

New Reactions of Tetrathiocyanatobismuthates(III) with Organic Compounds. I. Reactions of Caesium Tetrathiocyanatobismuthate(III) with Monocarboxylic Acid Salts

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Reactions of $\text{Cs}[\text{Bi}(\text{SCN})_4]$ with solutions of sodium formate, acetate, propionate and valerate were examined. Chemical, XRD and IR analyses were carried out. Two bismuth compounds are formed in the solid phase: caesium sodium hexathiocyanatobismuthate(III) $\text{Cs}_2\text{Na}[\text{Bi}(\text{SCN})_6]$ and BiX_3 or BiOX (X – organic anion). The composition of the precipitate depends on the kind of the ligand and its concentration. When NaX is used in excess of BiX_3 , the compound forms a double salt $m\text{BiX}_3 \cdot n\text{NaX}$ or $m\text{BiOX} \cdot n\text{NaX}$. Within a certain range of sodium salt concentration it remains unchanged. When the precipitate is separated, as least soluble $\text{Cs}_2\text{Na}[\text{Bi}(\text{SCN})_6]$ crystallizes from the solution. The compounds are of biological and analytical significance.

Synthesis and Characterization of Complexes of Transition Metal Ions with New Pentaazamacrocyclic Ligands

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New multidentate ligands 1,4,7,9,12-pentaaza-10,11-dioxo-8,9,12,13-bis-(1',3'-dioxo-6,6-diethyl-2'-hydropyrimidine)-trideca-7,13-diene, (L^1) and 1,4,7,9,13-pentaaza-10,12-dioxo-8,9,13,14-bis-(1',3'-dioxo-6,6-diethyl-2'-hydropyrimidine)-tetradeca-7,14-diene (L^2) have been prepared by the reaction of 5,5-diethylbarbituric acid, diethylenetriamine, diethyl oxalate and 5,5-diethylbarbituric acid, diethylenetriamine, diethyl malonate. Their coordination properties with the first row of transition metal ions have been explored. The macrocyclic complexes were characterized by elemental analysis, IR, ^1H NMR, UV-visible spectroscopy, magnetic moment measurements and molar conductance measurements. The electronic spectra and magnetic moment measurements are discussed with respect to assignment of square planar and tetrahedral structure except chromium(III), iron(III) ions. The chromium(III) and iron(III) complexes are considered to be octahedral. Molar conductance measurements suggest that the complexes of divalent metal ions are 1:1 electrolytes, while the trivalent metal ions are nonelectrolytes. The compounds have been tested against gram-positive bacteria *Staphylococcus aureus* and gram-negative bacteria *Escherichia coli*. The results show that all the compounds inhibit the growth of bacteria.

⁴⁵Sc NMR Study of Scandium Complexation by Podand Ligands

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The complexes of scandium trichloride with podand ligands (inorganic esters of poly-oxaethylene glycols) were prepared and studied by ⁴⁵Sc NMR. The species formed were subjected to structural investigation and the effect of the ligand type was discussed.

pH-metric and Spectrophotometric Studies on the Binary and Ternary Complexes of Copper(II) with 2,3-Pyrazinedicarboxylic Acid and Some Aliphatic and Aromatic Acids

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Formation and stability of binary and ternary complexes of copper(II) with 2,3-pyrazinedicarboxylic acid as a primary ligand and some biologically important aliphatic, aromatic and heteroaromatic carboxylic acids (succinic, malic, anthranilic, phthalic, salicylic, thiosalicylic and 2-hydroxynicotinic acids) as secondary ligands were determined by potentiometric and spectrophotometric techniques. The determination were performed in a 20% (v/v) ethanol-aqueous medium. $\Delta \log K$ and $\log X$ values indicate the favoured formation of ternary complexes, compared to the binary ones. The order of stability of the complexes under investigation in terms of the nature of secondary ligands is examined and discussed.

Supramolecular Copper(II) Complexes with Tetradentate Ketoenamine Ligands

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A new series of symmetric and unsymmetric supramolecular copper(II) complexes derived from β -diketones and aniline derivatives have been synthesized and characterized by elemental analyses, IR, UV-VIS spectra, magnetic moments, conductances, thermal analyses (DTA and TGA) and ESR measurements. The IR data show that the ligands behave as monobasic bidentate type towards copper(II) ion. The supramolecular structure is achieved through the dimerization of complexes **(1)**, **(3)**, **(5)** and **(6)** or polymerization of complexes **(2)**, **(4)** and **(7)** via intermolecular hydrogen bonding of the –OH and C=O of carboxylic groups. Molar conductances in DMF solution indicate that the complexes are non-electrolytes. ESR spectra of the solid complexes **(1)** and **(3)** at room temperature show axial-type with a d_{xz} ground state, however, the complexes **(2)**, **(4)**, **(5)** and **(6)** show axial-type spectra with $g_{\parallel} > g_{\perp} > 2.00$, indicating a $d_{x^2-y^2}$ ground state with significant covalent bond character. Electronic and ESR spectra show that the complexes represent square planar or tetragonally distorted octahedral geometry. The catalytic properties of the complexes **(1)** and **(5)** were investigated by decomposition of hydrogen peroxide.

Complexes of Cadmium(II), Mercury(II) and Lead(II) with Quercetin-5'-sulfonic Acid (QSA)

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QSA ($C_{15}H_{10}O_{10}S \cdot 5H_2O$), a ligand, which is non-toxic and well soluble in water, forms complex compounds with cations of toxic metals (Cd, Hg, Pb). New complex compounds with QSA: $Cd(C_{15}H_9O_{10}S)_2 \cdot 10H_2O$, $Hg(C_{15}H_9O_{10}S)_2 \cdot 8H_2O$, $Pb(C_{15}H_9O_{10}S)_2 \cdot 8H_2O$ and $Pb(C_{15}H_8O_{10}S) \cdot 4H_2O$ have been synthesized. Some of their physicochemical properties such as UV-VIS and infrared spectra, mass spectra, thermogravimetric analysis, and solubility were studied. It was found that the obtained compounds are sparingly soluble in water, which points out that QSA could be an antidote against cadmium, lead and mercury. The structures of the obtained compounds have been proposed.

New Complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III) with Quercetin-5'-sulfonic Acid

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New solid complexes of La(III), Ce(III), Tm(III), Yb(III) and Lu(III) with quercetin-5'-sulfonic acid at pH 1.4–1.5 were obtained. On the basis of the elementary analysis and thermogravimetric investigation, the following composition of the compounds was determined: $\text{Ln}(\text{C}_{15}\text{H}_9\text{O}_{10}\text{S})_3 \cdot n\text{H}_2\text{O}$ ($n = 14\text{H}_2\text{O}$ – La, Ce; $n = 13\text{H}_2\text{O}$ – Tm, Yb, Lu). UV and VIS suggest that complexes of CT type were acquired. IR spectra and magnetic and thermogravimetric investigations demonstrate that the obtained complexes are hexa-coordinated. Groups 3OH and 4CO of the ligand participate in binding Ln(III).

One-Step Synthesis and Regioselective Alkylation of Substituted 1*H*-Pyrazolo[4,3-*e*][1,2,4]triazine

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One-pot reaction between 5-acyl-3-(methylsulfanyl)-1,2,4-triazine (**1**) or its oxime (**8**) with hydrazine hydrochloride afforded 3-methyl-5-(methylsulfanyl)-1*H*-pyrazolo[4,3-*e*][1,2,4]triazine (**4**) in good yield. Treatment of the latter with alkyl halides in the presence of base gave 1- or 2-alkyl derivatives of **4** depending on the reaction conditions.

Interception of an Intermediate Thiocarbonyl Ylide by NH-Compounds

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By thermal decomposition of 1,1,3,3-tetramethyl-5-thia-7,8-diazaspiro[3.4]octan-2-one (**1**), 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methylide (**2**) was generated as an intermediate. This reactive “thiocarbonyl ylide” was trapped by protic agents such as alcohols, NH- and SH-acidic compounds to give 1,3-adducts of the acetal type. In a mixture of methanol and ammonia, the spiroheterocycle **1** was deprotonated and competitive ring opening of the 2,5-dihydro-1,3,4-thiadiazole and the cyclobutane ring occurred to give the hydrazono derivative **7** and the 1,3,4-thiadiazole **8**, respectively. Surprisingly, **2** was intercepted by maleimide in a 1,3-dipolar cycloaddition.

Influence of Chemisorption of Sulfite Ions on Electroreduction of Gold(I)–Sulfite Complexes

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Analysis of voltammograms, chronoamperograms and electrochemical impedance spectra (0.05–4000 Hz) indicate a slow stage of chemisorption of sulfite ions that reduces an active surface of gold electrode, and significantly influences a parallel stage of charge transfer of gold(I)–sulfite complexes. The proposed equivalent circuit representing electrochemical process well fits to experimental dependencies of real and imaginary parts of impedance on frequency. Values of elements of equivalent circuit at different potentials of gold electrode (0.1–0.5 V) were calculated. Cathodic voltammogram simulated by using the dependencies of elements of equivalent circuit on electrode potential rather well represents experimentally obtained voltammograms.

Kinetics and Mechanism of Oxidative Degradation of L-Proline by Alkaline Diperiodatonickelate(IV) – A Free Radical Intervention and Decarboxylation

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The kinetics of oxidation of L-proline by diperiodatonickelate(IV) (DPN) in aqueous alkaline medium at a constant ionic strength of 0.50 mol dm^{-3} was studied spectrophotometrically. The reaction is of first order in [DPN], zero order in [alkali] and less than unit order in [L-proline]. Addition of periodate has no effect on the rate of reaction. Effect of added products, ionic strength and dielectric constant of the reaction medium have been investigated. The main products were identified by spot test and IR spectra. A mechanism involving the diperiodatonickelate(IV) (DPN) as the reactive species of the oxidant has been proposed. The reaction constants involved in the different steps of mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also calculated. The isokinetic temperature was determined and discussed.

Hydrodechlorination of 1,2-Dichloroethane over Differently Reduced Pd/SiO₂ Catalysts

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Samples of 5 wt.% Pd/SiO₂ catalyst reduced at moderate (400°C) and high temperature (600°C) were investigated in the reaction of 1,2-dichloroethane hydrodechlorination (HDC). The highly reduced catalyst exhibited a higher selectivity towards ethylene, approaching 70% at 300°C, whereas the catalyst reduced at 400°C gave mainly ethane (S_{C₂H₆} ~90% at 300°C). Reduction of Pd/SiO₂ at 600°C leads to the formation of palladium silicide. In consequence, incorporation of Si in Pd surface lowers the hydrogenating strength of palladium, contributing to a higher ethylene selectivity. Such a behaviour resembles an analogous situation with Pd modified by Ag. It was shown that the catalysts deactivated rapidly at temperatures between 200 and 300°C. After reaction, much larger amounts of carbon were found in the sample reduced at 400°C. X-ray diffraction studies showed that a considerable part of this carbon was located in the bulk of palladium phase, *i.e.* forming a PdC_x solution.

Studies on the Electron Transfer Reaction Mechanism between NO_2 and NO_2^- Complexes in the Gas Phase

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The electron transfer (ET) reaction between NO_2 and NO_2^- complexes in the gas phase is investigated by Density functional theory (DFT). The geometry optimization of the nitrogen dioxide complexes and the precursor state in the process of ET reaction was performed at 6-311+G* basis set level. The nitrogen dioxide molecule separation distances computed using DFT method were found to agree with second order Moller-Plesset perturbation theory level (MP2) results. The 351.1 nm (3.532 eV) photoelectron spectrum of the nitrite anion (NO_2^-) is obtained. For the precursor complex of $\text{NO}_2 \cdots \text{NO}_2^-$, eight reasonable geometries on the potential energy surface are considered with the most stable structure being T1-type. The activation barriers and the coupling matrix elements in the electron transfer process are also calculated for four different transition states. Results indicate that the structures and properties of the precursor complex directly affect the electron transfer reaction mechanism and rate. The reacting system in the T1-type structure has lower activation barriers and greater coupling matrix elements than those in other type of structures. It is indicated that the most possible path of the electron transfer is the collision of NO_2 and NO_2^- to form the precursor complex with the T1-type structure, then the electron transfer and structure organization take place, the successor is obtained *via* the transition state with a Π_6^9 -conjugated system. Finally the product is attained.

Bell-shaped Dependence of the Quantum Yield of Fe(II) Formation in Irradiated Methanolic Solutions of Iron(III) Azido Complexes with *N,N'*-Ethylenebis(benzoylacetoneiminato) Schiff Base Derivatives

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The complexes *trans*-[Fe(4-R-benacen)(CH₃OH)N₃], where 4-R-benacen²⁻ are tetradentate open-chain N₂O₂-Schiff base *N,N'*-ethylenebis(4-R-benzoylacetoneiminato) ligands (R = H, Cl, Br, OCH₃, CH₃) are redox stable in the dark. Under the impact of ultraviolet and/or visible radiation they undergo photochemical reactions, yielding Fe(II) and formaldehyde CH₂O as final products. As an intermediate, [•]CH₂OH radicals were identified by EPR spin trapping technique. The efficiency of the photoredox processes, expressed by the quantum yield of Fe(II) formation, Φ_{Fe(II)} is strongly wavelength dependent and influenced by the peripheral groups R of the tetradentate ligands. It was found, that along with a frequently observed decrease in the quantum yield with decreasing the photon energy of incident radiation (Φ_{Fe(II)} at 313 nm < Φ_{Fe(II)} at 366 nm < Φ_{Fe(II)} at 436 nm), a substantial drop in Φ_{Fe(II)} was found, when shifting the wavelength of incident radiation from 313 nm to 254 nm. This drop is attributed to azido group decomposition competing with photoreduction of Fe(III) to Fe(II).

Oxidative Dehydrogenation of Propane on Supported Molybdena Catalysts: Effect of the Support Nature and of Additives

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Oxidative dehydrogenation of propane has been studied on molybdena deposited on SiO_2 , Al_2O_3 , TiO_2 , and MgO . The catalytic performance depended on the support nature, the selectivity to propene at iso-conversion decreasing in the sequence: $\text{MoO}_x/\text{SiO}_2 > \text{MoO}_x/\text{Al}_2\text{O}_3 \sim \text{MoO}_x/\text{TiO}_2 > \text{MoO}_x/\text{MgO}$. Introduction of the K, Cr, Ni and V additives to $\text{MoO}_x/\text{SiO}_2$ and Cr to MoO_x/MgO catalysts led to the increase of the total activity. The increase of the selectivity to propene was observed for the Cr and Ni additives, whereas the K and V in the $\text{MoO}_x/\text{SiO}_2$ catalysts decreased the selectivity (K and higher amounts of V), or did not affect it (lower amounts of vanadium).