

**Coordinating Behavior of a Macrocyclic Amide Ligand towards Lanthanide Ions: Synthesis and Spectral Studies of Lanthanide(III) Complexes with N,N'-Bis(2-hydroxyphenyl)pyridine-2,6-dicarboxamide**

by **K.B. Gudasi, R.V. Shenoy, R.S. Vadavi, S.A. Patil and V.C. Havanur**

*Department of Chemistry, Karnatak University, Dharwad 580003, Karnataka, India*

*(Received July 22nd, 2005; revised manuscript September 30th, 2005)*

Seven coordinate lanthanide(III) complexes with N,N'-bis(2-hydroxyphenyl)pyridine-2,6-dicarboxamide (BHPPDAH) with the general composition  $[\text{Ln}(\text{BHPPDA})(\text{H}_2\text{O})_2]\text{NO}_3$ , where Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Y(III), have been isolated. The complexes have been characterized based on magnetic susceptibility, conductivity studies, IR, NMR, UV-VIS, EPR and thermal studies. The ligand binds to the metal centre through pyridine and amide nitrogens and doubly deprotonated phenolic oxygens. Biological evaluation of the complexes indicates enhanced activity compared with that of free ligand.

**Key words:** lanthanide complexes, pyridine-2,6-dicarboxamide, spectral studies

## Synthesis, Characterization and Crystal Structures of Diorganotin(IV) Complexes with 2-Mercapto-4-methyl-5-thiazoleacetic Acid

by R.F. Zhang<sup>1</sup>, J.F. Sun<sup>1</sup>, C.L. Ma<sup>1,2</sup> and J.H. Zhang<sup>1</sup>

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

<sup>2</sup>*Taishan University, Taian 271021, P. R. China*

*(Received October 6th, 2005)*

The organotin(IV) complexes,  $[(C_4H_4NS_2CH_2CO_2)R_2Sn(OMe)OSnR_2]_2$  ( $R = Me$  **1**,  $n$ -Bu **2**, Ph **3**, PhCH<sub>2</sub> **4**), have been synthesized and characterized by IR and <sup>1</sup>H NMR spectroscopy. The structures of **1** and **2** have also been determined by X-ray crystallography. The structure analyses show that both complexes **1** and **2** feature a centrosymmetric core arranged as a ladder. Links between pairs of tin atoms are afforded by  $\mu_2$ -methoxy groups and each carboxylate anion coordinates an exocyclic tin atom exclusively, in the monodentate mode. Moreover, the packing of complexes **1** and **2** are stabilized by the hydrogen bonding interactions.

**Key words:** diorganotin, 2-mercapto-4-methyl-5-thiazoleacetic acid, crystal structure

## **Synthesis and Spectral Studies of a Novel 20-Membered Unsymmetrical Dinucleating [N<sub>8</sub>] Macrocyclic and Its Bimetallic Complexes, M<sub>2</sub>LCl<sub>n</sub>(ClO<sub>4</sub>)<sub>2</sub> (n = 2, M = Co, Ni or Cu; n = 4, M = Cr or Fe)**

**by Z.A. Siddiqi, M. Khalid and M.M. Khan**

*Division of Inorganic Chemistry, Department of Chemistry,  
Aligarh Muslim University, Aligarh - 202002, India*

*(Received October 10th, 2005)*

A 20-membered octaaza unsymmetrical Schiff base macrocycle, 6,10,16,20-tetramethyl-7,9,17,19-tetraphenyl[1,5,7,9,11,15,17,19]octaazacycloeicosa-5,10,15,20-tetraene dihydroperchlorate (L·2HClO<sub>4</sub>), has been obtained as an off-white amorphous solid by refluxing a mixture of 1,3-diaminopropane, N-acetylaniline and excess HCHO in the presence of HClO<sub>4</sub> in ethanol, characterized by physico-chemical and spectroscopic studies. Its reactions with transition metal salts have afforded air stable solids with stoichiometry M<sub>2</sub>LCl<sub>n</sub>(ClO<sub>4</sub>)<sub>2</sub> (n = 2, M = Co, Ni or Cu and n = 4, M = Cr or Fe). Magnetic moment, IR and UV-visible spectroscopic data confirm encapsulation of metal ions through chelation from unsymmetrical aza groups and additional coordination by counter ClO<sub>4</sub><sup>-</sup> which maintains hexa coordination around the metal ions. A low-spin distorted square-pyramidal geometry with distorted C<sub>4v</sub> symmetry of basal plane has been indicated for Co<sup>2+</sup> complex. EPR data on Cu<sup>2+</sup> complexes have indicated a tetragonal distortion with g<sub>||</sub> > g<sub>⊥</sub> > 2.0 and G < 4.0 with orbital reduction factor K<sub>⊥</sub> > K<sub>||</sub> favouring the presence of exchange coupling around the Cu<sup>2+</sup> environment.

**Key words:** dinucleating macrocycle, unsymmetrical [N<sub>8</sub>] macrocycle, metal-encapsulated complexes, polyaza-macrocyclic

## Novel Coordination Complexes of the Trivalent Ruthenium, Rhodium and Iridium with Hydrazones Derived from Isatin Hydrazide and Various Aldehydes with Spectral and Biological Characterization

by V.K. Sharma, S. Srivastava and A. Srivastava

Department of Chemistry, University of Lucknow, Lucknow – 226007, India

(Received July 26th, 2005; revised manuscript October 25th, 2005)

A series of several new ruthenium(III), rhodium(III) and iridium(III) complexes with hydrazones of general formula  $[M(LH)_3]Cl_3$  were synthesized in order to meet requirements essential for biological properties. Hydrazones were formed by isatin hydrazide and various aldehydes namely anisaldehyde, benzaldehyde, *o*-chlorobenzaldehyde, *p*-chlorobenzaldehyde and *p*-fluorobenzaldehyde. Physicochemical characterization of compounds has been carried out by elemental analyses, spectroscopic (IR, electronic,  $^1H$  NMR), thermogravimetric and magnetic studies. These complexes show higher conductance values, supporting their electrolytic nature. All the studies revealed octahedral nature of the complexes with nitrogen and oxygen of azomethine and carbonyl group as binding sites and exhibited monomeric nature of the complexes. Rhodium(III) and iridium(III) complexes were found diamagnetic and show intense absorptions while ruthenium(III) complexes show paramagnetic behaviour. In addition, antifungal and antibacterial studies have been carried out *in vitro* for investigated compounds against fungus *A. niger* and *F. oxysporium* and bacteria *E. coli* and *S. aureus*. Most of the metal chelates show higher biocidal activity for the above microorganisms than that of the free ligand.

**Key words:** hydrazone complexes, spectral, TGA and biocidal

## Dihydroisocoumarins from the Fungus *Cephalosporium sp.* AL031

by Y.-M. Bi<sup>1</sup>, X.-B. Bi<sup>2</sup>, Q.-R. Zhao<sup>1</sup>, Fang A<sup>1</sup> and Y.-G. Chen<sup>1</sup>

<sup>1</sup>Department of Chemistry, Yunnan Normal University, Kunming 650092, P. R. China

<sup>2</sup>Yunnan Animal Husbandry Veterinary Science Institute, Kunming 650224, P. R. China

(Received August 29th, 2005)

Three novel dihydroisocoumarins, (2*E*)-3-[(3*S*)-5-acetyl-3,4-dihydro-6-methoxy-1-oxo-1*H*-2-benzopyran-3-yl]-2-propenoic acid (**1**), (3*S*)-5-hydroxymellein (**3**) and (3*S*)-7-hydroxymellein (**4**) were isolated from the ethyl acetate extract of a culture broth of a strain of the fungus *Cephalosporium sp.* AL031, together with one known compound (3*S*)-mellein (**2**). Their structures were characterized by spectroscopic analysis and comparison of their spectral data with reported values.

**Key words:** *Cephalosporium sp.*, dihydroisocoumarins, fermentations

## **Butyrylcholinesterase Inhibitory C-Glycoside from *Symplocos racemosa***

**by V.U. Ahmad, M. Zubair, M.A. Abbasi, F. Kousar, M.A. Rasheed,  
N. Rasool, J. Hussain, S.A. Nawaz and M.I. Choudhary**

*H.E.J. Research Institute of Chemistry, International Center for Chemical Sciences,  
University of Karachi, Karachi - 75270, Pakistan*

*(Received September 12th, 2005)*

The re-investigation of the chemical constituents of *Symplocos racemosa* Roxb. led to the isolation of one new C-glycoside, symcososide (**1**) along with one known compound  $\beta$ -sito-glycoside (**2**). The structure of the new compound was determined by 1D and 2D-homonuclear and heteronuclear NMR spectroscopy, chemical evidences, and by comparison with the published data of the closely related compounds. The glycoside **1** displayed *in vitro* inhibitory activity against butyrylcholinesterase (BChE) enzyme with  $IC_{50}$  value of  $21.2 \pm 0.01 \mu\text{M}$ .

**Key words:** *Symplocos racemosa*, Symplocaceae, symcososide, butyrylcholinesterase

## **Recursterols A and B, Chymotrypsin Inhibiting Sterols from *Haloxylon recurvum***

by **S. Hussain<sup>2</sup>, E. Ahmed<sup>1</sup>, A. Malik<sup>1</sup>, S. Ferheen<sup>1</sup>, A. Jabbar<sup>2</sup>,  
M. Ashraf<sup>3</sup>, M.A. Lodhi<sup>1</sup> and M.I. Choudhary<sup>1</sup>**

<sup>1</sup>*International Centre for Chemical Sciences, HEJ Research Institute of Chemistry, University of Karachi,  
Karachi – 75270, Pakistan*

<sup>2</sup>*Department of Chemistry, Baghdad-ul-Jadid Campus, Islamia University, Bahawalpur, Pakistan*

<sup>3</sup>*Department of Pharmacy, Islamia University, Bahawalpur, Pakistan*

*(Received August 16th, 2005; revised manuscript October 24th, 2005)*

Recursterols A (**1**) and B (**2**), the new C-24 alkylated sterols, have been isolated from the chloroform-soluble fraction of *Haloxylon recurvum*. Their structures have been deduced through spectroscopic techniques including 2D NMR. Both **1** and **2** showed promising inhibitory potential against the enzyme chymotrypsin.

**Key words:** *Haloxylon recurvum*, Chenopodiaceae, recursterol A, recursterol B, chymotrypsin inhibition

## **Hydroperoxide Oxidation of Different Organic Compounds Catalyzed by Silica-Supported Selenenamide**

by **M. Giurg, M. Brząszcz and J. Młochowski**

*Department of Organic Chemistry, Faculty of Chemistry, Wrocław University of Technology,  
Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland*

*(Received November 11th, 2005)*

The recoverable heterogeneous silica-supported catalyst selenenamide **2** was prepared by the coupling of 3-aminopropylsilicate (**4**) with 2-chloroselenobenzoyl chloride (**6**). Its catalytic activity was demonstrated in *tert*-butyl hydroperoxide oxidation of aldehydes **8** to carboxylic acids **9** and benzylamines **17** to nitriles **18**. Moreover, it was employed for hydrogen peroxide oxidation of azomethine compounds such as tosylhydrazones **10**, oximes **13** and N,N-dimethylhydrazones **16** to parent ketones **12**, arenecarboxylic acids **11** and **15**, their methyl esters **14** and nitriles **18** depending on the substrate used and the reaction conditions. The catalyst was simply recovered by filtration and could be reused.

**Key words:** heterogeneous catalysis, oxidation, peroxides, selenium, supported catalysts

## Synthesis and *In Vitro* Cytotoxic Activity of Novel 6-Chloro-1,1-dioxo-1,4,2-benzodithiazin-3-ylhydrazine Derivatives

by E. Pomarnacka<sup>1</sup>, P.J. Bednarski<sup>2</sup>, R. Grunert<sup>2</sup>, Z. Brzozowski<sup>1</sup> and J. Lach<sup>1,2</sup>

<sup>1</sup>Department of Chemical Technology of Drugs, Medical University of Gdańsk,  
Al. Gen. J. Hallera 107, 80-416 Gdańsk, Poland

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

(Received November 25th, 2005)

The syntheses of 1-(6-chloro-1,1-dioxo-1,4,2-benzodithiazin-3-yl)-4-hydroxysemicarbazides **11–19**, hydroxybenzaldehyde *N*-(6-chloro-7-methyl-1,1-dioxo-1,4,2-benzodithiazin-3-yl)hydrazones **21–24** and 8-chloro-2-(1-naphthylamino)-5,5-dioxo[1,2,4]triazolo[2,3-*b*][1,4,2]benzodithiazine-7-carbonitrile (**26**) are described. All compounds were tested for their *in vitro* cytotoxic potency against 12 human cancer cell lines at the Institute of Pharmacy, University of Greifswald. The compounds **11–19** were inactive, whereas **22** and **24** exhibited weak tumor growth inhibitory properties. The compound **26** was screened at the National Cancer Institute and showed reasonable anticancer activity.

**Key words:** 6-chloro-1,1-dioxo-1,4,2-benzodithiazin-3-ylhydrazine derivatives, syntheses, cytotoxic activity

## **Dicyclopentadienylaluminium Chiral Alkoxides**

**by A. Kunicki, A. Cebulski, K. Leszczyńska, K. Kowalczyk and J. Zachara**

*Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw, Poland*

*(Received July 5th, 2005; revised manuscript November 30th, 2005)*

The reactions of  $\text{Cp}_3\text{Al}$  with *rac*-1-phenyl-1-propanol, *rac*-2-phenyl-1-propanol and *rac*-1-phenyl-2-propanol lead to the formation of dicyclopentadienylalkoxy bridged dimers containing chiral alkoxy groups; (*R,S*) and (*R*<sup>\*</sup>,*R*<sup>\*</sup>) diastereoisomers were found in the reaction mixture. The <sup>1</sup>H and <sup>13</sup>C NMR study showed a differentiation of signal patterns for diastereoisomers depending on the symmetry of a compound and of an anisotropic character of the chiral ligand.

**Key words:** aluminium, cyclopentadienyl, alkoxide

## Two New Steroids Dehydroadyneryzoid and Neristigmol from *Nerium oleander* Leaves

by B.S. Siddiqui<sup>1</sup>, N. Khatoon<sup>1</sup>, S. Begum<sup>1</sup>, R. Sultana<sup>2</sup>  
and S.A. Durrani<sup>1</sup>

<sup>1</sup>International Center for Chemical Sciences, H.E.J. Research Institute of Chemistry,  
University of Karachi, Karachi - 75270, Pakistan

<sup>2</sup>Applied Chemistry Research Centre, PCSIR-Laboratories Complex Karachi,  
Karachi - 75280, Pakistan

(Received August 29th, 2005; revised manuscript November 30th, 2005)

Two new steroids dehydroadyneryzoid (**1**) and neristigmol (**2**) have been isolated from the fresh, uncrushed leaves of *Nerium oleander* and their structures elucidated as 3 $\beta$ -O-( $\beta$ -D-2-deoxy-rhamnosyl)-8,14 $\beta$ -epoxy-5 $\beta$ -carda-16,20(22)-dienolide and hexyl *p*-stigmasteryloxy-benzoate, respectively. The structure elucidation is based on spectroscopic methods including 1D NMR (<sup>1</sup>H NMR, <sup>13</sup>C NMR) and 2D NMR (<sup>1</sup>H-<sup>1</sup>H COSY, NOESY, HMQC, HMBC and *J*-resolved) and chemical transformation.

**Key words:** *Nerium oleander*, Apocynaceae, fresh leaves, triterpenoids, steroids, 1D and 2D NMR

## **Mass Spectrometric Decompositions of Platinum(II) Complexes with 1,3,4-Thiadiazoles and Dimethyl Sulfoxide. Changes in the Complexation Mode**

by **R. Frański and B. Gierczyk**

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

*(Received October 3rd, 2005; revised manuscript December 7th, 2005)*

The platinum(II) complexes with 1,3,4-thiadiazoles and dimethyl sulfoxide have been studied by tandem mass spectrometry. Under the ion trap mass spectrometric condition, after the DMSO molecule(s) loss, changes have been observed in the complexation mode. They consisted in a fast conversion of one complex into another, provided that pyridine nitrogen atom contributes to the platinum cation complexation. The complexes studied have also shown a loss of the pyridine- or benzenenitrile molecule and HCl molecule. The eliminated HCl may contain a hydrogen atom originating from DMSO or from the aryl moiety. In the latter case, further decomposition of the ions formed involves (among others) a complex skeletal rearrangement yielding 2-thiopyridineplatinum cation.

**Key words:** 1,3,4-thiadiazoles, platinum(II) complexes, dimethyl sulfoxide, tandem mass spectrometry

## Isothermal Section of the $Y_2Se_3$ – $Cu_2Se$ – $GeSe_2$ System at 870 K and Crystal Structure of the $Y_3CuGeSe_7$ Compound

by O.S. Lychmanyuk, L.D. Gulay and I.D. Olekseyuk

*Department of General and Inorganic Chemistry, Volyn State University,  
Voli Ave 13, 43009 Lutsk, Ukraine*

*(Received July 6th, 2005; revised manuscript November 14th, 2005)*

The  $Y_2Se_3$ – $Cu_2Se$ – $GeSe_2$  system was investigated using X-ray powder diffraction. The existence of the  $Y_{(2+x)/3}Cu_{2-x}Se_2$  ( $0 \leq x \leq 1$ ) solid solution ( $Er_{2/3}Cu_2S_2$  structure type, space group  $P\bar{3}$ ) was confirmed in the  $Y_2Se_3$ – $Cu_2Se$  section. No compounds were found in the  $Y_2Se_3$ – $GeSe_2$  section. The formation of the  $Cu_8GeSe_6$  ( $Cu_8GeSe_6$  structure type, space group  $P6_3cm$ ) and  $Cu_2GeSe_3$  ( $Cu_2GeSe_3$  structure type, space group  $Imm2$ ) compounds was confirmed in the  $Cu_2Se$ – $GeSe_2$  section. The isothermal section of the  $Y_2Se_3$ – $Cu_2Se$ – $GeSe_2$  system at 870 K was constructed, based on data of the phase analysis of 54 samples. The formation of new quaternary  $Y_3CuGeSe_7$  compound ( $La_3CuSiS_7$  structure type, space group  $P6_3$ ,  $a = 1.02368(8)$  nm,  $c = 0.60569(3)$  nm) was established in the  $Y_2Se_3$ – $Cu_2Se$ – $GeSe_2$  system.

**Key words:** X-ray analysis, isothermal section, crystal structure, phase diagram

## Theoretical Determinations of Ionization Potential and Electron Affinity of Gaseous $\alpha$ -Alanine

by J.F. Lu<sup>1</sup>, S.L. Zhu<sup>2</sup>, Z.Y. Zhou<sup>1</sup>, Q.Y. Wu<sup>1</sup> and G. Zhao<sup>1</sup>

<sup>1</sup>Department of Chemistry, Qufu Normal University, Shandong, Qufu, 273165, and State Key Laboratory Crystal Materials Shandong University, Shandong, Jinan, 250100, P. R. China

<sup>2</sup>School of Biological and Chemical Engineering, Qingdao Technical & Vocational College, Qingdao 266555, P. R. China

(Received September 13th, 2005; revised manuscript November 16th, 2005)

Adiabatic (vertical) ionization potential (IP) and valence electron affinity (EA) of gaseous  $\alpha$ -alanine have been determined by density functional theory (B3LYP), *ab initio* Hartree-Fock (HF) calculations and *ab initio* third order algebraic diagrammatic construction [ADC(3)] Green function method with the 6-311++G\*\* and 6-311G\*\* basis sets, respectively. Eighteen possible conformers of  $\alpha$ -alanine and its charged states have been optimized, employing density functional theory (B3LYP) with 6-311++G\*\* and 6-311G\*\* basis sets, respectively. In the gas phase, the IPs of all  $\alpha$ -alanine calculated have positive values and all the EAs are negative, except for VEA<sub>2</sub> (+0.555 eV) of 6A, which indicates that all anions except for 6A<sup>-</sup> are unstable with respect to electron autodetachment vertically and adiabatically. All kinds of chemical quantities, associated with the IP and EA, such as electronegativity, chemical potential, chemical hardness, and chemical softness, have also been determined. Finally, we also report the infrared spectrum frequencies and vibrational modes for neutral states of  $\alpha$ -alanine 1A, 2A, 3A, 5A and their optimized cationic and anionic states in seven highest frequency regions, and analyzed the relationship between the vibrational frequencies when receiving or donating an electron.

**Key words:** B3LYP method, ionization potential, electron affinity,  $\alpha$ -alanine

## **Voltammetric Study of Interaction of Copper with Some Methyl-Substituted Ethylenediimine Compounds Using Nonlinear Least-Squares-Excel-Solver**

by **L. Fotouhi<sup>1</sup>, T. Bahmanpour<sup>1</sup>, J. Ghasemi<sup>2</sup>, S. Dehghanpour<sup>1</sup>**  
and **M.M. Heravi<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Faculty of Science, Alzahra University, P.O.Box 1993891167, Tehran, Iran*

<sup>2</sup>*Department of Chemistry, Faculty of Science, University of Razi, Kermanshah, Iran*

*(Received August 4th, 2005; revised manuscript December 9th, 2005)*

The complex formation of  $\text{Cu}^{2+}$  with some recently synthesized methyl-substituted ethylenediimines in binary dimethylformamide-ethanol mixtures was studied by differential pulse voltammetry. The stoichiometry and the stability of the complexes were determined by monitoring the increasing complex peak current against the ligand concentration using nonlinear least squares-Excel solver. In all studied cases, it was found that the stability of the resulting 1:1 complex decreases by increasing the amount of ethanol in the binary mixtures. The observed stability order is discussed in terms of the solvent binary mixtures and the nature of the substituted ethylenediimine structure.

**Key words:** ethylenediimine, voltammetry, stability constant, mixed solvent, complex

**Copper(II)-Catalyzed Promazine Oxidation by Dioxygen  
in Acidic Aqueous Solutions**

by **J. Wiśniewska and P. Kita**

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

*(Received August 29th, 2005; revised manuscript November 15th, 2005)*

**Influence of Oxygen on SiO<sub>x</sub> Thin-Film Formation  
in Pulsed Electric Discharges**

by **T. Opalińska<sup>1</sup>**, **B. Ulejczyk<sup>1</sup>**, **J.W. Sobczak<sup>2</sup>**, **A. Biliński<sup>2</sup>**  
and **K. Schmidt-Szałowski<sup>3</sup>**

<sup>1</sup>*Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warszawa, Poland*

<sup>2</sup>*Institute of Physical Chemistry PAS, Kasprzaka 44/52, 01-224 Warszawa, Poland*

<sup>3</sup>*Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warszawa, Poland*

*(Received June 24th, 2005; revised manuscript November 30th, 2005)*

**Kinetic Studies on Formation of Heterobimetallic  
Complexes Between Some Chromium(III) Bipyridine  
Species and Hexacyanoferrates(II)**

by **A. Topolski, H. Marai, J. Chatłas and P. Kita**

*Faculty of Chemistry, N. Copernicus University, Gagarina 7, 87-100 Toruń, Poland*

*(Received September 16th, 2005; revised manuscript November 30th, 2005)*