Synthesis and Magnetic Properties of Dinuclear Oxovanadium(IV) Complexes Bridged by Tetracarboxylato Groups

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Three novel μ-tetracarboxylato-bridged oxovanadium(IV) dinuclear complexes described by the overall formula [(VO)2(PMTA)L2], where PMTA stands for the tetraanion of pyromellitic acid, and L denotes 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy) or 1,10-phenanthroline (phen), respectively, have been synthesized and characterized by elemental analyses, molar conductivity and room-temperature magnetic moment measurements, IR, ESR and electronic spectral studies. It is proposed that these complexes have PMTA-bridged structures and consist of two oxovanadium(IV) ions, each in a square-pyramidal environment. The [(VO)2(PMTA)(bpy)2] (1) and [(VO)2(PMTA)(phen)2] (2) complexes were further characterized by variable temperature (4.2–300 K) magnetic susceptibility measurements and the observed data were fitted to the modified Bleaney-Bowers equation by the least-squares method, giving the exchange integral \( J = -2.75 \text{ cm}^{-1} \) for (1) and \( J = -3.91 \text{ cm}^{-1} \) for (2). This result indicates that there is a weak antiferromagnetic spin-exchange interaction between the two VO²⁺ ions within each molecule.
Synthesis of Ferromagnetic Cu\textsuperscript{II}Cr\textsuperscript{III}-Type Heterotetranuclear Complexes with Oxalato Bridges

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Three new \(\mu\)-oxalato-bridged \(\text{Cu}_3\text{II} \text{Cr}_3\text{III}\)-type heterotetranuclear complexes have been synthesized and identified as: \([\text{Cu}_3\text{Cr}(\text{ox})_3(\text{phen})_3](\text{ClO}_4)_3\) (\textit{1}), \([\text{Cu}_3\text{Cr}(\text{ox})_3(\text{Me}_2\text{phen})_3](\text{ClO}_4)_3\) (\textit{2}) and \([\text{Cu}_3\text{Cr}(\text{ox})_3(\text{NO}_2\text{phen})_3](\text{ClO}_4)_3\) (\textit{3}), where \(\text{ox}\) represents the oxalato dianions; \(\text{phen}\), \(\text{Me}_2\text{phen}\) and \(\text{NO}_2\text{phen}\) represent 1,10-phenanthroline; 2,9-dimethyl-1,10-phenanthroline or 5-nitro-1,10-phenanthroline respectively. These complexes are the first examples of \([\text{Cu}_3\text{II} \text{Cr}_3\text{III}]\) species bridged by oxalato groups. The three complexes have not yet been isolated in crystalline form suitable for X-ray structure analysis, but based on elemental analyses, molar conductivity and magnetic moment (at room-temperature) measurements, IR, ESR and electronic spectral studies, these complexes are proposed to have oxalato-bridged structure 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. Variable temperature magnetic susceptibility (4.2~300 K) measurements and studies of the complexes (\textit{1}) and (\textit{2}) revealed the occurrence of an intramolecular ferromagnetic interaction between the copper(II) and chromium(III) ions through the oxalato-bridge within each molecule. The magnetic data have been also used to deduce the indicated \(\mu\)-oxalato-bridged \([\text{Cu}_3\text{II} \text{Cr}_3\text{III}]\) tetranuclear structure. On the basis of the spin Hamiltonian operator, \(\mathbf{H} = -2J\mathbf{S}_{\text{Cu}1}\cdot\mathbf{S}_{\text{Cu}2} + \mathbf{S}_{\text{Cu}1}\cdot\mathbf{S}_{\text{Cr}} + \mathbf{S}_{\text{Cu}2}\cdot\mathbf{S}_{\text{Cr}}\), the magnetic analyses were carried out for the two \(\text{Cu}_3\text{II} \text{Cr}_3\text{III}\) heterotetranuclear complexes and the spin-coupling constants (\(J\)) were evaluated as +10.97 cm\(^{-1}\) for (\textit{1}) and +9.28 cm\(^{-1}\) for (\textit{2}), indicating that the bridging oxalato would be able to transmit ferromagnetic interaction in the strict orthogonality \([\text{Cu}_3\text{II} \text{Cr}_3\text{III}]\) tetranuclear system.
Synthesis and Catalytic Activity of Square-Planar Ni(II) Complexes of Bis-N,N'-disubstituted Oxamides and Related Ligands for Epoxidation of Olefins

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Four new monomeric square-planar nickel(II) complexes of two bis-N,N'-disubstitute oxamides and related ligands have been prepared and characterized, namely [NMe₄]₂[Ni(L)] · xH₂O, where L = dbopba = 3,5-dibromo-o-phenylenebis-(oxamate) and dbmeopba = 3,5-dibromo-o-phenylenebis-(N'-methyloxamidate), L = meopba = 3,5-dibromo-o-phenylenebis-(oxamate) and memeopba = 3,5-dibromo-o-phenylenebis-(N'-methyloxamidate). NMe₄ is the tetramethylammonium cation. Based on elemental analyses, IR and UV spectroscopies and molar conductance data, the complexes are proposed to have a square-planar structure. Their catalytic activities for aerob
Structures and Spectral Properties of (O-sec.-Butyldithiocarbonatio-S,S’)
Bis(triphenylphosphine) Copper(I) and Silver(I) Complexes

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New complexes (PPh₃)₂M(S₂COR) [R = sec.-butyl, M = copper (1), silver (2)] were synthesized by the reaction of excessive triphenylphosphine and copper(II) or silver(I) xanthate, and characterized using IR, EA, ¹H NMR and TG. Their crystal structures have been determined by X-ray diffraction. The light yellow crystal of the complex (1) is triclinic of space group P1, with parameters a = 10.300(2) Å, b = 13.120(3) Å, c = 14.570(3) Å, α = 89.53(3), β = 72.81(3), γ = 78.61(3), and Z = 2. The yellow crystal of the complex (2) is triclinic of space group P₁, with parameters a = 10.330(2) Å, b = 13.410(3) Å, c = 14.420(3) Å, α = 88.61(3), β = 73.60(3), γ = 78.93(3), and Z = 2. In the two complexes, the central Cu or Ag atom is in a distorted tetrahedral environment and chelated by two phosphorus atoms from the triphenylphosphine groups and two sulfur atoms from the O-alkyldithiocarbonate. IR and ¹H NMR results supported the structures. The thermal analytical data indicate that the complex (1) began to decompose at 122.3° and decomposition was complete at 370.9°, leaving Cu₂S, while the complex (2) began to decompose at 133.3° and decomposed completely at 290.3° to Ag₂S.
Carbonate-Containing Barium Hydroxyapatite Synthesized by Solid State Reactions

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The carbonate-containing barium hydroxyapatite was prepared by solid state reactions in air at 950°C. Obtained samples were investigated by X-ray powder diffraction and IR spectroscopy. The stoichiometry of these samples conforms to $\text{Ba}_5(\text{PO}_4)_{3-x}(\text{CO}_3)_x(\text{OH})_{1-x} \text{O}_x$ as the result of $\text{CO}_3^{2-}$ and $\text{O}_2^-$ substitution for $\text{PO}_4^{3-}$ and $\text{OH}^-$ in the hydroxyapatite lattice under the scheme: $\text{PO}_4^{3-} + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{O}_2^-$. The crystal structure of some carbonated barium hydroxyapatite patterns were refined by Rietveld method using X-ray powder diffraction data. The analysis of the crystallographic site occupation has shown that the single phase range of $\text{Ba}_5(\text{PO}_4)_{3-x}(\text{CO}_3)_x(\text{OH})_{1-x} \text{O}_x$ is limited by $x = 0.32$. 

Synthesis of 2-Oxa-4,6,8-triazabicyclo[3.3.0]octanes

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4,6,8-Triaryl-2-oxa-4,6,8-triazabicyclo[3.3.0]octanes (4) and 6,8-diaryl-2,4-dioxa-6,8-diazabicyclo[3.3.0]octanes (5) were synthesized by condensation of arylamines with glyoxal and formaldehyde in CH₃CN. Change of the reaction solvent to CH₃OH leads to dimethoxy imidazolidine (7). Depending on the reaction conditions, intermediates with different configuration are formed. The X-ray crystal structure determination of 5 shows a cis fusion of the two five-membered rings, in line with two anomic effect; a strong nN→σC-O* interaction and a weak nO→σC-N*. The compound 5 is a rare molecule containing N-C-N and O-C-O units adjacent to N-C-O anomeric moiety. The results show, that in the presence of anomic unit of N-C-O, the anomic effect of N-C-N and O-C-O moieties are negligible.
Structure, Thermal Stability and Water Solubility of (Tanshinone II-A)/(β-Cyclodextrin) Inclusion Complex

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The structure of the inclusion complex of tanshinone II-A and β-cyclodextrin formed under microwave irradiation was studied by the UV, IR, and NMR spectroscopy. The association constant of the complex in water is 210 M⁻¹, as determined from the double reciprocal curve by UV spectroscopy. The enhanced water solubility of the complex was found. Thermal studies proved the increased thermal stability of the inclusion complex.
Synthesis, Characterization and Crystal Structure of \((Z)-1-[2-(\text{Tri-o-tolylstannyl})\text{vinyl}]-1\text{-cyclopentanol and Its o-Tolylhalostannyl Derivatives}

by D.-S. Zhu\(^1,2\), C.-S. Lü\(^1\), Z.-M. Mei\(^1\), W. Gao\(^1\), Y.-T. Zhang\(^1\), Y. Mu\(^1,3\) and Z.-M. Wang\(^1\)

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\((Z)-1-[2-(\text{Tri-o-tolylstannyl})\text{vinyl}]-1\text{-cyclopentanol (1)}\) was synthesized by the additive reaction of 1-ethynylcyclopentanol with tri-o-tolyltin hydride. One or two of the o-tolyl groups of compound 1 was substituted by I, Br or Cl to yield derivatives of the type \(\text{CH}_2(\text{CH}_2)_3\text{CH(OH)CH=CHSn(o-tol)}_3\text{X}_n, n=1, X=I \text{(2)}, \text{Br (3)}, \text{Cl (4)}; n=2, X=\text{Br (5)}\). The compounds 1–5 were characterized by elemental analysis, \(^1\)H NMR and FT-IR spectroscopy. The crystal and molecular structures of 1 and 2 have been determined by single crystal X-ray diffraction analysis. The Sn atom in 1 exhibits a tetrahedral geometry distorted towards trigonal bipyramid, due to a weak intramolecular interaction between Sn and hydroxyl O atoms [2.813(4) Å], while the Sn atom in 2 adopts a trigonal bipyramidal geometry with a significant Sn(1)–O(1) interaction [2.553(4) Å].
Synthesis of Aryl 1-(tert-Butyl)-4,4-dimethyl-2,5-dioxo-3-pyrrolidinecarboxylates

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Reaction of tert-butyl isocyanide with isopropylidene Meldrum’s acid in the presence of phenols in dichloromethane leads to aryl 1-(tert-butyl)-4,4-dimethyl-2,5-dioxo-3-pyrrolidinecarboxylates in good yields.
Synthesis of New Trifunctional Ligands Based on 1,4,7,10-Tetraazacyclododecane

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Synthesis of 1,4,7,10-tetraazacyclododecane with different N-substituents: chelating groups, fluorescent, and long lipophilic chain with ω-hydroxyl group is reported.

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AM1 calculations suggest that the [2+3]-cycloaddition of C,C,N-triphenylnitrone (1) to (E)-3,3,3-trichloro-1-nitropropene-1 (2) in gas phase occurs in concerted manner. Kinetic factors favour the formation of cycloadduct with nitrogen group in position C4 of the isoxazolidine ring (path A). Introduction of toluene as a dielectric medium does not alter this preferable. However, the character of the energy profile for path A undergoes a critical change. In this case, two transition states and intermediate with zwitterionic character were localized by means of AM1/COSMO method.
Synthesis and Antifeedant Properties of N-Acylphenylisoserinates of Lactarius Sesquiterpenoid Alcohols

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The esterification of various sesquiterpenoid alcohols of Lactarius origin with N-benzoyl-[2R,3S]-phenylisoserine (side chain of Taxol®), N-acetyl-[2R,3S]-phenylisoserine and N-tert-butoxy-[2R,3S]-phenylisoserine (side chain of Taxotere®) produced compounds whose antifeedant properties against storage pests Tribolium confusum, Trogoderma granarium, Sitophylus granarius and Rhizoperta dominica were measured. The introduction of the ester moiety in these molecules, in comparison to original compounds, moderately enhanced their antifeedant activities, as well as changed their selectivity of activity towards the test insects.

Conductance Study of the Thermodynamics of Dibenzopyridino-18-crown-6 Complexes with K⁺, Tl⁺, Sr²⁺ and Ba²⁺ Ions in Acetonitrile Solution

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The complexation reactions between dibenzopyridino-18-crown-6 and Tl⁺, K⁺, Sr²⁺ and Ba²⁺ ions were studied conductometrically in acetonitrile solution at various temperatures. The formation constants of the resulting 1:1 complexes were calculated from the computer fitting of the molar conductance-mole ratio data at different temperatures. At 25°C, the stability of the resulting complexes varied in the order Ba²⁺ > Sr²⁺ > Tl⁺ > K⁺. The enthalpy and entropy changes of the complexation reactions were evaluated from the temperature dependence of formation constants. While, the bivalent alkaline earth complexes are both enthalpy and entropy stabilized, the univalent cation complexes used are enthalpy stabilized but entropy destabilized.
Catalytic Electrolysis-Free Copper Deposition Using Dispersions of Titanium Dioxide with Adsorbed Trespassing Metal Ions

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It has been found that modification of TiO₂ by impregnation with Pd²⁺, Cu²⁺, Fe²⁺, Fe³⁺ and Co²⁺ salts causes a significant rise of its catalytic activity in the reaction of metal copper deposition. Influence of nature of modifying cation, its concentration, counter-anion concentration and the effect of double modification by two different salts have also been investigated. Comparison of energetic characteristics of all intermediate compounds led us to a possible model of catalytic deposition of copper, explaining the increased catalytic activity of the modified examples.
Resolution of Quenched Fluorescence Mixtures of Two Conformers of trans-1-(2-Anthryl)-2-phenylethene by Constrained and Unconstrained Methods of Principal Component Analysis: a Comparative Study

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Two different methods of principal component analysis (PCA) were applied to resolve pure component spectra in the two-component spectral mixture of gradually quenched fluorescence. The two approaches differ by that in the first method one uses an additional physical constraint to arrive at the desired solution, while none of this but simple matrix transformations are used to this aim in the other. Both methods are classified as the approaches of Principal Component Analysis with Self-Modeling (PCA-SM). The first technique is known as PCA-SM-SV, where SV stands for a constraint related to the Stern-Volmer equation, the second method is known as Kubista’s approach to two same-sized correlated sets of spectral data matrices. The methods were applied to resolve the pure component fluorescence spectra in the fluorescence mixture of two conformers of trans-1-(2-anthryl)-2-phenylethene (t-APE) quenched by fumaronitrile in toluene. The results of the application of both methods to precisely measured spectra appear practically equivalent and eventually dispel the controversy existing in the literature about the fluorescence spectral profiles of the t-APEα and t-APEβ conformers in favour of the PCA-SM-SV method which results were earlier questioned by the outcome of other methods.
Cyclic Voltammetry and Electronic Absorption Spectroscopy in Investigations of the Nature of the Electrochemical Reduction of Phenylidiazonium and Phenyl-\textit{bis}-diazonium Cations

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The electrochemical reduction of phenylidiazonium and phenyl-\textit{bis}-diazonium cations on mercury drop and platinum cathodes exhibits a multistep nature, as demonstrate the results of polarographic and cyclic voltammetry measurements. The primarily formed radicals participate in various secondary processes, as a result of which occur species absorbing UV-VIS radiation. Electronic absorption in the visible region can be ascribed to entities forming from the recombination of two azophenyl or azophenyl and phenyl radicals, originating from the one- or two-electron reduction of primarily or secondary formed cations.
Oxidative Dehydrogenation of Propane over Pentasil Ring Co-Zeolites

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The activity of Co-zeolites with MFI, BEA, MOR and FER topologies was studied in propane oxidative dehydrogenation. The products of oxidative dehydrogenation of propane were propene, CO, CO₂ and a very small amount of ethene and methane as products of cracking, which play only a minor role. The sequence in ODH activity of Co-zeolites is CoH-BEA > CoH-MFI > CoH-MOR > CoH-FER. The difference in activity of various zeolite matrices is ascribed to the differences of channel diameter and architecture of Co-β sites in the pentasil zeolites. Rate limiting step of propene formation is not the reaction of propane or adsorbed species of propane with oxygen but desorption of propene.
Synthesis and Magnetic Property of a New Dialkoxo-Bridged Bicobalt(II) Complex with Triethanolamine as Ligand

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Carbon-Based Ruthenium Catalyst for Ammonia Synthesis Doped with Caesium Nitrate. Studies of the Catalyst Activation

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Further Sesquiterpene Lactones from *Dugaldia hoopesii*

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