Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 3(1), 2013, 1-15
ISSN 2277-2669

APPLICATIONS OF COPPER – SCHIFF's BASE COMPLEXES : A REVIEW

RISHU KATWAL[*], HARPREET KAUR[a] and BRIJ KISHORE KAPUR

Department of Chemistry, Shoolini University, SOLAN – 173212 (H.P.) INDIA
[a]Department of Chemistry, Punjabi University, PATIALA – 147002 (Punjab) INDIA

(*Received : 13.09.2012; Revised : 19.09.2012; Accepted : 21.09.2012*)

ABSTRACT

Schiff bases are versatile ligands synthesized from the condensation of an amino compound with carbonyl compounds and these coordinate to metal ions via azomethine nitrogen Schiff's base and their copper complexes possess remarkable properties as catalysts in various biological systems, polymers, dyes, antimicrobial activities, antifungal activities, antiviral activities insecticides, antitumor and cytotoxic activities, plant growth regulator, enzymatic activity and pharmaceutical fields. A variety of Schiff's base and its complexes have been studied extensively. Several model systems, including those with bidentate, tridentate, tetradentate, multidentate Schiff base ligands, and their coordination chemistry of copper attracts much attention because of its biological relevance and its own interesting coordination chemistry such as geometry, flexible redox property, and oxidation state. This review summarizes the application of copper Schiff bases complexes.

Key words: Schiff's bases, Copper, Antimicrobial activity, Antitumor activity, Catalytic properties, Application.

INTRODUCTION

Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively[1]. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethine has been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial activities[2-3]. The complexes of copper with Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical, anti-inflammable activity, antiradical activities and biological activities[4]. Schiff-base complexes are considered to be among the most important stereo chemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety[5]. Copper (II) complexes show distorted octahedral and tetrahedral symmetries due to d^9 configuration (Jahn-Teller effect). The distortion is usually seen as axial elongation consistent with the lability and geometric flexibility of the complex. Therefore, typical Cu (II) complexes have square planar or square pyramidal geometries with weakly associated ligands in the axial position (s), but some copper (II) complexes possess trigonal bipyramidal geometry. The fundamental role of copper and the recognition of its complexes as important bioactive compounds *in vitro* and *in vivo* aroused an ever-increasing interest in these agents as potential drugs for therapeutic intervention in various diseases. The vast array of information available for

Available online at www.sadgurupublications.com
[*]Author for correspondence; E-mail: rishu.katwal2@gmail.com

their bioinorganic properties and mode of action in several biological systems combined with the new opportunities offered by the flourishing technologies of medicinal chemistry, is creating an exciting scenario for the development of a novel generation of highly active drugs with minimized side effects, which could add significantly to the current clinical research and practice. A considerable number of schiff's base copper complexes have potential biological interest, being used as more or less successful models of biological compounds[6]. Not only they have played a seminal role in the development of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials[7].

Antimicrobial activities

Antibacterial activities

Tetradentate Schiff base ligands derived from Knoevenagel condensation of β-ketoanilides and furfural with *o*-phenylenediamine and diethylmalonate and their Cu (II) complexes showed antibacterial activity against *Escherichia coli, Salmonella typhi, Staphylococcus aureus, Klebsiella pneumoniae* and *Pseudomonas aeruginosa* by disc diffusion method. It has been reported that complexes have higher antibacterial activity than that of free ligand[8-9]. Bidentate Complexes of Cu (II) with Schiff bases derived from 2,6-diacetylpyridine (L^1), 2-pyridine carboxaldehyde, 3-amino-5-methyl isoxazole with 5-methyl furan-2-carboxyaldehyde, 5-methyl thiphene-2-carboxaldehyde and pyridine-2-carboxaldehyde coordinate through the azomethine nitrogen, furfural oxygen, thiophene sulphur and pyridine nitrogen, respectively show antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Mycobacterium Smegmatis*, *Pseudomonas aeruginosa*, *Enterococcus cloacae*, *Bacillus megaterium* and *Micrococcus leteus*. The results showed that L^1 ligand has a greater effect against *E. coli* than the other bacteria, while it has no activity against *S. aureus*. Metal complexes have a greater effect against almost all bacteria[10-11]. Schiff base of aroyl-hydrazone and its copper complexes has been screened for antibacterial activity against two Gram positive bacterial strains (*B. subtilis and S. aureus*) and two Gram-negative bacterial strains (*E. coli and P. fluorescence*) by the (MICs) method. Schiff base showed significant activity against two Gram-negative bacterial strains with MIC but inactive against two Gram positive bacterial strains[12]. Bidentate Schiff base complex derived by the condensation of Cinnamaldehyde hydrazone with different benzaldehyde Cu (II) compounds screened more active against gram positive bacteria *Bacillus subtilis* than gram negative bacteria *E. Coli*[13]. Azo Schiff's base ligand (N′E)-N′-(5-((4-chlorophenyl) diazenyl)-2-hydroxybenzylidene)-2-hydroxyl benzohydrazide complexes with VO (II), Co (II), Ni (II), Cu (II), and Zn (II) has been studied against several microorganisms by the well diffusion method. In general, the activity order of the synthesized compounds can be represented as Cu (II) > Co (II) > Ni (II) > Zn (II) > VO (II) > Ligand[14].

Bidentate complexes of Co (II), Cu (II) and Cd (II) with benzofuran-2-carbohydrazide and benzaldehyde [BPMC] or 3,4-dimethoxybenzaldehyde [BDMePMC] showed biological activities but Cu (II) complex of [BPMC] and [BDMeOPMC] are more active against *S. aureus* as compared to Co (II) and Cd (II) complexes. Bidentate ligand of 2-[(2-[1-(hydroxyphenyl) ethyl] aminophenyl) ethanimidoyl] phenol derived from o-phenylenediamine are effective against[15] *Bacillus cereus*, *Staphylococcus aureus* and *E. Coli*. Cu (II) complexes with o-phenylenediamine (L^1) and 2–hydcoxyacetophonone (L^2) has been screened for antibacterial activity against *Bacillus cereus, Staphylococcus aureus* and *E. Coli* and tested by Mueller-Hinton agar plates. *E. coli resistance* L^2 was given best results due to the presence of hydroxyl group (2 OH) in the compound and L^1 as free ligand is biological less effective than that of its coordinate with copper due to the presence of (Cu^{2+}) ion[16]. Antibacterial activity of the Clomiphene citrate copper complex has been determined against *E.coli, Staphylococcus aureus* and *Xanthomonas vesicatoria* by Disk diffusion method[17].

The mixed ligand complexes of Cu (II) with Schiff bases N-(2-hydroxy-1-naphthylidene)-4-chloroaniline (L^1) and N-(2-hydroxybenzylidene)-2,3-dimethylaniline (L^2) reported to show some antibacterial activity to certain extent against *E.coli*, *S. aureus*, *B. subtilis*, and *S. typhi.,* but their complexes exhibit comparatively greater amount of activity against these bacteria[18]. Mixed ligand complexes of Cu (II) Schiff base ligands derived from o-hydroxy benzaldehyde and amino phenols has been reported to show antibacterial activities[19]. Schiff bases derived from 2-formylindole, salicylaldehyde and N-amino rhodanine and their copper complexes have been screened for antimicrobial activities against *Bacillus cereus, Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Candida albicans*. The results indicated that the free ligands do not have any activity, where as their complexes showed more activity against same bacteria[20]. Mixed ligand complexes of o-vanillidene-2-aminobenzothiazole and 1,10-phenanthroline has been screened for their *in vitro* biological activities against bacterial activity against *Escherichia coli, Pseudomonas aeruginosa, Salmonella Typhi* and *Vibrio parahaemolyticus* by well diffusion method using agar nutrient[21].

It has been reported that the novel 14-membered macro cyclic Schiff base derived from 3-cinnamalideneacetanalide and *o*-phenylenediamine, gave good results in the presence of copper ion in the ligand system[22]. Twenty Schiff bases of 2-amino-5-aryl-1,3,4- oxadiazoles were synthesized with different aromatic aldehydes were investigated against *Proteus mirabilis* and *bacilius subtilis*[23]. Two thiocyanato-bridged dinuclear copper (II) complexes derived from 2,4-dibromo-6-[(2-diethylaminoethylimino)methyl] phenol and 4-nitro-2-[(2-ethylaminoethylimino) methyl]phenol showed wide range of antibacterial activity[24]. Complexes of a tridentate Schiff base from the condensation of S-benzyldithiocarbazate with salicylaldehyde showed very strong activity against bacteria[25]. Copper (II) complexes of Schiff's base derived from o-phenylenediamine and 5-bromosalicylaldehyde possess growth inhibitory activity against *E. coli* and staphylococcus aureus[26]. Schiff base, synthesized from 5-bromo-3-fluorosalicylaldehyde and benzidine and its complexes with transition metal ions such as; Cu (II) and Ni (II) has been tested against four pathogenic bacteria (*S. aureus* and *B. subtilis*) as Gram-positive bacteria and (*E. coli* and *K. pneumoniae*) as Gram-negative bacteria. Copper complex showed higher activity than Ni complex[27].

The metal complexes show higher activity than the free ligand against the same organism under identical experimental conditions, such increased activity of the metal chelates can be explained on the basis of chelation theory[28]. Antibacterial activity studies of Cu (II) complex of Schiff base derived from 3,3′-{1,2-phynylenebis-[nitrilo(*E*) methylylidine]} diquinolin-2-ol has been carried out. A cup plate method has been employed for the *in vitro* study of antibacterial effect against*, Staphylococcus aureus*, *E. coli.* Screening data indicated that the metal chelates exhibit a higher inhibitory effect than the free ligand[29]. Complexes of chlorosalicylidene aniline with Co (II) and Cu (II) screened for antibacterial activity against several bacterial strains, *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa.* The metal complexes showed enhanced antibacterial activity as compared to uncomplexed ligands. Copper complex showed greater activity against *Pseudomonas aeruginosa* as compared Co (II) complex[30]. Schiff bases ligands and their copper complexes synthesized from sulphonamide and resacetophenonehave been evaluated for their antimicrobial activity against both Gram-positive and Gram-negative bacteria *B. megaterium*, *E. coli, B. subtilis*, *P. fluoresces.* The comparison of antimicrobial activities of the free ligands and complexes shows that the presence of metal causes more inhibition i.e., more activity[31]. Similarly schiff base Cu (II) complexes of the type [$HLMClH_2O$] and [$HLMOAcH_2O$] synthesized by condensation of oxalyldihydrazide and 3-tert-butyl-2-hydroxy-3-(3-phenylpent-3-yl) benzaldehyde have been screened for their antibacterial activity against the bacteria *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aeruginosa, Escherichia coli* and *Salmonella typhi* (as gram negative bacteria). The results compared with standard drug (Imipenem) have indicated that compounds were more active than the standard drugs[32]. Copper (I) 4-benzylimino-2,3-dimethyl-l-phenyl pyrazal-5-one complex showed remarkably active

against *Staphylococcus aureus* as compared with zinc complex. The standard drug used (ciprofloxacin) did not show any inhibition[33] against *Staphylococcus aureus*. Schiff base derived from sulfonamide and their copper (II) complexes have been screened for their *in vitro* antibacterial activity against bacterial strains, *Escherichia coli*, *Shigella flexneri*, *Pseudomonas aeruginosa*, *Salmonella typhi*[34]. Copper (II) complexes with Schiff bases derived from pyrrole-2-carboxaldehyde and 2-hydroxy-1-naphthaldehyde and 2,3-diaminopyridine showed antibacterial activity[35].

Antifungal activities

The antimicrobial activity of the N-(2-hydroxy-1-naphthylidene) phenylglycine and its copper complexes has been investigated. The antifungal screening data indicated that the activity of the ligand has increased upon complexation. Cu (II) complexes have shown better antifungal activity compared to the ligand and the corresponding metal salts[36]. Tetradentate Schiff base and their Cu (II) complexes showed antifungal activity against *Aspergillus niger, Rhizopus stolonifer, Aspergillus flavus, Rhizoctonia bataticola* and *Candida albicans* by well diffusion method[9]. Antifungal activity of the Clomiphene citrate Cu compounds has been determined against two fungi, *A. flavus*and, *A. niger*, by Batemann poisoned food technique[17].

The fungicidal effect of salicylaldimine containing formaldehyde and piperazine moity and its metal polychelates has been determined against *Candida albicans, Aspergillus*. Cu (II) polychelate exhibited high activity against *Candida albicans* and the other show mild activity. The presence of N and O donor groups in the ligand and its metal polychelates inhibited enzyme production because enzymes that require free hydroxyl group for their activity appear to be especially susceptible to deactivation by the metal ion of polychelates. All the metal polychelates are more toxic than the ligand[37]. Neutral complexes of Cu (II) with Schiff bases derived from 3-nitrobenzylidene-4-aminoantipyrine and aniline or p-nitroaniline or p-methoxyaniline showed antifungal activity. A comparative study of the MIC values for the ligands and their complexes indicates that the complexes exhibit higher antifungal activity. Such increased activity of the complexes can be explained on the basis of overtone's concept and Tweedy's chelation theory[38]. Inhibition is enhanced with the introduction of an electron withdrawing nitro group in the phenyl ring[39]. Cu (II) complexes with Schiff base 3,3′-thiodipropionic acid bis (4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline showed antifungal activity against *Alternaria brassicae, Aspergillus niger* and *Fusarium oxysporum* and results indicate that the complexes show the enhanced activity in comparison to free ligand[40].

Copper Schiff base ligand like, 3-amino-5-methyl isoxazole with pyridine-2-carboxaldehyde, 5-methylfuran-2-carboxyaldehyde and 5-methylthiophene-2-carboxaldehyde were screened for antifungal activity[10]. Copper (II) complexes of Schiff base ligands derived from 2-substituted anilines and salicylaldehyde exhibit good broad-spectrum antifungal in *vitro*[41]. Cu (II) complexes has been synthesized by the addition of Cu (II) acetate to ligand, i.e., 1,10-phenanthroline and 2,2'-bipyridyl, which led to the precipitation of binary complexes. The complex has been tested for antifungal activity against the human and plant fungal pathogens. The [Cu(Sala)bpy] H_2O complex has been found to have some inhibitory effect against *Candida* sp. and *Mucor* sp., *Alternaria alternate, Fusarium* sp.*, Penicillum* sp. Copper (II) complex with binuclear Schiff base, synthesized from benzidine and 5-bromo-3-fluorosalicylaldehyde has been tested against stone pathogenic fungi; *A. fumigates*[27]. Mixed ligand complexes of o-vanillidene-2-aminobenzothiazole and 1, 10-phenanthroline has been screened for their *in vitro* antifungal activities against fungus: *Aspergillus niger*, *Penicillium*, *Trichoderma viride*[21].

Antifungal activity studies of Cu (II) complexes of Schiff base derived from 3,3′-{1,2-phynylenebis[nitrilo(*E*) methylylidine]} diquinolin-2-ol have been carried out. A cup plate method employed for the *in vitro* study of antifungal effect against*, C. albicans and A. niger* and the screening data

showed that the metal chelates exhibit a higher inhibitory effect than the free ligand[29]. Schiff's base synthesized from sulphonamide and resacetophenone and its metal complexes showed antifungal activity against *A. awamori*. The comparison of antimicrobial activities of the ligands and complexes shows that the presence of metal causes more inhibition i.e., more activity[31]. Copper (II) complexes of oxalyldihydrazide and 3-tert-butyl-2-hydroxy-3-(3-phenylpent-3-yl) benzaldehyde ligand show a significant degree of antifungal activity against *Aspergillus sp., Rizoctonia sp.* and *Penicillium sp*. The complexes are highly effective against *Aspergillus sp.* All the metal complexes exhibited greater antifungal activity against *Aspergillus sp.* as compared to the standard drug Miconazole[32]. Schiff base ligands derived from sulfonamide and their copper (II) complexes have been tested antifungal activity against fungal strains, *Trichophyton longifusus*, *Candida albicans*, *Aspergillus flavus*, *Microsporum canis*, *Fusarium solani* and *Candida glabrata*[34].

Antimalarial activity

It has been reported that thiosemicarbazones and its derivatives show antimalarial activities[42]. The primary task of researchers is to investigate new compounds in respect to their activity against malaria. A correlation between the structure and biological activity has been established indicating that the tridentate (NNS) 2-(N)-heterocyclic thiosemicarbazones and its complexes are most efficient as therapeutic agents[43].

Schiff base ligand 2-acetylpyridine thiosemicarbazones and their copper complexes possess significant antimalarial activities[44]. The presence of a 2-pyridylalkylidene moiety or selenocarbonyl group has been shown to be essential for antimalaria activities[45]. These features would also be expected to promote effective transition-metal chelating properties[46]. It has been reported that the presence of certain bulky groups at position N_4 of the thiosemicarbazones moiety greatly enhances the antimalarial activity[47]. Heterocyclic ligands based on ferrocene, pyridine and thiosemicarbazones derivatives and these compounds as ligands for the preparation of transition metal complexes and test their biological activities against malaria[48-52]. Acetylferrocenyl-4-phenyl thiosemicarbazone, acetylferrocenyl-4-methyl thiosemicarbazone, acetylferrocenyl-2-thiophene carboxyl semicarbazone, acetylpyridine-2-thiophenecarboxyl semicarbazone and their copper (II) complexes has been screened against malaria parasite *Plasmodium falciparum*[53]. Cu (II) complexes of buparvaquone 3-*trans* (4-*tert*.-butylcyclohexyl)methyl-2-hydroxy-1,4-naphthoquione has been tested for their in vitro antimalarial activity against *Plasmodium falciparum* strains[54].

Antitumor and cytotoxic activities

Metal complexes of Schiff's base derived from 2-thiophene carboxaldehyde and 2-aminobenzoic acid (HL) has been tested as anticancer activity[55]. L-glutamine schiff's base has proteasome inhibitory activity in human breast cancer and leukemia cells. The complex selectively inhibits the proteasomal activity and induces the cell death in cultured breast cancer cells, but not normal, immortalized breast cells[56]. A tridentate Schiff base derived from the condensation of S-benzyldithiocarbazate with salicyldehyde and its copper complexes showed cytotoxic properties[57]. Copper (II) complexes containing Schiff bases derived from S-benzylde thiocarbazate and saccharinate showed anticancer properties. These complexes have been active against the leukemic cell line (HL-60) but only [Cu (NNS) (sac)] found to exhibit strong cytotoxicity against the ovarian cancer cell line (Caov-3). The activities being higher than the standard anticancer drug Doxorubicin[58]. Complexes of copper (II), with isatin-thiosemicarbazones can inhibit cell proliferation of human leukemia U937cell lines[59]. Isatin-Schiff base copper (II) complexes, obtained from isatin and 1,3-diaminopropane or 2-(2-aminoethyl)pyridine possess pro-apoptotic activity[60].

Besides oxindoles, different Lewis bases coordinated to copper (II) ions have their biological activities enhanced, and some of them has been already studied as potential cancer chemotherapeutic agents[61].

A number of Cu (II) chelate complexes that exhibit cytotoxic activity through cell apoptosis or enzyme inhibition has been reviewed[62]. Copper complexes of pyridine-2-carbohidrazide derivatives inhibit the expression of cellular-Src, a non-receptor tyrosine kinase, which plays a significant role in growth-mediated signaling pathway, thereby, showing cytotoxicity against colon cancer cell lines. Similarly Cu (II) chelates of salicylaldoxime and resorcylaldoxime are potent antiproliferative agents, exhibiting strong cytotoxic effects comparable to that of standard drug adriamycin[63-64]. The diverse biological activity of these complexes compared to one of the widely used platinum anticancer drugs cisplatin, indicates different mechanism (s) of action, which have not been yet resolved. The complex 2,6-bis-(benzimidazo-2-yl) pyridine copper (II) chloride has been shown to exhibit metalloprotease activity[65].

Complexes of carboxamidrazones showed antiproliferative activity against B16F10 mouse melanoma cells[66]. Coordination of N-substituted adenines to Cu (II) also results in enhanced cytotoxic activity against various forms of human cancer[67].

Copper has been coordinated with phenanthroline, 8-hydroxyquinolinate, (pyridine-2-ylmethylamino) methyl phenolate pyrrolidine or dithiocarbamate. The free ligands themselves are not efficient inhibitors and the complex formation is necessary for proteasome inhibition[68]. Thus Schiff base complexes of thiosemicarbazones have been extensively studied to synthesize efficient anticancer drugs[69]. Such complexes have been also found to inhibit enzymatic activity and induce cell apoptosis[70], such activity is usually correlated with anticancer drug validity. Similarly Cu (II) complexes of nitrophenone thiosemicarbazones has been found to exhibit significant antitrypanosomal activity *in vitro*[71]. A number of binary Cu (II) Schiff base complexes of quinolone derivatives[72], 2-carboxaldehyde thiosemicarbazones derivatives[73] and benzene sulfonamide derivatives[74]. Binary Cu (I) complexes of N, N′-disubstituted thioureas and 1,3,5-triaza-7-phosphaadamantane exhibit moderate cytotoxicity against various human cell lines[75].

Copper complex with mixed ligands such as; phenanthroline or 2,2′-bipyridine and acetylacetonate or glycinate are known as casiopeinas[76]. They exhibit significant antineoplastic activity *in vitro* and *in vivo*, against a variety of tumor cell lines. The complex of o-iodohippuric acid exhibits both antitumor and nuclease activity. Healthy cells are not affected under the same conditions[77]. A number of mixed ligand complexes with Schiff bases and 2-amino-2-thiazoline were reported to show significant anticancer activity against various cell lines[78-82]. They have been found to exhibit cytotoxicity against human leukemia cells, with the sparfloxacin complex being the most potent[83]. Ferrocene-conjugated reduced Schiff base copper (II) complexes of L-methionine and phenanthroline bases showed cytotoxic in HeLa (human cervical cancer) and MCF-7 (human breast cancer) cells[84]. A few Cu (I) complexes has been tested *in vitro* as potential anticancer drugs. Mixed ligand Cu (I) complexes of triazolylborate and alkyl/aryl-phosphines has been found to be effective against A549 adenocarcinoma cells that are resistant to the widely used anticancer drug, cisplatin[85]. Copper (I) hydrazone complexes show antioxidant activities against ABTS, O_2^- and OH radicals and *in vitro* cytotoxic activity of compound was assessed using tumour (HeLa, A431) and non-tumour (NIH373) cell lines[86]. Pyrrolidine dithiocarbamate-copper complexes has been found[87] to suppress the proliferation of BE (2) C cells, a human neuroblastoma cell line, with an (half maximal inhibitory concentration) IC_{50} = 8.0 μM, which is more potent than cisplatin IC_{50} = 80 μM.

Anti- inflammable activity

Anti-inflammatory activity studies of Co (II) complexes of derived from 3,3′-{1,2-phynylene bis (nitrilo (*E*) methylylidine)} diquinolin-2-ol showed that the metal chelates exhibit a higher inhibitory effect than the free ligand. The anti-inflammatory activity data showed that the metal chelates showed significant anti-inflammatory activity than the free ligand when compared with that of standard diclofenac[29].

Complexes of Co (II), Ni (II), Cu (II) and Zn (II), have been synthesized from the Knoevenagel condensate Schiff base ligand derived from *β*-ketoanilide and furfural with *o*-phenylenediamine and diethylmalonate. Ligand and its complexe have been tested for their *in vivo* and *in vitro* anti-inflammatory activity against Male Wister Albino rats[9]. Among the metal complexes, copper complex has significant activity. Cu (II) schiff base complex showed wide range of anti-inflammatory activity[88-91]. Chelate Cu (II) complex of N-pyridinobenzamide-2-carboxylic acid (PBCA) has been tested *in vivo* for anti-inflammatory activity[92]. The complex showed a greater decrease (26.5%) in inflammation compared with free PBCA (20.2%) against the cotton pellet granuloma pouch test in rats. Copper (II) complexes with amino acids has been tested for antiinflammatory[93].

Catalytic activity

Many copper (II) Schiff base complexes are known to be useful reagents for oxidative[94] and hydrolytic cleavage of DNA. In addition to the biological properties a large number of copper (II) Schiff base complexes has been used as catalysts in the aziridination[95] and cyclopropanation of olefins[96] and in the per oxidative oxidation of phenol to dihydroxy benzenes[97], in which they act as models for catalase enzymes. Dinuclear Schiff base complexes of copper (II) ions has been used successfully in hydroxylation of phenol[98]. Copper (II) complexes of indoxyl thiosemicarbazone (ITSC) show one pair of well defined reduction peaks at different potential in the forward scan, which represent the reduction of Cu^{2+} to Cu^{+} by one electron process and subsequent oxidation of Cu^{+}. The quasireversible nature of the Cu^{2+}/Cu^{+} is due to inherent reducing tendency of thiosemicarbazone ligands[99]. Ternary complexes of Cu (II) containing NSO donor schiff base showed DNA cleavage activity. In the presence of 3- mercaptopropionic acid (5 mM) as a reducing agent, the complexes (40 μM) show efficient DNA cleavage activity giving the order NSO-dppz > ONO-dppz > NSO-dpq > ONO dpq[100]. Schiff base derived from 2-carboxybenzaldehyde and 3,3′,4,4′-tetraminobiphenyl binuclear Cu(II) complex cleaves pUC18 DNA in presence of the oxidant H_2O_2[101].

Copper-Schiff-base complexes has been used as catalysts for oxidation of alcohols and widely studied for the DNA-binding and DNA-cleaving properties and mimic of galactose oxidase[102].

Zeolite--encapsulated Cu(salen) and Cu(5-Cl-salen)[103], copper acetate monohydrate[104], copper phthalocyanines[105], copper salens[106-112], copper tetrahydro-salophen complexes showed catalytic activity and the activity for the decomposition of H_2O_2, *tert*-butylhydro peroxide, oxidation of phenol and *para*-xylene, oxidation of methane, propane, aliphatic and aromatic hydrocarbons, hydroxylation of phenols to diphenols, epoxidation of olefins, oxyhalogenation of aromatic compounds, oxidation of cyclohexane[113-114]. Copper (II) Schiff base complexes [*N*,*N*′-(ethylene)-bis-(5-nitro-salicylaldiimine)] showed excellent catalytic activity and product selectivity in the oxidation reactions and [*N*,*N*′-(ethylene)-bis-(3-methoxy salicylaldimine)] Cu(MeO-salen)-NaY showed excellent catalytic activity and product selectivity in the hydroxylation of phenol and 1-naphthol[115-116]. Self- activating nuclease activity (DNA cleavage) of Copper (II) Schiff base complexes has been reported[117]. According to Raman *et al*.[118], copper complexes of the Schiff base derivatives of anthranilic acid and acetoacetanilide bind to DNA in the and enhances nuclease activity of Thymus DNA (CT-DNA).

Copper complexes derived from 4-aminoantipyrine enhances DNA cleavage[119]. Some Schiff base-copper (II) complexes showed catalytic activity in the dismutation of superoxide radicals and disproportionation of hydrogen peroxide[120-123]. Copper (II) complex with a tridentate imine, was intercalated revealed an efficient catalyst for phenol oxidation using hydrogen peroxide as oxidant. Schiff base of amino-polystyrene with salicylaldehyde and their Cu (II) complex has been tested by studying the oxidation of cyclohexene, styrene and benzyl alcohol in the presence of *tert.*-butyl hydroperoxide as oxidant[124-125].

Catalytic activities of Schiff base aqua complexes of copper (II) towards hydrolysis of amino acid esters has been reported[126]. Dinuclear copper salicylaldehyde-glycine Schiff-base complex $[Cu_2(Sal\text{-}Gly)_2(H_2O)_2]$ has been used as glass carbon electrode exhibited good electrocatalytic oxidation properties to ascorbic acid[127]. Copper (II) Schiff's base complex catalyzed the atom transfer polymerization of methacrylate.

Catalytic oxidative polymerization of 2, 2′-dihydroxybiphenyl (DHBP) has been performed by using both the Schiff base monomer-Cu (II) complex and Schiff base polymer-Cu (II) complex compounds as catalysts and hydrogen peroxide as oxidant[128]. Polymer bound copper (I) azabis (oxazoline) ligands catalyzed asymmetric cyclopropanations and Cu (II)-Aza (bisoxazoline)-Catalyzed asymmetric benzoylations[129-130]. Binuclear copper complex with tetraglycol aldehyde-phenylalanine Schiff base has been used as a good catalyst polymerization of methyl methacrylate[131].

Complex stability for asymmetric copper-catalyzed cyclopropanations in ionic liquid i.e. bis (oxazoline)-azabis (oxazoline)[132] have been studied. Copper (II) complex was found to be efficient catalyst for the oxidation of alkenes, alkanes and aromatic alcohols in the presence of hydrogen peroxide as oxidant[133]. Copper (II)-bis (oxazoline) complexes for catalytic activity[134]. Chiral oxazoline-Schiff base copper (II) complex has been used as catalysts for asymmetric Henry reaction[135]. Development of bifunctional aza-bis (oxazoline) copper catalysts for enantioselective Henry reaction[136]. Chiral bis (oxazoline) copper (II) complexes used as a versatile catalysts for enantioselective cycloaddition, Aldol, Michael, and carbonyl ene reactions[137]. Oxidation product of the binuclear copper (I) complex $Cu_2L\ (ClO_4)_2$ (L = N,N'-bis-(6-methyl-2-pyridyl) (2′-pyridyl) methyl m-xylylidene imine) has been found to be a catalyst for the oxidation of 3,5-ditert.-butylcatechol to 3,5-ditert-butyl-o-benzoquinone by molecular oxygen[138].

Pesticidal activity

Copper complexes of semicarbazones and phenolic hydrazone have been used as herbicides, insecticides, nematocides, and redenticides[139-141]. Phenoxyacetic acid and its derivatives act as herbicides[142-143]. Aryloxyacetate anions as acid ligands in the corresponding (carboxylato) copper (II) complexes possess herbicidal activities[144-145]. Pesticidal activities of Schiff's bases like; N-(1-phenyl-2-hydroxy-2-phenylethylidine)-2′4′-dinitrophenyl hydrazine], N (1-phenyl-2-hydroxy-2-phenyl ethylidine)-2′-hydroxy phenylimine and [N-(2-hydroxybenzylidine)-2′-hydroxy phenyl amine] derived from benzoin, salicylaldehyde, 2-aminophenol and 2,4-dinitrophenyl hydrazine and their copper complexes has been studied against *Tribolium castaneum*[146-147]. 2-Hydroxybenzalmethylene-*O*,*O*′-diethyl phosphorohy drazono thionate (HL) and its complexes with copper (II) possess some insecticides activities[148]. The complex of copper and N-salicylidene-O,S-dimethylthio phosphorylimine (HSMa) showed much higher pesticidal rates on poisoning *Aphis fabae* and *Metatetranychus ulmi*, compared with methamidophos a commercial pesticide[149].

Miscellaneous applications

Popova and Berova reported that copper and its complexes are good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis hepatitis, leprosy, anemia and leukemia in children[150]. Semicarbazone Cu (II) complexes to mimic superoxide dismutase activity and use as hypnotic[151-152]. Copper (II) complexes with phenolic hydrazone; 4-[(2-(4,8-dimethylquinolin-2-yl) hydrazono)methyl] benzene-1,3-diol; (H_2L) has been used as dyes, bakelite, drugs, and stabilizers for polymers[153-154]. Some Schiff bases possess simple harmonic generation activity[155]. Amido-Schiff base form chelates with Cu (II) and act as a thrombin inhibitor[156]. Copper complex with isatin (1H-indole-2,3-dione) and its derivatives have shown a variety of biological effects, including inhibition of monoamine oxidase[157]. Magneto-spectral properties of Cu (II) complexes of 4-[N-(benzylidene)amino]-, 4-[N-(4-methoxy benzylidene)amino]- and 4-[N-(4-dimethylamino benzylidene) amino]- thiosemicarbazone[158] have been

reported. Antioxidant, pro-oxidant effect of (4-(1-phenylmethyl cyclobutane-3-yl)-2-(2-hydroxy benzylidene hydrazino) thiazole) and its metal complexes has been reported[159]. Copper (II) N-salicylidene-amino acidates, copper (II) complexes derived from salicylaldehyde, α- or β-alanine and its thioureas derivative and copper (II) complexes derived from pyruvic acid and β-alanine has been studied *in vitro* and *in vivo* methods for antiradical activity[160-161]. Plasticized membranes using Schiff's base complex derived from 2,3-diaminopyridine and o-vanilin act as copper (II) selective electrochemical sensors[162].

CONCLUSION

Schiff' bases and their transition metal complexes possess a number of biological applications. Metal complexes show higher activity than free ligands. Among transition metal complexes the activity of copper complexes is high. These compounds shows bright path towards pharmaceutical as well as chemical sciences. But still there is need to explore the biological properties of these already synthesized copper complexes and to synthesize new complexes with more properties.

REFERENCES

1. P. A. Vigato and S. Tamburini, Coord. Chem. Rev., **248**, 1717 (2004).
2. B. S. Bahl and A. Bahl, Elementary Organic Chemistry, Schand and Company Ltd., New Delhi (1993) p. 60.
3. C. T. Barboiu, M. Luca, C. Pop, E. Brewster and E. M. Dinculescu, Eur. J. Med. Chem., **31**, 597 (1996).
4. J. M. Gemi, C. Biles, J. B. Keiser, S. M. Poppe, S. M. Swaney, W. G. Tarapley, D. L. Romeso and Y. Yage, J. Med. Chem., **43**, 1034 (2004).
5. H. Keypour, M. Rezaeivala, L. Valencia, P. Perez Lourido and H. Raza Khavasi, Polyhedron, **28**, 3755 (2009).
6. K. S. Suslick and T. J. Reinert, J. Chem. Educ., **62**, 974 (1986).
7. J. Tisato, F. Refosco and F. Bandoli, Coord. Chem. Rev., **135**, 325 (1994).
8. N. Raman, J. Joseph, A. Sakthivel and R. Jeyamurugan, J. Chil. Chem. Soc., **54**, 4 (2009).
9. N. Raman, J. Ramaraj and Jeyasekaran Joseph, J. Iran. Chem. Res., **3**, 83 (2010).
10. Y. Prashanthi and Shiva Raj, J. Sci. Res., **2**, 126 (2010).
11. E. Ispir, S. Toroglu and A. Kayraldiz, Trans. Met. Chem., **33**, 953(2008).
12. M. V. Angelusiu, S. F. Barbuceanu, C. Draghici and G. L. Almajan, Eur. J. Med. Chem., **45**, 2055 (2010).
13. O. W. Salawu and A. O. Abdulsalam, J. Phy. Sci. & Inno., **3**, 51 (2011).
14. C. Anitha, S. Sumathi, P. Tharmaraj and C. D. Sheela, Int. J. Inorg. Chem., **2011**, 8 (2011).
15. K. Shivakumar, Shashidhar, P. Vithal Reddy and M. B. Halli, J. Coord. Chem., **61**, 2274 (2008).
16. A. M. Hamil, K. M. Khalifa, A. L. Houni and A. El- Ajaily, M. M. Rashayan, J. Chem., **2**, 261 (2009).
17. K. S. Prasad, L. S. Kumar, H. D. Revanasiddappa, B. Vijay and B. Jayalakshmi, Chem. Sci. J., **7**, 28 (2011).
18. K. M. Atmaram and V. Kiran Mangaonkar, Int. J. Chem. Tech. Res., **3**, 477 (2011).

19. M. S. Islam, M. A. Farooque, M. A. K. Bodruddoza, M. A. Mosaddik and M. S. Alam, J. Bio. Sci., **1**, 711 (2011).

20. E. A. Elzahany, K. H. Hegab, S. K. H. Khalil and K. N. S. Youssef, Australian J. Basic App. Sci., **2**, 210 (2008).

21. M. A. Neelakantan, M. Esakkiammal, S. S. Mariappan, J. Dharmaraja and T. Jeyakumar, Indian J. Pharm. Sci., **72**, 216 (2010).

22. N. Raman and C. Thangaraja, Trans. Met. Chem., **30**, 317 (2005).

23. P. Mishra, H. Rajak and A. J. Meth, Gen. Appl. Microbial., **51**, 133 (2005).

24. Z. Hong, Trans. Metal. Chem., **33**, 797 (2008).

25. T. F. H. Tarafder, M. A. Ali, D. J. Wee, K. Azahiri, S. Silong and K. A. Crouse, Trans. Metal. Chem., **25**, 456 (2000).

26. T. M. Fasina, O. O. Qundele, F. N. Ejiah and C. U. Dueke-Eze, Int. J. Bio. Chem., **6**, 30 (2012).

27. S. Vedanayaki, D. Sandhanamalar, P. Jayaseelan and R. Rajavel, Int. J. Pharm. and Tech., **2**, 1118 (2010).

28. E. Canpolat and M. Kaya, J. Coord. Chem., **57**, 1217 (2004).

29. B. H. M. Jayakumarswamy, F. Rahaman, V. K. Revankar and K. Vasantakumar Pai, Int. J. Pharm. Tech. Res., **3**, 1864 (2011).

30. J. Iqbal, S. A. Tirmizi, F. H. Wattoo, M. Imran, M. H. S. Wattoo, S. Sharfuddin and S. latif, Turk. J. Biol., **30**, 1 (2006).

31. S. Baluja, A. Solanki and N. Kachhadia, J. Irani. Chem. Soc., **3**, 312 (2006).

32. G. Kumar, D. Kumar, S. Devi, R. Vermaa and R. Johari, Int. J. Eng. Sci. and Tech., **3**, 1630 (2011).

33. E. E. Elemike, A. P. Oviawe and I. E. Otuokere, Res. J. Chem. Sci., **1**, 6 (2011).

34. H. C. Zahid, A. S. Hazoor and T. S. Claudiu, Labo. di. Chimica. Bioinorg., **27**, 58 (2012).

35. T. Jeewoth, K. W. H. Li, G. B. Minu, D. Ghoorohoo and K. Babooram, Syn. and Reac. Inorg. and Met. Org. Chem., **30**, 1023 (2000).

36. K. B. Gudasi, M. S. Patil, R. S. Vadavi, R. V. Shenoy and S. A. Patil, Trans. Met. Chem., **31**, 580 (2006).

37. T. Ahamad, N. Nishat and S. Parveen, J. Coord. Chem., **61**, 1963 (2008).

38. M. Fujiwara, H. Watika, T. Matsushitla and T. Shono, Bull. Chem. Soc. Jpn., **63**, 3443 (1990).

39. J. C. Dhanraj and S. M. Nair, J. Coord. Chem., **62**, 4018 (2009).

40. S. Chandra, D. Jain, A. K. Sharma and P. Sharma, Molecules, **14**, 174 (2009).

41. R. K. Parashar, R. C. Sharma, A. Kumar, Inorg. Chim. Acta, **151**, 201 (1998).

42. E. M. R. Kiremire, L. S. Daniel, A. Mu, H. Chibale and H. Kambafwile, J. Mat. Sci. Res., **4**, 263 (2007).

43. J. Bakir, A. Jerash and E. Ali, J. Coord. Chem., **56**, 1029 (2005).

44. P. S. John, L. K. Daniel and F. F. Charles, J. Med. Chem., **24**, 1261 (1982).

45. K. S. Vinod, S. Shipra and S. Ankita, J. Bioinorg. Chem. App., **13**, 1 (2003).

46. K. S. Soumitra, P. P. Om and K. S. Bimal, J. Trans. Metal. Chem., **23**, 349 (1998).
47. H. C. Zahid, P. Humayun, M. K. Khalid and T. S. Claudiu, J. Enzy. Inhi. & Med. Chem., **19**, 81 (2005).
48. S. James and L. Miller, Malaria Vaccine Development: Status Report. NIAID of 34 (2001).
49. Z. Chohan, J. Enzy. Inhi. and Med. Chem., **15**, 98 (2003).
50. M. C. Cardia, M. Begala, A. Delogu, E. Maccioni and A. Plumitallo, J. Pharmaceutical, **55**, 93 (2000).
51. M. T. Cocco, C. Congiu, V. Onnis, M. L. Pellerano and A. De Logu, J. Bioorg. & Med. Chem., **10**, 501 (2002).
52. A. Walcourt, M. Loyevsky, D. B. Lovejoy, V. R. Gordeuk and D. R. Richardson, Int. J. Biochem. and Cell Bio., **36**, 401 (2004).
53. E. M. R. Kiremire, L. S. Daniel, H. Muashekele, K. Chibale and H. Kambafwile, Mate. Sci. Res. J., **4**, 263 (2009).
54. N. H. Gokhale, B. P. Subhash, L. C. Simon, D. K. Howard, D. Wendy, E. A. Christopher and K. P. Annie, J. Inorg. Biochem., **95**, 249 (2003).
55. E. M. Hodnett, A. W. Wu and F. A. French, Eur J. Med. Chem. Ther., **13**, 577 (1987).
56. Y. Xiao, C. Bi, Y. Fan, C. Cui, X. Zhang and Q. Ping Dou, Int. J. Oncogy, **33**, 1079 (2012).
57. M. T. H. Tarafder, M. A. Ali, D. J. Wee, K. Azahari, S. Silong and K. A. Crouse, Trans. Met. Chem., **25**, 456 (2000).
58. C. Jovanovski, S. Tancera and B. Soptrajanov, Spectrosc. Lett., **28**, 1095 (1995).
59. M. C. Rodriguez Arguelles, A. Sanchez, M. B. Ferrari, G. G. Fava, C. Pelizzi, G. Pelosi, R. Albertini, P. Lunghi and S. Pinelli, J. Inorg. Biochem., **73**, 7 (1999).
60. G. Filomeni, G. Cerchiaro, A. M. D. Costa Ferreira, A. D. Martino, Z. P. Jens, G. Rotilio and R. C. Maria, The J. Bio. Chem., **282**, 12010 (2007).
61. G. F. Vílchez, R. Vilaplana, M. Gielen and E. R. T. Tiekink, Eds., J. Wiley, Chichester, England, **12**, 219 (2005).
62. L. Tripathi, P. Kumar and K. A. Singhai, Indian J. Cancer, **44**, 62 (2007).
63. H. Elo, Zeitschrift Fur. Naturforschung, **59**, 609 (2004).
64. D. Jayaraju and K. A. Kondapi, Current Science, **81**, 787 (2001).
65. H. Y. Shrivastava, M. Kanthimathi and U. B. Nair, Bio. Bio. Phy. Acta, **1573**, 149 (2002).
66. N. H. Gokhale, S. S. Padhye, S. B. Padhye, C. E. Anson and A. K. Powell, Inorg. Chim. Acta, **319**, 90 (2001).
67. Z. Travnicek, M. Malon and Sindelar, J. Inorg. Biochem, **84**, 23 (2001).
68. S. S. Hindo, M. Frezza and D. Tomco, Euro. J. Med. Chem., **44**, 4353 (2009).
69. F. Gonzalez-Vilchez and R. Vilaplana, ^{29}Cu Chemotherapeutic Copper Compounds in Metallotherapeutic Drugs and Metal-Based Diagnostic Agents, M. Gielen & E. R. T. Tiekink, Eds., John Wiley & Sons, New York, USA (2005) p. 236.
70. F. Tisato, C. Marzano, M. Porchia, M. Pellei and C. Santini, Med. Res. Reviews, **30**, 708 (2010).
71. A. Perez Rebolledo, R. L. Teixeira and A. A. Batista, Euro. J. Med. Chem., **43**, 939 (2008).

72. N. Jimenez Garrido, L. Perello and R. Ortiz, J. Inorg. Biochem., **99**, 677 (2008).

73. S. Sharma, F. Athar, M. R. Maurya and A. Azam, Euro. J. Med. Chem., **40**, 1414 (2005).

74. Z. H. Chohan, H. A. Shad, M. H. Youssoufi and B. T. Hadda, Euro. J. Med. Chem., **45**, 2893 (2010).

75. M. Porchia, F. Benetollo, F. Refosco, F. Tisato, C. Marzano and V. Gandin, J. Inorg. Biochem., **103**, 1644 (2009).

76. A. Marin Hernandez, I. Gracia Mora, L. Ruiz Ramirez and R. Moreno Sanchez, Biochem. Pharma., **65**, 1979 (2003).

77. M. Barcelo Oliver, A. Garcia-Rasa and A. Terron, J. Inorg. Biochem., **101**, 649 (2007).

78. A. Th, Chaviara, C. P. Christidis, A. Papageorgiou, E. Chrysogelou, D. J. Hadjipavlou Litina and C. A. Bolos, J. Inorg. Biochem., **99**, 2102 (2005).

79. G. Psomas, A. Tarushi, E. K. Efthimiadou, Y. Sanakis, C. P. Raptopoulou and N. Katsaros, J. Inorg. Biochem., **100**, 1764 (2006).

80. E. K. Efthimiadou, H. Thomadaki and Y. Sanakis, J. Inorg. Biochem., **101**, 73 (2007).

81. M. E. Katsarou, E. K. Efthimiadou, G. Psomas, A. Karaliota and D. Vourloumis, J. Med. Chem., **51**, 478 (2008).

82. E. K. Efthimiadou, M. E. Katsarou, A. Karaliota and A. Psomas, J. Inorg. Biochem., **102**, 920 (2008).

83. M. Patel, P. M. Parmar and D. S. Gandhi, Bioorg. & Med. Chem., 18, 1235 (2010).

84. P. Sathyadevi, P. Krishnamurthy, R. B. Rachel, H. C. Alan and Nallasamy, Metallomics, **4**, 511 (2012).

85. C. Marzano, M. Pellei and S. Alidori, J. Inorg. Biochem., **100**, 299 (2006).

86. D. Chen, F. Peng and Q. C. Cui, Frontiers in Biosci., **10**, 2939 (2005).

87. K. G. Tridib, S. Gadadhar, M. Roy, M. Nethaji, A. A. Karande and A. R. Chakravarty, Organometallics, **31**, 3021 (2012).

88. J. Sokolik and M. Blahova, (in Slovak) **42**, 133 (1993).

89. M. Blahova, M. Tumova and I. Sokolik, Pharmazie, **49**, 374 (1994).

90. M. Blahova, M. Tumova and I. Sokolik, Pharmazie, **45**, 45 (1998).

91. M. Blahova, M. Sokolík and J. Tumova, Pharmazie, **59**, 156 (1999).

92. G. Mohan and R. Nagar, Indian J. Pharm., **24**, 207 (1992).

93. J. R. J. Sorenson, Progress in Med. Chem., G. P. Ellis and G. B. West, Ed., Elsevier, **26**, 437 (1989).

94. S. Dhar, M. Nethaji and A. R. Chakravarty, Inorg. Chimica. Acta, **358**, 2437 (2005).

95. Z. Li, K. R. Conser, E. N. Jacobsen, J. American Chem. Soc., **115**, 5326 (1996).

96. Z. Li, Z. Zheng, B. Wan and H. Chen, J. Mol. Catal. A. Chem., **165**, 67 (2001).

97. C. R. Jacob, S. P. Varkey and P. Ratnasamy, Microporous and Mesoporous Materials, **22**, 465 (1998).

98. A. G. J. Ligtenbarg, E. K. Beuken, A. Meetsma, N. Veldman, W. J. J. Smeets, A. L. Spek and B. L. Feringa, J. Chem. Soc., Dalton Transactions, 263 (1998).

99. A. Gama, L. Z. Flores Lopez, G. Aguirre, M. Parra Hake, R. Somanathan and P. J. Walsh, Tetra. Asy., **13**, 149 (2002).

100. S. Dhar, M. Nethaji and R. Chakravarty, Inorg. Chem., **45**, 11043 (1996).

101. N. Mahalakshmi and R. Rajavel, Asian J. Biochem. and Pharm. Res., **1**, 525 (2011).

102. H. Eshtiagh Hosseinia, R. H. Mohammad, S. Ali Beyramabadib, S. Hamid Mir Tabatabaeia, A. E. Abbas and J. K. Malihe, Spectrochimica Acta Part A, **76**, 1046 (2011).

103. S. Deshpande, D. Srinivas and P. Ratnasamy, J. Catal., **188**, 261 (1999).

104. R. Raja and P. Ratnasamy, J. Mol. Catal. A. Chem., **100**, 93 (1995).

105. R. Raja and P. Ratnasamy, Appl. Catal. General A, **185**, L7 (1997).

106. R. Raja and P. Ratnasamy, J. Catal., **170**, 244 (1997).

107. R. Raja and P. Ratnasamy, Stud. Surf. Sci. Catal., **101**, 181 (1996).

108. C. R. Jacob, S. P. Varkey and P. Ratnasamy, Microporous Mesoporous Mat., **22**, 465 (1998).

109. C. R. Jacob, S. P. Varkey and P. Ratnasamy, Appl. Catal. A General, **168**, 353 (1998).

110. S. P. Varkey, C. Ratnasamy and P. Ratnasamy, J. Mol. Catal. A. Chem., **135**, 295 (1998).

111. C. R. Jacob, S. P. Varkey and P. Ratnasamy, Appl. Catal. A. General, **182**, 91 (1999).

112. S. N. Masoud, Z. Salimi, M. Bazarganipour and F. Davar, Inorg. Chimica. Acta, **362**, 3715 (2009).

113. N. M. Salavati, A. M. Shakouri and F. Davar, Microporous Mesoporous Mater, **116**, 77 (2008).

114. B. Dutta, S. Jana, R. Bera, P. Kumar Saha and S. Koner, App. Catal. A. Gen., **318**, 89 (2007).

115. S. P. Kumar, B. Dutta, S. Jana, R. Bera, S. Saha, K. I. Okamoto and S. Koner, Polyhedron, **26**, 563 (2007).

116. S. S. Tonde, A. S. Kumbhar, S. B. Padhye and R. J. Butcher, J. Inorg. Biochem., **100**, 51 (2006).

117. N. Raman, J. Joseph and K. Rajasekaran, Polish J. Chem., **81**, 149 (2007).

118. N. Raman, J. Joseph, S. M. Kumar, S. Sujatha and K. Sahayaraj, J. Biopesticides, **1**, 206 (2008).

119. N. Raman, S. Johnson Raja and A. Sakthivel, J. Coord. Chem., **62**, 5 (2009).

120. M. D. Patricia, K. Lilian, R. L. C. Vera, M. D. C. F. Ana, B. G. Marcos, R. N. Rafael, M. P. Helena, C. Marilia and C. G. F. Regina, Quimica Nova Quim. Nova, **33**, 5 (2010).

121. M. L. P. Santos, A. A. Faljoni, A. S. Mangrich and A. M. D. C. Ferreira, J. Inorg. Biochem., **71**, 71 (1998).

122. M. L. P. Santos, I. A. Bagatin, E. M. Pereira and A. M. D. C. Ferreira, J. Chem. Soc., Dalton Trans., 838 (2001).

123. M. A. A. Azzellini, I. A. Bagatin and A. M. D. C. Ferreira, Redox Report, **11**, 25 (1996).

124. M. A. Bizeto, W. A. Alves, C. A. S. Barbosa, A. M. D. C. Ferreira and V. R. L. Constantino, Inorg. Chem., **11**, 6214 (2006).

125. S. M. Islam, P. Mondal, S. Mukherjee, A. S. Roy and A. Bhaumik, Polym. for Adv. Tech., **22**, 933 (2011).

126. C. Haribal, N. Paul and L. M. Rahman, Trans. Metal. Chem., **19**, 524 (1994).

127. Z. Zhang, X. Li, C. Wang, C. Zhang, P. Liu, T. Fang, Y. Xiong and W. Xu, Dalton. Trans., **41**, 1252 (2012).

128. A. Bilici, I. Kaya and F. Dogan, J. Polym. Sci. Part A: Polym. Chem., **47**, 2977 (1994)

129. H. Werner, C. I. Herrerias, M. Glos, A. Gissibl, M. J. Fraile, I. Perez, J. A. Mayoral and O. Reiser, Adv. Syn. Catal., **348**, 125 (2006).

130. A. Gissibl, G. M. Finn and O. Reiser, Org. Lett., **7**, 2325 (2005).

131. D. Wei, N. Li, G. Lu and K. Yao, Sci. China. Series B., **49**, 225 (2006).

132. J. M. Fraile, J. I. Garcia, C. I. Herrerias, J. A. Mayoral, O. Reiser and M. Vaultier, Tetrahedron Lett., **45**, 6765 (2004).

133. S. M. Islam, S. K. Roy, P. Mondal, M. Mubarak, S. Mondal, D. Hossain, S. Banerjee and S. C. Santra, J. Mol. Catal. A. Chem., **336**, 114 (2011).

134. M. Hager, S. Wittmann, A. Schatz, F. Pein, P. Kreitmer and O. Reiser, Tetrahedron Asymmetry, **21**, 1194 (2010).

135. W. Yang, H. Liu and D. M. Du, Org. Biomol. Chem., **28**, 2956 (2010).

136. K. Lang, J. Park and S. Hong, J. Org. Chem., **1**, 6424 (2010).

137. R. Calero, A. Vega, M. A. Garcia, E. Spodine and J. Manzur, J. Chil. Chem. Soc., **48**, N 2 (2003).

138. J. Patole, S. Dutta, S. Padhye and E. Sinn, Inorg. Chim. Acta, **318**, 207 (2001).

139. J. T. Stevens, D. D. Sumner, Herbicides in, Handbook of Pesticide Toxicology, (W. J. Hayes, J. R. E. R. Laws, Eds.) Academic Press, New York, 1317 (1991).

140. L. G. Copping, J. C. Kerry, I. T. Watkins, R. J. Wllis and H. Bryan, US Patent No. 4394, 387 (1983).

141. M. Blahova and S. K. Varkonda, Pharmazie, **22**, 270 (1999).

142. K. Hedman, Toxicology, **91**, 87 (1994).

143. R. J. Anderson, I. S. Cloudsdale, R. J. Lamoreaux, K. Schaefer and J. Harr, US Patent No. 6, **110**, 869 (2000).

144. M. Blahova, I. Tumova and J. Sokolik, Pharmazie, **12**, 49 (1998).

145. M. M. Ali, M. Jesmin, S. M. A. Salam, J. A. Khanam, M. F. Islam and M. N. Islam, J. Sci. Res., **1**, 641 (2009).

146. M. Jesmin, M. M. Ali, M. N. Islam, N. Islam, S. M. S. Shahriar and J. A. Khanam, J. Sci. Foundation, **6**, 49 (2008).

147. M. Jesmin, M. M. Ali, M. S. Salahuddin, M. R. Habib and J. A. Khanam, Mycobiology, **36**, 70 (2008).

148. X. Zhu, C. Wang, W. Dong, F. Song, Z. Hu, Y. Dang, H. Li and Z. Liu, Syn. and Reac. Inorg. & Met. Org. Chem., **32**, 475 (2002).

149. X. Zhu, C. Wang, Y. Dang, H. Zhou, Z. Wu, Z. Liu, D. Ye and Q. Zhou, Syn. & Reac. Inorg. and Met. Org. Chem., **30**, 625 (2000).

150. E. Popova and S. Berova, Bulgarius Chemical Abstract, **84**, 184 (1981).

151. J. Patole, S. Dutta, S. Padhye and E. Sinn, Inorg. Chim. Acta, **318**, 207 (2001).

152. N. S. Pandeya, N. Aggarwal and J. S. Jain, Pharmazie, **54**, 4 (1999).

153. G. A. Al Hazmi and A. A. El-Asmy, J. Coord. Chem., **69**, 337 (2009).

154. K. M. Ibrahim, I. M. Gabr and R. R. Zaky, J. Coord. Chem., **62**, 1100 (2009).
155. X. Chen, N. Qi and L. Chen, Dalian Lingong Daxue Xuebao, **34**, 37 (1994).
156. E. Toyata, H. Sekizaki, Y. Takahashi, Kunihiko and K. Tanizawa, Chem. Pharm. Bull., **53**, 22 (2005).
157. G. Cerchiaro and D. M. A. Costa, J. Braz. Chem. Soc., **17**, 8 (2006).
158. R. K. Aggarwal, R. K. Garg and S. K. Sindhu, J. Iran. Chem. Soc., **2**, 203 (2005).
159. M. Karatepe and F. Karatas, Cell Biochem. and Fun, **24**, 547 (2006).
160. Z. Puterova, J. Valentova, Z. Bojkova, J. Kozisek and F. Devinsky, Dalton. Trans., **40**, 1489 (2011).
161. V. Jan, S. Olga, R. Eva, M. Jan and V. Jindra, J. Trace Elem. Med. & Bio., **18**, 155 (2004).
162. P. L. Singh and M. J. Bhatnagar, Talanta, **64**, 319 (2004).