

Kinetics and Mechanism of Complex Formation between Pentamminesuccinatocobalt(III) and Gallium(III)

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The reversible complexation between pentamminesuccinatocobalt(III) with gallium(III) was investigated by stopped flow technique in the temperature range $15 \leq t \leq 35^\circ\text{C}$, and over an acid range of $0.15 \leq [\text{H}^+] \leq 0.30 \text{ mol dm}^{-3}$. Consistent inverse rate dependence was observed with increasing $[\text{H}^+]$. The major path, as supported by the formation rate constant, is $[(\text{NH}_3)_5\text{CoOCO}(\text{CH}_2)_2\text{CO}_2\text{H}]^{2+} + \text{Ga}(\text{OH})^{2+} \rightarrow (\text{NH}_3)_5\text{CoOCO}(\text{CH}_2)_2\text{CO}_2\text{Ga}^{4+} + \text{H}_2\text{O}$. Results obtained here firmly corroborate the chelating nature of half bonded succinato moiety with the gallium ion. By comparing the ΔG^\ddagger values of k_1 and k_2 paths with the ΔG^\ddagger of the k_{ex} path and k_1 and k_2 with the k_{ex} (25°C), it was proposed that the substitution at Ga^{3+} centre is interchange dissociative (I_d).

Synthesis, Crystal Structure and Magnetic Properties of a Zinc(II) Complex with Nitronyl Nitroxide Radical

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A new mononuclear diamagnetic metal zinc compound $[\text{Zn}(\text{NITpPy})_4(\text{N}_3)_2]$ (NITpPy = 2-(p-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) has been synthesized and characterized. The crystal structure of this compound was determined by X-ray diffraction analysis. It crystallizes in the triclinic space group $P\bar{1}$ with the Zn^{II} ion octahedrally coordinated and bound to four radical ligands through the nitrogen atoms of the pyridine rings, and the azido groups occupy the apical positions. The compound exhibits weak intermolecular antiferromagnetic interaction between the radicals, in which the diamagnetic zinc(II) plays the role of bridge.

Synthesis and Magnetic Characterization of μ -Oxamido-Bridged Cu(II)–M(III) (M = Fe and Cr) Heterobinuclear Complexes

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Two new μ -oxamido-bridged heterobinuclear complexes have been synthesized and identified as [Cu(dmoxae)Cr(Ph₂phen)₂](ClO₄)₃ (**1**) and [Cu(dmoxae)Fe(Ph₂phen)₂](ClO₄)₃ (**2**), where dmoxae denotes N,N'-bis[2-(dimethylamino)ethyl]oxamido dianion and Ph₂phen represents 4,7-diphenyl-1,10-phenanthroline. Based on elemental analyses, IR, ESR and electronic spectra studies, and molar conductivity measurements, the complexes are proposed to have an extended oxamido-bridged structure consisting of planar copper(II) and octahedral chromium(III) or iron(III) ions. The two heterobinuclear complexes were further characterized by variable-temperature magnetic susceptibility (4.2–300 K) measurements and the magnetic data have been also used to deduce the indicated heterobinuclear structure. The results derived from least-squares fit of the experimental data have confirmed that the adjacent copper(II) and chromium(III) ions through the oxamido-bridge in complex (**1**) are ferromagnetically coupled with the exchange integral $J_{\text{(Cu-Cr)}} = +13.6 \text{ cm}^{-1}$, while an intramolecular antiferromagnetic coupling is detected between the copper(II) and iron(III) ions through the oxamido-bridge in complex (**2**) with the exchange integral $J_{\text{(Cu-Fe)}} = -17.5 \text{ cm}^{-1}$, on the basis of the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_{\text{Cu}} \cdot \hat{S}_{\text{M}}$ (M = Cr³⁺ and Fe³⁺). The influence of electronic-structural variation of the metal ions on the nature of spin-exchange interaction between the paramagnetic centers is also discussed.

**Spectroscopic, Magnetic and Thermal Properties of
New Thiocyanato Bridged Complexes of the Type
[M(diamine)₂]₃[Cr(NCS)₆]₂ · nH₂O,
where M = Cu(II), Ni(II)**

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Heteropolynuclear complexes of the type [M(diamine)₂]₃[Cr(NCS)₆]₂ · nH₂O, where diamine = *N*-methylethylenediamine (*N*-Me-en), 1,2-diaminopropane (pn); M = Ni(II), Cu(II) have been prepared by reacting [Cr(NCS)₆]³⁻ with the corresponding cationic [M(diamine)₂]²⁺ complex in an aqueous solution. They have been characterized by elemental analysis, IR, UV-VIS, EPR, variable temperature magnetic susceptibility and thermal analysis. Spectroscopic studies reveal thiocyanato bridges between M(II)–Cr(III) centres. The parameters determined from temperature dependence on magnetic susceptibility (80–300 K) indicate moderate antiferromagnetic interactions for Ni(II)–Cr(III) and negligibly small or very weak ones for Cu(II)–Cr(III) systems. Magnetic studies suggest also presence of diamagnetic Ni(II) ions in the structure of Ni(II)–pn–Cr(III) complex. Thermal analysis shows higher thermal stability of Ni(II)–Cr(III) than Cu(II)–Cr(III) compounds. The process of thermal decomposition after dehydration is multistage and yields NiO + NiCr₂O₄ and CuO + CuCrO₂ as final products, respectively.

Synthesis and Characterization of New d^n Metal Complexes with 4,4'-Bipyridine and Formates

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New mixed-ligand complexes of the stoichiometric formulae: $\text{Mn}(4\text{-bpy})_2(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Co}(4\text{-bpy})(\text{HCOO})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(4\text{-bpy})(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(4\text{-bpy})(\text{HCOO})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}_2(4\text{-bpy})_3(\text{HCOO})_4$ and $\text{Cd}(4\text{-bpy})(\text{HCOO})_2$ (where 4-bpy = 4,4'-bipyridine) have been isolated in pure state. The IR and VIS spectra (for compounds of Co(II), Ni(II), Cu(II)), molar conductivity measurements and other physical properties of these compounds are discussed. Thermal behaviour of all compounds was studied by means of DTA, DTG, TG techniques under static conditions in air. The resultant final products were the metal oxide in all cases. A coupled TG-MS system was used to analysis of principal volatile thermal decomposition (or fragmentation) products of Co(II) and Ni(II) complexes. The principal volatile mass fragments correspond to: C^+ , OH^+ , H_2O^+ , NO^+ , CO_2^+ and other.

The Antielectrostatic Effect of N-Alkanol-N-alkoxymethyl-N,N-dimethylammonium Chlorides and Their Ester Derivatives

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Several new quaternary ammonium chlorides, analogues of choline, were prepared by reaction of 2-(dimethylamino)ethanol and its derivatives with chloromethyl alkyl ethers. The obtained chlorides were examined in respect to their antielectrostatic effects: the surface resistance and half decay time on polyethylene film were measured. Application of rough set theory permitted to perform a comprehensive analysis of data and detection of structural-activity relationships. The obtained chlorides showed high antielectrostatic properties. The most active were quaternary ammonium chlorides with 11 and 12 carbon atoms in alkyl chain.

Synthesis of 5-(2-Hydroxyethyl)-1-thia-3,5,6,8-tetraaza- and 1,3,5,6,8-Pentaazaacenaphthylenes

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Synthesis of 5-(2-hydroxyethyl) derivatives of 1-thia-3,5,6,8-tetraaza- and 1,3,5,6,8-pentaazaacenaphthylenes from 4,6-dichloro-2-methylthiopyrimidine-5-carbonitrile *via* the corresponding thieno- and pyrrolo[2,3-*d*]pyrimidines is described.

**Silica Gel Supported γ -Picolinium Chlorochromate;
A New and Efficient Reagent for Selective Conversion
of Alcohols and Oximes into Carbonyl Compounds
under Mild and Non-Aqueous Conditions**

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The preparation of silica gel supported γ -picolinium chlorochromate and its application as an efficient reagent for selective oxidation of oximes and alcohols into carbonyl compounds is reported. The trimethylsilyloxy and ester groups survived under the reaction conditions.

An *ab initio* Post SCF Study on Stacking Interactions of 8-Oxo-9-methylguanine with Four Canonical DNA Bases

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Stacking properties of 8-oxo-9-methylguanine interacting with all four canonical nucleic acid bases were studied and compared to dimers formed by unmodified guanine. The impact of twist angle and base-base separation distance on the stacked dimers energies were analyzed based on MP2/6-31G*(d=0.25) quantum chemistry and Amber molecular mechanics single point calculations. Besides, solvent effects were taken into account within PCM formalism. Presented data lead to the conclusion that 8-oxo-9-methylguanine has significantly different stacking properties compared to standard guanine. Although the dimers stabilization energies are similar for standard and modified 9-methylguanine structural properties are significantly diverse. The most stable dimers formed by 8-oxo-9-methyl-G are characterized by different conformations compared to canonical 9-methylguanine. This may lead to complete alteration of stacking abilities. For example, 8-oxo-9-methyl-G if paired with 9-methyl-G exhibits strong stacking repulsion in the twist region, for which 9-methylguanine/9-methylguanine dimer has major attraction. The most stable stacking pair is formed by 8-oxo-9-methylguanine with 9-methylguanine, while the least stable one corresponds to 8-oxo-9-methylguanine/1-methylcytosine and 9-methylguanine/1-methylcytosine pairs. Besides, significant changes of stacked complexes polarities are observed, especially in case of pairs containing methylated pyrimidines. Polarities of dimer formed by two 9-methylated purines are much less sensitive to the environment but dipole moments of 9-methylpurine/1-methylpyrimidine stacking pairs are significantly altered by taking into account solvent effects. The observed differences in stacking properties between standard and modified guanine are related mainly to charge redistribution rather than direct interactions of O₈ oxygen. The correlation energies of stacking dimers are very high and are main source of pairs stabilization. Both 9-methylguanine and 8-oxo-9-methylguanine are characterized by similar values of correlation energy.

Fragmentation and Skeletal Rearrangements of the Protonated Spiro(2H-benzimidazole-2-4'-pyrazole)-5'-one Dyes Studied by Electrospray Ionization and Liquid Secondary Ion Mass Spectrometry

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The mass spectrometric decomposition of the titled compounds was studied by using electrospray ionization (ESI) and liquid secondary ion mass spectrometry (LSIMS) as a methods for $[M+H]^+$ ions generation. Low-energy collision induced dissociation (fragmentation "in source") mass spectra for ESI and B/E linked scan mass spectra of metastable ions for LSIMS were performed. In order to better understand the decomposition of the compounds studied, the mass spectra of isotopically labelled compounds were recorded. The fragmentation pathways of $[M+H]^+$ ions were found to be complex and skeletal rearrangements were observed. It was deduced that subsequent loss of NH_3 and H_2O molecules leads to the formation of ions with polycyclic structures. The fragment ion $[133]^+$ and its complementary fragment ion $[M+H-132]^+$ can be considered as protonated molecules of 3-methyl-1*H*-indazole and 2-hydroxyquinoxaline, respectively. Loss of the CH_3CN molecule also occurs and this is rather simply process. Aniline elimination ($H_2N-C_6H_5$) and formation of ions at m/z 146 are complex processes and it was difficult to propose plausible mechanisms for these reactions.

Electrochemical Behavior of Some Thioheterocyclic Compounds in Aqueous-Methanolic Media at Mercury Electrodes

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This paper presents the electrochemical behavior of 4-amino-3-thio-1,2,4-triazole (I), 4-amino-3-thio-5-methyl-1,2,4-triazole (II) and 4-amino-6-methyl-3-thio-1,2,4-triazin-5-one (III) at mercury electrodes. The study is performed in aqueous-methanolic solutions by differential pulse polarography (DPP), cyclic voltammetry (CV), chronoamperometry, coulometry and spectrophotometry. All three compounds exhibited one reversible oxidation peak, accompanied by a prepeak, due to the adsorption of these compounds on the electrode. The main peak in each case was found to be diffusion controlled. Their polarographic responses were similar to those of common thiol compounds and involved a one electron oxidation of mercury followed by a disproportionation step to form the mercury(II) salt and Hg, (EC mechanism). The protonation constants (pK), diffusion constants, the rate constants of coupled chemical reaction and transfer coefficients were also obtained.

Three-Dimensional Self-Assembly Supramolecular Structure of Hydrogen Bonded Melaminium Citrate

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The melaminium dihydrogen citrate, $(C_3H_7N_6)(HOOC-CH_2-C(OH)(COOH)-CH_2-COO)$, crystallizes from water solution at room temperature in the $P2_1/c$ space group of the monoclinic system with the lattice parameters of $a = 5.531(1)$, $b = 20.869(4)$, $c = 11.282(2)$ Å and $\beta = 99.96(3)^\circ$ and $Z = 4$. The crystals are built up from singly protonated at the one N-ring atom melaminium cations that interact in a near linear fashion through a pair of $N-H\cdots N$ hydrogen bonds to form the centrosymmetric dimeric structure. The dihydrogen citrate(–) anions interact in the head-to-tail fashion *via* the terminal dissociated (COO^-) and non-dissociated ($COOH$) carboxyl groups to form $O-H\cdots O$ hydrogen bonded zigzag infinite chains. The hydroxyl group of dihydrogen citrate(–) ions is involved into $O-H\cdots O$ hydrogen bonds that linked together the dihydrogen citrate(–) chains into two-dimensional network. The centrosymmetric dimers of melaminium moieties interact with the sheets of dihydrogen citrate(–) to form the three-dimensional hydrogen bonded network. The conformation of the dihydrogen citrate(–) ion in the crystal is compared with the conformation in the gas-phase obtained by the *ab-initio* molecular orbital calculation.

Formaldehyde Formation in Coupled Oxidation of Methane and Methanol over V_2O_5 and MoO_3 Silica Supported Catalysts

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The effect of methanol on partial oxidation of methane has been studied on standard molybdena and vanadia catalysts supported on silica. Prior to catalytic tests the catalysts were characterized by BET, SEM/EDAX and TPR/O methods. Three types of catalytic tests were performed giving temperature and contact time dependence on the catalyst activity and selectivity: partial oxidations of methane, methanol and methane/methanol mixtures. The methanol showed an activating impact on the partial oxidation of methane over all used catalysts samples, but the strongest one over MoO_3/SiO_2 . In the absence of CH_3OH the only catalyst, which exhibited HCHO selectivity, was a low loaded vanadia catalyst. It has been put forward that methanol may enhance formation of oxygen active species, prerequisites for activating methane molecules, through reducing vanadia cations and causing breakage of vanadium oxygen bonds.

Processing of Methane in Dielectric-Barrier Discharge

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Carbon Black Generation in Gliding Discharges

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**Complexes of Zn(II) and Cd(II) with Bipyridine Isomers
and Chloroacetates**

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