while the mixed monolayers and micelles formed from cationic/anionic mixtures (*SDSn/DTEAB*) possess more symmetrical composition than the mixed solution. As it was found the interactions between molecules both in the mixed monolayers and micelles are more attractive or less repulsive as compared to those in respective one-component monolayers and micelles and the strength of these interactions increases in the order: *SDSn/SDS* < *SDSn/DG* < *SDSn/DTEAB*.

Key words: mixed monolayers, micelles, surfactants, excess free energy of mixing

Polish J. Chem., **81**, 2171–2180 (2007)

The Electrochemical and Radiometric Study of Thiourea Adsorption on Polycrystalline Copper Electrode in Neutral Solution

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Adsorption of thiourea (TU) on a polycrystalline copper electrode from 0.01 M $NaClO_4$ solution has been studied by impedance spectroscopy and radiometric method. Differential capacity of copper electrode in 0.01 M $NaClO_4$ solution containing TU of concentrations from 10^{-6} to $5\cdot10^{-4}$ M has been measured. The dependencies of the surface concentration of TU on the electrode potential and the bulk concentration were determined radiometrically. The adsorption of TU on the copper electrode was studied in the range of potentials where no faradaic currents occurred. In this range the process of adsorption is practically reversible with respect to the potential and the bulk concentration of TU. The experimental data were described by the Langmuir and virial isotherms and the Gibbs energy of adsorption was calculated. In order to show the role of the metal the data of TU adsorption on different electrodes have been compared. The unusual behaviour of TU on Cu electrode in comparison with the urea was commented.

Key words: adsorption, thiourea, copper electrode, radiometry, impedance spectroscopy

Polish J. Chem., **81**, 2181–2194 (2007)

Oxygen Adsorption and H_2-O_2 Titration Method for Measurement of Ru Dispersion in Ru/γ-Al_2O_3 Catalysts

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Oxygen adsorption at room temperature (RT) and 0°C and H_2-O_2 titration were studied by volumetric technique on a colloidal 5.1% Ru/ -Al_2O_3 catalyst prepared from the $RuCl_3 \cdot 3H_2O$ precursor by a polyol reduction method. Adsorption properties of this catalyst were compared with those of the 4.6% Ru/γ-Al_2O_3 catalyst prepared by incipient wetness impregnation method using the same metal precursor. The colloidal catalyst, in contrast to traditionally prepared one, was free of chlorine contamination. Characterization by TEM, XRD and XPS showed high dispersion of ruthenium in both catalysts. It was found that at RT the O_2 adsorption coexists to some extent with the subsurface oxidation, but at 0°C the rate of the later, activated process was very low. In spite of this, the O_2 adsorption at both temperatures can be successfully used to determine the ruthenium dispersion in the colloidal Ru/γ-Al_2O_3 catalyst. Using a stoichiometry $O/Ru_s = 2$, good agreement was obtained between the average ruthenium particle sizes calculated from the O_2 adsorption and from TEM. The H_2-O_2 titration data confirm the formation of the surface oxide of stoichiometry close to RuO_2. In contrast, the presence of Cl ions in the traditionally prepared Ru/γ-Al_2O_3 catalyst decreases the capacity of Ru to O_2 adsorption ($O/Ru_s < 2$), and causes large discrepancies between the average particle size estimated from the O_2 uptake, H_2 chemisorption and TEM. The XPS data revealed that mainly Ru^{4+} was formed at the surface of the Ru particles after the O_2 adsorption.

Key words: Ru nanoparticles, oxygen and hydrogen adsorption, hydrogen-oxygen titration, Ru/γ-Al_2O_3 catalyst

Polish J. Chem., **81**, 2195–2205 (2007)

Oxidative Polymerization Studies of 8-Hydroxyquinoline in Different Media

by S.M. Ahmed* and S.A. Ahmed**

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Oxidative polymerization reaction of 8-hydroxyquinoline (HQ) in different media has been studied experimentally by spectrophotometric technique and confirmed computationally by molecular mechanics (MM+) calculations. MM+ calculations showed that the PE of the optimum molecular geometric (OMG) of the anionic HQ (HQ-NaOH) form is about two (1.985) times greater than the PE in the protonated (HQ-HCl) form. PE of the OMG structure of the PHQ was computed (–30.651 kJ mol^{-1}). These calculations indicate that the matrix is highly stable. The oxidation constant (K_{ox}) of the anionic form (HQ-NaOH) is about twice (2.02) greater than that of the protonated (HQ-H_2SO_4) form. The proposed procedure was successfully applied for the oxidation of diiodohydroxyquinoline in streptoquin (SQ) (anti-diarrhea, tablets). The K_{ox} of HQ in SQ was also found to be lower than the K_{ox} in synthetic (HQ) solution. Kinetic parameters of the oxidative polymerization of the anionic form of HQ (HQ-NaOH) were deduced on the basis of absorbance variations. The results of computer-oriented kinetic analysis indicate that the rate-controlling step of the HQ polymerization is governed by Ginstling-Bronstein equation representing the three-dimensional diffusion (D4). Activation parameters of the oxidative polymerization of the anionic form of HQ (HQ-NaOH) were computed and discussed.

Key words: 8-hydroxyquinoline, streptoquin, polymerization, MM+ calculations

Polish J. Chem., **81**, 2207–2214 (2007)

UV-Vis and Raman Spectroelectrochemistry of Electrodeposited Polypyrrole in Hexafluorophosphate

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UV-Vis and Raman spectroscopy are very useful and powerful techniques to characterize the structure of conjugated polymers in various states. Spectroelectrochemical measurements were performed in a three-electrode cell containing polypyrrole (PPY) films as active layers in contact with $NaPF_6$ aqueous electrolyte. UV-Vis spectroscopy was used to characterize the neutral (undoped) and oxidized (p-doped) states of polypyrrole upon electrochemical p-doping. Raman measurements were done with the excitation wavelengths of 514, 633 and 780 nm. It is shown how the vibrational modes of PPY were influenced by the applied laser wavelength. The neutral form was found to be strongly resonance enhanced with the 514 nm excitation wavelength and the corresponding Raman bands dominate the spectra. Spectra obtained using the 633 nm excitation wavelength displayed a strong contribution of the neutral form, but noticeable bands due to the radical cation and dication were also visible. The spectra recorded using the 780 nm excitation line are dominated by Raman bands of the radical cation and dication.

Key words: *in situ* spectroelectrochemistry, UV-Vis and Raman spectroscopy, conducting polymers, polypyrrole, sodium hexafluorophosphate

Polish J. Chem., **81**, 2215–2220 (2007) **COMMUNICATION**

Plasma-Catalytic System for Methane Conversion in Gliding Discharges

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