Synthesis and Ferromagnetic Interaction in Oxalato-Bridged Copper(II)–Chromium(III)–Copper(II) Heterotrinuclear Complexes

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The strategy of “complex as ligand” allowed us to synthesize four new µ-oxalato-bridged copper(II)–chromium(III)–copper(II) heterotrinuclear complexes described by the overall formula [Cu₂Cr(ox)₃L₂]ClO₄, where ox represents the oxalato dianions; L stands for 5-phenyl-1,10-phenanthroline (Ph-phen); 4,7-diphenyl-1,10-phenanthroline (Ph₂-phen), 5-chloro-1,10-phenanthroline (Cl-phen) and 5-bromo-1,10-phenanthroline (Br-phen). Based on elemental analyses, molar conductivity and magnetic moment (at room-temperature) measurements, IR, ESR and electronic spectra studies, it is proposed that these complexes have oxalato-bridged structure consisting of two copper(II) ions and a chromium(III) ion, in which the chromium(III) ion has an octahedral environment, and the two copper(II) ions have a square-planar environment. The [Cu₂Cr(ox)₃(Ph-phen)₂]ClO₄ complex was further characterized by variable temperature magnetic susceptibility (4.2~300 K) measurements and the observed data were simulated by the equation based on the spin Hamiltonian operator, $H = -2J(S_{Cu1} S_{Cr} + S_{Cu2} S_{Cr})$, giving the exchange integral $J = +12.8$ cm⁻¹. The result indicates the presence of a ferromagnetic spin-exchange interaction between the copper(II) and chromium(III) ions through the oxalato-bridge in the complex.
The complex formation of Hg$^{2+}$ ion with five recently synthesized benzo-substituted macrocyclic diamides in binary nitromethane + dimethylformamide mixtures was studied by differential pulse polarography at 25°C. The stoichiometry and stability of the complexes were determined by monitoring the shift in the Hg$^{2+}$ differential pulse peak potential against the macrocycles concentration. In all cases studied, it was found that the stability of the resulting 1:1 complex decreases drastically by increasing the amount of dimethylformamide in the binary mixtures. The observed stability order in a given solvent mixture is discussed in terms of the cavity size, structural flexibility and nature of the substituted on the macrocyclic diamide ring.
Rate and Equilibrium in Aqueous 1:2 Chelation of Copper(II) by 2-Pyridinecarboxylic Acid Hydrazide. Antituberculosis Activity

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Chelation reactions of 2-pyridinecarboxylic acid hydrazide, widely used drug in antituberculous regimens, with copper(II) have been investigated in aqueous solution at a temperature of 25°C. The ionization equilibria of the ligand and the stability of the metal-ligand complexes have also been characterized. Kinetic results show that the rate constant for monochelated complex formation is several times larger than the rate constant for dichelated complex formation. A detailed mechanism is proposed to account for the kinetic data.
Synthesis and Magnetic Studies of Binuclear Iron(II) Complexes Bridged by Tetracarboxylato Groups

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Four novel binuclear iron(II) complexes, namely \([\text{Fe}_2(\text{PMTA})\text{L}_4]\), where \(\text{L}\) denotes 4,4′-dimethyl-2,2′-bipyridine (Me₂-bpy); 1,10-phenanthroline (phen); 5-chloro-1,10-phenanthroline (Cl-phen) or 5-bromo-1,10-phenanthroline (Br-phen), respectively, and PMTA stands for the tetraanion of pyromellitic acid, have been synthesized and characterized. Based on elemental analyses, magnetic moments at room-temperature and molar conductivity measurements, and spectroscopic (electronic and IR spectra) studies, extended PMTA-bridged structures consisting of two iron(II) ions, each in a distorted octahedral environment, are proposed for these complexes. The variable temperature magnetic susceptibilities (4–300 K) of the complexes \([\text{Fe}_2(\text{PMTA})(\text{Me}_2\text{-bpy})_4]\) (1) and \([\text{Fe}_2(\text{PMTA})(\text{phen})_4]\) (2) were measured and the magnetic analysis was carried out by least-square method to the observed data with the susceptibility equation derived from the spin Hamiltonian operator, \(H = -2JS_S\), giving the exchange integrals \(J = -1.09 \text{ cm}^{-1}\) for (1) and \(J = -1.18 \text{ cm}^{-1}\) for (2). The results indicate that there is a very weak antiferromagnetic spin-exchange interaction between the Fe(II) ions within each molecule.
Thermal, Spectral and Magnetic Investigations of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes with 4-Methoxy-2-methylbenzoic Acid

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Conditions for the preparation of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with 4-methoxy-2-methylbenzoic acid were investigated and their quantitative composition, magnetic moments and solubilities in water at 293 K were recorded. IR spectra and powder diffractograms of the complexes, prepared with molar ratio of metal to organic ligand of 1.0 : 2.0 and general formula M(C₉H₉O₃)₂nH₂O, where n = 1 for Mn, Co, Ni, Cu, n = 2 for Cd and n = 0 for Zn, were recorded and their thermal decomposition in air was studied. During heating the complexes are dehydrated in one step and next the anhydrous complexes of Cu, Zn and Cd decompose directly to oxides (MO), whereas the complexes of Mn, Co and Ni decompose to oxides (M₂O₇, Co₃O₄, NiO) with intermediate formation of the mixture of free metals and their oxides. The effective magnetic moments the paramagnetic complexes of Mn(II), Co(II), Ni(II) and Cu(II) attain at 303 K values 5.65, 4.69, 3.18 and 1.27 B.M., respectively. On the basis of IR spectra it can be suggested that carboxylate groups are bidentate asymmetric bridging ligands.
The Efficient Synthesis of Azaamino Acids

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An efficient method of synthesis of N-t-butoxycarbonyl-azaamino acid ethyl esters has been described. This method consisted of three stages including: hydrazone formation, its reduction and acylation with ethyl chloroformate. The second step – reduction of the hydrazones to the appropriate hydrazides – was the most challenging. Some reducing agents have been tested, though NaBH₃CN was found to lead to the final products with the highest yields in relatively short time and even to allow the selective reduction of C–N bond in the presence of nitro group.
Three New Diterpenoids from *Euphorbia decipiens*

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Three new diterpene esters with a tricyclic myrsinol-type skeleton have been isolated from *Euphorbia decipiens* Boiss. & Buhse. The structure elucidation of the isolated compounds was based primarily on 1D and 2D-NMR analysis, including COSY, HMQC, HMBC and NOESY correlations. The compound 1 showed inhibitory activity against prolyl endopeptidase and compound 2 showed analgesic activity.
Preparation of Synthetically Useful Chiral Building Blocks – 5-Alkylated γ-Lactones via Catalytic Asymmetric Hydrogenation of 4-Oxo Esters

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Asymmetric hydrogenation of 4-oxo esters, catalyzed by cationic BINAP-Ru(II) complexes, afforded in a good overall yield and with excellent enantioselectivity (> 98% ee), the respective 5-alkylated γ-lactones, useful intermediates for the preparation of pheromones.
Hydrogen Peroxide Oxidation of N,N-Dimethylhydrazones Promoted by Selenium Compounds, Titanosilicalites or Acetonitrile

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Hydrogen peroxide oxidation of N,N-dimethylhydrazones \( \text{I} \) promoted by title reagents has been investigated. Depending on the substrate nitrile \( \text{II} \) and/or amide \( \text{III} \) accompanied with carboxylic acid \( \text{IV} \) and parent carbonyl compounds \( \text{V} \) were obtained. Formation of nitriles \( \text{II} \) with \( \text{H}_2\text{O}_2 \)-acetonitrile system is limited for a few more active substrates. The mechanism of the reaction, based on generated in situ per oxyiminoacetic acid, is presented. A broad spectrum of aliphatic, unsaturated and aromatic nitriles \( \text{II} \) was obtained by oxidation of corresponding N,N-dimethylhydrazones \( \text{I} \) with hydrogen peroxide in the presence of poly(bis-9,10-anthracenyl) diselenide (PADS) \( \text{VII} \) as catalyst.
Carbon and Chlorine Kinetic Isotope Effects and Solvent Effects on the Hydrolysis of Chloroformates

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Carbon and chlorine kinetic isotope effects and pseudo-first order rate constants were measured for the hydrolysis of ethyl, benzyl, and isopropyl chloroformate in various mixtures of the binary solvent water-1,4-dioxane. Rate constants decreased as the percentage of 1,4-dioxane increased for all three chloroformates. Carbon-13 kinetic isotope effects ($k_{12}/k_{13}$) for hydrolysis of these compounds were 1.039–1.042 for ethyl chloroformate (0–75% 1,4-dioxane), 1.034–1.039 for benzyl chloroformate (15–75% 1,4-dioxane), and 1.025–1.037 for isopropyl chloroformate (25–75% 1,4-dioxane). Chlorine-37 kinetic isotope effects ($k_{35}/k_{37}$) were measured for benzyl and isopropyl chloroformates in 25% 1,4-dioxane (1.0088, benzyl; 1.0080 isopropyl) and 75% 1,4-dioxane (1.0090, benzyl; 1.0102 isopropyl). These data are consistent with an associative mechanism for benzyl and ethyl chloroformates, but hydrolysis of isopropyl chloroformate appears to be dissociative in polar solvents.
Effect of Potassium Modification on Structure and Reactivity of $V_2O_5/\gamma-Al_2O_3$ for Isobutane Dehydrogenation to Isobutene


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Undoped and K-doped $V_2O_5/\gamma-Al_2O_3$ catalysts for the dehydrogenation of isobutane to isobutene were prepared by impregnation and characterized by means of BET, H$_2$-TPR, NH$_3$-TPD, XPS and ESR. It is found that potassium addition changes acidic and electric properties of $V_2O_5/\gamma-Al_2O_3$ and results in a better spreading of $V_2O_5$ over $\gamma-Al_2O_3$ surface. Small addition of potassium to $V_2O_5/\gamma-Al_2O_3$ catalyst (K:V = 0.05), consisting of 12 wt% $V_2O_5$, increased the activity and selectivity in dehydrogenation of isobutane to isobutene.
An Evaluation of the Kinetic Data for Hydrogen Abstraction from Germanes in the Gas Phase by CF$_3$ and C$_2$F$_5$ Radicals

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After the review of kinetic data for reaction of hydrogen abstraction from germano-organic compounds by trifluoromethyl and pentafluoroethyl radicals in the gas phase it was possible to determine the relative kinetic reactivity of the two radicals under consideration. The contributing factors are the thermochemical effects of the investigated reactions, steric hindrance derived mainly from the size of substrate molecules and the polar interaction between the polarized germane molecules and the radicals of different electrophilicity. The polar effects occurring in these radical reactions contribute primarily to the activation energy, but they have no significant contribution to the pre-exponential factor.
Synthesis, Crystal Structure and Fluorescence of 2-D Polymeric Eu(III) Complex with Fumarate and 2-Chlorofumarate as Bridging Ligands


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