

Synthesis and Magnetic Properties of μ -2-Nitroterephthalato-Bridged Binuclear Lanthanide(III) Complexes

by Y.-T. Li¹, J. Zhang² and C.-W. Yan³

¹Marine Drug & Food Institute, Ocean University of China, 5 Yushan Road, Qingdao, Shandong, 266003, P. R. China

²College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, P. R. China

³College of Marine Life Science, Ocean University of China, Qingdao, Shandong, 266003, P. R. China

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Nine new binuclear lanthanide(III) complexes described by the overall formula $[\text{Ln}_2(\text{NTPHA})(\text{Me}_2\text{bpy})_4(\text{ClO}_4)_2](\text{ClO}_4)_2$ (Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er), where Me₂bpy stands for 4,4'-dimethyl-2,2'-bipyridine, and NTPHA represents the 2-nitroterephthalate dianions, have been synthesized and characterized by elemental analyses, IR, ESR and electronic spectra, and molar conductance measurements. It is proposed that these complexes present NTPHA-bridged structures consisting of two lanthanide(III) ions. The variable-temperature magnetic susceptibilities (4–300 K) of complex $[\text{Gd}_2(\text{NTPHA})(\text{Me}_2\text{bpy})_4(\text{ClO}_4)_2](\text{ClO}_4)_2$ were measured and studied, demonstrating a very weak antiferromagnetic spin-exchange interaction between Gd(III)–Gd(III) ions within the complex. Based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, the exchange parameter (J) was evaluated as -0.12 cm^{-1} .

Cyclohexylethyl- and Hexamethyleneimine Nickel(II)dithiocarbamates with 1,6-Bis(diphenylphosphino)hexane

by R. Pastorek¹, J. Kameníček¹, J. Husárek¹, M. Pavlíček¹,
Z. Šindelář¹ and Z. Žák²

¹*Department of Inorganic and Physical Chemistry, Palacký University,
Křížkovského 10, 771 47 Olomouc, Czech Republic*

²*Department of Inorganic Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*

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A binuclear diamagnetic Ni(II) dithiocarbamates with 1,6-bis(diphenylphosphino)hexane (dpph) as a bidentate bridging P,P-ligand of composition $[\text{Ni}_2(\mu\text{-dpph})(\text{hmidtc})_2\text{X}_2]$ (hmidtc = hexamethyleneiminedithiocarbamate, dtc = S_2CN^- , X = Cl, Br, I, ClO_4 , NCS); $[\text{Ni}_2(\mu\text{-dpph})(\text{cetdte})_2\text{X}_2]$ (cetdte = cyclohexylethylidithiocarbamate, X = Cl, Br, I, NCS) and also the mononuclear diamagnetic complex $[\text{Ni}(\text{cetdte})(\text{dpph})]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ have been synthesized. The complexes have been studied by elemental analysis, IR and UV-VIS spectroscopy, thermal analysis, magnetochemical and conductivity measurements. X-ray structural analysis was solved for the $[\text{Ni}_2(\mu\text{-dpph})(\text{hmidtc})_2\text{Br}_2] \cdot 2\text{CHCl}_3$ and confirmed the presence of two NiS_2PBr chromophores bonded by the P-donor atoms of 1,6-bis(diphenylphosphino)hexane.

Competitive Spectrophotometric Study of Complexation of Dibenzopyridino-18-crown-6 with Ca^{2+} , Sr^{2+} , and Ba^{2+} in Binary Dimethylsulphoxide–Acetonitrile Solutions

by **J. Zolgharnein, F. Zahirredini and G. Azimi**

Department of Chemistry, Arak University, Arak, Iran

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The complexation of dibenzopyridino-18-crown-6 (DBPY18C6) with Ca^{2+} , Sr^{2+} and Ba^{2+} has been studied in binary dimethylsulphoxide – acetonitrile mixtures at 25°C by a competitive spectrophotometric technique, using murexide as a metal ion indicator. Stoichiometry and stability of the resulting complexes were evaluated by KINFIT program. The stability of 1:1 complexes prepared were found strongly solvent dependent. There is an inverse linear relationship between $\log K_f$ and mole fraction of dimethylsulphoxide (DMSO) in the solvent. In all these solvents the increase of %AN increases the stability of DBPY18C6 complexes with alkaline earth cations in the sequence $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$.

Synthesis, Structure and Spectroscopic Properties of Bis(2,4-dichloro-phenol-methylene- -1H-benzimidazole-N³)-dichlorocobalt(II)

by **F.F. Jian¹, F.L. Bei², X. Wang² and L.D. Lu²**

¹*New Materials & Function Coordination Chemistry Laboratory,*

Qingdao University of Science and Technology, Qingdao, 266042, P. R. China

²*Materials Chemistry Laboratory, Nanjing University of Science and Technology,
Nanjing, 210094, P. R. China*

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The title compound, CoL_2Cl_2 [L = (2,4-dichloro-phenol-methylene-1H-benzimidazole)], has been synthesized and structurally characterized by elemental analysis, IR and X-ray. The coordination geometry of cobalt(II) may be represented by slightly distorted tetrahedron with the CoN_2Cl_2 chromophore. In the solid state, the title compound forms infinite one-dimensional chains in the [101] direction through hydrogen bonds and potentially weak intermolecular interactions. The IR data agree with the crystal structure. The thermal gravimetry (TG) data indicate that there are two decomposition steps. The final product of thermal decomposition is Co_2O_3 . The magnetic properties of the title compound are also reported and discussed.

Synthesis, Crystal Structure and Magnetic Behavior of a One-Dimensional Cobalt(II) Complex with Mellitic Anion as Bridging Ligand

by **M.G. Zhao¹, J.M. Shi², C.Q. Liu¹, W. Xu² and Y.Q. Chen²**

¹*Department of Chemistry, Xinzhou Normal College, Xinzhou 034000, P.R. China*

²*Department of Chemistry, Shandong Normal University, Jinan 250014, P.R. China*

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A one-dimensional complex $\{[\text{Co}_3(\text{C}_6(\text{COO})_6)(\text{H}_2\text{O})_{12}]\} \cdot 6\text{H}_2\text{O}\}_n$ has been prepared and its crystal structure determined by X-ray crystallography. In the complex mellitic anion provides its six carboxylate groups to coordinate four cobalt(II) ions, in which a seven-membered ring was formed by two ortho-carboxylate groups to coordinate the same cobalt(II) ion. Through the four carboxylate groups bridging two cobalt(II) ions the one-dimensional chain structure was formed. The variable-temperature magnetic susceptibility of the complex was measured in the 4–300 K range and the magnetic data indicate the magnetic interaction between the bridged cobalt(II) ions displays an antiferromagnetic coupling.

Synthesis, Characterization, and SOD-like Activity Testing of Two Novel Copper(II) Complexes Bridged by Oxamide-N,N'-diacetic Acid

by **L.-Z. Zhang¹**, **S.-L. Ma¹**, **A.-Y. Shen¹**, **M. Fu¹**, **L.-J. Zhang²** and **X. Liu²**

¹*Department of Pharmaceutical Engineering, Tianjin University of Commerce, Tianjin, 300134, P.R. China*

²*Department of Biological Engineering, Beijing Institute of Technology, Beijing, 100081, P.R. China*

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To provide more complexes which are expected to yield better similarity to authentic SOD (Superoxide Dismutase) and to have certain SOD activity, two novel 1D linear complexes composed of binuclear copper(II) units are synthesized and characterized with the structural units bridged by oxamide-N,N'-diacetic acid. They are $\{\text{Na}[\text{Cu}_2(\text{oxaa})\text{OAc}] \cdot \text{H}_2\text{O}\}_n$ (I) and $\{\text{Na}[\text{Cu}_2(\text{oxaa})(\text{o-phenylenediamine})_2\text{OAc}] \cdot 2.5\text{H}_2\text{O}\}_n$ (II), where oxaa denotes oxamide-N,N'-diacetic acid tetraanion. The temperature dependence of the magnetic susceptibilities of $\{\text{Na}[\text{Cu}_2(\text{oxaa})(\text{o-phenylenediamine})_2\text{OAc}] \cdot 2.5\text{H}_2\text{O}\}_n$ was investigated between 4.99–299 K, giving the exchange parameter $J = -294.1 \text{ cm}^{-1}$. This result is demonstrated with an antiferromagnetic interaction between the adjacent copper(II) centers. In addition, the SOD-like activity of the complex (II) is discussed.

Synthesis and Characterization of New Thiocyanato Bridged Heterobimetallic Complexes with the General Formula: $[\text{Cu}(\text{diamine})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot n\text{H}_2\text{O}$

by G. Wrzeszcz

Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 7, 87-100 Toruń, Poland

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Four new thiocyanato bridged heteropolynuclear complexes with general formula $[\text{Cu}(\text{diamine})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot n\text{H}_2\text{O}$, where diamine = *N*-ethylethylenediamine (*N*-Et-en), *N*-isopropylethylenediamine (*N*-Pr^{*i*}-en), *N*-methyl-1,3-propanediamine (*N*-Me-tn), 1,3-diaminopentane (*C*-Et-tn), were prepared by treatment of corresponding cationic $[\text{Cu}(\text{diamine})_2]^{2+}$ complex with $[\text{Cr}(\text{NCS})_6]^{3-}$ in aqueous solutions. Solid products were formulated as $[\text{Cu}(\text{N-Et-en})_2]_3[\text{Cr}(\text{NCS})_6]_2$, $[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$, $[\text{Cu}(\text{N-Me-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$ and characterized by spectroscopic methods, magnetic measurements and thermal analysis. The formation of end-to-end thiocyanato bridges between tetragonal Cu(II) and octahedral Cr(III) is evident from IR and electronic spectra. The EPR spectra measured at room temperature on solid samples show broad, symmetric signal at $g = 2.01\text{--}2.03$. Variable-temperature magnetic susceptibility measurements reveal the presence of weak antiferromagnetic interactions in $[\text{Cu}(\text{N-Pr}^i\text{-en})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{C-Et-tn})_2]_3[\text{Cr}(\text{NCS})_6]_2 \cdot \text{H}_2\text{O}$. Thermal decomposition after dehydration is multi-stage and yields CuO and CuCrO₂ as final products.

Structural, Thermal, Biological and Semiconducting Properties of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and VO(IV) Complexes of Schiff Base Derived from Resdiacetophenone and S-Benzyldithiocarbazate

by **J.T. Makode, S.G. Bhadange and A.S. Aswar**

Department of Chemistry, Amravati University, Amravati – 444 602, India

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A series of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and VO(IV) complexes with Schiff base derived from resdiacetophenone and S-benzyldithiocarbazate have been synthesized and characterized by elemental analyses, magnetic moment, IR and electronic spectral studies and thermal analysis. The Schiff base functions as a binucleating tridentate chelating agent and coordinates *via* the deprotonated phenolic oxygen, azomethine nitrogen and thioenolate sulphur atoms to the metal ion favouring the formation of bimetallic complexes. From dynamic TG data, activation energy and other kinetic parameters have been computed using Freeman-Carroll, Sharp-Wentworth and Coats-Redfern methods. Electrical conductivity of the complexes have also been studied between 313–473 K in pellet forms and the complexes are found to exhibit semiconducting behaviour. The antimicrobial activity of the ligand and its complexes have been screened against various microorganisms and all of them were found to be moderately active against the organisms.

Synthesis of 3-Benzyl-1,3-thiazolidines by [2+3]-Cycloaddition of Sonochemically Generated Azomethine Ylides with Thiocarbonyl Compounds

by A. Gebert¹, A. Linden¹, G. Mlostoń² and H. Heimgartner¹

¹Organisch-chemisches Institut der Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

²Section of Heteroorganic Compounds, University of Łódź,
Narutowicza 68, PL-90-136 Łódź, Poland

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Sonification of *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)methyl]amine (**5a**) in the presence of LiF led to the formation of the reactive azomethine ylide **1d**, which was intercepted by cyclic thioketones to give spirocyclic 1,3-thiazolidines. In the case of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**13**), the 1:1- and 1:2-cycloadduct, respectively, was formed as the major product depending on the ratio of the starting materials. With 1,3-thiazole-5(4*H*)-thiones, **1d** undergoes stereoselective [2+3]-cycloadditions with the C=S group to yield spirocyclic 1:1-adducts. In the case of the 1,3-dipole generated from *N*-benzyl-*N*-(methoxymethyl)-*N*-[1-(trimethylsilyl)ethyl]amine (**5b**), the [2+3]-cycloaddition proceeded in a non-regioselective manner leading to a mixture of regio- and diastereoisomers.

New Bradykinin Analogues Modified in Position 6 and 7 with Naphthylalanine

by **A. Prahl**¹, **I. Derdowska**¹, **O. Dawidowska**¹, **K. Neubert**², **B. Hartrodt**²,
T. Wierzba³, **W. Juzwa**³ and **B. Lammek**¹

¹*Faculty of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland
E-mail: olad@chemik.chem.univ.gda.pl*

²*Institute of Biochemistry, Martin-Luther-University Halle-Wittenberg,
Kurt-Mothes-Straße 3, 06120 Halle (Saale), Germany*

³*Department of Physiology, Medical Academy of Gdańsk, Dębinki 1, 80-211 Gdańsk, Poland*

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We describe the synthesis and some pharmacological properties of eight new analogues of a previously synthesized bradykinin antagonist, D-Arg-Arg-Pro-Hyp-Gly-Thi-Ser-D-Phe-Thi-Arg. Two peptides were designed by substitution of Ser⁶ with L-1- and L-2-naphthylalanine. In two further analogues this modification was combined with placement in position 7 of D-naphthylalanine residue. We also obtained four analogues by acylation of N-terminus of the peptides mentioned above with 1-adamantaneacetic acid. The activity of analogues was assessed by their ability to inhibit vasodepressor response to exogenous bradykinin (rat blood pressure test). Our results indicate that the modifications proposed decreased significantly the B₂ antagonistic activity. Moreover, our earlier observation, suggesting that acylation of the N-terminus of many BK antagonists with bulky groups consistently improved the antagonistic potency, appears to be valid only for one pair of analogues.

^1H , ^{13}C and ^{15}N NMR Spectral and X-ray Structural Studies of 2-Arylsulfonylamino-5-chlorobenzophenones

by E. Kolehmainen¹, M. Nissinen¹, H. Janota¹, R. Gawinecki²
and B. Ośmiałowski²

¹Department of Chemistry, University of Jyväskylä,
P.O. Box 35, FIN-40014 Jyväskylä, Finland

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

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Six 2-(4-R-phenylsulfonylamino)-5-chlorobenzophenones were prepared and their ^1H , ^{13}C and ^{15}N NMR spectra recorded and assigned. The dependence between the chemical shift of the amide proton and Hammett σ substituent constants is of the V type. Substituent effect on the chemical shift of the amide nitrogen atom was found insignificant. X-ray analysis shows that the terminal benzene rings in 2-(4-nitrophenylsulfonylamino)-5-chlorobenzophenone are located close to each other. They are not, however, parallel, dihedral angle between them being equal to 10.86 deg (MP2/6-31G**//HF/6-31G** *ab initio* calculations show this to be 20.44 deg). This shows that the mutual orientation of two benzene rings in the molecule of this compound is caused by the π - π stacking. It is additionally reinforced by the intramolecular NH...O=C hydrogen bond. Except the dihedral angle between the benzene rings, X-ray determined structure of 2-(4-nitrophenylsulfonylamino)-5-chlorobenzophenone is very similar to this optimized by the *ab initio* calculations.

**Electrochemical Behaviour of Chloride and Bromide
Complexes of Palladium(II) with
4-Amino-6-methyl-3-thio-3,4-dihydro-1,2,4-triazin-5(2H)-
-one in Dimethylformamide at Glassy Carbon Electrode**

by **L. Fotouhi¹**, **M. Ghassemzadeh²** and **M.M. Heravi¹**

¹*Department of Chemistry, Faculty of Science, Alzahra University, P.O. Box 1993891176, Tehran, Iran*

²*Chemistry & Chemical Engineering Research Center of Iran, Tehran, Iran*

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The electrochemical behaviour of palladium(II) complexes of PdCl₂L (I) and PdBr₂L (II) (L = 4-amino-6-methyl-3-thio-3,4-dihydro-1,2,4-triazin-5(2H)-one) has been investigated in dimethylformamide at glassy carbon electrode. Under cyclic voltammetric conditions, complex PdCl₂L is found to undergo a one-electron oxidation at 1.27 V with a prewave, which is similar to oxidation of ligand L. The oxidation of ligand shows an oxidation wave at 1.25 V with EC mechanism. In the chemical reaction following the one electron irreversible oxidation of ligand, the electrochemical-generated cation radical forms a dimer, which is reduced at reverse scan at -0.66 V to reproduce the monomer. Thus, the nature of oxidation of both complexes I and II suggests a ligand-centered oxidation, because their oxidation behaviour is similar to oxidation of ligand L. However, the reduction of both complexes I and II shows a reduction peak at -1.31 V and -1.33 V respectively, which is related to reduction of metal center of complexes, Pd(II) to Pd(I).

Dehydrogenation of Isobutane to Isobutene over $V_2O_5/\gamma\text{-Al}_2O_3$ Catalysts: Effects of the Extent of Catalyst Reduction on Catalytic Performance

by **H.-C. Ma, Y.-H. Fu, Y. Li, Z.-L. Wang, W.-C. Zhu and G.-J. Wang**

Department of Chemistry, Jilin University, Changchun 130023, China

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$V_2O_5/\gamma\text{-Al}_2O_3$ catalysts for the dehydrogenation of isobutane to isobutene were prepared by impregnation and characterized by BET, H_2 -TPR, ESR and XPS. Based on our studies of the effects of the extent of catalyst reduction on catalytic performance, we conclude that the $V_2O_5/\gamma\text{-Al}_2O_3$ catalytic activity for the dehydrogenation of isobutane is related to the valence state of vanadium present in the catalyst, in the order of $V^{4+} > V^{3+}$. Furthermore, V^{4+} species are the main active sites of this reaction under the present reaction conditions.

Effect of Additives to VPO System on Its Catalytic Properties in Oxidative Dehydrogenation of Propane and Ethane

by **M. Gašior¹**, **I. Gressel¹**, **V.A. Zazhigalov²** and **B. Grzybowska¹**

¹*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
ul. Niezapominajek 8, 30-239 Kraków, Poland*

²*Ukrainian-Polish Laboratory of Catalysis, Institute of Sorption and Problems of Endoecology,
NASU, ul. Gen. Naumova 13, Kyiv-164, 03164, Ukraine*

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Oxidative dehydrogenation (ODH) of propane and ethane has been studied on VPO catalysts with additives of Bi, La, Mo and Zr. The catalysts show promising properties in the ethane ODH, with selectivities to ethene of ~85% at 10% conversion of ethane, but are poor in the propane ODH (maximal selectivities to propene of ~40%). For both alkanes introduction of the additives leads to an increase in the overall rate of the reaction. The effect of the additives on the selectivity to olefins is complex and depends on the reaction temperature, the additive content and the type of alkane. The same additive has in several cases an inverse effect on the selectivity for the propane and ethane ODH. The Mo additive and higher amounts of the La additive increase the selectivity to propene, whereas they decrease the selectivity to ethene. Low content of La additive gives rise to the increase of selectivity to ethene and decrease in that to propene. The differences between the selectivities to olefins in ODH of propane and ethane are discussed as being due to different acido-basic properties of the propene and ethene and their different strength of bonding to the catalyst surface.

**Synthesis, Characterization and Activity of Rare Earth
Complexes with Schiff Base from Picolinaldehyde
N-Oxide and 4,4'-Methylenedianiline**

by **Q. Yu¹, K. Chen² and M.Y. Tan¹**

¹*College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China*

²*College of Life Science, Lanzhou University, Gansu 730000, P. R. China*

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**Ammonia Synthesis over the Barium-Promoted
Ruthenium Catalyst Supported on Boron Nitride.
Effect of the Catalyst Activation**

by D. Szmigiel, W. Raróg-Pilecka, E. Maciejewska and Z. Kowalczyk

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

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**Synthesis, Crystal Structure and Magnetic Behavior
of a One-Dimensional Chain Complex:
 $\{[\text{Cu}(\text{N-m-en})_2\text{Fe}(\text{CN})_5(\text{NO})] \cdot \text{H}_2\text{O}\}_n$**

by C.Q. Liu¹, J.M. Shi², W. Xu², W. Xu² and Y.Q. Chen²

¹*Department of Chemistry, Xinzhou Normal College, Xinzhou 034000, P.R. China*

²*Department of Chemistry, Shandong Normal University, Jinan 250014, P. R. China*

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