Green chemistry: A step towards clean and sustainable development†

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Manuscript received 21 March 2012, accepted 23 March 2012

Quinonoid molecular diversity in Bignoniaceae and its taxonomic significance†

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Manuscript received 13 March 2012, accepted 15 March 2012

Abstract : The present brief review focus on isolation of a large number of naphthoquinones, anthraquinones and naphthoquinone dimers from more than 33 plant species of 16 genera of family Bignoniaceae. The following sixteen genera viz. Catalpa, Crescentia, Heterophragma (syn : Haplophragma), Kigelia, Lundia, Mansoa, Markhamia (syn : Dolichandrone), Newbouldia, Oroxylum, Paratecoma, Phyllarthron, Radermachera, Stereospermum, Tabebuia, Tecomella (syn : Tecoma) and Zeyheria have so far chemically investigated for more than sixty quinonoid constituents. Ten plant species belonging to seven genera namely Heterophragma, Kigelia, Markhamia, Phyllarthron, Stereospermum, Tabebuia and Tecomella have chemically been examined by our group during last three decades which have resulted in the isolation of two dozen of quinonoid compounds including some new naphthoquinones and their dimers. The structures of these compounds were unambiguously established from chemical and spectral evidences. Their taxonomic and biogenetic significance were discussed.

Keywords : Naphthoquinones, anthraquinones, naphthoquinone dimers, Bignoniaceae, taxonomy, biogenesis.

Role of biomarkers in the forensic investigation of arson mainly bride burning cases – in India†

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Abstract: Arson is a widely prevalent crime done for multiple reasons. Homicidal bride burning, a typical example of arson, particularly prevalent in India, Bangladesh and other South Asian countries for monetary reasons and on other pretexts.

The exhibits for bride burning cases from different parts of West Bengal and Delhi were received by the Central Forensic Science Laboratory, Kolkata for investigation. Gas chromatograph-Mass spectrometric measurements of the analyzates particularly fuels (kerosene) extracted from fire debris residues showed the presence of high boiling hydrocarbon fractions and particularly biomarkers in all exhibits in spite of the absence of low boiling fractions in some cases. The biomarkers were common as well as variable depending on the source of fuel. But the presence of biomarkers was the undisputable proof for the use of fire accelerators like kerosene in the burning cases.

Keywords: Forensic science, arson, biomarkers, bride burning, gas chromatograph-mass spectrometer, kerosene.

Kinetics of palladium(II)-catalyzed oxidation of sulfur(IV) by oxygen†

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Manuscript received 16 April 2012, accepted 20 April 2012

Abstract: The kinetics of the palladium(II) catalyzed autoxidation of sulfur(IV) has been studied using stopped flow spectrophotometric and conventional techniques. The observed kinetics is in agreement with the rate law

\[ R_{obs} = k_3 [\text{Pd}^{II}] [\text{S}^{IV}]^2 [\text{O}_2] [\text{H}^+]^{-1} \]

The stability constant for the formation of the complex \([\text{Pd(SO}_3]_3]^{4-}\) from \([\text{Pd(SO}_3]_2]^{2-}\) and \(\text{HSO}_3^-\) ions has been determined spectrophotometrically. The values of \(k_1\), \(k_{II}\) and \(k_{III}\) relating to following scheme have been determined from stopped-flow study.

\[ [\text{Pd(SO}_3]_n]^{(2n-2)-} + \text{O}_2 \rightarrow [\text{Pd(SO}_3]_n/(\text{O}_2)]^{(2n-2)-} \]

\(C_1\) appears to be intermediate of the type – \([\text{Pd(SO}_3]_n]^{(2n-2)-}[\text{O}_2]\) – in which \(\text{O}_2\) is weakly bonded to axial position and one sulfite group appears to be O-bonded instead of S-bonded. Subsequently, \(\text{O}_2\) moves to square plane and therefore intra-molecular rearrangement converts O-bonded complex into S-bonded complex. Following mechanism has been proposed to explain the autoxidation kinetics.

\[ [\text{Pd(SO}_3]_3]^{2+} + \text{SO}_3^{2-} \rightarrow [\text{Pd(SO}_3]_3]^{4+}; K_1 \]
\[ [\text{Pd(SO}_3]_3]^{4+} + \text{O}_2 \rightarrow [\text{Pd(SO}_3]_3(\text{O}_2)]^{4+}; K_2 \]
\[ [\text{Pd(SO}_3]_3(\text{O}_2)]^{4+} + \text{HSO}_3^- \rightarrow [\text{Pd(SO}_3]_3(\text{OSO}_3]_3)^{2-}; K_3 \]
\[ [\text{Pd(SO}_3]_3(\text{OSO}_3]_3)^{2-} \rightarrow [\text{Pd(SO}_3]_2]^{2+} + 2\text{SO}_4^{2-} + \text{H}^+; k \]

The effect of \(\text{NH}_3\), \(\text{C}_2\text{H}_5\text{OH}\) and \(\text{C}_6\text{H}_6\) has also been studied.

Keywords: Kinetics, sulfur(IV), palladium(II), oxygen, catalysis, ammonia, ethanol, benzene.

Kinetics and mechanism of the oxidation of substituted benzaaldehydes with bis(pyridine)silver permanganate†
Abstract: The oxidation of thirty-six ortho-, meta- and para-substituted benzaldehydes by bis(pyridine)silver permanganate (BPSP) resulted in the formation of the corresponding benzoic acids. The reaction is first order with respect to both BPSP and aldehydes. The reaction is catalyzed by hydrogen ions. The rate of reaction increases with an increase in the amount of acetic acid in the solvent. The correlation analyses of the rate of oxidation of thirty-six aldehydes were performed in terms of Chartron’s LDR and LDRS equations. The rate of oxidation of meta- and para-substituted benzaldehydes showed excellent correlation with Chartron’s LDR equation. The rates of ortho-compounds showed excellent correlation with LDRS equation. The oxidation para-compounds is more susceptible to the delocalization effect. The oxidation of ortho- and meta-compounds exhibited a greater dependence on the field effect. The polar reaction constants are negative indicating an electron-deficient centre in the rate-determining step. A mechanism involving a nucleophilic attack on the carbonyl group by a permanganate-oxygen and a subsequent hydride transfer has been proposed.

Keywords: Correlation analysis, kinetics, mechanism, oxidation, permanganate.


DNA binding/cleavage studies of known hexanuclear/trinuclear copper(II) complexes in presence of standard activators†

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Manuscript received 02 March 2012, accepted 09 March 2012

Abstract: The polynuclear copper(II) complexes of types [Cu₆Na₄(NTA)₂(µ-O)₂(bpy)₆(H₂O)₄(NO₃)₂]·3H₂O (1) and [Cu₃(C₂O₄)₂(bpy)₃(H₂O)₂](NO₃)₂ (2) (bpy = 2,2′-bipyridyl, H₃NTA = nitrilotriacetic acid and C₂O₄²⁻ = oxalate) recently reported by us, have been allowed to interact with calf thymus DNA. Their DNA binding properties are studied using absorption and emission spectral titrations. These complexes cleave supercoiled pBR322 DNA to nicked circular DNA under physiological conditions. Studies using standard radical scavengers suggest the involvement of hydroxyl radicals in the oxidative cleavage of DNA.

Keywords: Polynuclear, copper(II) complexes, nuclease property, oxidative cleavage, gel electrophoresis.


Treatment of waste water from coke oven plant – A case study†

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Abstract: Industrial progress has been accompanied by a growing negative impact on the environment in terms of its pollution and degradation. In our country number of coke oven batteries for production of low ash metallurgical coke is increasing day by day. During off gas cleaning there are different sources of generation of waste water. But the waste water is not treated before discharge. Naturally found coal is converted into coke in coke ovens and a large quantity of water is used for quenching hot coke and for washing gas. Effluent generated contains high value of TSS, BOD, COD, phenols, ammonia, cyanide, which cause serious water pollution problems. This study was carried out to focus on characteristics of the effluent produced by coke oven plant and a treatability study was conducted to find out an appropriate treatment procedure to achieve a depletion of pollutants for discharge to surface water bodies after meeting the level of standard. This study was done initially separating ammonia of raw effluent through natural zeolite for ammonia scrubbing water. After this treatment the treated water was mixed with coal tar separator effluent, quenching effluent and gas plant effluent for chemical treatment followed by two stages aerobic biodegradation process and finally adsorption process by activated carbon. Overall depletion rate of COD, BOD, phenol, cyanide, in the waste water achieved by this treatment process were 94.9%, 96.2%, 98.3%, 94.52%, respectively and discharge effluent met the Pollution Control Board standard. On the basis of the findings schematic treatment system was finalized.

Keywords: Waste water, coke oven batteries, chemical treatment, biological treatment, COD, BOD.

The reaction of heterocyclic amine with pendant naphthyl group in Pd(αβ-NaiR)Cl₂ (αβ-NaiR = 1-alkyl-2-(naphthyl-αβ-azo)imidazoles) and the product characterisation

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Manuscript received 06 February 2011, accepted 10 February 2011

Abstract: The reaction of Pd(αβ-NaiR)Cl₂ (1-alkyl-2-(naphthyl-αβ-azo)imidazoles, α-NaiR (1) and β-NaiR (2)) with m-aminopyridine (m-NH₂-Py) and o-aminopyrimidine (o-NH₂-Pym) in acetonitrile solution has synthesized a C-N coupled product, chloro[1-alkyl-2-(7-imidophenyl)pyridyl-αβ-azo]imidazole-N,N',N''[palladium(ii)], Pd(αβ-NaiR-N-Py-m)Cl (3, 4) and Pd(αβ-NaiR-N₂-Py-o)Cl (5, 6). The structural confirmation has been carried out by X-ray diffraction study. The solution electronic spectra of C-N fused products, 3-6, show transitions within 600–900 nm those are absent in Pd(αβ-NaiR)Cl₂. Cyclic voltammogram shows four successive redox couples, one of them (positive to SCE) is oxidative in nature and others (negative to SCE) are ligand reductions. Emission is observed from ligand centred orbitals and has been ascribed to π-π* excitation process. The excited state decays following radiative and nonradiative biexponential routes. Absorption and fluorescence spectra of pyridylamine fusion product show H⁺ and metal ion (Zn²⁺, Cd²⁺) sensitivity.

Keywords: Pd-naphthylazoimidazoles, C–N coupling reaction, LLCT, electrochemistry, luminescence, H⁺-sensitivity.

Syntheses, characterization and bioactivities of new copper(II) complexes of N’-[(1E)-1H-pyrrol-2-ylmethylidene]pyridine-3-carboxydrazone

Four copper(II) complexes viz. [Cu(PPC)$_2$(ClO$_4$)$_2$ (1), [Cu(PPC)(bipy)](ClO$_4$)$_2$ (2), [Cu(PPC)(phen)](ClO$_4$)$_2$ (3) and [Cu(PPC)(PMDT)](ClO$_4$)$_2$ (4) have been synthesized and characterized by various physico-chemical techniques, where PPC = N′′′-[(1E)-1H-pyrrol-2-ylmethylene]pyridine-3-carbodihydrazone, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline and PMDT = N,N,N′,N′′,N′′′,N′′′-pentamethylethylene diamine. The spectra of complexes exhibit the usual line spectra for mononuclear copper(II) complexes with $g || > g \perp > 2.3$. Bioactivities (superoxide dismutase, antibacterial and DNA cleavage) of these complexes have also been discussed.

Keywords: Schiff base, EPR, antibacterial activity, DNA cleavage.

Antiandrogenic effect and biological potency of some of the organogermainium(IV) complexes†

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Manuscript received 13 December 2011, accepted 10 February 2012

Abstract: An important study has been made in the search for the better fungicides, bactericides and antiandrogen agents on the organogermainium(IV) complexes of sulphonamide-imines. The complexes were screened in vitro against bacteria and fungi to test their antimicrobial property and in vivo on male albino rats to test their antifertility properties. The treatment with the sulphonamide-imines and their organogermainium complexes at the dose levels of 2 mg and 4 mg per day per rat did not cause any significant change in the body weight, but a significant reduction in the weights of reproductive organs was observed. Arrest of spermatogenesis was noted at various stages with the production of primary spermatocytes, secondary spermatocytes and step-19 spermatids found to be decreased. Biochemical parameters of tissues, i.e. protein, sialic acid, cholesterol, content of testes and seminal vesicular fructose also showed significant reduction. Further, the serum testosterone concentrations were also decreased after the treatment with the sulphonamide-imines and their organogermainium complexes.

Keywords: Antifertility, hematological studies, histopathological studies, sulphonamide-imines, tissue biochemistry, organogermainium compounds.

Reactions and structural studies of 4-(1H-benzimidazole-2-yl)-benzonitrile with metal nitrates†

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Manuscript received 02 March 2012, accepted 09 March 2012

Abstract: One pot synthesis of 4-(1H-benzimidazole-2-yl)-benzonitrile (1) under mild reaction conditions and metal-organic hybrid of 4-CN-BIBH with Cu$^{II}$ salt have been reported for the first time. In the metal-organic hybrid [Co(NO$_3$)$_2$.4H$_2$O . (4-CN-BIBH)] (3), there is no interaction between the metal and 4-CN-BIBH through dative bonds, 4-CN-BIBH afforded solvated species 4-CN-BIBH. DMSO, (2) in dimethylsulfoxide and reacted with Cu$^{II}$, Zn$^{II}$, Cd$^{II}$ and Ni$^{II}$ nitrates to form [(4-CN-
BIBH₂(NO₃)₃ (4) and M(OH)(NO₃)(H₂O)ₓ, Formation of [(4-CN-BIBH₂)NO₃ has been supported by theoretical studies.

Keywords: Synthesis, benzimidazole, structure, solvent co-crystallization, organic-inorganic hybrid, HNO₃ liberation, DFT calculations.


Synthesis, characterization and electrochemical studies of mixed-ligand copper(II) complexes of 6-chloronicotinic acid and diimines†

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Manuscript received 14 March 2012, accepted 19 March 2012

Abstract: Four new mixed-ligand copper(II) complexes involving 6-chloronicotinic acid (6-ClNA) and aromatic diimines and one binary Cu²⁺ complex with 5,5′-Me₂bipy have been synthesized in aqueous/nonaqueous media. Elemental analyses (Cu, C, H, N%), molar conductance, spectral (FT-IR, UV-Visible) and room temperature magnetic susceptibility measurements have been used for structural characterization of these complexes. FT-IR spectra of these complexes indicate the bidentate mode of coordination through carboxylate oxygen atoms of 6-chloronicotinate anion. On the basis of these measurements the following formulae have been proposed: [Cu(6-ClNA)(bipy)(H₂O)](NO₃) (1), [Cu(6-ClNA)(5,5′-Me₂bipy)(ONO₂)](H₂O) (2), [Cu(6-ClNA)(phen)(H₂O)](NO₃) (3), [Cu(6-ClNA)(dmp)(ONO₂)](H₂O) (4) and [Cu(5,5′-Me₂bipy₂)](ClO₄) (5), {where diimines = 2,2′-bipyridine (bipy); 5,5′-dimethyl-2,2′-bipyridine (5,5′-Me₂bipy); 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp)}. The observed room temperature (300 K) magnetic moments (µ_eff = 1.70 to 1.84 B.M.) correspond to mononuclear complexes with one unpaired electron. The distorted square-pyramidal coordination geometry around the Cu⁴⁺ ion has been proposed in solid complexes 1-4. In DMSO and DMF solutions, these complexes possess distorted octahedral geometry due to solvent coordination. The electrochemical behaviors of these complexes have also been studied at a glassy carbon working electrode (GCE) in DMSO and DMF media containing 0.2 M NaClO₄ as the supporting electrolyte using cyclic voltammetry. The electrochemical behavior of complex 4 involving dmp as the auxiliary ligand is different from rest of the three mixed-ligand Cu²⁺ complexes.

Keywords: Mixed-ligand Cu²⁺ complexes, 6-chloronicotinic acid, 5,5′-dimethyl-2,2′-bipyridine, 2,9-dimethyl-1,10-phenanthroline, cyclic voltammetry.


Synthesis of carbon nanotubes using spinach, characterization and study of magnetic properties†

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Manuscript received 09 April 2012, accepted 12 April 2012

Abstract: Nano Technology is growing at a faster pace and is leaving its impact on our day to day life. Nano materials are undoubtedly the most valuable resource in the development of this technology. So it is very essential to develop new methods to produce these materials. Keeping this view in mind CNTs were made by using protein present in spinach and metal ions as catalyst. The
chemical compound, so formed was decomposed at different temperatures to obtain CNTs. These CNTs were characterized using SEM and Micro Raman spectroscopy. Keywords : Carbon nanotubes, spinach, synthesis, characterization.

J. Indian Chem. Soc.,
Vol. 89, August 2012, pp. 1149-1154

Oxidation of some aliphatic aldehydes by tetrakis (pyridine) silver dichromate: A kinetic and mechanistic study†

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Manuscript received 28 March 2012, accepted 30 March 2012

Abstract : The oxidation of six aliphatic aldehydes by tetrakis (pyridine) silver dichromate (TPSD) in dimethyl sulfoxide (DMSO) leads to the formation of corresponding carboxylic acids. The reaction is first order each in TPSD. A Michaelis-Menten type of kinetics is observed with respect to the aldehydes. The reaction is catalysed by hydrogen ions, the hydrogen-ion dependence has the form : 

\[ k_{\text{obs}} = a + b[H^+] \]

The oxidation of deuteriated acetaldehyde, MeCDO, exhibited a substantial primary kinetic isotope effect \( k_D/k_H = 5.80 \) at 298 K. The oxidation of acetaldehyde has been studied in nineteen different organic solvents. The solvent effect has been analysed using Taft’s and Swain’s multiparametric equations. The rate constants correlate well with Taft’s \( \sigma^* \) values; reaction constants being negative. A mechanism involving transfer of hydride ion has been suggested.

Keywords : Aldehydes, correlation analysis, halochromate, kinetics, mechanism, oxidation.

Cyclic voltammetric and electronic absorption spectral investigations on binary and mixed-ligand copper(II) complexes with diethyldithiocarbamate and diimines†

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Manuscript received 05 March 2012, accepted 12 March 2012

Abstract : The electrochemical properties of binary and mixed-ligand CuII complexes involving diethyldithiocarbamate \((\text{Et}_2\text{-dtc}^-)\) as primary ligand and 2,2′-bipyridine/1,10-phenanthroline \((\text{bipy/phen})\) as coligands formed in different CuII : \(\text{Et}_2\text{-dtc} : \text{bipy/phen}\) molar ratios in acetone solution have been studied by using cyclic voltammetry. Cyclic voltammograms were recorded in acetone solution containing 0.2 \(M\) NaClO₄ as a supporting electrolyte at a platinum working electrode. On the basis of CV results, it is concluded that there are two complex species present in equilibrium in solution in mixed-ligand CuII : \(\text{Et}_2\text{-dtc} : \text{bipy/phen}\) \((1 : 1 : 1, 1 : 1 : 2\) and \(1 : 2 : 1\) molar ratios) systems. It is noteworthy that binary CuII(\(\text{Et}_2\text{-dtc})_1\) and mixed-ligand CuII(\(\text{Et}_2\text{-dtc})(\text{bipy/phen})\) complex species exhibit both oxidation \((\text{Cu}^{2+/3+})\) and reduction \((\text{Cu}^{2+/1+})\) processes while binary CuII(\(\text{bipy/phen})_1\) and \(2\) complex species show only \(\text{Cu}^{2+/1+}\) redox change. UV-Visible spectra of the above systems have also been studied in acetone.

Keywords : Cyclic voltammetry, diethyldithiocarbamate, bipyridine, phenanthroline, copper(II) complexes.