

Critical Behavior Studies of 2,4-Dichlorobenzoic Acid – Amines Hydrogen-Bonded Complexes Utilizing Fourier-Transform Infrared Spectroscopy

by **M.M. Habeeb**

Chemistry Department, Faculty of Education, Alexandria University, Alexandria, Egypt

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A series of crystalline 1:1 hydrogen-bonded complexes between 2,4-dichlorobenzoic acid (DCBA) and various quinolines and pyridines was prepared. Fourier-transform infrared spectra (FTIR) of these complexes are presented and analyzed in the ν_{OH} and $\nu_{\text{C=O}}$ regions. The correlation between the gravity center of the protonic vibrations ν_{cg} (cm^{-1}), the quantity $\Delta\nu/\Delta\nu_0$ and the pK_{a} values of the amines are presented. The integrated intensities in solution A ($\text{Lmol}^{-1} \text{cm}^{-2}$) and in the crystalline state A ($\text{kg mol}^{-1} \text{cm}^{-2}$) in the $\nu_{\text{C=O}}$ region were correlated with the pK_{a} values of the investigated amines. Striking anomalies are observed at the critical region (50% proton transfer). These results can be interpreted by assuming that quasi-symmetrical O..H..N bridge is formed with a single, flat minimum potential in the solid state and a double minimum potential in solution.

Spectrochemical Properties of Noncubic Transition Metal Complexes in Solutions. XIII. Angular Overlap Treatment of Diaquabis(salicylideneaminothiazole)cobalt(II)

by I. Kuźniarska-Biernacka and K. Kurzak

Department of Chemistry, University of Podlasie, PL 08-110 Siedlce, Poland

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Mixed ligand cobalt(II) complex with monodentate (water) and bidentate (Schiff base: salicylidene-2-aminothiazole) ligands has been characterized by elemental analyses, molar conductivities, ultraviolet (UV) and visible (VIS) spectroscopy. The electronic spectra of solids as well as solutions exhibit pseudo-octahedral coordination geometry for the cobalt centre. The molar conductivities indicate their non-electrolytic properties in solvents studied. Combined multi-technique experiments have been used to postulate the C_{2h} geometry for the species in solutions and to determine the coordination properties of ligands and their bonding abilities (ligand-field parameters).

Kinetic, Spectroscopic and Magnetic Properties of 1,4,8,11-Tetraazacyclotetradecanenickel Bi- and Trivalent Complexes

by **B. Banaś¹**, **M. Nahorska¹**, **B. Korybut-Daszkiewicz²** and **J. Mroziński^{1*}**

¹*Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland*

²*Institute of Organic Chemistry, Polish Academy of Sciences, M. Kasprzaka 44, 01-224 Warszawa, Poland*

**jmroz@wchuwr.chem.uni.wroc.pl*

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Nickel(II) and nickel(III) complexes of formula $[\text{Ni}^{\text{II}}\text{LCl}_2]$ and $[\text{Ni}^{\text{III}}\text{LCl}_2]^+$ containing tetraaza macrocyclic ligands with nitrogen donor atoms, where L = [14]aneN₄ (L¹), 2-Me[14]aneN₄ (L²), 5,12-Me₂[14]aneN₄ (L³), 5,7,7,12,14,14-Me₆[14]aneN₄ (L⁴), form stable crystals with a pseudo-octahedral geometry of central atom. This work concerns the methyl analogues of Ni(II) and Ni(III) complexes. Magnetic and spectroscopic measurements gave values of spectroscopic parameter g and paramagnetic temperature dependence characteristic for this type of compounds. Their properties were investigated using EPR, reflectance spectroscopy and IR techniques. The Faraday method was used for the investigation of magnetic susceptibility between 4.2–300 K.

**Predominance of Amino-Sulfonyl Hydrogen Bonding
in (*Z*)-2-Benzene-sulfonyl-1-phenyl-2-
(phenylhydrazono)ethanones in Crystals and in Solution:
An Experimental NMR and X-ray Crystallographic and
Theoretical *Ab Initio* and DFT/GIAO Studies**

by E. Kolehmainen¹, A. Zakrzewski², A. Zakrzewska², M. Nissinen¹,
B. Ośmiałowski² and R. Gawinecki²

¹Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40351 Jyväskylä, Finland

²Department of Chemistry, Technical and Agricultural University,
Seminaryjna 3, PL-85-326 Bydgoszcz, Poland

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¹H, ¹³C, and ¹⁵N NMR spectra show that (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanone is the only tautomeric form detected in chloroform solution. Substituent in the phenylhydrazono moiety does not affect this tautomeric preference. *Ab initio* calculations show that (*Z*)-2-benzenesulfonyl-1-phenyl-2-(phenylhydrazono)ethanone is really favoured over its proton transfer products in chloroform solution. This shows that N-H...OS(O) interaction is much stronger than the hydrogen bonds in other tautomeric forms. The (*Z*)-2-benzene-sulfonyl-1-phenyl-2-(phenylhydrazono)ethanone tautomer was also detected in the crystal state.

New Method for the Synthesis of Azocrown Compounds Containing Oxygen, Nitrogen and Oxygen, or Sulfur Atoms in the Macroring

by E. Luboch and A. Biedrzycka

*Department of Chemical Technology, Technical University of Gdańsk,
Narutowicza 11/12, 80-952 Gdańsk, Poland
E-mail: elub@chem.pg.gda.pl*

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A new method for the synthesis of azocrown ethers with different heteroatoms in macrocycle and of different size of molecular hole has been described. This method consists in reaction of 2,2'-difluoroazobenzene with diols, diamine, aminodiols and dithiol in the presence of base.

Syntheses of a New Series of *N*-Amino-*N'*-(benzenesulphonyl)guanidine Derivatives with Potential Antitumor Activity

by J. Sławiński¹, P. Bednarski², R. Grünert² and P. Reszka^{2,3}

¹Department of Chemical Technology of Drugs, Medical University of Gdańsk,
Al. Gen. J. Hallera 107, 80-416 Gdańsk, Poland; E-mail: jaroslaw@farmacja.amg.gda.pl

²Department of Pharmaceutical and Medicinal Chemistry, Institute of Pharmacy,
University of Greifswald, L.-John Str. 17, D-17487 Greifswald, Germany

³On leave from Medical University of Gdańsk

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Syntheses of novel *N*-amino-*N'*-(benzenesulphonyl)guanidines (**4a–h**, **5a–g**) from *N*-(benzenesulphonyl)cyanamide potassium salt and hydrazine derivatives are described. Compounds **4b**, **5a–c** and **5e** were evaluated by *in vitro* assays of growth inhibition against several human tumor cell lines. The highest *in vitro* cytotoxic activities were found for 3-phenylamino-1-(2-benzylthio-4-chloro-5-methylbenzenesulphonyl)guanidine (**5b**) (IC₅₀ = 2.35–8.14 μM) and 3-phenylamino-1-(4-chloro-2-ethoxycarbonylmethylthio-5-methylbenzenesulphonyl)guanidine (**5c**) (IC₅₀ = 2.74–10.6 μM), while other tested compounds (**5a**, **5e**) showed the moderate cytotoxic activities. The molecular orbital calculation of the possible tautomeric forms of the benzenesulphonylguanidine derivatives were also presented.

Photophysics of Lumichrome and Its Analogs

by E. Sikorska¹, D.R. Worrall², J.L. Bourdelande³ and M. Sikorski⁴

¹*Faculty of Commodity Science, Poznań University of Economics, al. Niepodległości 10, 60-967 Poznań Poland; Fax: +48 61 8543993, Tel: +48 61 8569040, E-Mail: sikorska@novci1.ae.poznan.pl*

²*Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE11 3TU, England*

³*Unitat de Química Organica, Universitat Autònoma de Barcelona, Barcelona 08193, Spain*

⁴*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*

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The spectroscopic and photophysical properties of lumichrome and its 1- and 3-methyl and 1,3-dimethyl derivatives in acetonitrile and in methanol are presented. In common with the parent molecule, the photophysics of the lumichrome methyl derivatives are dominated by non-radiative transitions in both methanol and acetonitrile. However, fluorescence yields in methanol are higher than in acetonitrile as a result of a reduction in the efficiency of non-radiative deactivation channels. These observations are discussed in terms of the available solvent-solute interactions.

Neutron Spectroscopy, IR, Raman and *Ab Initio* Study of L-Proline

by A. Pawlukojć^{1,2}, J. Leciejewicz², I. Natkaniec^{1,3} and J. Nowicka-Scheibe⁴

¹*Joint Institute for Nuclear Research, 141980 Dubna, Russia*

²*Institute of Nuclear Chemistry and Technology, 03 195 Warszawa, Poland*

³*H. Niewodniczański Institute of Nuclear Physics, Krakow, Poland*

⁴*Institute of Fundamental Chemistry, Technical University, Szczecin, Poland*

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Inelastic incoherent neutron scattering spectra (IINS) were obtained for normal and deuterated L-proline. Raman and infrared spectra were also recorded. Geometries were optimized for the zwitterion form using *ab initio* Hartree-Fock (HF) level with 6-31G*, 6-311G** and 6-311++G** basis sets. Force fields and normal modes were calculated and used as basis for an assignment of the spectral features. The theoretical frequencies of normal and d₂ – L-proline were compared with IINS spectra.

EPR and ESEEM Identification of Free Radicals and Molecular Structure of the Oligomers Formed During Polycondensation of 1-Chloro-4-nitrobenzene with Sodium Sulfides in N-Methyl-2-pyrrolidone

by **S.K. Hoffmann**¹, **I. Polus**², **W. Hilczer**¹, **J. Goslar**¹,
S. Kiczka¹ and **B. Doczekalska**³

¹*Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, PL-60179 Poznań, Poland, Fax: 48-61-8684 524; E-mail: skh@ifmpan.poznan.pl*

²*August Cieszkowski Agricultural University, Faculty of Wood Technology, Department of Chemistry, Wojska Polskiego 75, PL-60625, Poznań, Poland*

³*August Cieszkowski Agricultural University, Faculty of Wood Technology, Institute of Chemical Wood Technology, Wojska Polskiego 28, PL-60637, Poznań, Poland*

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The synthesis of derivative of poly (4-hydrazo-diphenylenedisulfide) by reaction of 1-chloro-4-nitrobenzene with sodium sulfide and disulfide in N-methyl-2-pyrrolidone leads to oligomeric products with average molecular weight of the homogeneous chains 1182 g/mol and 690 g/mol, respectively. The mechanisms of the reactive intermediates polycondensation reaction are described. The products were characterized by IR, ¹H NMR, and EPR spectroscopy and by elemental analysis. The final amorphous oligomer products contain mostly diamagnetic species and about 1% of paramagnetic species. The latter produce strong isotropic EPR signal at $g = 2.0025$ from free radical with concentration of about 10^{18} radicals/gram. Pulsed EPR spectroscopy allowed identifying the radical by analysis of the electron spin echo envelope modulation spectrum. The radical is localized on the carbon atom of the C=O-group of the N-methyl-2-pyrrolidone moiety with broken internal C–N bond of the lactam ring.

**Formation of Binuclear EDTA and Cu(II) Complexes
in Aqueous Solutions**

by **O. Gylienė** and **J. Aikaitė**

*Department of Environmental Chemistry, Institute of Chemistry,
Goštauto 9, LT-2600 Vilnius, Lithuania, E-mail: gyliene@ktl.mii.lt*

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**Nickel/Alumina Catalyst for Carbon Oxides Methanation.
Flash Calcination of the Catalyst Precursor**

by **R. Narowski¹, Z. Kowalczyk¹, J. Zieliński², A. Gołębiowski³ and K. Stolecki³**

¹*Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland*

²*Institute of Physical Chemistry PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland*

³*Fertilizers Research Institute, Al. Tysiąclecia P.P., 24-100 Puławy, Poland*

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**Complexation Behaviour of
5(2'-Hydroxyphenyl)-3-phenylpyrazoline
with Some Metallic Moieties**

by U.N. Tripathi¹, K.V. Sharma¹, A. Chaturvedi² and T.C. Sharma¹

¹*Synthetic Inorganic and Organometallic Laboratory, School of Studies in Chemistry,
Vikram University, Ujjain – 456 010, India*

²*Department of Chemistry, Govt. PG. College, Ajmer, India*

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Diffuse Reflectance Spectroscopy Applied to Solid-State 2-Methylsparteine Metal Complexes

by **B. Jasiewicz¹**, **E. Sikorska²**, **I.V. Khmelinskii³** and **M. Sikorski¹**

¹*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
Tel: +48 61 8291309, Fax: +48 61 8658008, E-Mail: Sikorski@amu.edu.pl*

²*Faculty of Commodity Science, Poznań University of Economics,
al. Niepodległości 10, 60-967 Poznań, Poland*

³*Universidade do Algarve, FCT, 8000–117 Faro, Portugal*

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Phase Transitions in Guanidinium Bromoantimonate(V)
[C(NH₂)₃]SbBr₆

by **R. Jakubas, G. Bator and P. Ciapala**

Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

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