

Standard Molar Enthalpy of Formation of Hydrated Sodium Cupric Arsenate [NaCuAsO₄·1.5H₂O(s)]

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A new compound (NaCuAsO₄·1.5H₂O) was synthesized, and its composition was determined by means of the methods of ignition loss-in-weight and chemical analysis. The standard molar enthalpies of dissolution of the mixtures {Na₃AsO₄·12H₂O(s) + CuSO₄·5H₂O(s)} and {NaCuAsO₄·1.5H₂O(s) + Na₂SO₄(s)} in 1.498 mol·dm⁻³ HCl solution at 298.15 K have been determined to be respectively ${}_{\text{s}}H_{\text{m},1}^0 = (64322 \pm 63) \text{ J}\cdot\text{mol}^{-1}$ and ${}_{\text{s}}H_{\text{m},2}^0 = -(20558 \pm 25) \text{ J}\cdot\text{mol}^{-1}$ using an isoperibol solution-reaction calorimetry. From these values and other thermodynamic data, the standard molar enthalpy of formation of NaCuAsO₄·1.5H₂O(s) has been derived: ${}_{\text{f}}H_{\text{m}}^0(\text{NaCuAsO}_4\cdot 1.5\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}) = -(1469.33 \pm 0.65) \text{ kJ}\cdot\text{mol}^{-1}$. In addition, UV/Vis spectra and refractive indexes of solution A and solution A' were measured to examine the reliability of the designed thermodynamic cycle.

Key words: NaCuAsO₄·1.5H₂O(s), isoperibol solution-reaction calorimetry, standard molar enthalpy of dissolution, standard molar enthalpy of formation, UV/Vis spectroscopy

**Synthesis and Characterization of
(1*E*,2*E*)-*N*¹,*N*²-Bis(2-formylphenyl)-*N*¹,*N*²-dihydroxy-
ethanediimidamide and Its Complexes with Ni(II), Co(II),
Cu(II), Zn(II), Cd(II), Hg(II) and U(VI)O₂**

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A new vicinal dioxime ligand (1*E*,2*E*)-*N*¹,*N*²-bis(2-formylphenyl)-*N*¹,*N*²-dihydroxyethanediimidamide (**H₂L**) has been synthesized by the reaction of *o*-anisidine with dichloroglyoxime. Mononuclear complexes with some transition metal ions have been prepared. This compound forms square-planar metal complexes (M(HL)₂), with Ni(II), Co(II) and Cu(II), with a metal ligand ratio of 1:2. Also, the tetrahedral complexes of Hg(II), Cd(II) and Zn(II) have been prepared and were found to have a metal ligand ratio of 1:1. The results indicated that the metal ions are coordinated through two N atoms of the ligand, as do most of the *vic*-dioximes. **H₂L** forms the binuclear nonplanar N, O coordinating complex [(H₂L)(OH)₂M₂] and a metal ligand ratio of 1:1 with M = U(VI)O₂. The composition and structural formula of these complexes were confirmed by elemental analysis, IR, MS, and NMR spectroscopic methods.

Key words: *vic*-dioxime, (1*E*,2*E*)-*N*¹,*N*²-bis(2-formylphenyl)-*N*¹,*N*²-dihydroxyethanediimidamide, transition metal complex

Sol-Gel Synthesis and Superconducting Properties of Bi-2212 High- T_C Superconductors

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A novel aqueous sol-gel synthesis technique has been refined to prepare heterometallic $(\text{Bi}_{1.75}\text{Pb}_{0.25})\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $(\text{Bi}_{1.8}\text{Pb}_{0.33})\text{Sr}_{1.87}\text{CaCu}_2\text{O}_x$ (Bi-2212) oxides. The formation of Bi-2212 phase depending on synthesis conditions (duration of annealing, stoichiometry of metals) has been estimated. The synthesized products were characterized by powder X-ray diffraction analysis (XRD) and resistivity measurements. It was demonstrated, that the investigated synthesis conditions only slightly influence on the phase purity and superconducting properties of Bi-2212 phase.

Key words: high- T_C superconductors, Bi-2212, sol-gel synthesis

Preparation of Truncated Triangular Silver Nanoparticles by a Simple and Rapid Method in Aqueous Solution

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The paper brings details of a simple method for rapid synthesis of triangular silver nanoparticles and their characterization. The method presented proceeds with a simple reaction in aqueous solution at ambient temperature and nanotriangles are synthesized in a few minutes. The formation of triangular nanoparticles was investigated by UV-VIS spectroscopy. Transmission electron microscopy (TEM) images of nanoparticles show that resulting triangles are truncated. The concentration of reactants and pH were found to have influence on the shape of resulting nanoparticles. These results indicate that hydrazine and citrate are necessary for formation of triangular nanoparticles.

Key words: triangular silver nanoparticles, aqueous solution, citrate, hydrazine

**Hydrothermal Synthesis, Structure Characterization of
a New Mixed Mo/V Metal-Oxygen Cluster Compound:
[Co(phen)₃]₂[HPMo₄^VMo₄^{VI}V₆^{IV}M₂O₄₄]₂·4H₂O,
(M = 0.78Mo^V + 0.22V^{IV})**

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A new polyoxometalate [Co(phen)₃]₂[HPMo₄^VMo₄^{VI}V₆^{IV}M₂O₄₄]₂·4H₂O (M = 0.78Mo^V + 0.22V^{IV}) **1** was hydrothermally synthesized and characterized by IR, elemental analyses, X-ray photoelectron spectrum, ESR and single crystal X-ray diffraction. The title compound is in the triclinic space group *P* $\bar{1}$ with *a* = 12.0953(7) Å, *b* = 14.0182(6) Å, *c* = 14.6468(7) Å, *V* = 2402.55(18) Å³, α = 105.134(2), β = 91.841(3), γ = 91.401(2), *Z* = 1, and *R*₁ (*wR*₂) = 0.0617 (0.1701). The compound was prepared from tetra-capped pseudo-Keggin with phosphorus-centered polyoxoanions [PMo₈V₆M₂O₄₄]⁵⁻, [Co(phen)₃]²⁺ cations and linked through hydrogen bonds and π - π stacking interaction into three-dimensional supramolecular framework. A study of the magnetic properties of **1** demonstrates that it exhibits antiferromagnetic coupling interactions.

Key words: hydrothermal synthesis, polyoxometalate, crystal structure, transition metal, cobalt

Solid-phase Synthesis and Self-assembly Formation of Tyrocidines

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A facile and efficient method was applied for parallel total synthesis of natural cyclic decapeptides, tyrocidine A-E, on safty-catch resin. Synthetic products were equally active as the natural products isolated from the bacterial source and found to possess similar bacterial selectivity as other members in the amphipathic antimicrobial cyclic decapeptide family. At the same time, the self-assembling nanotubes of them were observed under a transmission electronic microscopy.

Key words: solid-phase synthesis, cyclic decapeptide, antibiotics, bionanomaterial

Synthesis of Silylated Alkylboronic Acids and Esters *via* Hydroboration of Allylic and Vinylic Trimethylsilanes

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Representative allylic trimethylsilanes and isopropenyltrimethylsilane were hydroborated with dichloroborane, and the products were transformed into the corresponding β - or γ -trimethylsilylboronates. Synthesis of 2-trimethylsilylethylboronic acid and its diethyl ester *via* hydroboration of trimethylvinylsilane with diisopinocampheylborane, followed by liberation of α -pinene is described.

Key words: trimethylsilylalkylboronic acids, trimethylsilylalkylboronates, dichloroorganoboranes dichloroborane, diisopinocampheylborane

Expedient Synthesis of Glycidonitriles by Darzens Condensation of α -Halogenonitriles with Aldehydes and Ketones

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Chloroacetonitrile (**1**), α -halogenopropionitriles **4**, and α -chlorophenylacetonitrile (**6**) react with aldehydes **2a,b,h–o** and ketones **2c–g,p–t** in the presence of solid NaOH in THF or DME, without any added catalyst, affording substituted glycidonitriles **3a–t**, **5a, c–g,r,s** and **7a,b,i,j,u,v**, respectively (*Darzens* condensation). The glycidonitriles **3a–h**, prepared from **1** and carbonyl compounds **2a–h**, are obtained in high yields, exceeding those reported in the literature (Table 5). Expedient results of the reactions studied are due to increased reactivity of anions with Na⁺ as counterion in ethereal solvents. Investigation of the concentration of NaOH and the carbanion of diphenylacetonitrile in selected solvents reveals that ethereal solvents may increase the solubility of the anions participating in *Darzens* condensation.

Key words: *Darzens* condensation, solid-liquid two-phase system, uncatalyzed reactions

A Study on the Electrochemical and Structural Properties of a Schiff Base SAM on Au(111) Surface

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The electrochemical and structural properties of Schiff base V-hp self-assembled monolayer (SAM) on Au(111) surface have been studied using electrochemical technique and electrochemical scanning tunneling microscopy (ECSTM) in 0.1 M HClO₄ solution. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements revealed that the adlayer of V-hp on Au(111) surface inhibits the oxidation of Au and reduces the surface double-layer capacitance. The electronic charges for V-hp-SAM covered Au(111) electrode, resulting from capacitive charging and discharging process involved in the double-layer potential region, become one or more orders of magnitude lower than that for bare Au(111). STM investigation demonstrated that V-hp molecules can adsorb with a flat-lying orientation on Au(111) and formed a long-range two-dimensional ordered SAM with a $(2\sqrt{3}\times\sqrt{21})$ adlattice symmetry structure. A model structure with one molecule per unit cell was proposed, which yields a surface concentration of 1.28×10^{-10} mol/cm².

Key words: Schiff base, Au(111), molecular adsorption, SAM

Separation of Organic Species from Wastewater Using a Polyol Supported Liquid Membrane

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This paper examines the application of supported liquid membrane for the removal of organic compounds in the aqueous waste effluents. Polypropylene glycol was employed as carrier mounted on PTFE supports. It has been demonstrated that polyols act as efficient carrier for selective removal of organic compounds having an acidic –OH group. Mass transfer coefficient increased when the number of carbon atoms increased from 4 to 6. A correlation between pK_a, pH and flux of permeating species has been demonstrated. Aromatic compounds showed higher transport rates as compared to similar aliphatic compounds. Effect of temperature on the transport rates has been studied. It has been shown that a mock waste solution can be transported up to >90% under the conditions studied.

Key words: SLM, polyol, phenols, carboxylic acids

Compressibility Data and Virial Coefficients for Helium – Nitrogen Mixtures

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A detailed experimental study of the pressure and density of He – N₂ mixtures at 0°C, 25.0°C and 50.0°C is reported. The pressures are measured with a dead-weight tester. The densities are determined from knowledge of the precise volume and weight measurement of the mixtures. Statistical analysis of the experimental data yielded very precise values for the second and third density virial coefficients. Experimentally determined virial coefficients are compared with those of the literature. Unlike interaction second virial coefficients, B₁₂, are determined from the mixture virial coefficients by using the like interaction virial coefficients, B₁₁ and B₂₂, of the pure components. The deduced B₁₂ values agree very well with those computed from potential functions with quantum corrections.

Key words: He – N₂ mixtures, second virial coefficient, third virial coefficient

The Mechanism and Kinetics of the Reaction of ClONO₂ with Cl⁻

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Three original three-dimensional Potential Energy Surfaces (PESEs) of the reaction have been obtained by Density Functional Theory calculation using the 6-311+G(d) basis to prove an assumption that the reaction of ClONO₂ + Cl⁻ → NO₃ + Cl₂ in a gas phase is built up of two simpler reactions: ClONO₂ + Cl⁻ → (O₂NOCICl)⁻ and (O₂NOCICl)⁻ → NO₃ + Cl₂. The PESEs indicate that the intermediate compound (O₂NOCICl)⁻ called Potential Well Compound (PWC) is trapped by a potential energy well of -13.2 kcal/mol deep. The (O₂NOCICl)⁻ PWC in a gas phase is a stable compound at low temperatures and will be examined in the low-temperature infrared spectra. The decomposition of (O₂NOCICl)⁻ in a gas phase is dominated by its dynamic effects, and its kinetics is predicted in the present work. In heterogeneous chemistry however, the (O₂NOCICl)⁻ PWC cannot be stable even at ~180 K, due to H₂O solvation, leading to decomposition of the PWC. Solvation mechanism for the total reaction has been suggested in this paper.

Key words: chlorine nitrate, chloride ion, potential energy well, potential well compound, mechanism, kinetics, solvation

Tautomeric Equilibria and π -Electron Delocalization for the Substrate (Pyruvate) and Inhibitor (Oxamate) of Lactate Dehydrogenase – DFT Studies

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Keto-enol tautomerism for the substrate (pyruvate) of lactate dehydrogenase (LDH) and amide-iminol tautomerism for its inhibitor (oxamate) were studied at the DFT(B3LYP)/6-31++G(d,p) level. Both anions (and also both radicals) prefer the C=O forms, *i.e.* the keto and amide form, respectively. The OH forms (enolpyruvate and iminloxamate) have higher Gibbs free energies. Their amounts in the tautomeric mixtures are larger than 0.01% for anions and lower than 0.001% for radicals. π -Electron delocalization for OCO fragments is greater than that for XCO fragments for both anions and radicals.

Key words: prototropic tautomerism, pyruvate-enolpyruvate, oxamate-iminloxamate, anions, radicals, π -electron delocalization, DFT

Investigation on the Hydrogen Bonding Interaction of Complexes of 2-Butanimine with Water

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The hydrogen bonding of 1:1 complexes formed between 2-butanamine and water has been investigated using DFT and MP2 methods at varied basis set levels from 6-311G to 6-311++G(d,p). Four reasonable geometries were considered with the global minimum being a cyclic double-hydrogen bonded structure. The optimized geometric parameters and interaction energies for various isomers at different levels were estimated. The IR intensities and vibrational frequency shifts are reported. The solvent effects on the geometries of the complex have also been investigated using SCRF calculations at the B3LYP/6-311++G(d,p) level. The results indicate that the polarity of the solvent has played an important role on the structures and the relative stabilities of different isomers.

Key words: 2-butanamine, hydrogen bonding, water, complexes

Systematically Exploring Decomposition Routes of HMX Explosive Molecule

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This investigation performs three quantum chemical calculations to determine an unrealizable profile of the HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) unimolecular decomposition. First, the bonding energies of HMX and its corresponding decomposition species were calculated using the differential overlap (INDO) program, which identifies the weakest bonding site for reference and determines the site of easiest cleavage. Second, the molecular energies of all species were estimated by performing density-functional theory (DFT) calculations, yielding an accurate enthalpy of formation following calibration according to a five-parametric equation. Finally, all decomposition transition states were sought using Quasi-Newton and Synchronous Transit approaches (QST3 procedure). Computational results reveal that the activation energy of direct *cis*-form HONO elimination is lower than that of direct *trans*-form HONO elimination and that of the two-stage elimination of two forms of HONO (N–N bond fission combined with C–H bond breaking) in the initial decomposition step, which are 234.7 kJ/mol and 147.9–171.4 kJ/mol, respectively.

Key words: decomposition route, INDO program, parametric equation, QST3 procedure