

## Synthesis and Crystal Structure of Five-Coordinated Triorganotin Complexes with 2,5-Dimercapto-4-phenyl-1,3,4-thiadiazole

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Reactions between triorganotin chloride and 2,5-dimercapto-4-phenyl-1,3,4-thiadiazole gave complexes  $R_3Sn(S_3N_2C_8H_5)$  (**4**: R = Ph; **5**: R = PhCH<sub>2</sub> and **6**: R = *n*-Bu), respectively. All products were characterized by elemental analysis, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and two of them ((**4**) and (**5**)) have been determined by X-ray crystallography. Including the Sn–N interaction, the tin atoms of three complexes all have five-coordinated distorted trigonal bipyramidal geometry. All three complexes have antitumor activity in bioactivity measurements. Crystal data for complex (**4**): monoclinic, space group  $P2(1)/c$ ,  $a = 9.696(2)$  Å,  $b = 14.773(3)$  Å,  $c = 17.466(4)$  Å,  $\beta = 92.599(3)^\circ$ , and  $Z = 4$ . Crystal data for complex (**5**): triclinic, space group  $P-1$ ,  $a = 9.744(6)$  Å,  $b = 16.338(10)$  Å,  $c = 17.957(12)$  Å,  $\alpha = 90.000(12)^\circ$ ,  $\beta = 100.735(11)^\circ$ ,  $\gamma = 90.000(12)^\circ$  and  $Z = 4$ .

## Antiferromagnetically Coupled Chromium(III)–Chromium(III) Binuclear Complexes with Tris(oxalato)chromate(III)

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Three new binuclear chromium(III) complexes bridged by tris(oxalato)chromate(III),  $[\text{Cr}(\text{ox})_3]^{3-}$  and end-capped with 2,2'-bipyridine (bpy); 4,4'-dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{bpy}$ ) or 5-methyl-1,10-phenanthroline (Mephen), have been synthesized and characterized, namely  $[\text{Cr}_2(\text{ox})_3(\text{bpy})_2]$  (**1**),  $[\text{Cr}_2(\text{ox})_3(\text{Me}_2\text{bpy})_2]$  (**2**) and  $[\text{Cr}_2(\text{ox})_3(\text{Mephen})_2]$  (**3**). At present, the three complexes have not yet been isolated in crystalline form, suitable for X-ray structure analysis, but based on elemental analyses, molar conductance and magnetic moments of room-temperature measurements, and spectroscopic studies, extended ox-bridged structures consisting of two chromium(III) ions, each in an octahedral environment are proposed for these complexes. The complexes  $[\text{Cr}_2(\text{ox})_3(\text{bpy})_2]$  (**1**) and  $[\text{Cr}_2(\text{ox})_3(\text{Me}_2\text{bpy})_2]$  (**2**) were further characterized by variable temperature magnetic susceptibility (4.2–300 K) measurements and the observed data were successfully simulated by the equation based on the spin Hamiltonian operator,  $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ , giving the exchange integrals  $J = -9.73 \text{ cm}^{-1}$  for (**1**) and  $J = -5.29 \text{ cm}^{-1}$  for (**2**). This result indicates the presence of weak antiferromagnetic spin-exchange interaction between the metal ions within each molecule. The influence of the methyl substituents in the terminal ligand on magnetic interactions between the metals is also discussed.

**Study of Phase Equilibria in the System  
Nd<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O–P<sub>2</sub>O<sub>5</sub>. The Partial System  
NdPO<sub>4</sub>–NaPO<sub>3</sub>–Nd(PO<sub>3</sub>)<sub>3</sub>**

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A partial system of NdPO<sub>4</sub>–NaPO<sub>3</sub>–Nd(PO<sub>3</sub>)<sub>3</sub> in the ternary system Nd<sub>2</sub>O<sub>3</sub>–Na<sub>2</sub>O–P<sub>2</sub>O<sub>5</sub> was investigated and its phase diagram is proposed. Thermoanalytical methods and X-ray powder diffraction were employed. In the composition range under examination, two ternary compounds occur, which melt incongruently and have the formulae NaNd(PO<sub>3</sub>)<sub>4</sub> (m.p. 866°C) and NaNdP<sub>2</sub>O<sub>7</sub> (m.p. 790°C). Two quasi-binary sections, NdPO<sub>4</sub>–NaNd(PO<sub>3</sub>)<sub>4</sub> and NaNdP<sub>2</sub>O<sub>7</sub>–NaNd(PO<sub>3</sub>)<sub>4</sub> have been identified.

## Synthesis, Structure and Non-Linear Optical Properties of a Copper(II) Ethyl Bisulfate Two-Dimensional Supramolecular Compound [Cu(Him)<sub>4</sub>(CH<sub>3</sub>CH<sub>2</sub>OSO<sub>3</sub>H)<sub>2</sub>]

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A novel copper(II) ethyl bisulfate complex [Cu(Him)<sub>4</sub>(Eb)<sub>2</sub>] **1** (Him = imidazole, Eb = ethyl bisulfate) has been prepared and characterized by means of elemental analysis, IR and ESR. The structure was determined by single crystal X-ray diffraction analysis, which suggests that compound **1** exhibits a two-dimensional supramolecular structure through hydrogen bonds. Compound **1** displays strong third-order non-linear optical (NLO) absorption and refraction with absorption coefficient  $\alpha_2$   $1.10 \times 10^{-11} \text{ m} \cdot \text{w}^{-1}$  and refractive index  $n_2$   $-5.60 \times 10^{-16} \text{ m}^2 \cdot \text{w}^{-1}$ . The third-order non-linear optical susceptibility  $\chi^{(3)}$  of compound **1** is  $3.07 \times 10^{-10}$  esu.

## **Phase Equilibria in the Quasi-Binary Thallium(I) Selenide – Bismuth(III) Selenide System**

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The phase equilibrium diagram for the system  $\text{Tl}_2\text{Se} - \text{Bi}_2\text{Se}_3$  has been constructed from the results of thermal analysis. The diagram has been compared with that for the analogous system  $\text{Tl}_2\text{Te} - \text{Bi}_2\text{Te}_3$ , as well as with that published earlier for the same  $\text{Tl}_2\text{Se} - \text{Bi}_2\text{Se}_3$  system, delineated from the data obtained by other methods.

## **Competitive Potentiometric Study of a Series of 18-Crown-6 with $\text{Pb}^{2+}$ , $\text{Ag}^+$ , and $\text{Tl}^+$ Ions in Methanol Using $\text{Ag}^+/\text{Ag}$ Electrode**

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The complexation of  $\text{Ag}^+$ ,  $\text{Tl}^+$  and  $\text{Pb}^{2+}$  with 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexyl-18-crown-6 (DCY18C6), and dibenzopyridino-18-crown-6 (DBPY18C6) in methanol solution have been studied by a competitive potentiometry, using  $\text{Ag}^+/\text{Ag}$  electrode as a sensor. The stoichiometry and stability constants of resulting complexes have been evaluated by MINIQUAD program. The stoichiometry for all resulting complexes was 1:1. The order of stability of  $\text{Ag}^+$  complexes with used crown ethers varied as  $\text{DBPY18C6} > \text{DCY18C6} > \text{18C6} > \text{DB18C6}$ . For  $\text{Pb}^{2+}$ , and  $\text{Tl}^+$ , the sequence of stability of complexes with each of these crown ethers (except of DBPY18C6) varied in the order  $\text{Pb}^{2+} > \text{Ag}^+ > \text{Tl}^+$ . The major trend of stability of resulting complexes of these macrocycle with  $\text{Pb}^{2+}$  and  $\text{Tl}^+$  varied in the order  $\text{DCY18C6} > \text{18C6} > \text{DBPY18C6} > \text{DB18C6}$  with few exceptions.

## Selective Formation of Isopropyl $\alpha$ - and $\beta$ -Glucofuranosides in One Pot Reaction from D-Glucose and Propanol-2 Promoted by $V_2O_5$

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Reaction of D-glucose with propanol-2 promoted by  $V_2O_5$  gives rise exclusively to isopropylglucofuranosides. Their tetraacetates were prepared; X-ray structure of one of tetraacetates was determined. <sup>1</sup>H and <sup>13</sup>C NMR signals assignment was done by COSY and GMBC techniques. Mechanism of selective glucosidation was discussed.

## Studies on Reactions of 3-Benzoyl-4-hydroxypyrido[3,2-*e*]-1,2-thiazines with Primary Amines and N-Methylhydrazine

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Reaction of the appropriate 3-benzoyl-4-hydroxypyrido[3,2-*e*]-1,2-thiazine-1,1-dioxides **2** bearing a methyl or a 3-(4-arylpiperazin-1-yl)propyl group at the nitrogen atom of the thiazine ring with primary amines resulted in enamines of type (E)-**3**. The related products **8** were obtained by alkylation of 3-phenylpyrazolo[4,3-*c*]pyrido[3,2-*e*]-1,2-thiazine-5,5-dioxide **7** with the corresponding 1-aryl-4-(3-chloropropyl)piperazines **9**. The structures of the new heterocycles **3** and **8**, synthesized for pharmaceutical purposes, and of the model compounds **4–6**, prepared for comparison of spectral properties, were proven through elemental, IR, <sup>1</sup>H NMR and, in some cases (**3d**, **8a**), X-ray data.

## **Transformation of $\alpha$ -Hydroxymethylamino Acids into $\alpha$ -Mercaptomethylamino Acids ( $\alpha$ -Alkylcysteines)[1]**

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N-Boc- $\alpha$ -alkylserines ( $\alpha$ -hydroxymethylamino acids) undergo a cyclization reaction without racemization to N-Boc- $\alpha$ -alkylserine- $\beta$ -lactones in 90–98% yield using Mitsunobu conditions ( $\text{Ph}_3\text{P}$ , diethyl azodicarboxylate). Treatment of the corresponding  $\beta$ -lactones with sulphur nucleophiles (thiolacetic acid or 4-methoxybenzylmercaptan) gives S-protected N-Boc- $\alpha$ -alkylcysteines ( $\alpha$ -mercaptomethylamino acids) in high yield. These chimeric  $\alpha,\alpha$ -disubstituted amino acids, being incorporated into peptide chain, are able to close the cyclic structure as a disulfide bond.

## **Studies on 2,3-Dioxopyrrolidines. Synthesis of Piperazine, Pyrrolo[4,5-*b*]indole, Pyrazino[5,6-*b*]indole and Arylazo Derivatives of Amino Acids**

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2,3-Dioxopyrrolidines **1** convert into 2,4-diketopiperazines **2** in one pot-reaction with hydrazoic acid. The pyrrolo[4,5-*b*]indole **6** was obtained by cyclization of *p*-methoxyphenylhydrazone **4** prepared *via* Japp-Klingemann reaction of **1a** with *p*-methoxyphenyldiazonium chloride. Compound **5** undergoes Schmidt reaction to give the pyrazino[5,6-*b*]indole derivative **6**. Reaction of **1b** with some aryldiazonium chlorides yields arylhydrazono- $\beta$ -alanines **8** and **9**. Phenylhydrazonoglycine derivative **11** was synthesized *via* Schmidt reaction to **10** with hydrazoic acid.

## **1H-Pyrazolo[3,4-b]quinolines and Their Performance in Electroluminescent Devices**

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A series of highly luminescent pyrazolo[3,4-b]quinolines were prepared and used as luminophores in fabrication of three-layer electroluminescent devices. The devices were fabricated using the basic structure of indium tin oxide (ITO)/TPD/Pyrazoloquinoline/ALQ/Mg:Ag, where TPD (3-methylphenyl)-1,1'-biphenyl-4,4'-diamine was used as a hole transport layer and ALQ (8-hydroxyquinoline) as an electron transport layer. Bright blue-green and blue emissions were obtained from all the devices with such configurations. The devices with **6d** and **6f** pyrazoloquinoline derivatives achieved  $L_{\max} = 20800 \text{ cd/m}^2$  and  $8550 \text{ cd/m}^2$  at a current density of  $30 \text{ mA/4 mm}^2$ . The luminance efficiency was 3.38 and 1.70 lm/W respectively.

**Photodegradation Kinetics of *o*-Nitroaniline (ONA),  
*m*-Nitroaniline (MNA), *p*-Nitroaniline (PNA),  
*p*-Bromoaniline (PBrA) and *o*-Chloroaniline (OCIA)  
in Aqueous Suspension of Zinc Oxide**

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Photodegradation of several aniline derivatives including *o*-nitroaniline (ONA), *m*-nitroaniline (MNA), *p*-nitroaniline (PNA), *p*-bromoaniline (PBrA) and *o*-chloroaniline (OCIA) have been studied in aqueous solution using zinc oxide. Rate constants span the range from  $6.46 \times 10^{-3} \text{ min}^{-1}$  to  $2.59 \times 10^{-2} \text{ min}^{-1}$ . The slower degradation rate of *p*-bromoaniline (PBrA),  $6.46 \times 10^{-3} \text{ min}^{-1}$  could be related to oxidation potential of the corresponding aromatic rings. The Langmuir-Hinshelwood (L-H) rate constant  $k$ , and adsorption constant, ( $K_A$ ) for all five aniline derivatives are reported.

## **Effect of Residual Na on Cu-ZnO Catalyst in Dehydrogenation of 2-Butanol**

**by Z.-L. Wang, G.-J. Wang, W.-C. Zhu, P.-P. Yang, H.-C. Ma, G.-Z. Liu,  
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A series of residual Na on Cu-ZnO catalysts were prepared by co-precipitation method. The effect of residual Na on catalysts was examined in dehydrogenation of 2-butanol. The catalysts were characterized by BET, ICP, XRD, TPR and XPS techniques. The TPR result showed that residual Na made CuO exists in different phases, the higher the content of Na the harder the reduction of CuO. For reduced or used catalyst with a high content of Na, the XPS result indicated that Na diffused to the catalyst surface and inhibited the interaction between Cu and ZnO. The sharp decrease in catalytic activity by Na incorporation could be interpreted mainly in terms of the copper particle size increasing during reaction. Interaction between Cu and ZnO could have stabilized the copper species. The Na free catalyst shows high and stable activity in dehydrogenation of 2-butanol.

**Synthesis and Structure of  
3,4-(Methylenedioxy)benzaldehyde  
2,4-Dinitrobenzalhydrazone**

by **J.-L. Wang<sup>1</sup>** and **Y.-J. Jia<sup>1,2</sup>**

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**Catalytic and Plasma-Catalytic Processing  
of Nitrous Oxide**

by **K. Krawczyk and O. Kawczyńska**

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**Chemistry and Mathematics: Two Scientific Languages of the 21<sup>st</sup> Century**  
**Nova Acta Leopoldina, N.F. 88, Nr 330 (2003) p. 160**

The book concerns the special symposium on the subject given above, organized by Leopoldina on 11–13. October 2001 and published two years later. The contents of this book are:

Roesky, Herbert W.: Introduction. ..7  
Ourisson, Guy: Chemistry as an Ideographic Language ...11  
Collin, Jean-Paul, Dietrich-Buchecker, Christiane, Gavina, Pablo Jimenez-Molero, Maria Consuelo, and Sauvage, Jean-Pierre: Transition Metal-Based Machines and Motors at the Molecular Level.....19  
Delgado-Friedrichs, Olaf: Virtual Crystallography ....39  
Deuflhard, Peter: A comparison of Related Concepts in Computational Chemistry and Mathematics...51  
Haber, Jerzy: The Essence of Chemical Thinking Beyond Mathematical Equations .... 67  
Warnatz, Jürgen: Analysis of Chemical Reaction Systems - What Are Mathematics Able to Do, How Far Has Chemistry to Help? ... 81  
Thomas, Sir John Meurig: Poetic Suggestion in Chemical Science ... 109  
Wolfrum, Jürgen: Combustion: From Mathematical Models to Practical Devices ... 141

From the above 8 contributions only 4: Delgado-Friedrichs, Deuflhard, Warnatz and Wolfrum can be treated as connected with „Chemistry and Mathematics” The other four contributions oscillate between an „Ideographic Language” and “Poetic Suggestion” – thus, they are rather beyond mathematics in the common sense.

In “Virtual Crystallography” a review of a new discipline, based on a mathematical theory is given, concerning crystals, networks and related space structures.

In the article of Deuflhard the relation between chemistry and mathematics is studied, whereby some examples from chemical kinetics, polymer chemistry and medical chemistry are discussed.

Warnatz treats the computer simulation in complex reacting systems on examples of oxidation of hydrocarbons, whereby both the reaction steps and the accompanying macroscopic balance equations are taken into account, including turbulence.

Wolfrum discusses in his contribution the possibility of a more detailed treatment of combustion processes by a combination of elementary kinetic steps with the macroscopic transport phenomena. This could lead to an improvement of the control of the processes involved.

Summing up – the book discussed contains valuable results and suggestions for the interaction between mathematics and chemistry and has in some parts interesting philosophical aspects of the two scientific languages treated.

*B. Baranowski*