Peculiarities of Components’ Interaction in Rare Earth–Transition Metal–Silicon Systems in $R(M_xSi_{1-x})_2$ Composition Region

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The explanation of ternary compounds, forming with AlB$_2$ structure type in the rare earth metal–transition metal–silicon systems, implements on base of analysis of the dependence of the valence-electron concentration versus the kind of the transition metals in their solid solutions in the binary compounds with AlB$_2$, $\alpha$-ThSi$_2$, and $\alpha$-GdSi$_2$ structure types appropriate to the rare earth–silicon systems. There is shown that the silicon content (as the electron donor) during formation of the ternary compounds with AlB$_2$ structure type is dependent on the kind of transition metal and this content is decreased in the series of the compounds with Fe, Co, Ni, and Cu consecutively. The experimental data on concentrational intervals of the stability ranges of these ternary compounds are proposed to the qualitative evaluation of the effective valency of the transition metal atoms.
Metal Complexes of C-Functionalized Macrocyclic Dioxotetraamines Bearing 8-Hydroxyquinoline: Stability in Aqueous Solutions


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Two novel 8-hydroxyquinoline connected dioxotetraamines have been designed and synthesized, and have been characterized by elemental analysis, IR, mass spectra and 1H NMR. The two ligands L1 and L2 have two chelating groups. Each can react with a transition metal ion forming complexes. Potentiometric titrations have been performed in 0.1 mol/L NaNO3 at 25°C giving the 1:1 stability constants. Coupled with UV spectroscopy the affinity of 8-hydroxyquinoline and dioxotetraamines to transition metal ions were compared and the possible structure of the metal complex species in solution was discussed. The results show that as to Mn²⁺, Zn²⁺ and Co²⁺, 8-hydroxyquinoline is a stronger chelating reagent than dioxo[13] or [14]tetraamine macrocycles and at 1:1 molar ratio (M:L), the former binds in 100% to the metal ions, while the dioxotetraamines can be only partially or not coordinated.
New hexagonal ternary phases $R_{2-y}Mn_xAl_{17-x}$ have been obtained in the Mn-rich regions of the $R$–Mn–Al ($R = \text{Gd, Tb, Dy, Ho, Er}$) systems: $\text{Gd}_{2-y}Mn_xAl_{17-x}$ ($0 \leq y \leq 0.15$, $13.0 \leq x \leq 15.1$); $\text{Tb}_{2-y}Mn_xAl_{17-x}$ ($0 \leq y \leq 0.23$, $13.2 \leq x \leq 15.2$); $\text{Dy}_{2-y}Mn_xAl_{17-x}$ ($0 \leq y < -0.2$, $11.9 \leq x \leq 14.6$); $\text{Ho}_{2-y}Mn_xAl_{17-x}$ ($0 \leq y < -0.2$, $11.5 \leq x \leq 14.2$) and $\text{Er}_{2-y}Mn_xMn_{17-x}$ ($0 \leq y \leq 0.27$, $0 \leq z \leq 0.54$, $11.3 \leq x \leq 14.1$). $\text{Th}_2\text{Ni}_{17}$-type of structure occurs in alloys with the content of $R = 10.5$ at.% (ideal $R_2X_{17}$ stoichiometry). When $R < 10.5$ at.% two ways of structure constitution are possible: i) formation of the $\text{Th}_2\text{Ni}_{17}$-type structure with defective $2(b)$ atomic position (solid solution of subtraction); ii) formation of the $\text{Th}_2\text{Ni}_{17}$-related type structure with the substitution of part of $R$ atoms by the Mn-Mn pairs (solid solution of multiple substitution).
Cine-Substitution of Nitro Group in 1-Aryl-2-methyl-4-nitroimidazoles by Thiols; X-ray Diffraction Proof for the Product Structure

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1-Aryl-2-methyl-4-nitroimidazoles react with 2-amino- or with 2-hydroxyethanethiols to give products of cine-substitution of the nitro group. 5-(2'-Hydroxyethylthio)-2-methyl-1-phenylimidazole has been isolated as a free base, other products in the form of dipicrates. A structure of 5-(2'-aminoethylthio)-2-methyl-1-phenylimidazole dipicrate was proved by X-ray diffraction.

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The reaction of neryl (3), geranyl (4), (+)-carvotanacetyl (5), (–)-carvyl (6) and perillyl (7) chlorides with phenylseleno- (1) or phenyltellurosodium (2), and then with chloramine-T afforded α,β-unsaturated toluenesulfonamides 8–11, which were reduced with sodium in liquid ammonia to allylic amines 12–15. Allylic phenyltellurides were oxidized by air to carbonyl compounds 29–31 or alcohol 28.
Synthesis of 2,2′-Diselenobisbenzamides and 4,4′-Diselenobisbutyramides with Sulfamoyl Groups as New Potential Virucides and Cytokine Inducers

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The synthesis of 2,2′-diselenobisbenzamides and 4,4′-diselenobisbutyramides with sulfamoyl functions, two new groups of potential antiviral agents and cytokine inducers, based on the acylation of the 4-aminobenzenosulfonamides with corresponding chlorocarbonylaryl or chlorocarbonylalkyl diselenides, has been elaborated. In a similar way dithiobenzamide and diphenic acid bisbenzamide were obtained from dithio-2,2-bisbenzoic acid and diphenic acid dichlorides respectively.
Application of Bromotrimethylsilane and Trialkyl Phosphites for Convenient and Effective Synthesis of Aminophosphonic Acids and Corresponding Monoalkyl and Dialkyl Esters

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Application of bromotrimethylsilane (Br-TMS) in a mixture with trialkyl phosphate for synthesis of various aminophosphonic acids and esters was investigated. It was found, that appropriate mixtures of Br-TMS and trimethyl phosphate or triethyl phosphate were effective reagents for phosphorylation of various aldimines, obtained from aromatic and heteroaromatic aldehydes. Products of these reactions were corresponding aminophosphonic acids, or corresponding dialkyl or monoalkyl esters, respectively.
Cine-Substitution of 2-Methyl-1,4-dinitroimidazole in Dimethylsulfoxide Solution. Synthesis of 4(5)-(Azol-1-yl)-5(4)-nitroimidazoles

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4(5)-(Azol-1-yl)-5(4)-nitroimidazoles were obtained in moderate yields by nucleophilic cine-substitution of 2-methyl-1,4-dinitroimidazole. Nucleophilic azole anions were generated from salts of parent heterocycles with 1,8-diazabicyclo[5.4.0]-undec-7-ene.
Synthesis of Ortho-, Meta- and Paracyclo(1,1’)-ferrocenophanes Containing Sulfide Bonds

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The title dithiaferrocenophanes (1–5) have been synthesized in reactions of 1,1’-di(hydroxymethyl)ferrocene with o-, m- and p-dithiophenols, applying high dilution technique and small amount of trifluoracetic acid as catalyst. As by-products insoluble ferrocene polysulphides formed in competitive intermolecular condensations were isolated in all cases. In reactions of isomeric dithiophenols with ferrocenylmethanol acyclic model compounds (6–10) were prepared for spectral comparisons. The complexing ability of the synthesized ortho- and meta(1,1’)ferrocenophanes 1 and 3 with metal cations was measured by a solvent-extraction method, and was found to be poor with alkali cations but significantly better with Ag⁺ cations.
Coupling of the C6 and C6′ Positions of Sucrose by Metathesis Reaction

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1′,2,3,3′,4,4′-Hexa-O-benzylsucrose (7) was converted into diallyl ether 11 and subjected to metathesis reaction with the Grubbs’ catalyst. The expected macrocyclic product (12) was obtained in a good yield as a cis/trans mixture of olefins, hydrogenation of which gave fully deprotected saturated compound 13.
Polymerization of acrylonitrile (AN), without and in the presence of CuCl$_2$, CoCl$_2$, and NiCl$_2$, formed polyacrylonitrile homopolymer (PAN) and polymer complexes of AN–CuCl$_2$, AN–CoCl$_2$ and AN–NiCl$_2$, respectively. These polymer complexes were characterized using spectroscopic techniques. Electrical conductivity and cyclic voltammetry on untreated and heat treated polymers, carried out at different temperatures, showed that the conductivity increased with temperature, presumably due to conjugation and cyclization during heat treatment.
Electrochemical Behavior of Mixed Self-Assembled Monolayers of Azobenzene and Alkanethiol

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The self-assembly and electrochemical properties of mixed self-assembled monolayer (SAMs) of 4-methoxy-4′-(N-(2′-mercaptoethyl)amino)carbonyl)azobenzene (C1AzoC2SH) and 1-butanethiol (C4SH) were studied on the gold electrode by cyclic voltammetry. Usually the azobenzene groups exhibit very sluggish electron-transfer kinetics in the densely packed films. The alkanethiol as the spacer molecule was introduced to the azobenzene monolayer system to weaken the intermolecular interaction in order to enhance the electrochemical activity of the azobenzene group. Under the different molar ratios of C1AzoC2SH and C4SH we obtain a different electrochemical response and an apparent surface electrochemical rate constant. The experimental results suggested that the azobenzene groups exhibit a higher electrochemical activity in the mixed SAMs systems.
Dipole Moment, Molar Kerr Constant, Crystal and Molecular Structure of
3-Chloro-N-methyl-N-nitroaniline

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Dipole moment, molar Kerr constant, crystal and molecular structure of m-
ClC₆H₄N(CH₃)NO₂ (or C₇H₇ClN₂O₂) are studied. Comparison the data obtained by di-
pole moment and molar Kerr constant measurement, X-ray crystallographic investiga-
tion and quantum-chemical calculation show that the molecule contains a planar NNO₂
nitroamino group which is twisted around the N–C phenyl bond by ca 61.4° from the plane
of the aromatic ring. The structural data are compared with the data for p-
ClC₆H₄N(CH₃)NO₂ and the influence of the substituent on the structural parameters of
the molecule is established.
Synthesis and Surface Acidity of Amorphous Fluorine-Containing Aluminium Borates

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A series of fluorine-containing aluminium borate samples with Al$_2$O$_3$/B$_2$O$_3$ = 3 and HF/B$_2$O$_3$ = 0.05–0.50 molar ratios has been synthesized by an impregnation method using NH$_4$F. The materials obtained are amorphous up to 840–1130 K. Their thermal transformations were investigated by DTA and MSA. There are Lewis and Brönsted acid sites present in these samples. The very strong Lewis sites are due to formation of trigonal B$^{3+}$, bonded with F$^-$ on the surface of fluorine-containing aluminium borates. Dehydration of isopropyl alcohol was used as a probe reaction to measure the acidity. The results of measurements have shown that these materials were more acidic and catalytically active than the starting aluminium borate.
Methanol Synthesis from CO$_2$ and H$_2$ on Cu/ZnO/Al$_2$O$_3$ – ZrO$_2$ Catalysts. Catalytic Activity and Adsorption of Reactants

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Effect of preparation method and substitution of Al$_2$O$_3$ by ZrO$_2$ on the adsorption of CO, CO$_2$, H$_2$O and methanol on the Cu/ZnO/Al$_2$O$_3$ – ZrO$_2$ catalysts as well as their activity in the synthesis of methanol from CO$_2$ and H$_2$ were investigated. The catalytic activity increases in the series: Cu/ZnO/Al$_2$O$_3$ obtained by co-precipitation < Cu/ZnO/Al$_2$O$_3$ – ZrO$_2$ obtained by the amorphous precursor (citric acid) method < Cu/ZnO/ZrO$_2$ obtained by the amorphous precursor (citric acid) method. It has been found that catalysts obtained by using citric acid as complexing agent show higher adsorption of methanol compared to water than the catalysts obtained by the co-precipitation. A partial substitution of Al$_2$O$_3$ by ZrO$_2$ evidently decreases the reversible adsorption of water and CO. A correlation between adsorptive and catalytic properties has been established. With increasing ratio of reversible CO$_2$/CO or CH$_3$OH/H$_2$O adsorption, an increase of the catalysts activity in the synthesis of methanol from CO$_2$ and H$_2$ is observed.

Thermodynamic Study of the Interaction Between Some Recently Synthesized Benzo-Substituted Macrocyclic Diamides with Some Pyridinium Ion Derivatives in Acetonitrile Solution

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The formation of pyridinium, 2-methyl pyridinium, 2,4-dimethyl pyridinium and 2,4,6-trimethyl pyridinium complexes with the some recently synthesized benzo-substituted macrocyclic diamides was investigated conductometrically in acetonitrile solution at various temperatures. The formation constants of the resulting 1:1 complexes were determined from the computer fitting of the molar conductance-mole ratio data. In all cases studied, the stability of complexes decreases in the order Py$^+$ > 2m-Py$^+$ > 2,4dim-Py$^+$ > 2,4,6trim-Py$^+$. The enthalpy and entropy of complexation reaction were determined from the temperature dependence of the formation constants. In all cases, the complexes were enthalpy stabilized but entropy destabilized.
Structure of O,O-Diethylthionophosphorylhydrazine o-Vanillin Schiff Base Copper(II) Complex: 
\( \text{Cu}[(\text{C}_2\text{H}_5\text{O})_2\text{PSHNCHPh}(\text{o-O})\text{OMe}]_2 \)


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N,N-Bispropylidithiocarbamato Bis(triphenylphosphine)
Copper(I) Dichloromethane Solvate:
\[(n-\text{Pr})_2\text{dtc(PPh}_3)_2\text{]}\text{Cu-CH}_2\text{Cl}_2\text{, (dtc = Dithiocarbamate)}

by L.Z. Xu\textsuperscript{1}, J.H. Lin\textsuperscript{1}, S.S. Zhang\textsuperscript{1}, K. Jiao\textsuperscript{1} and F.F. Jian\textsuperscript{2}

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Investigation of Pyridinium Tetrachloroferrates(1-)

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The Synthesis and Characterization of a New Ladder-Type Structure of Compound [FeMoO₄(phen)]ₙ (phen = 1,10-phenanthroline)

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