

Several Trivalent Rare Earth Complexes with 2,6-Diaminopyridine

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Several trivalent rare earth complexes of the formula $[\text{LnCl}_2(\text{dap})_2]\text{Cl}\cdot 4\text{H}_2\text{O}$, where Ln = Y, La, Ce, Eu, Ho and Yb; dap = 2,6-diaminopyridine, have been synthesized and characterized by elemental analysis, conductivity measurements and spectroscopic methods (IR, ^1H -NMR and ^{13}C -NMR). The spectral data show that the ligand coordinates to the metal ions through the pyridine and amino nitrogens.

Key words: rare earth complexes, 2,6-diaminopyridine

Hydrazinium Complexes of Lanthanide and Transition Metal Squarates

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Reaction of the ligands, squaric acid and hydrazine with $\text{Ln}(\text{NO}_3)_3$ where $\text{Ln}(\text{III}) = \text{La}$, Pr, Nd, Sm, Gd and Ce results in the formation of the complexes of the formula, $\text{N}_2\text{H}_5[\text{Ln}(\text{C}_4\text{O}_4)_2] \cdot x\text{H}_2\text{O}$ where $x = 3, 5$ and 6 and their reaction with transition metal nitrates, $\text{M}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, where $\text{M}(\text{II}) = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ and Cd in aqueous solution yields the squarates of the types, $[(\text{N}_2\text{H}_5)_3\text{M}(\text{C}_4\text{O}_4)_{2.5}] \cdot 2\text{H}_2\text{O}$ where $\text{M}(\text{II}) = \text{Co}, \text{Ni}$ and Cd ; $[(\text{N}_2\text{H}_5)_2\text{Zn}(\text{C}_4\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ and $[(\text{N}_2\text{H}_5)\text{Cu}(\text{C}_4\text{O}_4)_{1.5}]$. Neutralization of the acid with hydrazine hydrate gives dihydrazinium squarate hydrate, $(\text{N}_2\text{H}_5)_2(\text{C}_4\text{O}_4) \cdot \text{H}_2\text{O}$. All the above complexes, except Cd, are sparingly soluble in water and are characterized by IR, UV-visible, ESR and thermoanalytical methods. The squarates appear to behave as bis-monodentate and tetrakis-monodentate bridged ligands in transition metal and lanthanide complexes respectively. Hydrazinium cation acts as a coordinating ligand in transition metal complexes whereas it is a charge compensating species in lanthanide squarates. This fact is revealed from their IR spectra by displaying N-N frequency at 1000 cm^{-1} in the former case and at 950 cm^{-1} in the latter. Squarate compounds exhibit very high exothermic decomposition. Hydrazinium lanthanide squarates show weight losses due to dehydration and dehydrazination from 68°C to 258°C and a strong exothermic decomposition between 176°C and 700°C leading to the formation of metal oxides/oxy carbonates as the end products possibly *via* $\text{H}[\text{Ln}(\text{C}_4\text{O}_4)_2]$ intermediate. Transition metal compounds loose water and hydrazine in the range of $50\text{--}275^\circ\text{C}$, and then undergo strong exothermic decomposition above 200°C with no stable intermediate formation. Simple hydrazinium salt decomposes completely exothermally at 179°C . The electronic spectra indicate the coordination number (CN) and geometry; CN 8 with square anti-prism for lanthanides and CN 6 with octahedral arrangement for transition metals. The geometry of the complexes is substantiated by their electronic spectra, magnetic susceptibility values and ESR study. Isomorphism among the complexes is shown by their XRD.

Key words: electronic spectra, ESR, IR, squarates, thermal analysis

Synthesis, Characterization and Catalytic Activity of Salen-type Schiff Base Polychelates

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Polymeric complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with Schiff base derived from 4,4'-bis-[(salicylaldehyde-5)azo]biphenyl and 1,3-diaminopropane have been synthesized and characterized by microanalysis, IR, and electronic spectra and magnetic moment data. All these complexes are dark coloured and insoluble in water and most of the common organic solvents. Thermogravimetric analysis indicated the presence of coordinated water in complexes. The solid-state conductivity of the ligand and its polychelates was studied in the temperature range 313–413 K and chelates were found to show semiconducting behaviour. The Mn(II), Fe(II), Co(II) and Ni(II) polychelates have also been assessed for the catalytic epoxidation of styrene.

Key words: Schiff base, polychelates, TGA, conductivity, catalytic activity

Particular Features of Formation of the Anhydrous Solid Solutions of Mg, Mn(II), Co(II) and Zn Diphosphates

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The sequence of physical and chemical as well as structural transformations accompanying the formation of solid solutions of anhydrous Mg, Mn(II), Co(II) and Zn diphosphates by thermal dehydration of corresponding hydrated salts was investigated. The interconnection between state of water in crystalhydrate, on one side, and mechanism of its removal, on the other side, was considered. The peculiarities controlling the processes of formation of solid solutions of anhydrous divalent metal diphosphates were established.

Key words: anhydrous, diphosphate, solid solution, thermolysis

The Silver(I) – Complexes of Cyclic Polyamines with Pendant-arm Modification

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The complex formation for two different groups of cyclic polyamines with four or six nitrogen atoms and with pendant-arm modification and silver(I) ions in propylene carbonate has been studied by electron spray ionization mass spectrometry (ESI MS), potentiometric and Austin Model 1 (AM1d) semiempirical methods. The stability constants of complexes are determined by potentiometric method. The structure of those complexes are visualised by AM1d semiempirical calculations.

Key words: supramolecular chemistry, potentiometric method, macrocyclic polyamines, silver(I) complexes, AM1d calculations, stability constant

**The Synthesis and Characterization of
(1Z,2Z)-N'-1~,N'-2~Dihydroxy-N~1~,N~2~
dipyridin-2-ylethanedimidamide and Its Mono and
Dinuclear Zn(II), Cd(II) and Hg(II) Complexes**

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A new *vic*-dioxime, (1Z,2Z)-N'-1~,N'-2~dihydroxy-N~1~,N~2~dipyridin-2-ylethanedimidamide (**H₂L**) has been synthesized from (*E,E*)-dichloroglyoxime and 2-aminopyridine in acetonitrile. Mononuclear complexes of Zn(II), Cd(II) and Hg(II) have been prepared and were found to have a metal-ligand ratio of 1:1. The synthesis of mixed M,M' dinuclear complexes was achieved with Zn(II), Cd(II) and Hg(II) depending on the manner of addition of salts. The complexes were characterized by IR, MS, ¹H and ¹³C NMR.

Key words: (1Z,2Z)-N'-1~,N'-2~dihydroxy-N~1~,N~2~dipyridin-2-ylethanedimidamide, *vic*-dioxime, Zn(II), Cd(II) and Hg(II) complexes

Synthesis and Characterization of a New 4-Methoxysalicyliden-*p*-aminoacetophenoneoxime and Its Complexes with Co(II), Cu(II) and Zn(II)

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The novel Schiff base ligand, 4-methoxysalicyliden-*p*-aminoacetophenoneoxime (LH) was synthesized starting from *p*-aminoacetophenoneoxime and 4-methoxysalicylaldehyde. Mononuclear cobalt(II), copper(II) and zinc(II) complexes of the ligand have been prepared by using Co(II), Cu(II) and Zn(II) salt with a metal to ligand ratio of 1:2. The structures of the ligand and its complexes were identified by using elemental analyses, IR, ¹H- and ¹³C-NMR spectra, magnetic susceptibility measurements, UV spectra and thermogravimetric analyses (TGA).

Key words: Schiff bases, cobalt(II), copper(II) and zinc(II) complexes of Schiff bases

Transition Metal Manganese(II), Nickel(II), Copper(II) and Zinc(II) Complexes of a New Schiff Base Ligand: Synthesis, Characterization and Antitumor Activity Studies

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Four transition metals complexes ([Mn(L)₂] (complex **1**), [Ni(L)₂·0.5H₂O] (complex **2**), [Cu(L)₂·4H₂O] (complex **3**) and [Zn(L)₂·0.5H₂O] (complex **4**)), which contain a new Schiff base ligand (**HL**) derived from 2,4-dihydroxyacetophenone with triaminotriethylamine, have been synthesized and subsequently characterized by element analysis, ¹H NMR and mass spectra. Their properties have been investigated by IR, UV and TG-DTA techniques. Tentative structures for the complexes have been proposed based on the experimental results. The antitumor activity against HL-60 human leukemia cells of free ligand (L) and its Mn(II), Ni(II), Cu(II) complexes were also studied by MTT method. The Ni(II) complex shows the best antitumor activity properties among these complexes.

Key words: Schiff base ligand, transition metals complexes, synthesis, characterization, antitumor activity

The Mixed-Valence Rhenium(IV, V) Complexes

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Reaction of $\text{K}_4[\text{Re}_2\text{OCl}_{10}]$ with oxidizing agents in hydrochloric acid produced binuclear compounds: $\text{Cs}_3[\text{Re}_2\text{OCl}_{10}]$ **1**, $(\text{Ph}_4\text{As})_3[\text{Re}_2\text{OCl}_{10}]$ **2**, $(\text{ChinH})_3[\text{Re}_2\text{OCl}_{10}]$ **3**. These complexes had been characterized by kinetic and magnetic investigations. The low-temperature magnetic susceptibility measurements have revealed, that $\text{Cs}_3[\text{Re}_2\text{OCl}_{10}]$ complex is antiferromagnets, with Néel temperature at 10 K. The temperature dependence of the magnetic moment for **2** and **3** complexes indicates the existence of a magnetically isolated exchange-coupled dimer. In the electronic spectra, the intensive band at 20150 cm^{-1} is associated with the presence of the two different oxidation states. In agreement with the evidence from the oxidation of oxochlororhenate ion and the disproportionation in solution, it is proposed that the compound should be considered as a Re(IV)–Re(V) mixed-valence system.

Key words: bimetallic complexes, rhenium(IV), rhenium(V), mixed-valence system

Triterpenoid Acids from *Kadsura ananosma*

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Ananosic acid D, a new 18 (13→12) abeo lanostane triterpenoid acid was isolated from the stem barks of *Kadsura ananosma* and assigned the structure 3 α -hydroxy-18 (13→12) abeo lanost-7 (8), 12 (18), 24 (Z)-trien-26-oic acid (**1**) by spectroscopic analysis including HR-ESI-MS and 2D-NMR. In addition, known lanostane triterpenoid acids 24(E)-3-oxo-lanosta-8, 24-dien-26-oic acid (**2**) and anwuweizic acid (**3**) were also obtained from this species. **2** was obtained as a new natural product and **3** was isolated from the plant for the first time.

Key words: Schisandraceae, *Kadsura ananosma*, triterpenoid acid, lanostane, ananosic acid D

New Thiocarbonyl Ylides Derived from 3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione; Generation and Reactions

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The reaction of 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**1**) with diazo compounds yielded spirocyclic 2,5-dihydro-1,3,4-thiadiazoles **3**, which decomposed at *ca.* 45°C to give the corresponding thiocarbonyl ylide of type **4**. In the absence of trapping agents, these thiocarbonyl ylides underwent a 1,3-dipolar electrocycloaddition to yield spirocyclic thiiranes **5**. On the other hand, the thiocarbonyl methanide **4a** was efficiently intercepted with C≡C, C=C, C=O, C=S, and N=N dipolarophiles leading to the [2+3] cycloadducts. A non-stereoselective cycloaddition took place when **3a** was decomposed in the presence of the very electron-deficient dicyanofumarate or maleate, indicating a two step mechanism *via* an intermediate zwitterion. Furthermore, the thiocarbonyl methanide **4a** could be trapped by the imidazole-2-thione **7** to give the 1,3-adduct **8**. Treatment of **3a** with secondary amines led to amidrazones of type **25** *via* base-catalyzed ring opening and condensation reaction.

Key words: [2+3] cycloaddition, 1,3-dipolar electrocycloaddition, 2,5-dihydro-1,3,4-thiadiazoles, thiocarbonyl ylides

Reactions of Aza-*ortho*-xylylenes Generated from 3-Aryl-2,1-benzisothiazoline 2,2-Dioxides

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3-Methyl-3-(4-nitrophenyl)-2,1-benzisothiazoline 2,2-dioxides **1a,b** undergo thermal extrusion (180°C) of SO₂ to form aza-*ortho*-xylylenes, which after [1,5]-hydrogen shift give 1,1-diarylethylenes **9a,b**. The corresponding 3-(nitropyridinyl) benzosultams undergo transformation into dihydro-azepino[2,3-*b*]indole derivatives **17**.

Key words: benzosultams, extrusion, [1,5] sigmatropic hydrogen shift, aza-*ortho*-xylylenes, electrocyclization, indoloazepine, aryloindole

Investigation of the $\text{Tm}_2\text{Se}_3\text{--Cu}_2\text{Se--PbSe}$ and $\text{Lu}_2\text{Se}_3\text{--Cu}_2\text{Se--PbSe}$ Systems at 870 K

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Phase equilibria in $\text{Tm}_2\text{Se}_3\text{--Cu}_2\text{Se--PbSe}$ and $\text{Lu}_2\text{Se}_3\text{--Cu}_2\text{Se--PbSe}$ systems at 870 K were investigated, using X-ray powder diffraction. $\text{R}_{(2+x)/3}\text{Cu}_{2-x}\text{Se}_2$ ($0 \leq x \leq 1$) solid solutions (space group $P\bar{3}$) were found in $\text{R}_2\text{Se}_3\text{--Cu}_2\text{Se}$ ($\text{R} = \text{Tm}$ and Lu) sections of both systems. Crystal structure determinations for terminal RCuSe_2 compositions of these solid solutions were performed. $\text{Er}_{2/3}\text{Cu}_2\text{Se}_2$ structure type was confirmed for TmCuSe_2 . LuCuSe_2 crystallizes in the same structure, but with one extra position for Lu atoms. Crystal structures of R_2PbSe_4 (space group $Pnma$) in $\text{R}_2\text{Se}_3\text{--PbSe}$ sections were determined using X-single crystal and powder diffraction for $\text{R} = \text{Tm}$ and Lu , respectively. The existence of $\text{R}_{3,33}\text{CuPb}_{1,5}\text{Se}_7$ ($\text{Lu}_{3,33}\text{CuPb}_{1,5}\text{Se}_7$ structure type, space group Cm), RCuPbSe_3 ($\beta\text{-BaLaCuSe}_3$ structure type, space group $Pnma$) and $\text{Tm}_5\text{CuPb}_3\text{Se}_{11}$ ($\text{Er}_5\text{CuPb}_3\text{Se}_{11}$ structure type, space group $Cmcm$) compounds in $\text{R}_2\text{Se}_3\text{--Cu}_2\text{Se--PbSe}$ ($\text{R} = \text{Tm}$ and Lu) systems was confirmed.

Key words: X-ray structure analysis, isothermal section, crystal structure, phase diagram

Electrochemical Examination of the Influence of H_2SeO_3 on Molybdenum Electrodeposition on Tin Oxide Electrode from Aqueous Citrate Electrolyte

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Cyclic voltammetry and chronoamperometry have been used to evaluate the electrochemical reactions taking place under SnO_2 /glass electrode polarization in a solution of Na_2MoO_4 , H_2SeO_3 , sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) and in solutions consisting of their mixtures. According to our study, the presence of a small concentration of H_2SeO_3 in the electrolyte is necessary to induce the reduction of MoO_4^{2-} ions. Experimental data support an assumption that the reduction of MoO_4^{2-} ions to molybdenum could occur when selenium nuclei are initially formed on the electrode. Eventually selenium nuclei induce the electrodeposition of molybdenum, giving finally thin Mo–Se film layers. AAS analysis confirms that in the potential interval between -1.0 and -1.2 V, thin films with a Mo/Se atomic ratio 0.63 and 0.57, respectively, are obtained.

Key words: thin Mo–Se film layers, electrodeposition, cyclic voltammetry, chronoamperometry

Investigation of Phase Equilibria in the System Nd₂O₃–Na₂O–P₂O₅. Quasibinary Section NdPO₄–Na₃PO₄

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Quasibinary section NdPO₄–Na₃PO₄ has been investigated by thermoanalytical methods (DTA, TG, DTG), X-ray powder diffraction and microscopy. Its phase diagram is proposed. It is found, that the parent orthophosphates react in the molar ratio 1:1 yielding an intermediate compound of Na₃Nd(PO₄)₂. This phosphate melts incongruently at 1485°C, giving NdPO₄ and an Na₃PO₄-rich liquid. Na₃Nd(PO₄)₂ compound is stable down to room temperature and exhibits a polymorphic transition at about 1040°C.

Key words: phase diagram, DTA, TG, DTG, X-ray powder diffraction, neodymium-sodium orthophosphate

Fluorescence Properties of Derivatives of Anthroic Acids

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Fluorescence behaviour of 9-anthracenecarboxylic acid (H-ANCOOH), 10-bromoanthracene-9-carboxylic acid (Br-ANCOOH) and 10-cyanoanthracene-9-carboxylic acid (CN-ANCOOH) in solvents of different polarities was investigated, using the steady state and time-resolved methods. The dual fluorescence of the acids originates clearly from the fluorescence of the undissociated acids and the anions. From the ground-state absorptiometric titration the pK_a values have been obtained, whereas for the values of pK_a in the excited singlet state (pK_a^*) the Förster cycle was used. Introduction of the electron withdrawing groups (Br and CN) shifts the pK_a values both in the ground and singlet excited states to the lower values compared to the parent molecule. On the other hand, the presence of the electron accepting groups in anthracene moiety influences the spectral position of the bimolecular exciplexes (excited state complexes) formed between the excited acids and the electron donor molecule, such as *p*-cyano, *N,N*-dimethylaniline (DMABN) in nonpolar solvents. A correlation between the decreasing pK_a values in the excited singlet state and the position of the charge transfer luminescence of the intermolecular exciplexes has been found.

Key words: anthracenecarboxylic acids, Förster cycle, excited state acid dissociation, exciplex formation

Conductance Study of the Thermodynamics of Dibenzo-21-crown-7 Complexes with Na⁺, K⁺, Rb⁺ and Cs⁺ Ions in Acetonitrile Solution

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A conductance study of the interaction between Na⁺, K⁺, Rb⁺ and Cs⁺ ions and dibenzo-21-crown-7 in acetonitrile solution has been carried out at various temperatures. The formation constants of the resulting 1:1 complexes were determined from the molar conductance-mole ratio data and, in the entire temperature range, found to vary in the order Rb⁺ > K⁺ > Cs⁺ > Na⁺. The enthalpy and entropy of complexation reactions were determined from the temperature dependence of the formation constants. In all cases, the resulting complexes were found to be both enthalpy and entropy stabilized.

Key words: dibenzo-21-crown-7, alkali complexes, stability, enthalpy, entropy, acetonitrile, conductance

Coupled Discharge for Nitrous Oxide Processing

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