

## **Morphological Classification of Chemical Structural Units**

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*(Received May 24th, 2000; revised manuscript October 24th, 2000)*

A new classification of chemical structural units (csu), based on their elemental chemical transformations, is presented. It originates from a new uniform numerical definition of acids, bases, oxidators and reducers and a new numerical approach to the periodic chart of elements. According to these assumptions csu and their combinations are distributed in a multi-dimensional classification space. Much attention has been paid to prove experimentally that the virtual classification steps present the real steps of chemical reactions of csu. Thermal decomposition stages as well as syntheses of salts in solid state were investigated. Applications of classification presented in research and didactics have been discussed.

## **Spectroscopic and Polarographic Studies of Novel Imidazole Adduct of Ammonium Trioxovanadate(V). A Solution and Solid State Study**

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*(Received July 24th, 2000; revised manuscript September 26th, 2000)*

Complex formation between ammonium trioxovanadate(V) and imidazole has been studied and characterized by FT IR, UV/Vis, thermal analysis (TG, DTA, DTG) and polarographic techniques. Species formed in solid phase yield a yellow coloured product exhibiting an absorbance maximum at 400 nm. The FT IR spectra show that the inclusion of imidazole has a significant influence on the structure and the hydrogen bonding pattern in  $\text{NH}_4\text{VO}_3$ . Species formed in aqueous solution has been examined by voltammetry. Formation of an adduct of trioxovanadate(V) with imidazole onto dropping mercury electrode followed by reduction of the sample in DCP of the complex in 0.05 M  $\text{NH}_3/\text{NH}_4\text{Cl}$  buffer (pH 9.08) resulted in a single peak at  $-0.875$  V.

## **New Polymeric Copper(II) Complexes with Tributyl Phosphite and Perfluorinated Carboxylates**

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*(Received April 21st, 2000; revised manuscript October 2nd, 2000)*

New Cu(II) complexes with tributyl phosphite and aliphatic perfluorinated carboxylates  $[\text{Cu}\{\text{P}(\text{OBu})_3\}(\mu\text{-OH})(\mu\text{-RCOO})]_n$ , where  $\text{R} = \text{CF}_3, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7, \text{C}_6\text{F}_{13}, \text{C}_7\text{F}_{15}$ , were obtained and their spectroscopic (UV-VIS, EPR, MS, IR) and thermal properties were studied. Mass spectra were in favour of the bridging coordination carboxylates and monodentate phosphite and suggest a polymeric structure. EPR spectra and magnetic susceptibility measurements indicate the formation of pentacoordinated Cu(II) in polymeric complexes. Examination of COO absorption bands suggests bridging carboxylates as well as a hydroxo group, whereas tributyl phosphite is monodentately bonded. Thermal decomposition is a multistage process, which in nitrogen and air yields a mixture of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{P}_2\text{O}_7$ .

## Synthesis and Magnetic Properties of Heterobinuclear Copper(II)–Manganese(II) Complexes with N,N'-Bis[2-(dimethylamino)ethyl]oxamide as Ligand

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*(Received September 9th, 2000; revised manuscript October 17th, 2000)*

Four new copper(II)–manganese(II) heterobinuclear complexes bridged by N,N'-bis[2-(dimethylamino)ethyl]oxamido dianion (dmoxae) and end-capped with 2,2'-bipyridine (bpy); 4,4'-dimethyl-2,2'-bipyridine (Me<sub>2</sub>-bpy); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen), respectively, namely, [Cu(dmoxae)MnL<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (L = bpy, Me<sub>2</sub>-bpy, Cl-phen, Br-phen), have been synthesized and characterized by elemental analyses, IR and electronic spectra studies and molar conductivity measurements. The electronic reflectance spectrum indicates the presence of exchange-coupling interaction between bridging copper(II) and manganese(II) ions. The cryomagnetic measurements (4.2–300 K) of [Cu(dmoxae)Mn(bpy)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complex demonstrated the operation of an antiferromagnetic interaction between the adjacent manganese(II) and copper(II) ions through the oxamido-bridge within the complex. On the basis of spin Hamiltonian,  $\hat{H} = -2JS_1 \hat{S}_2$ , the magnetic analysis was carried out for the complex and the spin-coupling constant (J) was evaluated as  $-36.9 \text{ cm}^{-1}$ . The influence of methyl substituents in amine groups of the bridging ligand on magnetic interactions between the metal ions of this kind of complexes is also discussed.

## Solvatochromism of 1-(*p*-Aminostyryl)pyridinium Salts

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*(Received August 29th, 2000; revised manuscript October 5th, 2000)*

Solvatochromism of eighteen 1-methyl-(*p*-aminostyryl)pyridinium perchlorates was studied. For each solvent the  $\tilde{\nu}_{\max}$  values follow the  $\sigma_r^0$  substituent constants of the amino groups present in the molecule. The  $\tilde{\nu}_{\max}$  values for compounds are usually highest and lowest in water and in methylene chloride, respectively. The substituent bathochromic shifts in some solvents are as large as  $5700\text{ cm}^{-1}$ . No inverted solvatochromism is observed. Analysis of the spectra do not confirm also this effect to be negative. Dependence between the band position and solvent polarity, hydrogen bond donor acidity and hydrogen bond acceptor basicity is of low quality. There is no simple relationship between the  $\tilde{\nu}_{\max}$  values and the solvent dielectric constants.

## **New Photosensitive Methacrylate Monomers with 4-Aminoazobenzene Type Chromophore Group**

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*(Received June 26th, 2000; revised manuscript October 10th, 2000)*

Photosensitive methacrylate monomers, derivatives of azobenzene, were synthesized. The route of syntheses was based on coupling of diazonium salts of sulfathiazole, sulfomethoxazole, sulfadiazine, 4-aminobenzoic acid and 4-nitroaniline with N-alkyl-N-[2-(methacryloyloxy)ethyl]aniline. The *trans*↔*cis* isomerization of the monomers in DMSO solution was investigated by UV-VIS spectroscopy recording their spectra during illumination and thermal recovery periods. It was found that except for nitro derivatives the yield of *trans-cis* isomerization was *ca.* 50% and that the reverse reaction was a result of thermal relaxation. The spectroscopic studies were accompanied by quantum chemical calculations.

## **Synthesis and Transformation of 1-Monosubstituted Tetrazoles to Pyrimidinones, Benzoxazoles and Quinazolinediones Through 1,4-Disubstituted Tetrazolium Salts**

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*(Received January 10th, 2000; revised manuscript October 16th, 2000)*

Synthesis and some new transformations of 1-aryltetrazoles into other heterocycles through 1,4-disubstituted tetrazolium salts are described. 1-Aryltetrazoles, quaternized with *tert*-butanol and diacetone alcohol in perchloric acid media, gave pure 1,3- or 1,4-disubstituted tetrazolium salts or their mixtures. 1,3-Disubstituted tetrazolium salts are slowly converted into the corresponding 1,4-salts under dissolving in perchloric acid. 1,4-Disubstituted tetrazolium salts are recycled to 2-alkylaminobenzoxazoles, 3-monosubstituted 2,4-quinazolinediones and mixtures of di- and tetrahydropyrimidin-2(1H)-ones in basic conditions.

**Cyclic Analogue of Human Heat Shock Protein 70(29–42)  
Fragment.  
Synthesis, Conformational Studies and Evaluation  
of Its Immunogenicity**

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(Received September 7th, 2000; revised manuscript October 23rd, 2000)

The cyclic hexadecapeptide containing human heat shock protein 70(29–42) fragment cyclized by the disulfide bridge between two L-cysteine residues introduced at the N- and C-termini was synthesized by the solid phase method. It was established that the cyclic analogue, contrary to its linear counterpart, had much lower ability to generate immune response in rabbits. Conformational studies of cyclic peptide performed using 1D and 2D <sup>1</sup>H-NMR spectroscopy in conjunction with theoretical conformational analysis revealed that the cyclization constrained the 3D structure of this peptide, reflected by the observed rate of *cis/trans* isomerization of Arg<sup>9</sup>–Thr<sup>10</sup> peptide bond and the presence of Gly<sup>7</sup>–Asn<sup>8</sup> peptide bond in *cis* geometry. We, therefore, postulate that the conformational flexibility in the case of Human Heat Shock Protein fragments is a key element for their immunogenicity.



## **On Amination and Diazotization of Azulene and Its Derivatives**

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*(Received October 27th, 2000)*

A practical procedure for synthesis of 6-aminoazulene (**3**) via Vicarious Nucleophilic Substitution of Hydrogen (VNS) amination of azulene with 4-amino-1,2,4-triazole is reported. Amination with use of *N,N,N*-trimethylhydrazinium iodide (TMHI) of more electrophilic azulene derivatives, substituted at position 1- with CN or CPh group, afforded a mixture of 4-, 6-, and 8-aminoazulenes. Attempts to convert 6-aminoazulene (**3**) into diazonium salt failed, only formation of small quantities of the "auto-coupling" product, 1-(azulen-6-ylazo)-azulen-6-yl-amine, was observed.

## **Effect of Thermal Treatment of the Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> Supports on Properties of Dispersed Chromium Oxide in Oxidative Dehydrogenation of Isobutane**

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*(Received August 31st, 2000)*

Chromium oxide has been dispersed on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> supports, heated between 500–1200°C, and the catalysts obtained have been tested in oxidative dehydrogenation of isobutane at 280°C. For the CrO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> system the thermal treatment of alumina, which leads to the decrease in the specific surface area and polymorphic transformations of the initial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into  $\theta$ ,  $\Delta$  and  $\alpha$  modifications, does not affect the catalytic performance of the catalysts in the reaction under study. On the other hand, the transformation of anatase-TiO<sub>2</sub> into rutile-TiO<sub>2</sub>, occurring on heating at 1000°C, leads to catalysts of a higher activity and selectivity to isobutene. Amelioration of the catalytic properties for CrO<sub>x</sub>/rutile-TiO<sub>2</sub>, as compared with CrO<sub>x</sub>/anatase-TiO<sub>2</sub> catalysts, has been ascribed to changes in the structure of the CrO<sub>x</sub> active centres, evidenced by ESR.

**Kinetic Studies on Mechanism of Electron Transfer  
Between  $\text{Cr}_{(\text{aq})}^{2+}$  and  $[\text{Cr}(\text{bpy})_3]^{3+}$  – Ions**

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*(Received September 7th, 2000)*

## **Preparation, Structure and Thermal Decomposition of Zinc(II) Complex with 2,5-Dichlorobenzoic Acid**

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*(Received February 4th, 2000; revised manuscript October 25th, 2000)*



