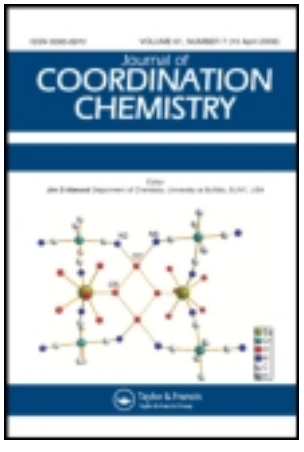

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REVIEW

Cadmium and tin complexes of Schiff-base ligands

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This review highlights the structural properties and biological aspects of Schiff-base ligands of cadmium and tin derived from the azomethine group. It also presents extensive studies on syntheses, spectral, magnetic structural characteristics, and biological activities of the cadmium and tin complexes with Schiff bases, which have appeared in the literature.

Keywords: Cadmium and tin metal complexes; Structural properties; Syntheses; Biological activities; Schiff bases

Abbreviations: PLSC, pyridoxal semicarbazone; PLTSC, pyridoxal thiosemicarbazone; PLBTSC, pyridoxal bisthiosemicarbazone; PLITSC, pyridoxal isothiosemicarbazone; SMDTC, S-methyldithiocarbazate; 4-Mpipzcdt, 4-methylpiperazine-1-carbodithioate; PHMTSC, phthalaldehyde-bis-(4-methyl-3-thiosemicarbazone); DPMAMT, 2,6-diacetylpyridine-bis-(3-methylsulfhydryl-4-amino-5-mercapto-1,2,4-triazol); DPHB, 2,6-diacetylpyridine-bis-(2-hydrazinobenzothiazole); $HTSCZ_1$, 2-(1,2-dihydro-2-oxo-3H-indol-3-ylidenyl) thiosemicarbazone; $HTSCZ_2$, 1,3-dihydro-3-[2-(4-fluorophenyl)-2-oxo-ethylidene]-2H-indol-2-one thiosemicarbazone; $HTSCZ_3$, 1,3-dihydro-3-[2-(4-fluoro-3-methylphenyl)-2-oxoethylidene]-2H-indol-2-one thiosemicarbazone; CT, charge transfer; TBP, trigonal bipyramidal; PLTSCEt, pyridoxal N_4-ethylthiosemicarbazone; $PLTSCMe_2$, pyridoxal N_4-dimethylthiosemicarbazone; CEM-SS, human cell T-lymphoblastic leukemia cell line; HELA, cervical cancer cells.

1. Introduction

The use of coordination compounds as biological probes represent one of the most important applications of bioinorganic chemistry [1]. Coordination complexes are gaining increasing attention particularly in the design of repository, slow release, or long-acting drugs in nutrition and in the study of metabolism [2, 3]. Nitrogen-, sulfur-, and oxygen-donor systems pertain to both biological and chemical properties. Heterocyclic chelated ligands have been extensively studied for biological applications, such as antiviral, antibacterial, antifungal [4], antimalarial agents [5], anti-leukemic [6], antifertility [7], anti-tubercular [8], antipyretic, antitumor, and anticancer [9]. Schiff bases constitute one of the most important classes of biologically active ligands due to their facile synthesis and good solubility. Thus, they have played an important role in

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the development of coordination chemistry [8] and readily form stable complexes with most metals.

Schiff bases described by Hugo Schiff in 1864 [10] have been extensively used as a chelating ligand in coordination chemistry and their metal complexes are of great interest [8]. Nitrogen and sulfur donors play a key role in coordination with metal at the active sites of numerous metallobiomolecules. The design of Schiff-base complexes in the twenty-first century will be focused on directed variation of the binding of azomethine derivatives to allow different chelate ring sizes and combinations. Thereupon, the problem of selectively obtaining tetra-, penta-, and hexa-coordinated chelate structures as well as standard and non-standard metal binding with chelating ligands will be resolved [11].

Schiff bases derived from the reaction of aromatic aldehydes and primary amines represent an important series of organic base ligands and their relevant transition metal complexes are of great interest in synthetic inorganic chemistry. Schiff bases and their metal complexes are active as antibiotic, antiviral, and antitumor [8] agents because of their specific structures. These ligands show broad biological activity and bind to metal ions in a variety of ways. Complexes of biologically active compounds bound to metal ions enhance their activities. The variety of Schiff-base metal complexes, with wide choice of ligands and coordination environment, has attracted much attention. The ease of formation of metal complexes from these ligands has attracted considerable interest in the development of the chemistry of chelate systems. These complexes have wide applications in food industries, dye industry, analytical chemistry, catalysis [4], agrochemical fields, potential antitumor, antibacterial, antiviral, fungicidal, antimalarial, and pharmacological activities [8]. Research dealing with Schiff-base metal complexes has broad interest in bioinorganic chemistry, catalysis, and magnetochemistry. In bioinorganic chemistry, Schiff-base metal complexes provide synthetic models for metal-containing sites in metalloproteins and enzymes.

Transition and non-transition metal complexes of azomethine moieties have biological and pharmacological properties, important in catalysis, medicine [12] (diagnosis and therapy), design of highly valuable materials, analytical chemistry as model compounds for structure and function of metalloproteins [13, 14]. The pronounced biological activity of metal complexes of ligands derived from thiamines has created considerable interest in their coordination chemistry. The chemistry of main group elements with various nitrogen and oxygen donors are the subject of increasing interest due to the striking structural features exhibited by this class of compounds and also on account of their biological significance [5, 8].

2. Broad aspects of heterocyclic and non-heterocyclic Schiff bases

Heterocyclic compounds are widely distributed in nature and are essential in many biochemical processes. These compounds have biological activities. As many drugs are heterocycles, sulfur, oxygen, nitrogen, amino-nitrogen, azomethine nitrogen, and alcohol or phenol oxygen-donors are of interest. A number of pharmaceutical compounds have been introduced with five-, six-, and seven-membered rings such as piperazines, piperidines, imidazoles, benzodiazepines, and other heterocycles containing nitrogen, sulfur, and oxygen. Compounds containing these heterocycles have important

physiological properties ranging from anti-histamine, analgesic, anti-inflammatory, anti-hypertensive to anticancer. Such compounds are also used as models for important bioinorganic systems, such as metalloproteins, and find applications as photosensitizers and catalysts. From early days, the physiological properties of piperazines have generated interest since they exert, even in small dosage, physiological effects, including accelerated pulse, breathing, and hypersensitivity to external stimuli [15]. Some current examples of promising candidates containing a piperazine moiety includes HIV protease inhibitor indinavir [16], a compound that blocks farnesyl transferase activity (anticancer) [17], ipsapirone (antidepressant) [18], and buspirone (anxiolytic drug) [19]. The most thoroughly studied heterocyclic ring system is pyrimidine, which serves as the building unit of many chemotherapeutic agents (bleomycin), vitamins (vitamin B_{12}), drugs (antibacterial, antimalarial), and nucleic acids (cytosine and uracil). Pyrazolone is an active moiety especially in non-steroidal, anti-inflammatory agents, used in the treatment of arthritis and other musculoskeletal and joint disorders. Some drugs show increased activity when administered as metal chelates. Schiff bases as multidentate ligand, having delocalized π-orbitals, are used as models for biological systems in catalysis and materials chemistry [20–24].

Non-heterocyclic compounds are also of interest as shown by the large number of reviews and papers. Isothiosemicarbazides and isothiosemicarbazones with diverse chemical and structural characteristics were the subject of a monograph [25], with potential and proven applications as biologically active molecules with wide spectrum of activity. This is especially true for thiosemicarbazones and their metal complexes, for which the relationship between structural and biological activities has been covered [26, 27]. Semicarbazone and thiosemicarbazone form stable-colored metal complexes, proposed as analytical reagents by Singh *et al*. [28]. The coordination chemistry of semi-, thiosemi-, and isothiosemicarbazones is very interesting for the number of metal complexes and the diversity of ligand systems (among them also macrocyclic ones) [29–33], i.e., the donors providing stabilization of various oxidation states of metals [33–35].

3. Synthesis and physico-chemical characteristics of Schiff bases and their complexes

The majority of pyridoxal semicarbazones (PLSC), pyridoxal thiosemicarbazones (PLTSC), pyridoxal bisthiosemicarbazones (PLBTSC), and pyridoxal isothiosemicarbazones (PLITSC) are obtained in good yield by the condensation of aqueous or alcoholic solution of pyridoxal and the corresponding semicarbazide derivative as described by Ferrari Belicchi *et al*. [36], Leovac *et al*. [37], and Knezevic *et al*. [38], who have shown that depending on the form (neutral, protonated) of the ligand precursor, i.e., the presence of a proton acceptor, it is possible to obtain either neutral or protonated form of ligands [39]. PLTSC in trihydrated and anhydrous [40] forms have been reported. All the ligands (pyridoxal semi-, thiosemi-, and isothiosemicarbazones) are yellowish substances, sparingly soluble in water and organic solvents, with protonated forms exhibiting somewhat higher solubility. On heating, especially in the presence of metal ions, due to the complexation, their solubilities increase. Both neutral and protonated forms are characterized by enhanced thermal stability, melting in the range from 212°C ($PLITSC \cdot H_2O$) to 245°C ($PLSC \cdot HCL \cdot H_2O$) [38]. In addition to the

unsubstituted derivatives of PLTSC, some, mainly N_4-substituted (alkyl and aryl), derivatives have been prepared [41].

3.1. *Physico-chemical properties of Schiff-base complexes of cadmium*

Cadmium, which is naturally present in the environment and also as the result of human activities, is extremely toxic. Development of chelating agents is essential for the treatment of cadmium intoxication [8]. Complexes of Cd(II) (**1**) with S-methyldithiocarbazate (SMDTC) and 2-hydroxyl-5-chloro acetophenone have been synthesized by Makode *et al*. [3]. The resulting complex has been characterized by elemental analysis, molecular weight, infrared (IR) spectra, reflectance spectra, magnetic susceptibilities, molar conductance measurement, and thermogravimetric analysis. This Schiff base is tridentate dibasic providing coordination through the deprotonated phenol oxygen, thioenolic sulfur, and azomethine nitrogen. The antimicrobial activities of free ligands and metal complexes were screened against a number of microorganisms to assess their potential as antimicrobial agents. Tetrahedral complexes are active against all strains; in general, metal complexes are more potent than their ligands and activate ligand as principal cytotoxic initiator [3]. Bidentate isomeric NS and NS' Schiff bases were derived from the condensation of S-methyldithiocarbazate (SMDTC) with 5-methyl-2-furylaldehyde and 2-furylmethyl ketone. The reaction of NS ligand with Cd(II) gives solid complex. Single-crystal X-ray diffraction of $[Cd(NS)_2]$ (**2**) showed that the complex was bis-chelated with a distorted tetrahedral structure. This Schiff base, with proton adjacent to thione groups, is relatively unstable in monomeric forms and tends to more stable thiol form by enthiolization in solution. The absence of ν(SH) at approximately 2570 cm^{-1} in solid state indicates thiones were the major tautomers. However, in the presence of KOH the Schiff bases form the thiolate anion in solution-enhancing nucleophilicity of the ligands affording bidentate uninegative chelation with metals [42]. Cd(II) complex of $[Cd(mpsme)_2]$ (**3**) (mpsme = the anionic form of tridentate ONS donor ligand formed from S-methyldithiocarbazate (SMDTC) and methyl pyruvate) has been prepared and characterized by conductance, IR, electronic, and NMR spectroscopic techniques. Spectral evidence supports a six-coordinate distorted octahedral geometry in which ligands are arranged meridional around cadmium.

This ligand coordinates to metal as a uninegatively charged tridentate ONS chelate *via* carbonyl oxygen, azomethine nitrogen, and thiolate sulfur. Methyl pyruvate Schiff bases have a proton adjacent to the thione group and consequently is capable of exhibiting thione (figure 1) and thiol tautomerism (figure 2) [43].

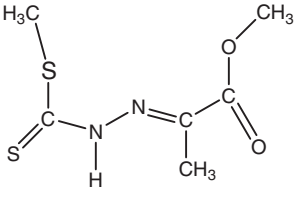


Figure 1. Thione form of the methylpyruvate Schiff base S-methyldithiocarbazate.

Dithiocarbamates are frequently used in analysis as analytical reagents, in agriculture as pesticides, in rubber industries as vulcanization accelerators, and in other industrial processes.

4-Methylpiperazine-1-carbodithioate (4-Mpipzcdt) complexes of general formula $[Cd(4\text{-}MpipzcdtH)_2]Cl_2$ (**4**) have been screened for their anti-leukemic activity by Kalia *et al*. [44].

According to available data the coordination geometry of Cd(II) complex of 2-(E)-(2-(2-pyridine-2-yl)-ethylthio)ethylimino)methyl)-4-bromophenol (PytBrasalH) (**5**) with N, S, O donors is octahedral [45].

Monomeric complex of phthalaldehyde-bis-(4-methyl-3-thiosemicarbazone) (PHMTSC) was synthesized, $[Cd(PHMTSC\text{-}2H^+)]$ (**6**). The PHMTSC has been deprotonated at two hydrazide nitrogen sites; consideration of the composition of PHMTSC indicates (figure 3) that any of the six nitrogens or two sulfurs could coordinate to a metal. The mode of bonding and overall tetrahedral geometry of **6**, shown in figure 4, was determined through spectroscopic methods [46].

Schiff base 2,6-diacetylpyridinebis(3-methylsulfhydryl-4-amino-5-mercapto-1,2,4-triazole) (DPMAMT) is shown in scheme 1. This Schiff base has potential binding sites toward transition metal ions as a pentadentate SNNNS ligand with two thione sulfurs, two azomethine nitrogens, and one pyridine nitrogen.

$[Cd(DPMAMT)] \cdot 3H_2O$ (**7**) was synthesized and characterized on the basis of elemental analysis, magnetic properties, spectral (IR, ^1H NMR, UV-Vis, EPR, and FAB mass), and thermal studies. As shown in figure 5, compound **7** exhibits octahedral geometry around cadmium.

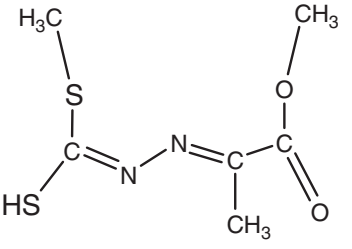


Figure 2. Thiol form of the methylpyruvate Schiff base of S-methyldithiocarbazate.

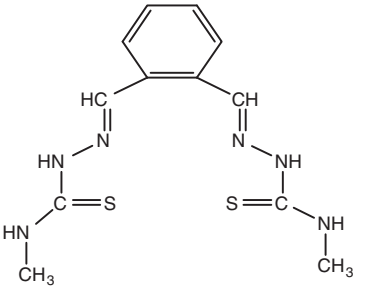


Figure 3. General structural formula of PHMTSC.

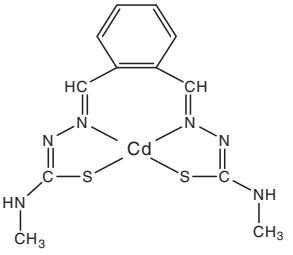
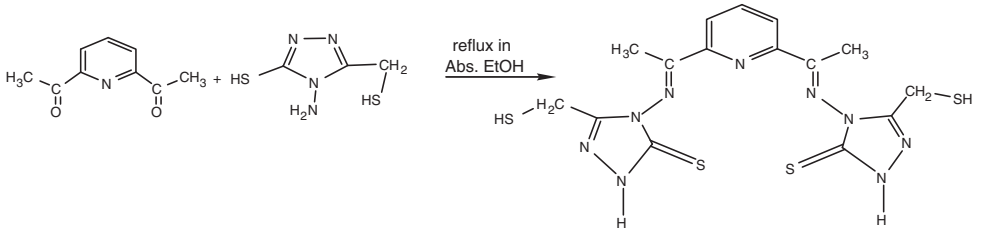


Figure 4. Proposed structure of the cadmium(II) complex (**6**).



Scheme 1. Synthetic route of DPMAMT.

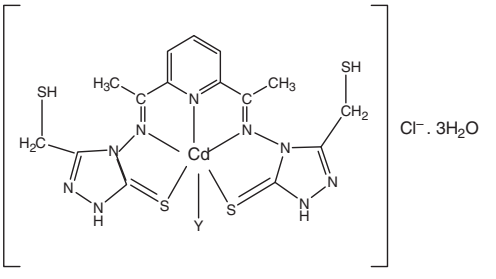
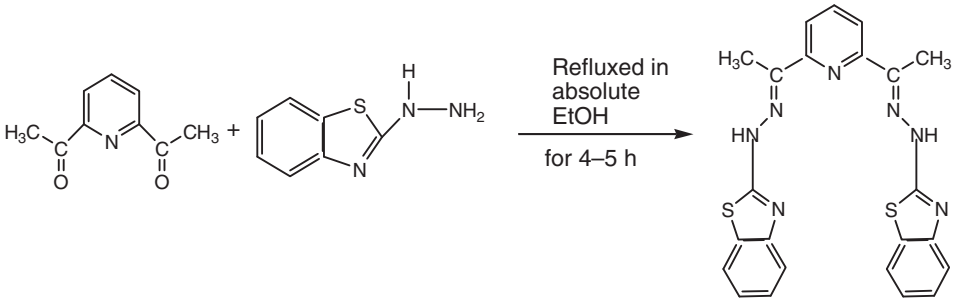


Figure 5. Structure of the Cd(II) complex [Y = Cl^-] (**7**).

The pentadentate behavior of the ligand was confirmed on the basis of spectral studies. Triazoles and their derivatives have proved to be effective bactericides [47], pesticides [48], fungicides, and insecticides [49]. This compound with two pendent arms can be a precursor for a macrocyclic compound. The existence of DPMAMT in thione form or thiol form or a mixture of the two on complexation makes its study more interesting [50].

[Cd(DPHB)] · H_2O (**8**), having N,N,N,N and N donor 2,6-diacetylpyridine bis(2-hydrazinobenzothiazole (DPHB), has been achieved as shown in scheme 2. DPHB is pentadentate through two azomethine nitrogens, pyridine nitrogen, and two hydrazinobenzothiazole nitrogens. The structure has been elucidated on the basis of spectral and thermal studies.

Compound **8** exhibits octahedral environment of ligands around cadmium as illustrated in figure 6 [51]. The chemical and electrochemical synthesis of Cd(II)



Scheme 2. Synthetic route of DPHB.

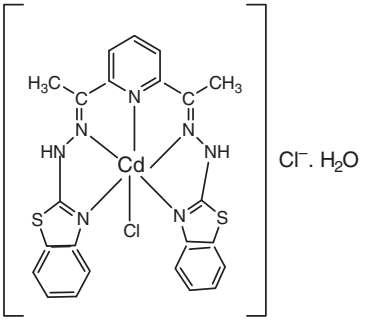


Figure 6. Structure of **8**.

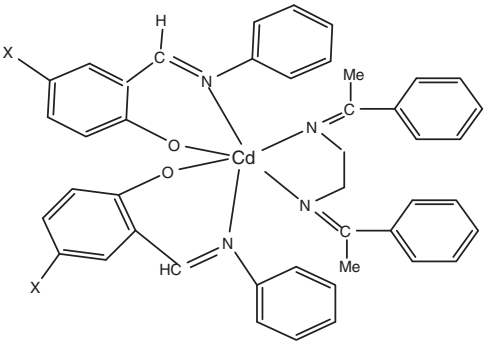


Figure 7. Proposed octahedral structure of the cadmium complex. $[Cd(SB1)_2(acphen)]$ (X = Cl) (**10**) or $[Cd(SB2)_2(acphen)]$ (X = Br) (**11**).

complex with the condensation product of 4,6-di-tert-butyl-2-aminophenol with the salicylaldehyde derivatives gave **9**. Electrochemical dissolution of zero valent Cd in methanol, in the presence of equimolar amounts of ligand, made it possible to isolate dimeric complexes [52]. Diamagnetic $[Cd(SB1)_2(acphen)]$ (**10**) and $[Cd(SB2)_2(acphen)]$ (**11**), shown in figure 7 [53], have been prepared from Cd(II) with monobasic neutral Schiff bases bis-(acetophenone)ethylenediamine (figure 8), 5-chlorosalicylideneaniline, or 5-bromosalicylideneaniline (figure 9) (yellow). Antimicrobial activities of the

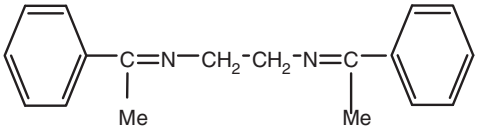


Figure 8. Bis-(acetophenone) ethylenediamine (acphen).

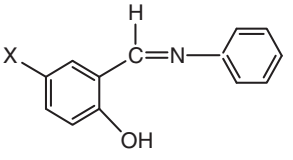


Figure 9. 5-Chlorosalicylideneaniline (HSB1) (X = Cl) 5-bromosalicylideneaniline (HSB2) (X = Br).

complexes and the ligand were tested against *Salmonella typhi* (bacteria), *Saccharomyces cerevisae* (yeast) and two fungal species.

Recently a new reduced amino acid Schiff base was obtained from the condensation of N-(4-hydroxybenzaldehyde) with l-glycine and used to synthesize $[Cd(H_2L)(H_2O)_3]\cdot 2H_2O$ (**12**). In **12**, two bidentate mono-anionic Schiff-base ligands coordinate to cadmium through the secondary amine nitrogen and carboxylate oxygen. The binding interaction of **12** to CT-DNA was studied by UV-Vis absorption and fluorescence spectroscopy. The solution of CT-DNA gave a ratio of UV absorption at 260 and 280 nm, A_{260}/A_{280} of 1.8–1.9, indicating that DNA was sufficiently free of protein; binding constant is determined using the following equation:

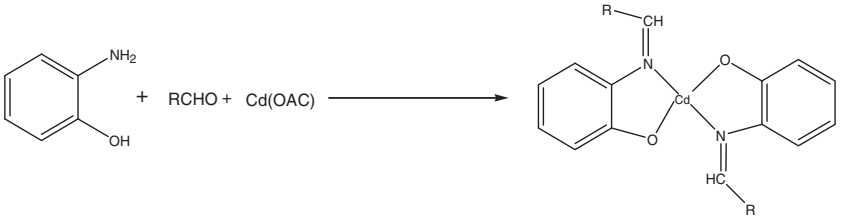
$$[DNA]/(\epsilon_a - \epsilon_f) = [DNA]/(\epsilon_a - \epsilon_f) + 1/kb(\epsilon_b - \epsilon_f).$$

Here, ϵ_a, ϵ_f, and ϵ_b correspond to $A_{obsd}/$[complex], the extinction coefficient for free complex, and the extinction coefficient for complex in fully bound form, respectively.

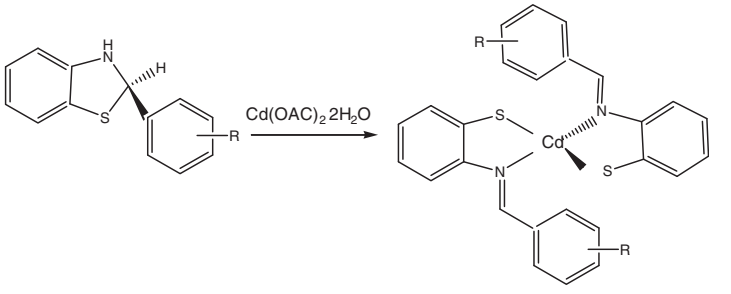
The seven-coordinate Cd complex **13** with an N_2O_5 donor set can be regarded as a highly distorted pentagonal bipyramid. Cadmium usually has coordination number four to seven; in this complex, axial positions are occupied by N_1 and N_1A with axial bond angle of 165.9°. The distortion from ideal pentagonal bipyramidal geometry is also reflected in the angle around Cd in the equatorial plane [54].

CT-DNA-binding abilities and super-coiled plasmid DNA cleavage activities of the complexes have been studied. The results suggest that the complex binds to CT-DNA by intercalation. The agarose gel electrophoresis studies show that these complexes can promote oxidative cleavage of plasmid DNA at physiological pH and temperature in the presence of H_2O_2/sodium ascorbate. Investigation of the DNA cleavage mechanism suggests that singlet oxygen is the reactive oxygen species that leads to DNA cleavage.

The reaction of 2-aminophenol with Cd(II) in the presence of 4-benzyloxybenzaldehyde and 2-butenal yields $[Cd(L)_2]$ (**14**) and $[Cd(L')_2]$ (**15**) (where $L = C_6H_5CH_2OC_6H_4CH{=}NC_6H_4O$ and $L' = CH_3CHCHCH{=}NC_6H_4O$) shown in scheme 3. These cadmium complexes have been synthesized by template methods not *via* ligand formation. Synthesized yellow $[Cd(L)_2]$ and yellow orange $[Cd(L')_2]$ are tetrahedral and both are biologically active against six pathogenic bacteria



Scheme 3. Synthetic route of Cd complex, where R = 4-benzyloxybenzaldehyde or 2-butenal.



Scheme 4. Synthetic route of Cd complex, where R = 2,4,6-triMe (**16**).

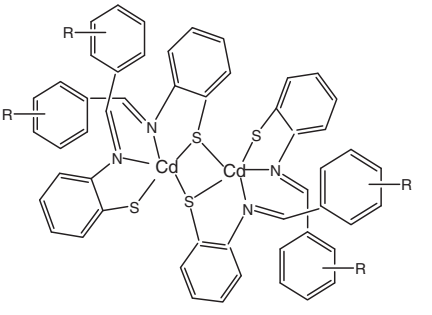


Figure 10. Structure of Cd complex, where R = 4-NMe_2 (**17**), R = 4-OMe (**18**), R = 4-Et (**19**).

(*Shigella dysenteriae*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Sternbergia lutea*, and *Staphylococcus aureus*). [$Cd(L')_2$] shows good activity as compared to ligand precursor [55]. N_2O_3 type Schiff base and complexes with Cd(II) are characterized by spectroscopic determinations and cyclic voltammetry. Cadmium(II) forms chelated complexes with 4-aminoantipyrine, thiosemicarbazone, and 2-amino benzothiazole. Complexes of cadmium with 3-hydroxy-4-nitrobenzaldehyde and *o*-phenylenediamine have been synthesized and structural features were obtained. The reaction of cadmium(II) acetate with 2-substituted benzothiazolines were carried out to synthesize complexes as shown in scheme 4. While $Cd(RsPhsC(H)dNsC_6H_4S)_2$] (R) 2,4,6-triMe (a) (**16**) with bulky substituents at ortho positions of the pendent phenyl ring had a tetrahedral mononuclear structure, other cadmium complexes, $Cd_2(RsPhsC(H)dNsC_6H_4S)_4$] (R) 4-$NMe_2$ (b) (**17**), 4-OMe (c) (**18**), and 4-Et (d) (**19**), as shown in figure 10, possessed S-bridged binuclear structures in

the solid state. These cadmium(II) complexes, which are assumed to be mononuclear in solution, showed photophysical properties, giving emission spectra in the CH_2Cl_2/toluene glass at 77 K. Cadmium(II) complexes with N_2S_2-Schiff bases are a new class of luminescent compounds, and careful derivatization of the substituents on the pendent phenyl rings permits fine tuning of the emission wavelength [56].

Binuclear $Cd_2(HL)_2(NO_3)_4{\cdot}(CH_3OH)_2$ complex based on N'-(pyridin-2-ylmethylene)-2-(1H-1,2,4-triazol-1-yl)acetohydrazide (HL) and Cd(II) salt has been synthesized and characterized by single-crystal X-ray diffraction. Cadmium complex exhibits a 3-D architecture constructed by intermolecular hydrogen bonds and π–π interactions. Quenching phenomena were observed in DMF at room temperature [57]. Similarly cadmium(II) complexes $[Cd_2(L1)(\mu_2\text{-}Cl)Cl_2]$, $[Cd_2(L2)(\mu_2\text{-}Cl)Cl_2]$, $[Cd_2(L3)(\mu_2\text{-}Cl)Cl_2]$, and $[Cd_2(L4)_3ClO_4]$, where HL1 = 4-methyl-2,6-bis(1-(2-piperidinoethyl)iminomethyl)-phenol, HL2 = 4-methyl-2,6-bis(1-(2-pyrrolidinoethyl)iminomethyl)-phenol, HL3 = 4-methyl-2,6-bis-(1-(2-morpholinoethyl)iminomethyl)-phenol, and HL4 = 4-methyl-2,6-bis-(cyclohexylmethyl)iminomethyl)-phenol, were synthesized. The fluorescence spectra of these cadmium complexes were recorded in solid state at room temperature [58].

Cadmium complexes of the type $MLL'Cl_2$, where M = Cd(II), L = TMeOBFC, and L′ = opd or 2,6-dap, were prepared. TMeOBFC is neutral bidentate, coordinating through the azomethine nitrogen and oxygen of –CONH–, whereas opd or 2,6-dap coordinate through amino groups. On the basis of analytical data and spectral studies, octahedral structure was proposed for the complex. Antibacterial and antifungal activities by agar diffusion in DMF against *E. coli* and *S. aureus* bacteria and *Aspergillus niger* and *Aspergillus flavus* fungi showed that complexes are more active than parent ligands. Analytical data show that the Cd complexes have 1 : 1 : 1 (metal : primary ligand : secondary ligand) stoichiometry. The molar conductance value was too low to account for dissociation of the complexes in DMF, indicating the presence of non-electrolytes. Complexes were stable, non-hygroscopic, possess high melting points, and are insoluble in common organic solvents but soluble in DMF and DMSO [59].

Schiff base {1-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]-4-phenyl-2-thioxo-1, 2-dihydro-pyrimidin-5-yl}-phenyl-methanone has been synthesized from N-amino pyrimidine-2-thione and 2-hydroxynaphthaldehyde. The analytical data, electronic spectra, magnetic susceptibility, IR, NMR, and API-ES mass spectral data reveal that ligand coordinates to cadmium by hydroxyl oxygen, azomethine nitrogen, and thione sulfur to form octahedral complexes [60]. Reduced amino-acid Schiff-base complex of $[Cd(HL)_2]\cdot H_2O$, where HL is a reduced Schiff base derived from condensation of N-(2-hydroxybenzaldehyde) and l-histidine, have been synthesized and characterized by elemental analysis, UV-Vis absorption spectra, and single-crystal X-ray diffraction. Cadmium is six-coordinate with O_2N_4 donors in slightly distorted octahedral geometry. The intrinsic binding constants K_b obtained from spectral titration are much smaller $4.56 \times 10^2\,(\text{mol L}^{-1})^{-1}$ for Cd complex than those reported for typical classical intercalators (EB–DNA, $3.3 \times 10^5\,(\text{mol L}^{-1})^{-1}$, indicating that the interaction of these complexes with DNA is a weak intercalative mode [61].

3.2. *Physico-chemical properties of Schiff-base complexes of tin*

Tin complexes exhibit a broad spectrum of biological activities [8] and are studied in view of their structural diversity and their possible biological applications. In this

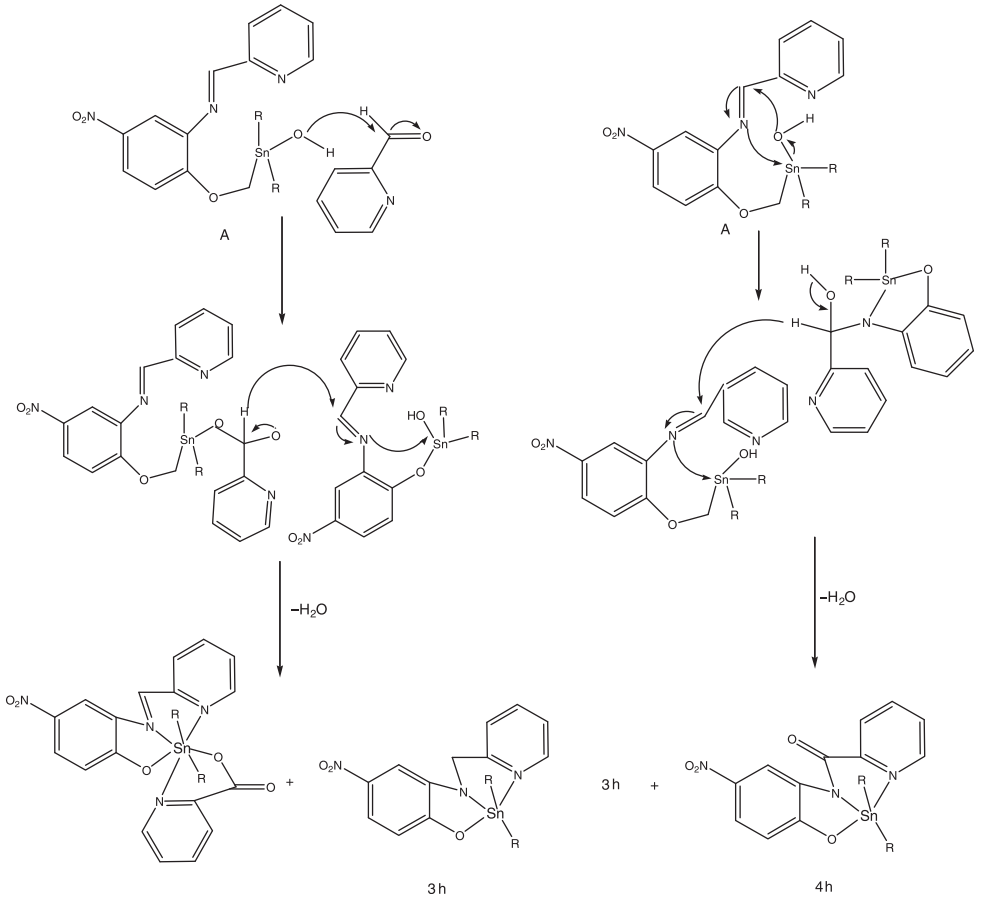
regard, compounds which exhibit antimicrobial [62–67], anti-inflammatory [68–72], bactericidal [73, 74], cardiovascular [62, 66–76], biocidal [77], anti-tubercular [78, 79], antifungal [8, 80], and cytotoxic [81–84] biological activity have been described. Different complexes have been investigated for the treatment of diseases, such as trypanosomiasis [85] and jaundice [86]. Pyridine ligands, which have been used in the coordination chemistry of a variety of metals [87–91], occupy a unique position in the synthesis of biologically active compounds [92]. The chemistry of organostannyl carboxylates is one of the most fascinating fields, and pyridine tin carboxylates are the focus of many studies due to their different coordination geometries and their structural diversity, which depends upon the reaction conditions. 2,6-Pyridine dicarboxylic acid reacts with diorganotin oxide or diorganotin diacetate, generating structures with a pentagonal bipyramidal environment [93–100]. Interestingly, the presence of alkaline alkoxides favors the formation of complexes with octahedral geometry [101]. The reaction of 2,5-pyridine dicarboxylic acid with dimethyl, dibutyl, or diphenyl tin oxides gives cyclotrimeric or polymeric seven-coordinate tin derivatives [102]. In addition, the 2,4-, 3,4-, and 3,5-pyridine dicarboxylates react with organotin chlorides giving oligomeric structures with distorted TBP geometries [103]. Some organotin complexes derived from picolinic acid possess octahedral or five-coordinate TBP structures, where the carboxylate is monodentate [104, 105]. Seven-coordinate tin complexes exhibit higher activity toward some cancer cell lines, when 2,6-pyridine carboxylate is part of the molecule [106]. Other studies have focused on the structural aspects of hypervalent Schiff-base organotin complexes [107, 108]. These classes of compounds are important due to their biological and catalytic applications.

Synthesis of the Sn(IV) complexes with Schiff-base derivatives has been achieved in one pot by the reaction of 2-amino-4-R-phenol ($R = H, Me, Cl, NO_2$), 2-pyridinecarboxaldehyde, 2-picolinic acid and dimethyl-, dibutyl-, and diphenyltin oxides as shown scheme 5. A good crop of crystals enabled X-ray diffraction to determine their molecular structures, which exhibited pentagonal bipyramidal geometry, where butyl groups occupied axial positions and nitrogen and oxygen donors occupied equatorial positions. The reaction of Schiff base with dibutyltin oxide led to pentacoordinate complex. An unusual oxidation reduction reaction took place by the reaction of 2-amino-4-nitrophenol, dibutyltin oxide, and 2-pyridinecarboxaldehyde, which produced the corresponding amine and amide tin(IV) derivatives. The structures of these complexes were established by X-ray crystallography and exhibited distorted trigonal-bipyramidal geometry [109].

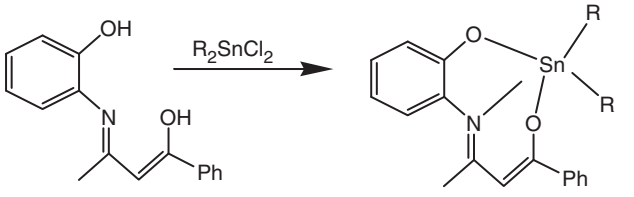
The coordination chemistry of tridentate amino acid-derived Schiff bases [110–112] and related tridentate Schiff bases [113–117] with diorganotin(IV) centres have been discussed widely. Much interest arises from their pharmacological activity [114], where several organotin(IV) complexes show antitumor and antiviral activity [115]. Diorganotin(IV) complexes $R_2Sn[Ph(O)CCH\text{-}C(Me)N\text{-}C_6H_4(O)]$ ($R_2 = Ph, Me$) (**20**) have been synthesized from the corresponding diorganotin(IV) dichloride and the ligand 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one in methanol at room temperature in the presence of triethylamine as shown in scheme 6.

Both compounds have been characterized by elemental analyses, IR, and ^{1}H, ^{13}C, ^{15}N, ^{119}Sn NMR spectra. The structures of the free ligand and complexes have been confirmed by single-crystal X-ray diffraction (figure 11).

An intermolecular hydrogen bond exists with phenolic hydrogen. The crystal structure is trigonal and a new polymorph; triclinic and monoclinic forms have been



Scheme 5. Synthetic routes for the synthesis of different coordination complexes of tin.



Scheme 6. Synthetic route for synthesis of Schiff-base tin complex (**20**).

published. The central tin adopts distorted trigonal-bipyramidal coordination geometry whereas other dimeric structures are distorted octahedral when including the intermolecular Sn–O (phenolic) bond (2.7998(20) Å). The δ (^{119}Sn) values are −306.6 and −127.9 ppm, respectively, thus indicating five-coordinate Sn centres in solution [118]. Synthesis and crystallographic characterization of hydrazone Schiff-base organotin(IV) compounds under ambient conditions have been discussed extensively [119–124]. The reactions of pyruvic acid hydrazones [pyruvic acid

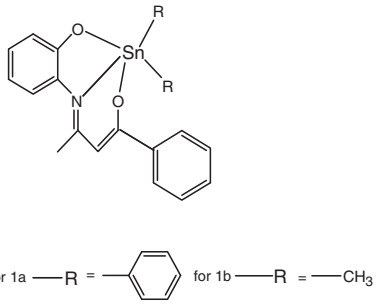


Figure 11. Compounds **1a** and **1b** and numbering scheme for NMR assignments.

thiophenecarbonyl hydrazone (L1), pyruvic acid 4-hydroxybenzoylhydrazone (L2), pyruvic acid salicyloylhydrazone (L3), pyruvic acid benzoylhydrazone (L4)], or salicylaldehyde hydrazone Schiff-base ligand [salicylaldehyde isonicotinoylhydrazone (L5)] with different alkyltin salts result in new organotin(IV) compounds, $\{(n\text{-Bu})_2\text{Sn}[2\text{-SC}_4\text{H}_3\text{CON}_2\text{C(CH}_3)\text{CO}_2](\text{HOC}_3\text{H}_7\text{-}i)\}_2$ (**21**). The molecular structure of **21** has tin coordinated by one isopropyl alcohol oxygen, one nitrogen, and two oxygens from tridentate pyruvic acid Schiff-base ligand, and two carbons of *trans n*-butyl groups. The structure of **21** can be described as a weak-bridged dimer with tin and the coordination geometry of tin can be described as a *trans*-$\text{C}_2\text{SnO}_4\text{N}$ pentagonal bipyramid with two *n*-butyl groups occupying *trans* positions. These data indicate that the tin is in a distorted pentagonal-bipyramidal configuration.

When the reaction of pyruvic acid hydrazone ligand with di-*o*-chlorobenzylltin chloride or di-*n*-octyltin oxide was carried out, $\{(o\text{-ClBz})_2\text{Sn}[4\text{-HOC}_6\text{H}_4\text{CON}_2\text{C(CH}_3)\text{CO}_2](\text{HOC}_2\text{H}_5)\}_2$ (**22**) and $\{(n\text{-C}_8\text{H}_{17})_2\text{Sn}[2\{(n\text{-HOC}_6\text{H}_4\text{CON}_2\text{C(CH}_3)\text{CO}_2](\text{H}_2\text{O})\}_2$ (**23**) were obtained. Compounds **22** and **23** have similar weak-bridged dimeric structures, which also present identical structure geometry of *trans*-$\text{C}_2\text{SnO}_4\text{N}$ pentagonal bipyramids with that of **21**, except for different coordinated solvents, isopropyl alcohol for **21**, ethanol for **22**, and water for **23**, as well as the different alkyl groups. The nature of the alkyl group and the coordinated solvent do not exert a great influence on the overall structure of weak-bridged dimers. In **22** and **23**, the para- or ortho-position phenolate oxygens do not participate in coordination to tin.

Single-crystal X-ray analyses reveal that $\{[(n\text{-Bu})_2\text{Sn}[\text{C}_6\text{H}_5\,\text{CON}_2\text{C(CH}_3)\text{CO}_2][\text{HOSn}(n\text{-Bu})_3]\}_2$ (**24**) presents a weak-bridged dimer. However, it shows a different structure from **21**, **22**, or **23**. The asymmetric unit of **24** consists of two different tins, which are linked by the hydroxyl group derived from the decomposition of "bis-(tri-*n*-butyltin) oxide". Tin 1 lies in a distorted pentagonal-bipyramidal coordination environment, in which one tridentate pyruvic acid benzoyl hydrazone, two *trans n*-butyl groups, the hydroxyl oxygen, and the carboxylate oxygen from the neighboring molecule, coordinate to Sn. In contrast to compounds **21–24** reported here, $\{[(n\text{-C}_4\text{H}_9)\text{SnCl}_2]^-[4\text{-NHC}_5\text{H}_4\text{CON}_2\text{CH}(\text{C}_6\text{H}_4\text{O-2})]^+$ (**25**) is isolated from the reaction of salicylaldehyde isonicotinoyl hydrazone with *n*-butyl tin trichloride in ethanol in the presence of triethylamine. X-ray single-crystal structure analysis reveals a simple monomer. To maintain neutrality, **25** is present as a zwitter ion with the ionization of nitrogen of pyridine in the Schiff base. In the crystal structure, the tin is six-coordinate, bound to one *n*-butyl, two chlorides, one nitrogen, and two oxygens from the enolic

hydrazone ligand. The geometry around tin is distorted octahedral, with the butyl lying in the molecular plane and two chlorides *trans*. The two Sn–Cl distances are not equivalent; one has a longer bond length due to hydrogen bond interaction [125].

Organotin complexes are toxic to a variety of microorganisms and find widespread applications in biocidal compositions [126–129]. Coordination behavior of biologically potent sulfonamide imine having N, N donation to diorgano and triorganotin(IV) has been investigated. The unimolecular and bimolecular reactions of di and triorganotin chlorides with monobasic bidentate imine resulted in the formation of colored solids soluble in DMSO, DMF, and MeOH which have been characterized. Structures have been proposed using spectral studies. Both complexes are monomeric as indicated by their molecular weight determinations. The pathogenicity and virulence of certain microbial infections associated with the ions of the complexes have been found to be potent, like broad spectrum antibiotics. These results made it desirable to delineate a comparison between the ligand and its metal complexes. The ligands and their complexes have been screened against antibacterial, nematocidal, and antifungal activities. On the basis of results, complexes are more active on *Helminthosporium gramineum* than *Alternaria alternaria*.

Six-coordinate complexes display better results than the five-coordinate complexes [130]. The organotin(IV) complexes $[n\text{-}Bu_2Sn(C_9H_8N_3O_3)(H_2O)]_2$ (**26**) and $\{[R_2Sn(C_9H_8N_3O_3)O]SnR_3\}_2$ (**27**) were prepared by the reaction of pyruvic acid isonicotinoylhydrazone with $n\text{-}Bu_2SnO$ or $(R_3Sn)_2O$ in the molar ratios of 1 : 1 and 1 : 2. The crystal (1 : 1) belongs to orthorhombic and its structure shows a distorted pentagonal-bipyramidal geometry with seven-coordinate tin. The crystal (1 : 2) is monoclinic and exhibits a dimeric structure containing distannoxane with two types of tin, one seven-coordinate with distorted pentagonal-bipyramidal geometry, and the other five-coordinate with distorted trigonal-bipyramidal geometry; Schiff bases function as tridentate chelates with O, N, and O donors [131]. Three adducts, $[SnMe_2Cl_2(Hcdacacen)]$ (**28**), $[SnBu_2Cl_2(Hcdacacen)_2]$ (**29**), and $[SnPh_2Cl_2(Hcdacacen)_2]$ (**30**), have been synthesized by the reaction of $SnCl_2$ with methyl-2-(aceylacetonimino)ethylamino]-1-cyclopentene-1-dithiocarboxylate (Hcdacacen). In this reaction, only 1 : 1 condensation occurs even when an excess of amine was used. Condensation products of (2,4-pentenedione) and related β-ketones with mono and diamines have been subject to many studies. Paramount in the consideration of these Schiff bases are questions of the positions of the keto-enol or amino-imine equilibrium and nature of the hydrogen bond in a six-membered chelate ring. It was reported earlier that, in common solvents, bis-(acetylacetone) ethylenediamine and related Schiff bases exist in appreciable amounts in the ketamine form [132, 133]. Spectroscopic data suggest that Hcdacacen exists predominantly in the ketamine tautomeric form and is monodentate neutral coordinating to metal through oxygen atom, while the sulfur and the imine nitrogen are not involved in coordination [134].

$[Ph_2Sn(2\text{-}OC_6H_4C(CH_3)dNCH_2COO)]$ (**31**), with a distorted trigonal-bipyramidal geometry in the solid state, reacts with Ph_3SnCl to yield a 1 : 1 adduct in which two tins are joined *via* the carbonyl of the ligand to form a mixed diorgano/triorganotin species (**32**). Similarly, $[t\text{-}Bu_2Sn(2\text{-}OC_6H_4C(CH_3)dNCH_2COO) \cdot t\text{-}Bu_2SnCl_2]$ (**33**), which has been characterized crystallographically, is dissociated in solution. In contrast to the above behavior, monomeric $[Vin_2Sn(2\text{-}OC_6H_4C(CH_3)dNCH_2COO)]$ forms an adduct with water to yield $[Vin_2Sn(2\text{-}OC_6H_4C(CH_3)dNCH_2COO)OH_2]$ (**34**) in the solid state.

The geometry found about tin in **31** is almost identical to that found about the Sn (1) in **32**. A comparison of chemically equivalent geometric parameters for **31** with those for Sn (1) in **32** shows a remarkable consistency. The presence of bidentate bridging carboxylate residues in organotin carboxylate structures is well-established; however, this is the first example of an isolated ditin structure held together in this fashion, i.e., in which the two tins are not connected *via* an organo link. Further, crystal structures of mixed diorgano/triorganotin tin are also rare, with one example containing a Sn–Sn bond and the other having the tin centers linked *via* a central platinum. A similar structure to **32** is found for **33**. In this case, the adduct involves two diorganotin centers and a distorted trigonal-bipyramidal geometry is found about Sn.

The structure of **34** was shown to be five-coordinate in solution but six-coordinate in the solid state, owing to the coordination of water. The geometry is distorted octahedral with two vinyl groups occupying *trans* positions above and below a NO_3 equatorial plane [135].

Six-coordinate organotin derivatives have been synthesized, $Me_2Sn[TSCZ^1][TSCZ^2]$ (**35**), $Me_2Sn[TSCZ^1][TSCZ^3]$ (**36**), $Ph_2Sn[TSCZ^1][TSCZ^2]$ (**37**), $Ph_2Sn[TSCZ^1][TSCZ^2]$ (**38**), by reacting with 2-(1,2-dihydro-2-oxo-3H-indol-3-ylidenyl) thiosemicarbazone ($HTSCZ_1$), 1,3-dihydro-3-[2-(4-fluorophenyl)-2-oxo-ethylidene]-2H-indol-2-one thiosemicarbazone ($HTSCZ^2$), and 1,3-dihydro-3-[2-(4-fluoro-3-methyl-phenyl)-2-oxo-ethylidene]-2H-indol-2-one thiosemicarbazone ($HTSCZ^3$). Thus, bidentate ligand coordinated to tin *via* sulfur and nitrogen. These synthesized ligands and their metal complexes were tested for antifungal and antibacterial activities. A six-coordinate environment has been suggested around Sn by Tweedy [136]. The resulting product is liphophilic in nature. An enhancement of the activity on complexation is due to chelation [136, 137]. These results reveal that compounds even at lower concentration inhibit the growth of microorganisms, showing good activity against pathogenic human bacteria (*S. aureus*), and fungus (*Aspergillus* species) [138].

A series of diorganotin(IV) complexes has been synthesized by the reaction of R_2SnCl_2 (R = Me, Bu, Ph) with O, N, O tridentate carbohydrazone. In the solid state, carbohydrazone exists as a keto tautomer, but in solution in the presence of base and diorganotin(IV) chloride it is converted to the enol tautomer and coordinated to tin in its deprotonated enolate form. X-ray crystallographic analysis shows that the diphenyltin(IV) complex $[Ph_2Sn(H_2CBS)]$ (**39**) is five-coordinate and has a distorted trigonal-bipyramidal geometry with the ligand coordinated to the tin(IV) as tridentate dinegative through its phenolic-O, enolic-O, and imine-N [139].

[*n*-$BuSnCl_2$(PAP)] (**40**) has been synthesized by direct reaction of *n*-$BuSnCl_3$ with pyruvic acid-2-pyridylhydrazone in the presence of KOH under nitrogen. Single-crystal X-ray diffraction studies indicate that **40** is six-coordinate and adopts a distorted octahedral configuration with coordination *via* carboxylic-O, imine-N, and pyridyl-N from the ligand [140].

Diorganotin dichlorides react with Schiff bases, synthesized from pyrrole-2-carbaldehyde with 2-amino-4-chlorophenol, 2-hydroxy-1-naphthaldehyde with 2-amino-4-chlorophenol, and 2-hydroxy-1-naphthaldehyde with 2-(aminomethyl)pyridine in 1 : 1 ratio. In complexes, the Schiff bases are completely deprotonated and coordinate tridentate *via* phenolic oxygen, pyrrolic, and imine and pyridine nitrogens. In view of the biological activity, these new complexes have applications, such as medicinal or biocidal agents. The characterization of ligands and their complexes and the nature of bonding in complexes were examined by spectroscopic

investigations [141]. New organotin(IV) complexes with empirical formula $Sn(SNNNS)R_2$, where SNNNS is the dianionic form of 2,6-diacetylpyridine Schiff bases of S-methyldithiocarbazate (H_2dapsme) or S-benzyldithiocarbazate (H_2dapsbz) and R=Ph or Me, have been prepared and characterized. Schiff bases derived from S-alkyl esters of dithiocarbazic acid remain as the thione tautomer in both the solid state and solution. However, in the presence of organotin(IV) dichlorides they are converted to the iminothiol form, deprotonate and coordinate to tin(IV) as dinegative pentadentate SNNNS chelating agents. The tendency of the ligands to deprotonate even in neutral solution may be attributed to the extra stability gained through π-electron delocalization along the –C–N–N–C–S– chains in the two arms of these ligands. Complexes with organotin(IV) dichlorides with the elimination of HCl indicate that these ligands are capable of coordinating with non-transition metals, such as tin, even though they have soft sulfur donors in their backbones. The molecular structures of these complexes have been determined by single-crystal X-ray diffraction. Both complexes have a distorted pentagonal-bipyramidal geometry in which the tin is coordinated by a dinegative pentadentate chelating agent *via* pyridine nitrogen, two azomethine nitrogens, and two thiolate sulfurs [142].

4. Spectroscopy of complexes

4.1. *Electronic absorption spectra*

The spectra of numerous transition metal complexes containing different Schiff-base ligands have been described by Salman and Mahmoud [143] and Herzfeld [144]. The obtained spectra display electronic transitions characteristic of ligands and metal ions in coordination. These spectra are sensitive to the type of ligand and have proved to be useful in the identification of particular complex species. The electronic spectra of 4-aminoantipyrine-derived ligands show four main absorptions in ethanol between 200 and 400 nm. The first (210–234 nm) and second (240–281 nm) absorptions are assigned to π–π^* transition of the aromatic ring. The band at 301–334 nm involves π–π^* transition of the C=O and C=N groups; the longer wavelength band (325–396 nm) can be assigned to an intermolecular charge transfer, originating from the 4-aminoantipyrine ring to C=O as a sink. This was confirmed by determining the energy of the CT band from λ_{max} value using the relation $E_{CT} = 1241.6/\lambda_{max}$ CT and comparing the values thus obtained with those calculated from the Brieleg relation [145].

$$E_{CT} = I_P - (E_A + C),$$

where I_P is the ionization potential of the donor part and E_A is the electron affinity.

The oscillator strength (f) of the CT band also was determined from the relation [146] $f = 4.6 \times 10^{-9}\ \varepsilon_{max(delta)}\ V_{1/2}$.

Numerous authors have studied changes in spectra upon the addition of metal ions. The electronic spectra of the complexes caused either bathochromic or hypsochromic shifts of ligand bands. The appearance of new medium intensity bands at lower wavenumbers were observed either merged or slightly separated from the intraligand (π–π^*) band. These bands were mainly attributed to charge-transfer transitions. Further bands with very low extinction coefficients appeared in the visible and near

IR region. These bands were attributed to ligand field (d–d) transitions. Electronic spectra of PHMTSC and their cadmium complex were recorded in DMF. The electronic spectrum of the Cd(II) complex exhibited bands related to the ligand (π–π^*) (n–π^*) transitions at 31,746 and 28,571 cm^{-1}, respectively. The additional band at 25,641 cm^{-1} was assigned to the charge-transfer transition. No ligand field transitions are observed because of the filled d orbital. Since the d^{10} configuration affords no crystal field stabilization, the stereochemistry depends on the size and polarizing power of the M(II) cation and steric requirement of the ligand.

4.2. *IR spectroscopy*

Practically all ligands and complexes of Schiff bases have been characterized in detail by recording IR spectra. A common feature of all these spectra is that between 3500 and 3100 cm^{-1} they possess several bands, which are ascribed to $\nu_{(OH)}$ of hydroxymethyl group and H_2O, along with the $\nu_{(NH2)}$ vibrations. The $\nu_{(NH)}$, which in spectra of free PLSC and PLTSC has been observed by Gopalakrishnan *et al.* [147] at 3150 cm^{-1}, Agarwal *et al.* [148], and Raman *et al.* [149], is missing from spectra of singly deprotonated ligands. This also holds for $\nu_{(NH)}$ from the pyridine ring, which in spectra of free ligands and complexes involving monoanionic ligands is observed at 2850 cm^{-1}; this is absent from the spectra of complexes with dianionic form of ligands. A common feature of all these spectra is the absorption in the medium range, i.e., 1700–1680 cm^{-1} [150–152] ascribed to ν(C=O) while coordinating with metal shifts the ketonic band of free ligand to lower wavenumber, a strong evidence that the ligand is coordinated to the metal ion *via* the ketonic oxygen. Shift of ν(C=N) to lower wavenumber (1600–1520 cm^{-1}) indicates coordination of the ligand *via* the azomethine nitrogen.

In order to study the binding of the Schiff base PHMTSC to metal, the IR spectrum of the free ligand was compared with spectra of the complex. The IR spectrum of the ligand shows a band at 3309–3151 cm^{-1} assigned to ν(NH). Bands due to ν(C=N) and ν(C=S) are located at 1543 and 1325 cm^{-1}, respectively. The (C=S) group is lower than the (C=O) group and has a less intense band. Therefore, identification is difficult and uncertain. The spectra of compounds in which the (C=S) group is attracted to a nitrogen show an absorption in the general (C=S) stretching region. In addition, several other bands in the broad region of 1563–700 cm^{-1} can be attributed to vibrations involving interaction between (C=S) and (C–N) stretches [153]. In spectra of Schiff-base complexes, the ν(C=N) of ligand shifts to higher wavenumbers once the azomethine nitrogen coordinates to metal [154, 155]. In the far IR region, all complexes exhibit bands around 466–420 and 403–400 cm^{-1}, which could be assigned to the vibrations of ν(M–N) and ν(M–S), respectively [156–158].

In the IR spectra of HTCSZ, a broad band at 3250–3100 and 2700 cm^{-1} assigned to ν(NH) and ν(SH), respectively, disappear in the complexes, which indicates deprotonation of ligand on complexation and the formation of (M–S) and (M–N) bonds. Several new bands observed in far IR spectra of complexes at 325, 415, 540, and 581 cm^{-1} were assigned to ν(Sn–S) and ν(Sn–N).

For DPMAMT the sulfydryl ν(SH) is at 2600 cm^{-1} and remains unchanged after complexation, suggesting non-involvement in coordination. In spectra of all metal complexes the ν(NH) band was not observed, perhaps obscured by the broad band at 3450–3100 cm^{-1} due to lattice water [159].

4.3. *^{1}H NMR and ^{13}C NMR spectroscopy*

Apart from IR and UV-Vis, diamagnetic complexes of Sn and Cd as well as the corresponding ligands have also been characterized by NMR spectroscopy. NMR spectra of the Cd(II) complex shows absence of signals due to $N_{(2)}H$ in ^{1}H NMR spectrum and (C=S) in ^{13}C NMR spectrum, which were observed in the spectra of free ligand (PHMTSC), indicating thiolization of (C=S) followed by deprotonation and complexation with metal ions [160, 161].

4.4. *^{119}Sn NMR spectra*

The ^{119}Sn{^{1}H} NMR spectra of $[Sn(R)_2Cl_2(Hcdacacen)]$ (R = Me, Ph, Bu) show sharp singlets at 9.5, 70.6, and 141.8 ppm for the complexes, respectively. These resonances are at significantly lower frequency than that of $SnMe_2Cl_2$ (+137 ppm), $SnBu_2Cl_2$ (+123 ppm), and $SnPhCl_2$ (−27 ppm). In ^{119}Sn NMR the chemical shift strongly depends on the coordination number of tin and an increase in coordination number produces a large upfield shift. The ^{119}Sn moves upfield by 60–150 ppm with a change in the coordination number of tin from four to five and by 130–200 ppm from five to six. On the basis of these chemical shift ranges, it appears reasonable to assume that for the methyl complex the coordination number of tin is five in solution. However, the ^{119}Sn signal for R=Ph and Bu lie at higher frequencies than that of six-coordinate complexes of phenyl and butyl tin derivatives, suggesting that in chloroform the adduct partially dissociates and loses the six-coordinate structure, even though the presence of only one set of signals for the ligand in ^{1}H NMR spectra of the complexes indicates that the free and coordinated ligands are involved in fast interchange. In all the complexes, Hcdacacen seems to be a monodentate neutral ligand, coordinating to metal as dangling through oxygen while an intramolecular hydrogen bond still exists between O and N.

4.5. *Electrochemistry*

In order to characterize the redox processes which may occur on the ligands and complexes, as well as to examine the stability of complex species in solution, electrochemical investigations in suitable solvents are frequently performed. Although thiosemicarbazone-based ligands and their complexes have been characterized by polarographic and voltammetric studies [162, 163], the title Schiff bases and their complexes have only been described in a few articles. Although there are several reports on electrochemical (in particular, polarographic) behavior of PL alone [164, 165], no data were found on its condensation products with semi- or thio-semicarbazide. By analogy of the structures of the Schiff-base ligands and with salicylaldehyde condensation products [166], it could be supposed that the new ligands and, consequently, their complexes can be more easily reduced, which was confirmed in some cases.

5. Biological aspects of Schiff-base ligands and their Cd and Sn metal complexes

Pioneering work on the anti-tubercular activity [167] of *p*-acetoamidobenzaldehyde thiosemicarbazone in 1946 led to a number of papers concerning pharmacological use

of these compounds, due to the wide spectrum of their biological activity [168, 169]. Thiosemicarbazone shows antitumorous, antiviral, antifungal, antibacterial, and antimalarial activities. The primary task of researchers was to investigate the new compounds with respect to their activity against tumors and viruses. A correlation between the structure and biological activity has been established and the tridentate NNS 2-(N)-heterocyclic thiosemicarbazones being apparently most efficient therapeutic agent.

Semicarbazones have a rather limited biological activity spectrum [168, 169]. They are mainly used as anticonvulsants, antiprotozoal agents, radio protector, and radiopharmaceuticals. There are also several reports on their anti-leukemic activity in mice [170], as well as on antimicrobial [171] and pesticide effects [172]. Until recently, it was assumed that isothiosemicarbazones are biologically inactive. However, Italian authors [173–175] found good antimicrobial potential in some tested compounds with the 5-nitrofuryl derivative the most efficient. The ligands PLTSCEt and $PLTSCMe_2 \cdot H_2O$ have been tested *in vitro* against the U937 human leukemic cell lines. Studies involving both inhibition of cell proliferation and apoptosis showed that both ligands inhibited cell growth, but neither of them induced apoptosis [41].

Free ligand derived from 2-hydroxy-5-chloroacetophenone and S-methyldithiocarbazate and its metal complexes were screened against *E. coli*, *S. aureus*, *Proteus mirabilis*, and *S. typhi* to assess their potential as antimicrobial agents. The results reveal the ligand is reactive toward all bacterial strains. Cd(II) complexes are more active toward all strains except *S. aureus*. In general, the metal complexes are more potent than their ligands and hence may serve as vehicles for the activation of ligand as principal cytotoxic species [176].

Compounds having CD_{50} values of less than $5\,\mu g\,cm^{-3}$ are considered highly active, 5–10 $\mu g\,cm^{-3}$ moderately active, 10–20 $\mu g\,cm^{-3}$ weak, and more than $20\,\mu g\,cm^{-3}$ inactive [177]. $[Cd(NS)_2]$ (**2**) was strongly active against CEM-SS with a CD_{50} value of $4.95\,\mu g\,cm^{-3}$ (table 1); qualitative antimicrobial assay results are shown in tables 2 and 3.

[Cd(NS)] was also tested against HELA (cervical cancer cells) and was found to be very active with a CD_{50} value of $4.0\,\mu g\,cm^{-3}$. Epoxide was used as standard in the screening against HELA [43]. The ligands $4\text{-MPipzcdtNa.}H_2O$, 4-MPipzcdtH and their metal complexes with cadmium have been screened to assess their antimicrobial activity against the pathogenic fungus *Candida albicans*, the pathogenic gram negative *E. coli*,

Table 1. Screening test against leukemic (CEM-SS) and colon cancer cells (HT-29).

	CD_{50} ($mg\,cm^{-3}$)	
Compound	CEM-SS	HT-29
NS	3.10	–
NS′	12.00	–
$[Cd(NS)_2]$	4.95	Not available
Metal salt		
$CdBr_2$	14.0	3.5
Standard		
Doxorubicin	0.10	6.00
Tamoxifen	36.00	36.00

Table 2. Qualitative antimicrobial assay results (diameter in mm).

Compound	MRSA	B29	B28	60690	C.A.	398	20341	2075
NS						17		16
$[Cd(NS)_2]$	21	19	22	20	26	15	18	–
Streptomycin (antibacterial control)	31	30	30	30	–	–	–	–
Nystatin (antifungal control)	–	–	–	–	21	25	24	27

Table 3. Quantitative antimicrobial assay results (MIC values in $mg\,cm^{-3}$).

Compound	MRSA	B29	B28	60690	C.A.	398	20341	2075
NS						25,000		25,000
$[Cd(NS)_2]$	12,500	25,000	50,000	781	n.a.	50,000	25,000	–
Streptomycin (antibacterial control)	12.2	48.8	48.8	12.2	–	–	–	–
Nystatin (antifungal control)	–	–	–	–	3125	3125	6250	6250

Methicillin-resistant staphylococcus (MRSA); *B. subtilis* wild type (B29); *Streptococcus mutant* (mutant defective DNA repair-B28); *P. aeruginosa* (60690); *C. albicans* (C.A.); *Aspergillus ochraceous* (398); *Saccaromyces ceciricaee* (20341); *Candida lypolytica* (2075), inactive. Diameter of 15 mm and above considered active. n.a., not available.

P. aeruginosa and gram positive *S. aureus*, *Enterococcus faecalis* using the agar dilution method. The results show that the ligands and complexes are potential antimicrobial agents. The results of *in-vitro* anti-leukemic activity in terms of cell viability of $Cd(4\text{-}MPipzcdt)_2$ on freshly isolated leukemic cells have been reported. The data as compared to control are quite encouraging, further necessitating the need to extend the research activity on leukemic-cell-line-induced mice [45]. Microbial activities of metal complexes or metal chelates are usually greater than the ligands and depend upon the metal ions, i.e., size, charge distribution, shape, and redox potential of the metal chelates [178, 179]. Microbial activities of the ligand precursor 2-aminophenol have been tested against six pathogenic bacteria; gram negative (namely *S. dysenteriae*, *E. coli*, *P. aeruginosa*) and gram positive (namely *B. subtilis*, *S. lutea*, *S. aureus*). Complexes show good biological activities against these bacteria. The antibacterial activity increases with increase in concentration of the tested compounds. The results are comparable with that of the standard compounds [56].

4-Aminoantipyrine-derived complexes are richer and more diverse than other pyrazole rings showing antimicrobial, antimalarial, and antitumorous activities. Antimicrobial activities of Schiff base 4-aminoantipyrine derivatives were tested against *S. aureus*, *Klebsilla pneumoniae*, *S. typhi*, *P. aeruginosa*, and *B. subtilis*. The complexes show higher inhibitory activity than that of the ligands and have higher activity than ampicillin, except for *K. pneumoniae* and *P. aeruginosa* [180]. Some of the isolated metal-4-amino antipyrine derivatives were tested for activity against a variety of microorganisms, and some other biotests have also been performed. In most tests, the activity of complexes is comparable to free 4-amino antipyrine derivatives. In certain examples, the activity increased but there is no evidence of further clinical tests [181].

The efficacy of metal-based therapeutic agents change considerably by making small changes in the Schiff-base ligand attached to the metal [182]. Most of the newly

synthesized compounds were tested for antibacterial activity *in vitro* against bacterial strains such as *S. aureus*, *E. coli*, and *K. pneumoniae* and fungi *C. albicans* and *Rhizopus stolonifer*, employing the nutrient agar disk diffusion method in DMSO. The results showed that all compounds exhibit marked activity against bacteria in comparison to amphotericin, as a standard drug.

Schiff base reported by Saxena and Shrivastava [183] derived from furylglyoxal and *p*-toluidine show antibacterial activity against *E. coli*, *S. aureus*, *B. subtilis*, and *Proteus vulgaris*. Tridentate Schiff bases [184–187] and their complexes show antibacterial activities against *E. coli*, *S. aureus*, *B. subtilis*, and *Bacillus pumpilis*. Some aldimines [188] (E and Z forms), pyrazine [189], amino-acid-derived Schiff bases [190–192], and heterocyclic-ketone-derived Schiff bases [193, 194] show antibacterial activity. Heterocyclic Schiff bases [195–197] and isatin-derived Schiff bases [198, 199] possess anti-HIV activity and antibacterial activity. Schiff bases benzimidazole [200], toluidinones [201], quinazolinones [202], furfuraldehyde [203], thiazole [204, 205], pyridine [206], benzyldithiocarbazate [207, 208], glucosamine [209], pyrazolone [210, 211], hydrazide [212], furfuraldiamine [213], halogenated [214] thiazolidiones or azetidiones [215], indole, *p*-fluorobenzaldehyde, *p*-anisidine, thio-semicarbazone, thiadiazolines, and imidazolinones show positive antibacterial activity. Schiff bases [216] containing cyclobutane and thiazole rings show antimicrobial activity. Schiff bases of pyrrolidinone, pyridone with *o*-phenylenediamine and their metal complexes show antibacterial activity. Cd(II) complexes with furfural-, semicarbazide-, and furfurylidenediamine-derived [217] Schiff bases show antibacterial activities. Salicylidene derivatives, neutral tetradentate ligand, and metal complexes [218] show antibacterial activities against *S. typhi*, *S. aureus*, *K. pneumoniae*, *B. subtlis*, and *Shigella flexneri*.

Thiazole and benzothiazole Schiff bases [219] possess effective antifungal activity. The presence of methoxy, halogen, and naphthyl enhances fungal activity toward curvularia species. Pyrandione Schiff bases [220] show physiological activity against *A. niger*. Some Schiff bases of quinazolinones show antifungal activities against *C. albicans*, *Trichophyton rubrum*, *Trichophyton mentagrophytes*, *A. niger*, and *Microsporum gypseum*. Furfurglidene nicotinamide Schiff base shows antifungal activity against *A. niger*, *Alternaria solani*, and *Collectotricum capsici*. Schiff bases and their metal complexes [221] formed between furan and furylglyoxal with various amines show antifungal activity against *H. gramineum* (causing stripe diseases in barley), *Syncephalostrum racemosus* (causing fruit rot in tomato), and *C. capsici* (causing die back diseases in chillies). Moreover, hydrazine and carbothioamide [222] and their metal complexes show antifungal activity against *A. alternate* and *H. graminicum*.

Benzothiazole- or phenyl-azo-thiazol-derived Schiff bases and metal complexes show microbiological activity against *A. niger* and *Aspergillus alternate* [223]. Schiff bases [224] derived from sulfane thiazole and salicylaldehyde or thiophene-2-aldehyde and their complexes show toxicities against insects. α-Amino acids [225] are intermediates in the synthesis of photostable parathyroid insecticides. Fluorination [226] on aldehyde of Schiff base enhances insecto-acracidal activity. N-acetylated compounds show growth-inhibitory activity with seedling of wheat, rye, and barley. Schiff bases show remarkable activity on plant hormones such as the auxins on the root growth. Schiff bases [227] of the ester and carboxylic acid derivatives show remarkable activities as plant growth hormones. Schiff bases of thiadiazole have good plant growth regulator activity toward auxin and cytokine [228, 229]. Thiazole-derived Schiff bases show analgesic and anti-inflammatory activity. Schiff base of the chitosan and carboxymethyl-chiosan give

antioxidant activity, such as super oxide and hydroxyl scavenging [230]. Furan semicarbazone metal complexes exhibit significant anthelmintic and analgesic activities [231]. Amino-Schiff-bases-derived with aromatic and heterocyclic amines possess high activity against human tumor cell lines. Aryl azo Schiff bases [232] exhibit anticancer activity. Schiff bases of indol-2-carboxaldehyde show inhibitor activities to K B cell lines. Diorganotin(IV) complexes and Schiff bases show antitumor activities *in vitro*, inhibiting interaction to K B HCT-8 and BEL-7402 tumor cell lines [233].

6. Concluding remarks: perspectives of Schiff bases and their metal complexes with cadmium and tin

Apart from their biological activity which can be used for pharmacological purposes, cadmium and tin Schiff-base complexes are sensitive analytical tools for determining traces of metals in several complex materials. In some cases, the *in situ* formation of ligand alone in the reaction of its constituent parts can also be exploited for analytical purpose [234]. The obtained semicarbazones not only enhance fluorescence effects in comparison with vitamins alone, but also increase their stability, thus enabling quantitative plasma PLP determinations even in B6-deficient patients. Pyridoxal, N4-methylthiosemicarbazide, and pyridoxal N4-methylthiosemicarbazone exhibit interesting features in a study of inhibition of mild steel corrosion [235]. Metal complexes of Schiff bases play important roles in agriculture, pharmaceutical, and industrial chemistry. Uses of Schiff bases and their metal complexes as polymers, dyes, catalysts, and in various biological systems, including some use as antifertility and enzymatic agents, have been reported.

Photochemical degradation of natural rubber yields amine-terminated liquid natural rubber (ATNR) [236] when carried out in solution, in the presence of ethylenediamine. ATNR on reaction with glyoxal yields ploy Schiff base, which improves aging resistance. Complexes with tridentate Schiff bases act as inhibitors of emulsion polymerization and copolymerization of dienyl and vinyl monomers. Azo-containing metal complexes are used for dying cellulose polyester textiles. Some metal complexes are used to mass dye polyfibers. Tetradentate Schiff base acts as a chromogenic reagent for the determination of nickel in some natural food samples [237].

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