A three-dimensional coordination polymer of cobalt(II) dicyanamide containing an in situ generated didentate Schiff base: Synthesis, structure and magnetic property

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\textbf{Abstract :} One 3D coordination polymer of cobalt(II) dicyanamide of the type [Co(L)(\mu-1,5-dca)]\textsubscript{2} \textsubscript{n} (1) (L = phenyl(pyridin-2-yl)methanimine, dca = dicyanamide) has been isolated using a 1 : 1 : 1 : 2 molar ratio of CoCl\textsubscript{2}.6H\textsubscript{2}O, 2-aminopyridine (ap), 2-benzoylpyridine (bp) and Na(dca) respectively in alcoholic solvent at room temperature. Single crystal X-ray crystallographic analysis shows that 1 crystallizes in the orthorhombic unit cell, space group P2(1)\textsubscript{1}2(1)\textsubscript{1}2(1) with unit cell dimensions, \(a = 8.506(5)\) Å, \(b = 12.736(7)\) Å, \(c = 15.635(9)\) Å and \(\beta = 90^\circ\). Each cobalt(II) center in 1 adopts a distorted octahedral geometry with CoN\textsubscript{6} chromophore coordinated by two N atoms of didentate Schiff base and four nitrile N atoms of four different dca units. 1 affords a 3D network structure where four \(\mu-1,5\)-dca bridges connect four different metal(II) centers. Variable-temperature magnetic susceptibility measurement of 1 shows weak antiferromagnetic coupling among the cobalt(II) centers mediated through \(\mu-1,5\)-dca bridges. The compound exhibits (\(\pi-\pi^*\)) fluorescence in solid states at room temperature.

\textbf{Keywords :} Cobalt(II) coordination polymer, \textit{in situ} generated Schiff base, dicyanamide, X-ray structure, antiferromagnetism, luminescence.

Fabrication of a new Pr\textsuperscript{3+} nanocomposite carbon paste electrode based on bis(salicylaldehyde)thiocarbohydrazone as a material sensing

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Abstract: The fabrication and electrochemical behavior of nanocomposite CP-electrode modified with MWCNT/nanosilica was investigated for bis(salicylaldehyde)thiocarbohydrazone (STCH) as a new ionophore in the presence of various alkaline, lanthanide and transition metal ions. Pursuant obtained results the best electrode behavior was belonged to Pr$^{3+}$-carbon paste electrode (PrCPE) with composition of STCH : 3%, binder (paraffin oil) : 30%, modifier (MWCNT : 2%, NS : 0.3%), and graphite powder : 64.7%. This PrCPE displayed a Nernstian response by the slope of 19.6 ± 0.2 mV decade$^{-1}$ in linear range $1.0 \times 10^{-8}$ to $1.0 \times 10^{-2}$ mol L$^{-1}$ with a lower detection limit $8.5 \times 10^{-9}$ mol L$^{-1}$. The pH range of this new praseodymium sensor was gained 2.1 to 8.9 with a response time about 6 s. To assessment the response of new prepared electrode toward different cations the matched potential method ($K_{MPM}$) was applied. Obtained results show good selectivity for this PrCPE with respect to a number of lanthanide and transition metal ions. It was successfully used as an indicator electrode in potentiometric titration of Pr$^{3+}$ ions with EDTA and determination of Pr$^{3+}$ content in several blends of ions.

Keywords: Praseodymium, ion selective electrode, bis(salicylaldehyde)thiocarbohydrazone, nanocomposite carbon paste electrode, potentiometry sensor.

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Synthetic, spectral and biological activities of binuclear imidazolate-bridged complexes as Cu,Zn-SOD models possessing tris(2-aminoethyl)amine and amino acid derived ligands

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Abstract: Synthetic, spectral and superoxide dismutase activities of the imidazolate-bridged binuclear copper(II)-zinc(II) complexes viz. [(L)Cu-Im-Zn(tren)]$^+$ 1; [(L')Cu-Im-Zn(tren)]$^{2+}$ 2; [(L)Cu-Im-Zn(tren)]$^{3+}$ 3, derived from (E)-2-(5-bromo-2-hydroxybenzylideneamino)acetic acid (H$_2$L); (S,E)-2-(5-bromo-2-hydroxybenzylideneamino)propanoic acid (H$_2$L$^1$); (R)-2-(5-bromo-2-hydroxybenzylideneamino)-3-methylbutanoic acid (H$_2$L$^2$); tren = tris(2-aminoethyl)amine, Im = imidazolate ion, have been achieved.

Magnetic moment values of hetero-binuclear complexes indicate that the imidazolate group can mediate antiferromagnetic interactions ($S = 1/2$) state. X-band EPR spectra of the complexes at different pH values in frozen solution showed that the metal complexes was stable in the pH range 6.50–11.00. Schiff base ligands (H$_2$L-H$_2$L$^2$) were synthesized by the condensation of equimolar (1 : 1) ratio of 5-bromosalicylaldehyde with glycine, alanine and valine, respectively, dissolved in ethanol. Biological (superoxide dismutase, antibacterial and antifungal) of these complexes have also been measured and compared with reported complexes.

Keywords: Cu$^{II}$-Zn$^{II}$ hetero-binuclear complexes, antibacterial, antiferromagnetic spin exchange, copper,zinc-superoxide dismutase, tridentate Schiff bases.
Kinetic study for the oxidation of dl-mandelic acid by tripropylammonium fluorochromate in the absence and presence of picolinic acid and 1,10-phenanthroline

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Abstract: The oxidation of dl-mandelic acid (MA) by tripropylammonium fluorochromate (TriPAFC) has been studied in aqueous acetic acid medium. The oxidation leads to the formation of the phenyl glyoxalic acid. The reaction is first order with respect to TriPAFC, MA and [H⁺] and the reaction is catalyzed by hydrogen ions. The reaction has been studied in the presence of picolinic acid (PA) and 1,10-phenanthroline (Phen) as promoters. The promoters used in this oxidation reaction, picolinic acid (PA) and 1,10-phenanthroline (Phen) are strong chelating ligands which form complexes with most transition metal ions. Among the two promoters oxidation is much faster with 1,10-phenanthroline. The low dielectric constant of the medium assists the complex formation and enhances the reactivity. Various thermodynamic parameters have been determined at different acetic acid-water composition. A suitable mechanism has been proposed.

Keywords: Tripropylammonium fluorochromate, dl-mandelic acid, picolinic acid, 1,10-phenanthroline.

Kinetics and thermodynamics of oxidation of 4-oxo-4-phenyl butanoic acid by benzimidazolium fluorochromate in acetic acid-water medium

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Abstract: Kinetics of oxidation of 4-oxo-4-phenyl butanoic acid (4-oxo acid) by benzimidazolium fluorochromate (BIFC) in acetic acid-water medium in the presence of perchloric acid has been studied. The reaction is first order each in [BIFC], [4-oxo acid] and [H⁺]. The reaction has been found to be catalyzed by H⁺ ions. The stoichiometry of the reaction is 1 : 1 and the product of oxidation is benzoic acid. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. The reaction rates have been determined at different temperatures and the activation
parameters were calculated. The reaction failed to induce the polymerization of acrylonitrile, i.e. absence of free radicals. From the observed kinetic results a suitable mechanism has been proposed.

Keywords: 4-Oxo acid, kinetics, oxidation, benzimidazolium fluorochromate.

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Effect of aromatic alcohols and carboxylic acids on light induced isomerisation of 1-alkyl-2-{(o-thioalkyl)phenylazo}imidazole

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\textbf{Abstract:} Light irradiated trans-to-cis isomerisation of 1-alkyl-2-{(o-thioalkyl)phenylazo}imidazole in presence of phenol, catechol, benzoic acid and salicylic acid (act as co-factor) in methanol solution has been studied in this work. The rate of trans $\rightarrow$ cis photoisomerisation is decreased in presence of co-factor in the medium and is dependent on the concentration of active quotient about photochrome. The decrease in rate follows catechol $>$ benzoic acid $>$ phenol $>$ salicylic acid. This trend is due to the effects of dissociation ability of -O-H /-COOH and intermolecular association of the molecules. The reverse change, cis-to-trans is very slow in light irradiation and has been carried out by thermal process at dark. The quantum yield of isomerisation observes same sequence of effects of co-factor as it is seen in case of rate of photoisomerisation.

Keywords: Photochromism, 1-alkyl-2-{(o-thioalkyl)phenylazo}imidazole, co-factors, quantum yield.

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Planar intramolecular charge transfer effects on meloxicam and piroxicam drugs with $\alpha$- and $\beta$-cyclodextrins: Spectral and molecular modeling studies

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\textbf{Abstract:} Inclusion complexation of meloxicam and piroxicam with $\alpha$-CD and $\beta$-CD were studied by UV-Visible, fluorescence, time resolved fluorescence and molecular modeling techniques. Dual emission noticed in the CD solutions recommended that the energy of the intramolecular charge transfer (ICT) state is lower than that of the locally excited state. The shorter wavelength band was originated from the locally excited state and the longer wavelength band was due to the planar intramolecular charge transfer.
(PICT) state emission. The ratio of the PICT emission to the normal emission marginally increased with β-CD concentration, while it was slightly increased upon addition of α-CD. The above behavior indicating the formation of different 1:1 drug:CD inclusion complexes. The size of the benzamido ring suggested that the orientation of the drug in the β-CD complex is different from that in the α-CD complex. PM3 calculations were also carried out to assign the encapsulation of the drug molecules.

Keywords: Meloxicam, piroxicam, cyclodextrin, inclusion complex, molecular modeling.

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Chemical fractionation and distribution of metals in contaminated urban soil in Zhuzhou City, South Central China

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Abstract: The present study was conducted to determine the chemical fractions of heavy metals, to assess the current and potential environmental risks and to evaluate the mobility and bioavailability of metals in contaminated urban soils. Sequential extraction procedure was applied to fractionate the metal content into exchangeable fraction, carbonate fraction, fraction bound to Fe-Mn oxides, fraction bound to organic matter and residual fraction. Chemical speciation (Tessier, 1979) study revealed that Cd in soil prevails mostly in exchangeable fractions (26.383%). The overall percentage of metal content in different sequential fractions is in the sequence of Residual > Organic > Fe-Mn Oxides > Carbonate. Exchangeable and the order of metals in each fractions are as follows – Exchangeable: Cd > Cu > Pb > As, Carbonate: Cd > Pb > Cu > As, Fe-Mn Oxides: Pb > Cd > Cu > As, Organic: As > Cu > Pb > Cd and Residual: As > Pb > Cu > Cd. Elemental concentrations from each sequential extraction step were measured using inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP, USA). The pH value of the soils in the study area ranged from 6.44 to 7.05 (mean 6.67), indicating an acidic to neutral type of surface soils. The eco-toxicological assessment of the studied soil using the mobility factor indices revealed the following sequence: Cd (40.627) > Pb (14.941) ≥ Cu (14.399) > As (5.377). Mobility factor indices for soil metals revealed a high environmental contamination risk for Cd, which indicates a serious environmental threat.

Keywords: Heavy metals, soil, speciation, mobility, sequential extractions, ICP-OES.

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Correlation analysis of reactivity in the oxidation of aliphatic primary alcohols by imidazolium dichromate

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Abstract: The oxidation of nine aliphatic primary alcohols by imidazolium dichromate (IDC) in dimethylsulphoxide leads to the formation of corresponding aldehydes. The reaction is first order with respect to IDC. A Michaelis-Menten type kinetics is observed with respect to alcohols. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form $k_{obs} = a + b[H^+]$. The oxidation of [1,1-2H₂]ethanol (MeCD₂OH) exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.79$ at 298 K).

The reaction has been studied in nineteen different organic solvents. The solvent effect was analysed using Taft’s and Swain’s multiparametric equations. The rate of oxidation is susceptible to both polar and steric effects of the substituents. A suitable mechanism has been proposed.

Keywords: Alcohols, dichromate, imidazolium, kinetics, mechanism, oxidation.

De-chelation of diphenyldithiophosphate from nickel(II) complex by 1,10-phenanthroline

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Abstract: The reaction of [{3,5-(CH₃)₂C₆H₃O}₂PS₂]₂Ni with 1,10-phenanthroline in chloroform in 1:3 molar ratio resulted in the formation of ionic complex [Ni(phen)]₃[S₂P(OCH₂CH₃)₂-3,5]₂·CHCl₃ in which all the diphenyldithiophosphate ligands were displaced by N-donor bidentate ligand. The complex has been characterized by elemental analysis, magnetic moment, IR and single crystal X-ray analysis. The complex was crystallized in the triclinic space group $P\overline{1}$. Crystal structure reveals that the complex consists of cationic Ni\textsuperscript{II} ion chelated by six N atoms of the three N-donor bidentate ligands to form octahedral geometry whereas the two diphenyldithiophosphate counter-anions are non-coordinating, which are displaced from nickel(II) atom.

Keywords: Diphenyldithiophosphate, phenanthroline, single crystal X-ray.

Asymmetric hydrogenation of N-heterocycles with sodium cyanoborohydride and S-(−)-binol

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Abstract: The reaction of [{3,5-(CH₃)₂C₆H₃O}₂PS₂]₂Ni with 1,10-phenanthroline in chloroform in 1:3 molar ratio resulted in the formation of ionic complex [Ni(phen)]₃[S₂P(OCH₂CH₃)₂-3,5]₂·CHCl₃ in which all the diphenyldithiophosphate ligands were displaced by N-donor bidentate ligand. The complex has been characterized by elemental analysis, magnetic moment, IR and single crystal X-ray analysis. The complex was crystallized in the triclinic space group $P\overline{1}$. Crystal structure reveals that the complex consists of cationic Ni\textsuperscript{II} ion chelated by six N atoms of the three N-donor bidentate ligands to form octahedral geometry whereas the two diphenyldithiophosphate counter-anions are non-coordinating, which are displaced from nickel(II) atom.

Keywords: Diphenyldithiophosphate, phenanthroline, single crystal X-ray.
Abstract: Asymmetric hydrogenation of indole-3-aldehydes, indazole-3-aldehyde and aza indole-3-aldehydes with sodium cyano borohydride and S-binol under glacial acetic acid over a period of 1–2 h gave enantiomeric excess of 3-substituted 2,3-dihydro alcohols in good yields. This is the first report for the hydrogenation of aromatic compounds like indoles, indazoles and aza indoles with mild reducing catalyst sodium cyano borohydride.

Keywords: Asymmetric hydrogenation, NaCNBH₃, dihydro compounds, enantiomeric excess.

Use of Zwitterionic-type molten salt at room temperature for the one-pot synthesis of N-substituted decahydroacridine-1,8-diones in aqueous-ethanol

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Abstract: Zwitterionic-type molten salt – 4-(1-imidazolium) butane sulfonate acts as an excellent catalyst for the synthesis of N-substituted decahydroacridine-1,8-diones through condensation of dimedone, aromatic aldehyde and amine via multi-component condensation strategy in aqueous-ethanol as solvent. The key advantages of this process are high yields, room-temperature reaction, reusability of catalyst, environmental friendliness, easy work-up and purification of products by non-chromatographic methods.

Keywords: Zwitterionic-type molten salt, acridines, multi-component reactions, one-pot.