

## Synthesis and Magnetic Analysis of $\mu$ -Oxamido-Bridged Cu(II)–Fe(II) Heterodinuclear Complexes

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The strategy of “complex as ligand” allowed us to synthesize two new  $\mu$ -oxamido-bridged heterodinuclear complexes identified as [Cu(bmap)Fe(bpy)<sub>2</sub>]SO<sub>4</sub> (**1**) and [Cu(bmap)Fe(phen)<sub>2</sub>]SO<sub>4</sub> (**2**), where bmap represents the N,N'-bis(2-methyl-2-amino-propyl)oxamido dianion; bpy and phen stand for 2,2'-bipyridine and 1,10-phenanthroline, respectively. These complexes are the first examples of copper(II)–iron(II) species bridged by bmap groups. Based on elemental analyses, IR and electronic spectra studies, magnetic moments at room temperature and molar conductivity measurements, these complexes are proposed to have an extended oxamido-bridged structure consisting of planar copper(II) and octahedral iron(II) ions. The two heterodinuclear complexes have been further characterized by variable temperature magnetic susceptibility (4.2–300 K) and the observed data were least-squares fitted to the susceptibility equation derived from the spin Hamiltonian including single-ion zero-field interaction for the iron(II) ion,  $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 - D\hat{S}_{Z1}^2$ , giving the exchange integrals  $J = -18.9 \text{ cm}^{-1}$  for (**1**) and  $J = -20.1 \text{ cm}^{-1}$  for (**2**). These results indicated that the spin coupling between the adjacent copper(II) and iron(II) ions through the oxamido-bridge in both complexes (**1**) and (**2**) is antiferromagnetic. The influence of methyl substituents in the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

**Key words:**  $\mu$ -oxamido-bridge, copper(II), iron(II), heterodinuclear complexes, magnetic properties

## Synthesis and Magnetism of Ferromagnetically Coupled [Cu<sup>II</sup><sub>3</sub>Cr<sup>III</sup>] Heterotetranuclear Complexes with N,N'-Bis(aminoalkyl)oxamidatocopper(II)

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The strategy of “complex as ligand” allowed us to synthesize two new  $\mu$ -oxamido-bridged copper(II)–chromium(III) heterotetranuclear complexes formulated as [Cu<sub>3</sub>(oxae)<sub>3</sub>Cr](ClO<sub>4</sub>)<sub>3</sub> (**1**) and [Cu<sub>3</sub>(oxpn)<sub>3</sub>Cr](ClO<sub>4</sub>)<sub>3</sub> (**2**), where oxae and oxpn represent N,N'-bis(2-aminoethyl)oxamido and N,N'-bis(3-aminopropyl)oxamido dianions, respectively. Based on elemental analyses, molar conductivity and magnetic moment (room-temperature) measurements, IR, ESR and electronic spectral studies, these complexes are proposed to have oxamido-bridged structures consisting of three copper(II) ions and a chromium(III) ion, in which the chromium(III) ion has an octahedral environment and the three copper(II) ions have a square-planar environment. The two heterotetranuclear complexes were further characterized by variable-temperature magnetic susceptibility (3~300 K) measurements and the magnetic data have been used to deduce the indicated heterotetranuclear structure. The results derived from least-squares fit of the experimental data have confirmed the ferromagnetic interaction between the adjacent copper(II) and chromium(III) ions through the oxamido-bridge within each molecule. On the basis of the spin Hamiltonian operator,  $\hat{H} = -2J(\hat{S}_{Cu_1} \cdot \hat{S}_{Cr} + \hat{S}_{Cu_2} \cdot \hat{S}_{Cr} + \hat{S}_{Cu_3} \cdot \hat{S}_{Cr})$ , the magnetic analyses were carried out for the two copper(II)–chromium(III) heterotetranuclear complexes and the spin-coupling constants (*J*) were evaluated as +13.98 cm<sup>-1</sup> for (**1**) and +12.65 cm<sup>-1</sup> for (**2**). The results indicate that the bridging oxamido should be able to transmit ferromagnetic interaction in the strict orthogonality [Cu<sup>II</sup><sub>3</sub>Cr<sup>III</sup>] system. The influence of the symmetry of the magnetic orbitals on the nature of the magnetic interaction between the paramagnetic centers is preliminarily discussed.

**Key words:**  $\mu$ -oxamido-bridge, copper(II), chromium(III), heterotetranuclear complexes, magnetic properties, ferromagnetic coupling

## Synthesis and Magnetism of Cu(II)–Ln(III)–Cu(II) (Ln = La, Nd, Gd, Tb, Ho, Er) Trinuclear Complexes Bridged by N,N'-Bis[3-(dimethylamino)propyl]oxamido

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Six new  $\mu$ -oxamido-bridged copper(II)–lanthanide(III)–copper(II) heterotrinnuclear complexes described by the overall formula  $\text{Cu}_2(\text{dmoxpn})_2\text{Ln}(\text{NO}_3)_3$  {Ln = La, Nd, Gd, Tb, Ho, Er; dmoxpn = N,N'-bis[3-(dimethylamino)propyl]oxamido dianions} have been synthesized and characterized by elemental analyses, molar conductivity measurements, IR and electronic spectral studies. The variable-temperature susceptibility (4.2–300 K), ESR measurements, and studies of the  $\text{Cu}_2(\text{dmoxpn})_2\text{Gd}(\text{NO}_3)_3$  complex have revealed that the central gadolinium(III) and terminal copper(II) ions are ferromagnetically coupled with the exchange integral  $J_{(\text{Cu-Gd})} = +6.85 \text{ cm}^{-1}$ , while an antiferromagnetic coupling is detected between the terminal copper(II) ions with  $J'_{(\text{Cu-Cu})} = -0.27 \text{ cm}^{-1}$ , on the basis of the spin Hamiltonian operator [ $\hat{H} = -2J(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Gd}} + \hat{S}_{\text{Cu2}} \cdot \hat{S}_{\text{Gd}}) - 2J'(\hat{S}_{\text{Cu1}} \cdot \hat{S}_{\text{Cu2}})$ ]. A plausible mechanism for the ferromagnetic coupling between copper(II) and gadolinium(III) is discussed in terms of spin polarization.

**Key words:**  $\mu$ -oxamido-bridge, copper(II), lanthanide(III), heterotrinnuclear complexes, magnetism

**Atomic Core Based Periodic System of Elements.  
A Contradictory Approach to the Arbitrary  
1–18 Group Numbering in the Long Form  
of Atom Based Periodic System**

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Problems connected with the long version of atom-based Periodic System of chemical elements with arbitrary 1–18 group numbering recommended by IUPAC are discussed. Introducing the atomic cores of elements instead of atoms to the Periodic Table enables to define unequivocally the Periodic System as a triparametric classification resulting from three numbers: the number of core electron shells  $n$ , the core charge  $q$ , and the number of valence subshells  $l$ . The core based periodic chart is free of any imperfections and limitations of the atom based system and it enables reasonable numeration of groups and periods according to the  $nql$  parameters.

**Key words:** Periodic System of elements, atomic core, elements classification

## **Coordination States and Apparent Molar Volumes of Cobalt(II) Perchlorate and Cobalt(II) Chloride in *N,N*-Diethylacetamide Solutions at 25°C**

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Visible absorption spectra and apparent molar volumes for  $\text{CoCl}_2$  and  $\text{Co}(\text{ClO}_4)_2$  in *N,N*-diethylacetamide (DEA) as well as the spectra for the  $\text{Co}(\text{ClO}_4)_2 - \text{CoCl}_2 - \text{DEA}$  and  $\text{CoCl}_2 - \text{LiCl} - \text{DEA}$  systems were studied. The results indicate formation of the electrically neutral  $\text{CoCl}_2(\text{DEA})_2$  complex, being the predominating chloro-complex of cobalt(II) in the solutions of  $\text{CoCl}_2$  in DEA. The formation constants of the consecutive chloro-complexes of cobalt(II) have been determined:  $\log K_1 = 5.28(\pm 0.10)$ ,  $\log K_2 = 6.10(\pm 0.08)$ ,  $\log K_3 = 3.31(\pm 0.05)$  and  $\log K_4 = 0.74(\pm 0.05)$ .

**Key words:** cobalt(II) perchlorate, cobalt(II) chloride, *N,N*-diethylacetamide, DEA, electronic absorption spectra, apparent molar volumes, complex formation, formation constant

## Determination of Thermodynamic and Kinetic Parameters of Inclusion Complex Formation of 2-Mercaptobenzothiazole with $\beta$ -Cyclodextrin

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The inclusion of 2-mercaptobenzothiazole by  $\beta$ -cyclodextrin was studied by spectrophotometry. The absorbance of inclusion complex decreased when  $\beta$ -cyclodextrin was dissolved in water and the complex was diluted with ethanol. The same result was obtained by using water as the solvent and diluent. The absorbance decrease in ethanol was greater than that in water. The absorbance increased with the increase of the content of  $\beta$ -cyclodextrin when DMSO was used both as the solvent and diluent. Although the absorbance of the complex was higher than that of the guest when  $\beta$ -cyclodextrin was dissolved in DMSO and inclusion complex was diluted with water, the absorption decreased when the concentration of  $\beta$ -cyclodextrin was increased. Stability constants of the inclusion complex in different solvents changed in the order  $K_{\text{DMSO}} < K_{\text{H}_2\text{O}} < K_{\text{EtOH}}$ . Further studies showed that formation of the inclusion complex was spontaneous and exothermic. Thermodynamic parameters and the rate constants of the inclusion reaction were determined.

**Key words:**  $\beta$ -cyclodextrin, 2-mercaptobenzothiazole, inclusion complexes, thermodynamics, kinetics

## Lipoxygenase Inhibiting Steroidal Glycosides and Naphthene Derivatives from *Haloxylon salicornicum*

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Allostigmasterol glycosides **1** and **2** and monocyclic naphthene derivatives **3** and **4** have been isolated from methanolic extract of *Haloxylon salicornicum* and their structures elucidated through spectroscopy. Triacontanoic acid **5**, ergosterol peroxide **6** and lupeol **7** were also obtained for the first time from this species. Both **1** and **2** showed moderate lipoxygenase inhibiting activity.

**Key words:** *Haloxylon salicornicum*, Chenopodiaceae, steroidal glycosides, naphthenes, lipoxygenase inhibition

## **Electrooxidative Conversion of Dibenzoylbenzene Dihydrazones into the Corresponding Bis-Diazo Compounds and Bis-Dimethyl Acetals**

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Several dibenzoylbenzene dihydrazones were electrochemically oxidized into the corresponding bis-dimethyl acetals in a methanolic solution containing sodium methoxide and catalytic amount of KI. During electrolysis, the anolyte exhibited a characteristic deep purple, which strongly suggested that formation of a diazo compound as an intermediate. Interestingly, some of the diazo compounds could be isolated directly from the anolyte.

**Key words:** electrooxidation, dibenzoylbenzene dihydrazones



## **Addition of Diazomethane to Phosphonodithioformates and Reactions of Phosphonylated Thiocarbonyl *S*-Methylides**

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The reaction of phosphonodithioformates **14** with diazomethane at  $-60^{\circ}\text{C}$  yielded 2,5-dihydro-1,3,4-thiadiazoles **15** as unstable intermediates. Their structure was evidenced by the base-catalyzed elimination of methylsulfane leading to 1,3,4-thiadiazole-2-phosphonates. At *ca.*  $-35^{\circ}\text{C}$ , thermal decomposition of **15** by  $\text{N}_2$ -elimination led to reactive thiocarbonyl *S*-methylides **17**. In the absence of trapping reagents, these 1,3-dipoles undergo a head-to-head dimerization leading to 1,4-dithianes **18**. An intermediate zwitterionic dimer **19** was detected by  $^{31}\text{P}$  NMR spectroscopy. The initially formed thiocarbonyl *S*-methylide **17** as well as an open-chain zwitterionic dimer **20** was intercepted by methanol. Stable interception products were also obtained with *S*- and *N*-nucleophiles.

**Key words:** addition reactions, dimerization, thiocarbonyl ylides, 1,3-dipoles, sulfur heterocycles

## **Ammonia Decomposition over Iron in the Presence of Water Vapor**

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The ammonia decomposition over iron in the presence of water vapor has been studied. Water vapor retards this process, though no change of the apparent activation energy is observed. Despite noticeable influence of the water vapor on the rate of ammonia decomposition the sticking coefficient of ammonia on iron is not affected. Those observations were explained by the retardation of nitrogen molecules recombination on the iron surface due to the presence of oxygen atoms. The positive influence of water vapor on the rate of iron nitriding is also elucidated.

**Key words:** ammonia decomposition, iron, water vapor

## **Applicability of the NRTLmKW Method for Prediction of Binary and Ternary Vapour-Liquid Equilibria Data**

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A new local composition model NRTLmKW has been used for prediction of 28 binary and ternary vapour-liquid equilibrium data. The data have been selected to give a wide representation of various kinds molecular interactions in solution. The results have been compared with correlation results of these systems given by well-known equation of states (Schmidt-Wenzel, Stryjek-Vera, Anderko) and have been discussed from the point of view of intermolecular interactions. Some recommendations have been made on the use of the equations investigated for such calculation.

**Key words:** correlation and prediction of VLE data, NRTLmKW model

## **Adsorption of Urea on the Gold Electrode and Air/Solution Interface**

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The adsorption of urea on gold from aqueous 1 M LiClO<sub>4</sub> has been determined from measurements of cyclic voltammetry and electrochemical impedance spectroscopy. The film pressure and the Gibbs excess are determined as functions of urea concentrations and potential. The standard free energy of adsorption is a quadratic function of charge with maximum adsorption occurring at a charge of  $+6\mu\text{C cm}^{-2}$ . These data are interpreted in terms of the partially oriented urea dipoles (with the CO group directed towards the metal) and the contribution of water dipoles.

**Key words:** gold, urea, differential capacity, adsorption

**Spectroscopic Studies on the Charge-Transfer  
Complex  $[\text{VO}(\text{acac})_2]\text{I}_5$  Formed in the Reaction  
of Oxovanadium(IV)acetylacetonate with Iodine**

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**Stability of Valinomycin – Proton Complex  
in Nitrobenzene Saturated with Water**

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**Synthesis and Crystal Structure of a New Mononuclear Silver(I) Complex with a Schiff Base Ligand Derived from 2-Fluorobenzaldehyde and Ethylenediamine**

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**Barrier-Discharge Reactor for Deposition of  
Gas-Tight Coatings on Plastic Foils**

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**Sesquiterpenoids and Phenolics from  
*Taraxacum rubicundum***

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