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Coordination Chemistry of Schiff Base Tin Complexes[1]

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Abstract—The most important results of extensive studies of tin metal complexes with Schiff base ligands are reviewed. A large number of inorganic compounds are known but still there is a need of new compounds to develop various efforts in different fields for biomedical applications.

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INTRODUCTION

In 1864, Hugo Schiff studied the condensation of primary amines and carbonyl compounds to form typical products. Therefore, these compounds are referred as Schiff bases. After that synthesis, chelating behavior and other properties of many Schiff bases have been studied by many researchers [1]. In this context, much work has been done all over the World. Some of the work is reviewed as follows. It is well known from the literature that nitrogen and sulfur atoms play a key role in the coordination with metal at the active site of numerous metallobiomolecules. Molecular design of Schiff-base complexes in the 21st century will be focused on directed variation of the binding of azomethine derivatives to allow buildup of different chelate ring size and combinations. Thereupon, the problem of selectively obtaining tetra, penta and hexa-coordinated chelate structures will be resolved, as well as standard and non-standard metal binding with chelating ligands [2]. Chelated ligands have been extensively studied for their biological applications as antiviral, antibacterial, antifungal [3], antimalarial agents [4], anti-leukemic [5], antifertility [6], anti-tubercular [7], antipyretic, antitumor and anticancer. Schiff bases constitute one of the most important class of biologically active ligands due to their facile synthesis and good solubility in uncommon solvents. Thus, they have played an important role in the development of coordination chemistry [8] and they readily form stable complexes with most of the metals. These compounds are worth of attention for many reasons, chief among them are their biological activities. As many drugs are heterocyclic their sulphur, oxygen, nitrogen, amino-nitrogen, azomethine nitrogen, and alcoholic or phenolic oxygen are some of the donor atoms of interest. The past few decades have seen the introduction of a number of pharmaceutical compounds which contain five, six and seven-membered rings, such as piperazines, piperidines, imidazoles, benzodiazepines and other heterocycles containing nitrogen, sulfur and oxygen [9–13].

Non-heterocyclic compounds are also the subject of great interest to many researchers for a number of years. The coordination chemistry of semi, thiosemi, isothiosemicarbazones appeared to be very interesting from the point of view of both the number of metals forming complexes with them and the diversity of the ligand systems themselves (among them being also macrocyclic ones) [14–17], i.e., set of donor atoms providing stabilization of various oxidation states of metals and reactions of coordination ligands [18–20]. The in vitro anti-HIV activities indicates that compound (3-(2-(4methylaminobenzylideneamino)-6-(cyclopropylamino)-9*H*-purin-9-yl)cyclopentyl)methanol was found to be most potent compound with selectivity index of >2000 and was found to be 32 times more potent than the parent drug [21].

One of the most important goals of pharmacological research is the search for new molecular structures which exhibit effective antitumor activities [22]. This has driven inorganic and organometallic chemists to look for new metal compounds with good activities, preferably against tumors that are responsible for high cancer mortality. Organotin(IV) compounds are a widely studied class of metal-based antitumor drugs and their intensive investigation has led to the discovery of compounds with excellent in vitro antitumor activity, but, in many cases, disappointingly low in vivo potency or high in vivo toxicity. It is well established that organotin(IV) compounds are very important in cancer chemotherapy because of their apoptotic inducing character [23–27]. The design of improved or-

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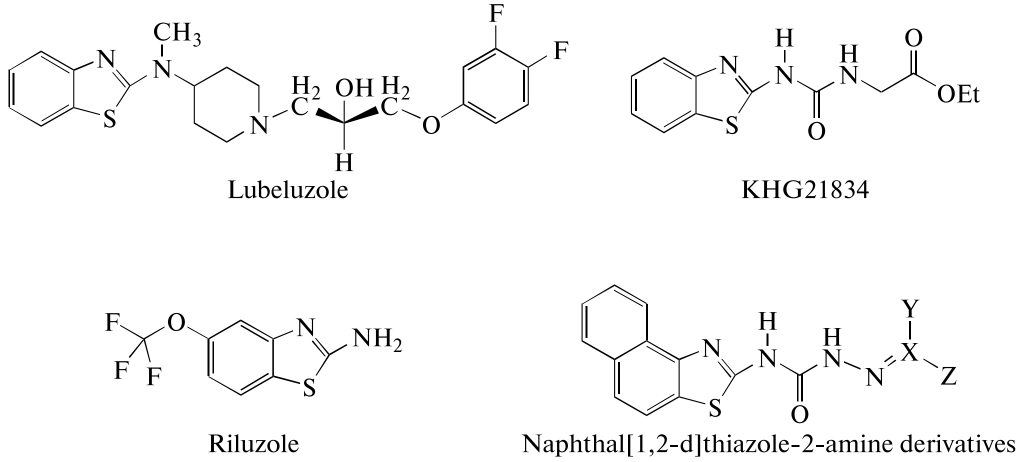


Lubeluzole KHG21834

Riluzole Naphthal[1,2-d]thiazole-2-amine derivatives

Fig. 1. Structure of some benzothiazoles based drugs.

ganotin(IV) antitumour agents occupies a significant place in cancer chemotherapy, as revealed from their remarkable therapeutic potential reflected in recent research reports. The binding ability of organotin(IV) compounds towards DNA depends on the coordination number and nature of the groups bonded to the central tin atom. The phosphate group of DNA sugar backbones usually acts as an anchoring site and the nitrogen of DNA base binding is extremely effective, this often resulting in the stabilization of the tin center as an octahedral species. Low doses of organotins can exhibit anti-tumoural activity [28–30] and have suggested an action mode via a gene-mediated pathway in the cancer cells, opening a new research sub-area on organotin(IV) compounds. The chemical and biochemical aspect of DNA inhibition, including biotechnological aspects of organotin(IV) cancer chemotherapy, has also been described. When organotin(IV) halides are dissolved in water, the pH of the solution decreases dramatically because they are converted slowly into organotin(IV) hydroxides and then to bis(triorganotin)oxides or diorganotin oxides. In contrast, di- and tri-organotin(IV) carboxylates do not suffer from this disadvantage and generally remain intact in water for long periods, i.e., days. Consequently, a large number of organotin(IV) carboxylates have been investigated for their antitumor potential. Among organotin(IV) carboxylates, triorganotin(IV) carboxylates are quite well known as bactericides and fungicides and subsequently several such derivatives were found to be potent when screened for their cytotoxicity [31–36].

Scope of Schiff base ligands. Parkinson's disease (PD) is the most common neurodegenerative movement disorder, characterized by a specific loss of dopaminergic neurons in the substantia nigra pars compacta and affecting the population above the age of 60 years [37]. Benzothiazoles are highly interesting molecules for drug development, because they are known to be useful for treating neurodegenerative disorders [38]. Among the most efficient compounds, lubeluzole has been shown experimentally to preserve neurological function and reduce infarct volume in animal models of focal brain ischemia [39], while other derivatives, such as KHG21834 were capable of protecting PC12 cells and cortical and mesencephalic neurons from amyloid b-induced degeneration [40].

In addition, the study of naphthalene derivatives has become of much interest in recent years on account of their antioxidant and antiparkinsonian activities. Many anticancer and anti-bacterial drugs are known to behave as versatile ligands [41] some of which exhibit increased anticancer activity when administered in the complex form with the metal ions [42, 43]. It has been suggested [44] that certain type of cancers are caused by viruses. The interaction between metal ion and their ligands with cancer associated viruses might represent an important route in designing [45] new anticancer therapies for tumors that becomes resistant to the conventional drugs. A recent methodology to design novel antiviral therapies is achieved by coordinating a metal ion from an important biomolecule, for instance a zinc finger protein with antiviral agent, usually containing sulphur functionalities with good complexing behavior. All these observations have attracted our attention to report antibacterial thiazole derived Schiff bases [46]. The structure of all these compounds is shown in Fig. 1.

Physico-chemical properties of Schiff base complexes of tin. Tin complexes exhibit a broad spectrum of biological activities and are studied in view of their structural diversity and their possible biological applications. In this regard, compounds which exhibit antimicrobial [47], anti-inflammatory [48], bactericidal

[49, 50], cardiovascular [51], biocidal [52], antitubercular [53], antifungal [54], and cytotoxic [55–58] biological activity have been described. Different complexes have been investigated in the search of treatments for diseases, such as trypanosomiasis [59] and jaundice [60]. 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. The 2,6-pyridine dicarboxylic acid reacts with diorganotin oxide or diorganotin diacetate, thereby generated structures with a pentagonal bipyramidal environment [61–68]. Interestingly, the presence of alkaline alkoxides favors the formation of complexes with octahedral geometry [69]. The reaction of 2,5-pyridinedicarboxylic acid with dimethyl, dibutyl or diphenyl tin oxides gives cyclotrimeric or polymeric seven-coordinated tin derivatives [70]. In addition, the 2,4/3,4 and 3,5-pyridine dicarboxylates react with organotinchlorides giving oligomeric structures with distorted trigonal bipyramidal geometries [71].

Some organotin complexes derived from picolinic acid possess octahedral or five-coordinated TBP structures, where the carboxylate acts as a monodentate ligand [72, 73]. It has been reported that seven-coordinated tin complexes exhibit higher activity towards some cancer cell lines when the 2,6-pyridine carboxylate moiety is part of the molecule [74]. Other studies have focused on the structural aspects of the hypervalent species of the Schiff-based organotin complexes [75, 76]. Binuclear and polynuclear transition metal complexes with macrocyclic ligands have been synthesized and show biological importance [77–83]. Synthesis, spectroscopic characterization, crystal structures, and in vitro cytotoxic activity of self-assembly of extended Schiff base amino acetate skeletons, 2-{[(2Z)-(3-hydroxy-1-methyl-2-butenylidene)]amino} phenylpropionate and 2-{[(E)-1-(2-hydroxyaryl)alkylidene]amino}phen-ylpropionate skeletons incorporating organotin(IV) moieties have been reported [84].

The crystal structures of complexes reveal that the complexes exist as polymeric chains in which the L-bridged Sn-atoms adopt a *trans*-R_3SnO_2 trigonal bipyramidal configuration with R groups in the equatorial positions and the axial locations occupied by carboxylate oxygen from the carboxylate ligand and the alcoholic or phenolic oxygen of the next carboxylate ligand in the chain. The carboxylate ligands coordinate in the zwitterion form with the alcoholic/phenolic proton moved to the nearby nitrogen atom. A polymeric zig-zag *cis*-bridged chain structure is observed without considering the weak Sn—O interaction; the Sn atom has a slightly distorted trigonal bipyramidal coordination geometry with the two O atoms of tridentate amino propionate ligand in axial positions. On the other hand, the structure of other complexes reveals a monomeric molecule in which the Sn atom has a distorted octahedral coordination geometry involving the tridentate carboxylate ligand, two *n*-butyl ligands occupying *trans*-positions and one water ligand. The in vitro cytotoxic activity of triphenyltin(IV) compounds against WIDR, M19 MEL, A498, IGROV, H226, MCF7 and EVSA-T human tumor cell lines are described in [85, 86].

The rigid, potentially tridentate ONS isatin derived Schiff bases ligands of S methyldithiocarbazate (Hisasme, A) and S-benzyldithiocarbazate (Hisasbz, B) exhibit variable coordination in complexes with transition metals and main group metals are shown in Fig. 2. The inflexibility of the ligand leads to a competition between the distal donor atoms (O and S) for the metal with the central N-donor being an effective pivot. This arrangement leads to breakage of the M–O coordinate bonds as the metal ion covalent radius increases as seen in the Zn(II) and Sn(IV) complexes of the monoanionic ligands. Elongation of the Co(II)–O and Ni(II)–O coordinate bonds is also apparent and it is clear that the ligands represent interesting examples where ‘pseudocoordination’ of the O-donor effectively blocks access by any other ligand to a coordination site leading to a low coordination number. These features may be useful in designing low coordination number complexes without the requirement of sterically demanding functionality attached to the ligand backbone [87].

Synthesis of the Sn(IV) complexes with Schiff bases derivatives have 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. A good crop of crystals enabled to use X-ray diffraction to determine their molecular structures, which exhibited pentagonal bipyramidal geometry where the butyl groups occupied the axial positions whereas the nitrogen and the oxygen atoms occupied the equatorial positions. An unusual reduction oxidation reaction took place by the reaction of 2-amino-4-nitrophenol, dibutyltin oxide and 2-pyridinecarboxaldehyde, which produced the corresponding amine and the amide tin(IV) derivatives. Structures of these complexes were established by X-ray crystallography and exhibited distorted trigonal bipyramidal geometry [88].

The coordination chemistry of tridentate amino acid-derived Schiff bases [89, 90] and related tridentate Schiff base [91–95] with diorganotin(IV) centres

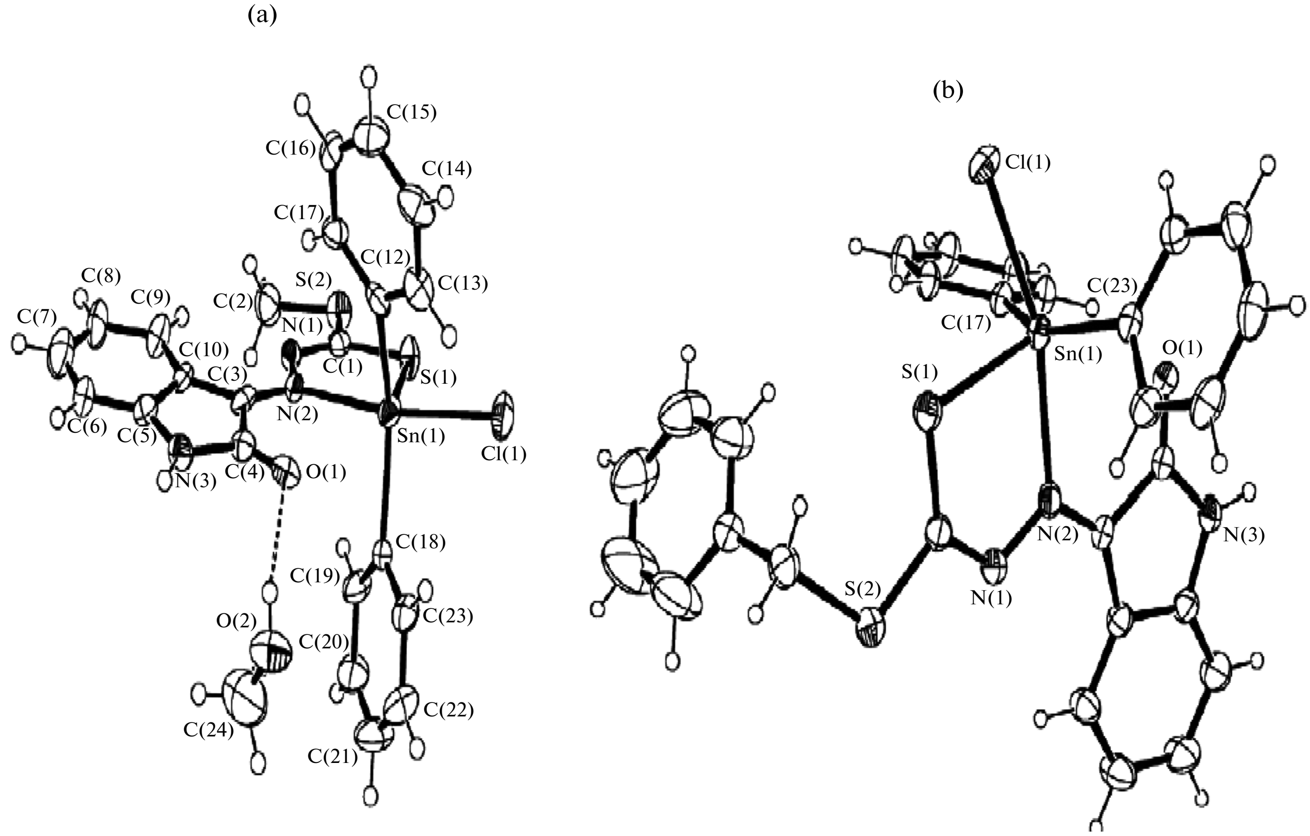
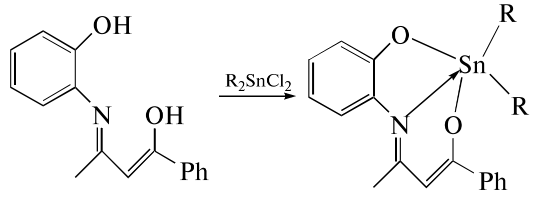


Fig. 2. Schiff based ligands of [Sn(Hisasme)Ph_2Cl] · CH_3OH (a) and [Sn(Hisasbz)Ph_2Cl] (b).

have been discussed widely. Much interest arises from their pharmacological activity, where several organotin(IV) complexes have shown antitumor and antiviral activity. Diorganotin(IV) complexes of the general formula $R_2Sn[Ph(O)C{-}CH{-}C(Me)N{-}C_6H_4(O)]$ (R = Ph, Me) 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 presence of triethylamine. Schematic reaction of tridentate chelated diorganotin(IV) complexes preparation is shown below:



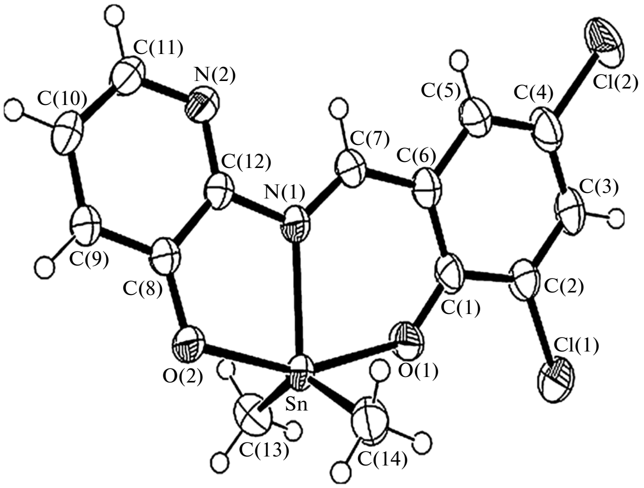


Fig. 3. The molecular structure of [Me_2Sn(2-OC_6H_2(3,5-Cl_2)$CHNC_5H_3NO$)].

New dimethyltin(IV) compounds of N-(3-hydroxypyridine-2-yl)-salicylideneimine derivatives have been synthesized and the crystal structure of [Me_2Sn(2-OC_6H_2(3,5-Cl_2)$CHNC_5H_3NO$)]Me_2SnL also been determined by X-ray single crystal diffraction analyses as shown in Fig. 3. It has found that the tin atoms are five-coordinated in a square pyramidal geometry. The monomeric [Me_2Sn(2-OC_6H_2(3,5-Cl_2)$CHNC_5H_3NO$)] units are linked into dimers by weak intermolecular interactions with Sn···O bonding. The in vitro antibacterial and antifungal tests of the synthesized dimethyltin complexes have been carried

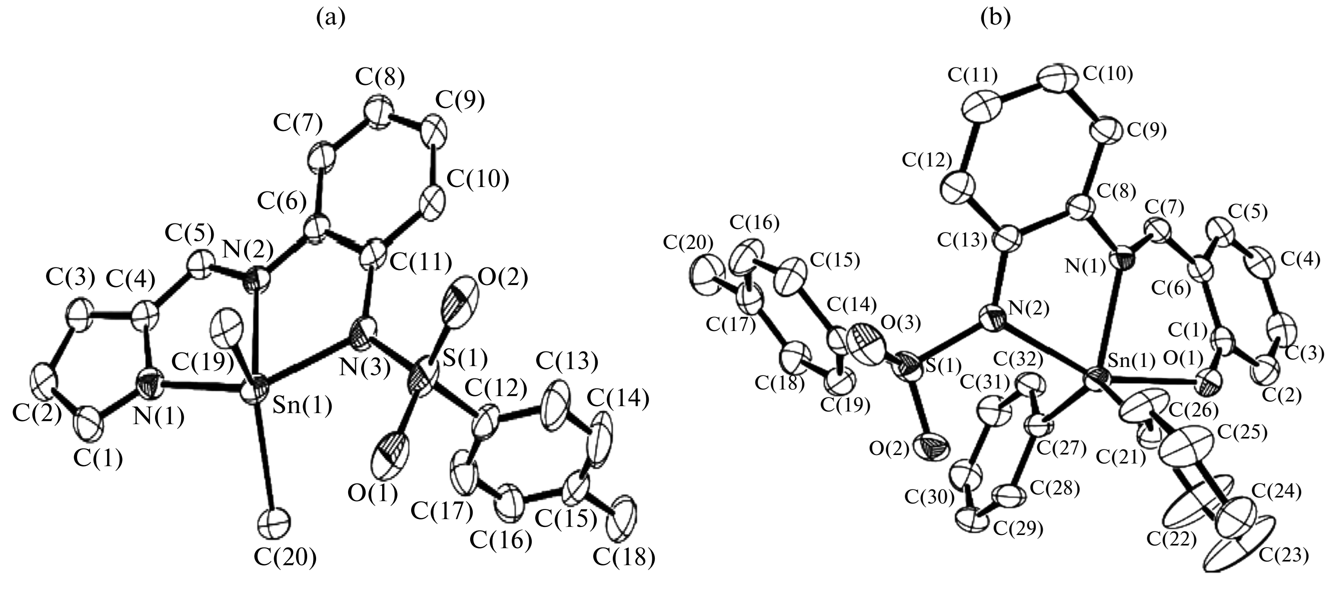


Fig. 4. Molecular structure of $[Sn(L^1)Me_2]$ (a) and $[Sn(L^2)Ph_2]$ (b).

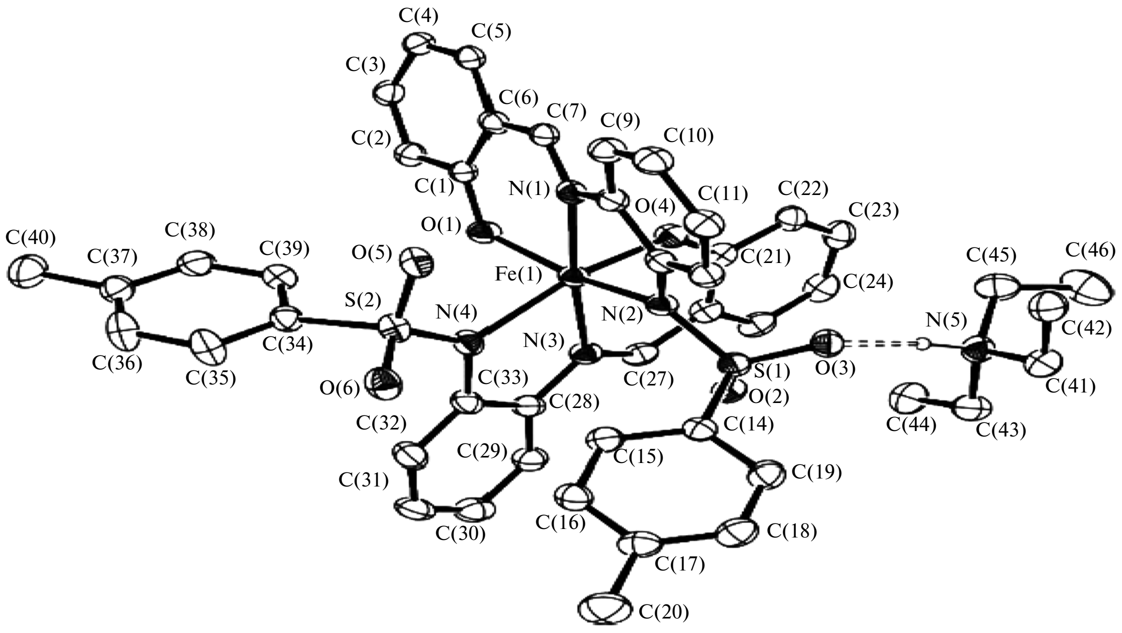


Fig. 5. Molecular structure of $[Et_3NH]Fe(L^2)]$.

out. $[Me_2Sn(2\text{-}OC_6H_2(3,5\text{-}Cl_2)CHNC_5H_3NO)]$ showed higher activity against *S. aureus* ATCC 25923 than the standard drug gentamisin. The results of antifungal screening indicated that complex showed more activity against all *Aspergillus* [96, 97].

Diorganotin(IV) complexes with terdentate Schiff bases *N*-[(2-pyrroyl)methylidene]-*N*'-tosylbenzene 1,2-diamine (L^1) and *N*-[(2-hydroxyphenyl)methylidene]-*N*'-tosylbenzene-1,2-diamine (L^2) are well known and have been synthesized in [98]. Molecular structure of these complexes shown in Fig. 4. However, the reaction between the precursor $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$ and the Schiff bases in the presence of triethylamine gave $[Et_3NH]FeL$. The crystal structures of the ligands and complexes have been studied by X-ray diffraction and is shown in Fig. 5. The structure of tin complexes shows the tin to be five-coordinate in a distorted square pyramidal environment with the dianionic ligand acting in a terdentate manner. In Fe complex iron atom is in a slightly distorted

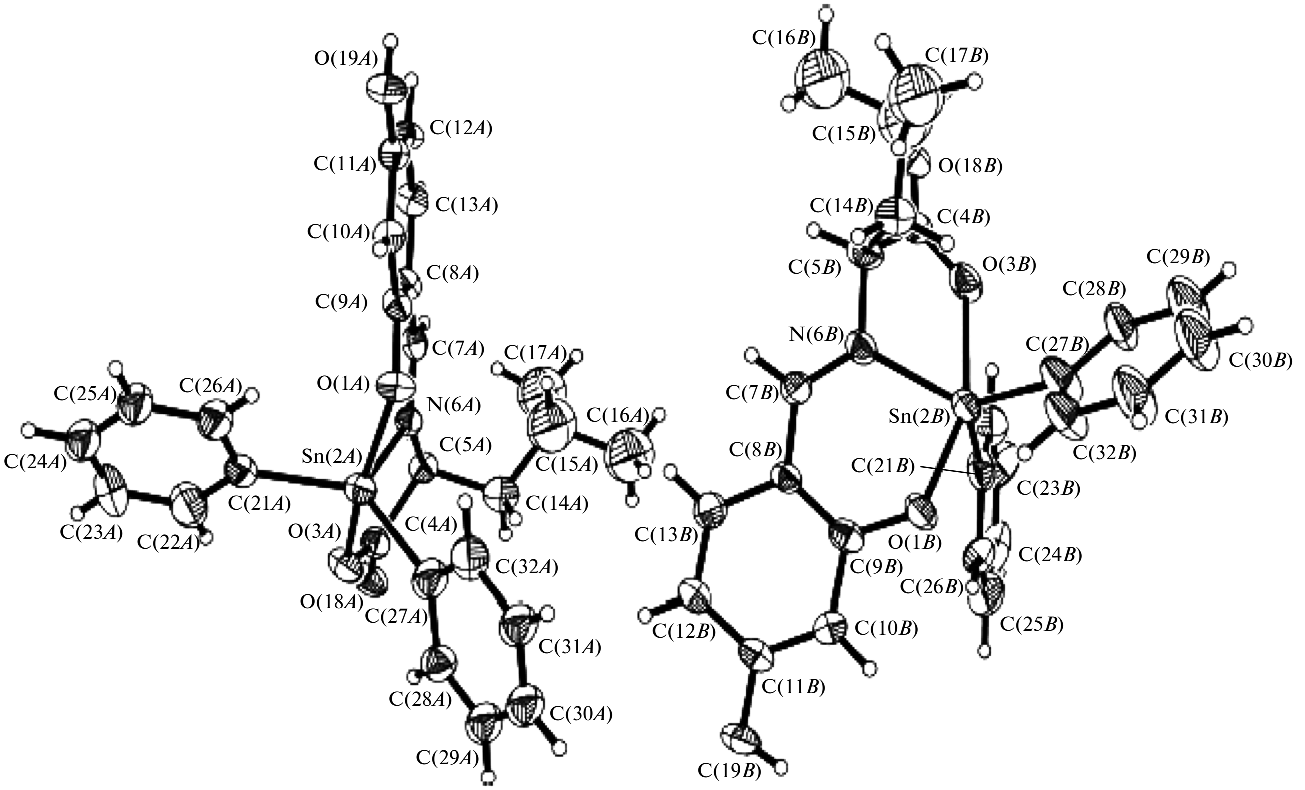
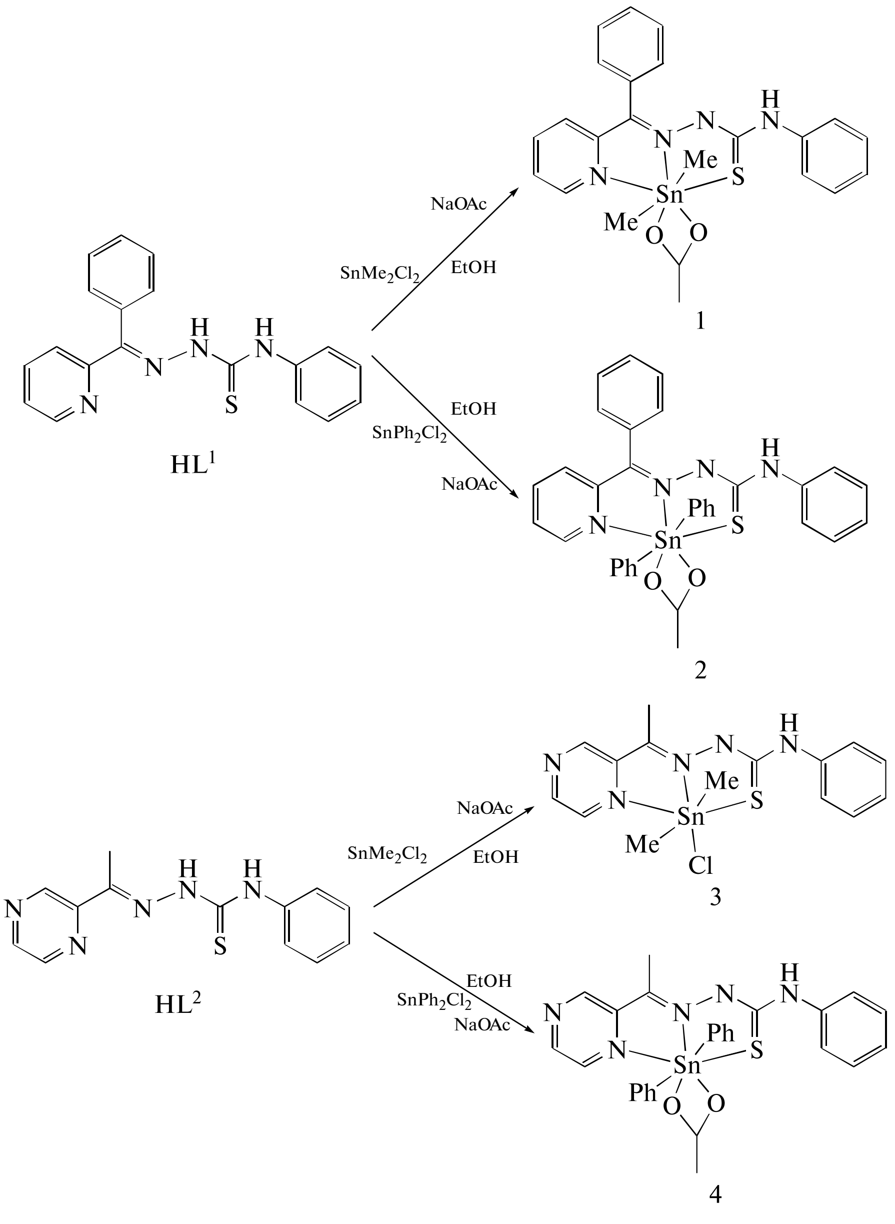


Fig. 6. Molecular structures of the penta-coordinated diorganotin(IV) compounds.

octahedral environment and is meridionally coordinated by two ligands [98–100].

The synthesis of twenty new penta-coordinated diorganotin(IV) compounds are reported in [101]. The molecular structure of one of them is given in Fig. 6. The chemical name and formulae of these compounds are as (5S)-6-Aza-2,2-di-*n*-butyl-11-hydroxy-5-isobutyl-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{21}H_{33}NO_4Sn$(1), (5S)-6-Aza-2,2-di-*n*-butyl-5-isobutyl-11-methoxy-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{22}H_{35}NO_4Sn$(2), (5S)-6-Aza-11-hydroxy-5-isobutyl-1,3-dioxa-2,2-diphenyl-2-stannabenzocyclononen-4-one, $C_{25}H_{25}NO_4Sn$(3), (5S)-6-Aza-5-isobutyl-11-methoxy-1,3-dioxa-2,2-diphenyl-2-stannabenzocyclononen-4-one, $C_{26}H_{27}NO_4Sn$(4), (5S)-6-Aza-2,2-di-*n*-butyl-5-[(20S)-but-20-yl]-11-hydroxy-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{21}H_{33}NO_4Sn$(5), (5S)-6-Aza-2,2-di-*n*-butyl-5-[(20S)-but-20-yl]-11-methoxy-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{22}H_{35}NO_4Sn$(6), (5S)-6-Aza-5-[(20S)-but-20-yl]-11-hydroxy-1,3-dioxa-2,2-diphenyl-2-stannabenzcyclononen-4-one, $C_{25}H_{25}NO_4Sn$(7), (5S)-6-Aza-5-[(20S)-but-20-yl]-11-methoxy-1,3-dioxa-2,2-diphenyl-2-stannabenzocyclononen-4-one, $C_{26}H_{27}NO_4Sn$(8), (5S)-6-Aza-2,2-di-*n*-butyl-5-(2-methylsulfanylethyl)-11-hydroxy-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{20}H_{31}NO_4SSn$(9), (5S)-6-Aza-2,2-di-*n*-butyl-5-(2-methylsulfanylethyl)-11-methoxy-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{21}H_{33}NO_4SSn$(10), (5S)-6-Aza-5-(2-methylsulfanylethyl)-11-hydroxy-1,3-dioxa-2,2-diphenyl-2-stannabenzocyclononen-4-one, $C_{24}H_{23}NO_4SSn$(11), (5S)-6-Aza-5-(2-methylsulfanylethyl)-11-methoxy-1,3-dioxa-2,2-diphenyl-2-stannabenzocyclononen-4-one, $C_{25}H_{25}NO_4SSn$(12), (5S)-6-Aza-5-benzyl-2,2-di-*n*-butyl-11-hydroxy-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{24}H_{31}NO_4Sn$(13), (5S)-6-Aza-5-benzyl-2,2-di-*n*-butyl-11-methoxy-1,3-dioxa-2-stannabenzocyclononen-4-one, $C_{25}H_{33}NO_4S$(14), (5S)-6-Aza-5-benzyl-11-hydroxy-1,3-dioxa-2,2-diphenyl-2-stannabenzocyclononen-4-one, $C_{28}H_{23}NO_4Sn$(15), (5S)-6-Aza-5-benzyl-11-methoxy-1,3-dioxa-2,2-diphenyl-2-stannabenzocyclononen-4-one, $C_{29}H_{25}NO_4Sn$(16), (5S)-6-Aza-2,2-di-*n*-butyl-11-hydroxy-1,3-dioxa-5-phenyl-2-stannabenzocyclononen-4-one $C_{23}H_{29}NO_4Sn$(17), (5S)-6-Aza-2,2-di-*n*-butyl-11-methoxy-1,3-dioxa-5-phenyl-2-stannabenzocyclononen-4-one, $C_{24}H_{31}NO_4Sn$(18), (5S)-6-Aza-11-hydroxy-1,3-dioxa-2,2,5-triphenyl-2-stannabenzocyclononen-4-one, $C_{27}H_{21}NO_4Sn$(19) and (5S)-6-Aza-11-methoxy-1,3-dioxa-2,2,5-triphenyl-2-stannabenzocyclononen-4-one $C_{28}H_{23}NO_4Sn$(20). These compounds have been prepared by the reactions of α-amino acids (isoleucine, leucine, methionine, phenylalanine and aminophenylacetic acid), 2,4-dihydroxybenzaldehyde, 2-hydroxy-4 methoxy benzaldehyde and either di-(*n*-butyl)tin(IV) oxide or diphenyltin(IV) oxide. They also reported that organotin compounds have high antineoplastic activity. All compounds show a high antineoplastic activity and these compounds were also tested in tumoral cell lines, HeLa, HCT-15 and MCF-7, in order to evaluate the antiproliferative activity and to obtain the medial inhibitory concentrations (IC_{50}) values. Selectivity was observed in the activities of some compounds over particular cell lines, which is very important for the future medicinal applications in order to avoid the side effects.

The structure of diorganotin(IV) complexes of N(4)-phenylthiosemicarbazones derived from 2-benzoylpyridine and 2-acetylpyrazine are given in Fig. 7 and reaction scheme for the synthesis of these complexes is shown below:



Biological studies of these complexes, carried out in vitro against selected bacteria and K562 leukaemia cells, respectively, have shown that different substituted groups attached at the thiosemicarbazone moieties and different diorganotin(IV) groups displayed distinctive differences in the biological properties. Further study is in progress and could be helpful in designing more potent antibacterial and antitumor agents for therapeutic use [102].

In [103], it was reported that potassium 2-{[(2Z)-(3-hydroxy-1-methyl-2-butenylidene)]amino}-4-methyl-pentanoate and potassium 2-{[(E)-1-(2-hydroxyphenyl)alkylidene]amino}-4-methyl-pentanoates underwent reactions with Ph_nSnCl_{4-n} ($n = 2$ and 3) to give the amino acetate functionalized Schiff base organotin(IV)

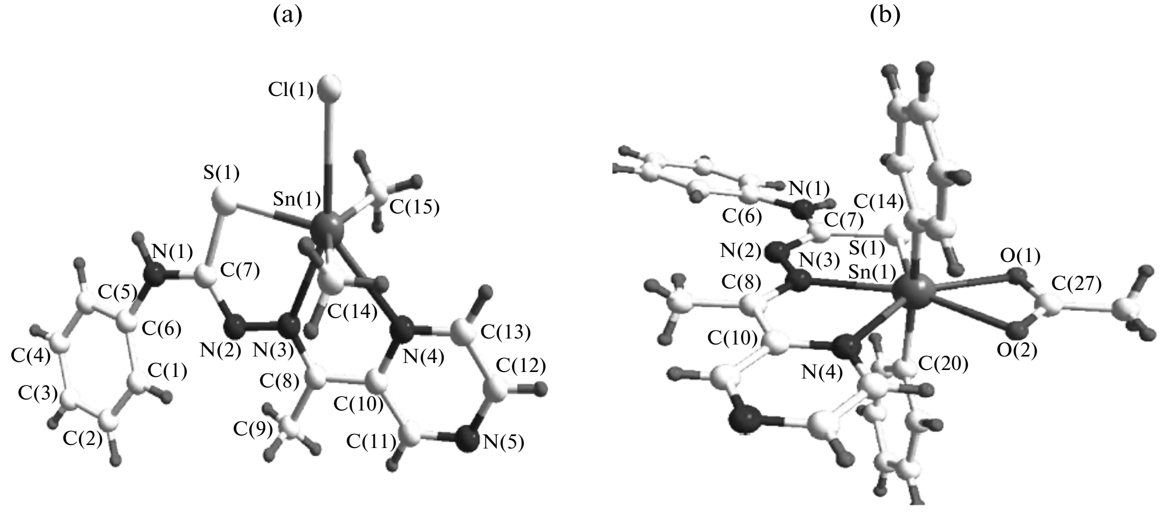
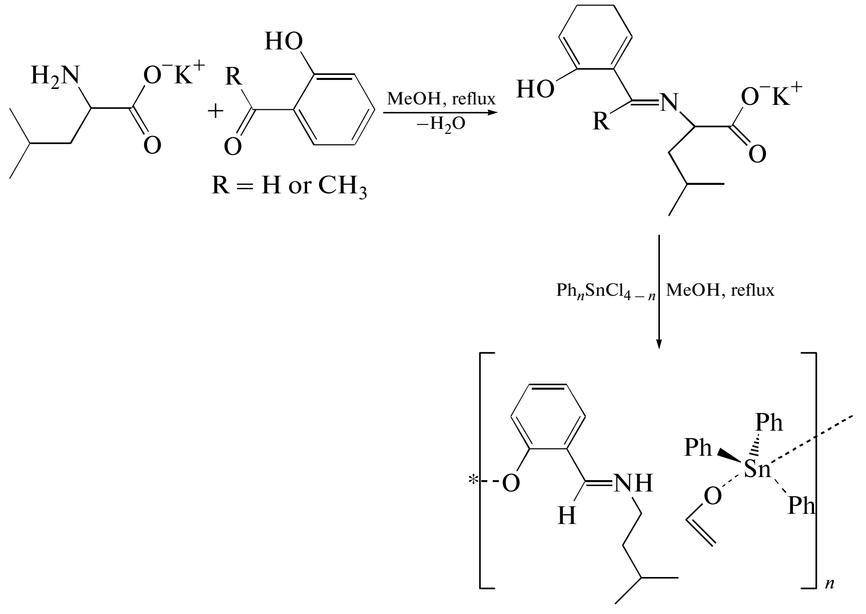


Fig. 7. Structures of tin complexes with N(4)-phenylthiosemicarbazones.

complexes. These complexes were tested against A498, EVSA-T, H226, IGROV, M19MEL, MCF7 and WIDR human tumor cell lines, the average ID_{50} values obtained were 55, 80 and 35 mg/mL for triphenyltin(IV) compounds. The most cytotoxic triphenyltin(IV) compound in the present report with an average ID_{50} value of around 35 mg/mL is found to be more cytotoxic for all studied cell lines than doxorubicin, cisplatin, 5-fluorouracil and etoposide. Schematic diagram of synthesis of triphenyltin(IV) complexes is shown below:



Diorganotin(IV) complex with *N*-(5-bromo-2-hydroxybenzylidene) benzoylhydrazone ligand, which coordinates to the metal centre in enolate form via the phenolic O, imino N and enolic O atoms, was synthesized in [104] and its structure is shown in Fig. 8. The central tin atom is in distorted trigonal bipyramidal geometry with two oxygen atoms of the ligand in axial positions, while the imino nitrogen atom of the ligand and two methyl groups on tin occupy the equatorial sites [105, 106].

All compounds of tin with 2-(9*H*-carbazol-9-yl) acetic acid were characterized by X-ray crystallography, confirming that complex $\{[n\text{-}Bu_2SnOL]_2O\}_2$ is tetra nuclear one with ladder framework, complex $[n\text{-}BuSn(O)OL]_6$ is a hexanuclear organotin(IV) complex with drum structure and complex $[n\text{-}Bu_3SnOL]_6$ is a macrocyclic with 24-membered stannoxane ring. Furthermore, these novel compounds have been synthesized in [107] and screened for their in vitro antitumor activity, using human hepatocellular carcinoma cell line (BEL-7402) and human hepatocellular liver carcinoma cell line ($HepG_2$). Complex $[n\text{-}BuSn(O)OL]_6$ displayed the best cytotoxicity and can be pointed out as a promising substrate to be subject of further investigations [107]. Four new organotin(IV) complexes of the type MeSnCl(Dact)], [BuSnCl(Dact)], [PhSnCl(Dact)], and $[Ph_2Sn(Dact)]$ were synthesized by the direct reaction of 2-hydroxyacetophenone-N(4)-cyclohexylthiosemicarbazone $[H_2Dact]$ and organotin(IV) chloride(s) in absolute methanol [108]. Salam et al. have also been published a paper on organotin(IV) complexes with pyruvic acid phenylhydrazine (HPAPD): synthesis, spectral characterization, and in vitro antibacterial activity. Four new triphenyltin(IV) complexes of composition Ph_3SnLH (LH = 2-/4-[(E)-2-(aryl)-1-diazenyl] benzoate) were synthesized [109]. The ^{119}Sn NMR spectroscopic data indicate tetrahedral coordination geometry in non-coordinating solvents. The crystal structures of three complexes, Ph_3SnL^1H, Ph_3SnL^3H, Ph_3SnL^4H, were determined. All these complexes display an essentially tetrahedral geometry with angles ranging from 93.50° to 124.5° and ^{119}Sn Mössbauer spectral data support this assignment [110].

In [111], electron-deficient tin(IV) tetraphenylporphyrin perchlorate, $[Sn^{IV}(TPP)(ClO_4)_2]$, was synthesized and used as a highly efficient catalyst for chemical fixation of carbon dioxide. The bifunctional catalytic system $[Sn(TPP)(ClO_4)_2]$–tetrabutylphosphonium bromide (TBPB) was applied for preparation of cyclic carbonates from epoxides and carbon dioxide. The effect of reaction parameters was also investigated [111]. They gave a conclusive remarks on this work that the catalytic activity of $[Sn(TPP)(ClO_4)_2]$ complex for synthesis of cyclic carbonate from epoxides and carbon dioxide was investigated. The nature of co-catalysts and temperature influenced the catalytic activity. The $[Sn(TPP)(ClO_4)_2]$–TBPB catalytic system was found to be more active than the others in DMF at 50°C. The reaction rates for linear epoxides were higher than that of cyclic epoxides with this catalytic system. The yield of cyclic carbonate is closely linked to the nature of the axial ligand and co-catalyst/catalyst molar ratio. The triorganotin(IV) Schiff-base complexes have been synthesized and characterized in [112]. All these complexes were found to be monomeric, colored viscous liquids and are soluble in polar solvents (methanol, ethanol, DMSO, and DMF). On the basis of ^{119}Sn NMR observations, a five coordination geometry around tin(IV) atom in these complexes is proposed tentatively. Five new chlorodiorganotin(IV) complexes derived from dithiocarbamate ligands have been prepared and structurally characterized in [113]. The complexes **I**–**V** with the general formula $\{(Ph_2SnCl)Dtc\}$ ($Dtc = R^1R^2(NCS)_2$; R^1 = Bn, R^2 = 9-anthrylmethyl (**I**); R^1 = Bn, R^2 = 9-phenanthrylmethyl (**II**); R^1 = Bn, R^2 = 1-pyrenylmethyl (**III**); R^1 = 1-naphthylmethyl, R^2 = 1-pyrenylmethyl (**IV**); $R^1 = R^2$ = 1-pyrenylmethyl (**V**)) have been obtained from Ph_2SnCl_2 and the sodium dithiocarbamate salts of benzyl(9-anthrylmethyl)amine, benzyl(9-phenanthrylmethyl) amine, benzyl(1-pyrenylmethyl)amine, 1-naphthylmethyl(1-pyrenylmethyl)amine, and di(1-pyrenylmethyl)amine.

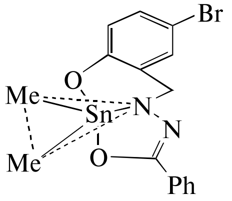


Fig. 8. Proposed structure of penta-coordinated dimethylorganotin(IV) complexes.

Two new diorganotin(IV) complexes have been synthesized from the reaction of diorganotin(IV) dichlorides with the Schiff base 3-(3-hydroxypyridin-2-ylamino)-1-phenylbut-2-en-1-one in [114]. On the basis of spectral and structural investigations, the Schiff base exists in the keto-amine form in both solution and the solid phase, and is coordinated to tin as dianionic tridentate via the imine nitrogen and phenolic and enolic oxygen atoms. On the basis of ^{119}Sn NMR data, the coordination number of tin is retained as five in solution. The synthesized organotin complexes are specialized in inhibiting both Gram-positive (*B. subtilis* and *S. aureus*) and Gram-negative (*E. coli* and *P. aeruginosa*) bacterial species, and the diphenyl complex exhibits a greater inhibitory effect. In view of the fact that diphenyltin(IV) derivatives are often less toxic than other diorganotin(IV) derivatives, it is suggested that the new diphenyltin(IV) complex **I** may be good candidate for anticancer studies. Homobimetallic carboxylates with general formulae $(R_3Sn)_2L$ (where R = Me, *n*-Bu, Ph; L = acetylene dicarboxylate dianion) have been synthesized by refluxing disodium salt of acetylene dicarboxylic acid with triorganotin chlorides in 1 : 2 (L : M) molar ratio in methanol under reflux in [115]. The unhydrated $[K(\mu_3\text{-}S,O\text{-}HTBA)]_n$ and corresponding hydrate $[K(\mu_2\text{-}S,O\text{-}HTBA)(\mu_2\text{-}S,O\text{-}H_2TBA)(\mu\text{-}H_2O)]_n$ have been isolated from slow evaporation of the filtrate derived from the reaction in water between H_2TBA (H_2TBA = terephthaloylbisanaline) and equimolar potassium hydroxide, depending on the absence or presence of methanol. Hydrogen bond patterns in hydrated complex: (a) formation of the bilayer by means of N–H–O hydrogen bonds and (b) water molecules join the bilayers into pairs of O–H–O hydrogen bonds. The crystal structures show that coordination occurs through the S and O donors. The potassium have distorted tetragonal bipyramidal and distorted cubic coordination environments in unhydrated and distorted square antiprism coordination environment in hydrated complex. Thermal analysis shows that the unhydrated is more stable than the corresponding hydrate [116].

A new series of tin(IV) complexes of general formulae $[Sn(L\text{-}1)(Opr^i)_2]$, $[Sn(HL\text{-}1)_2(Opr^i)_2]$, $[Sn(L\text{-}2)(Opr^i)_2]$, $[Sn(HL\text{-}2)_2(Opr^i)_2]$ (L is dianion of Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde with glycine (L-1) and β-alanine (L-2); Opr^i = isopropoxide) was synthesized by reaction of tin(IV) tetraisopropoxide with the ligands, in appropriate stoichiometric ratios (1 : 1 and 1 : 2). This would result in the replacement of the isopropoxide group from the tin(IV) tetraisopropoxide and hydrogen(s) from ligand with the azeotropical removal of isopropanol [116]. Recently, six new tin complexes of the formulae $[(Ph_3Sn)_2(PhSn)_{10}(Sn)_2(\mu_2\text{-}O)_8(\mu_3\text{-}O)_{18}(C_7HCl_3O_3)_2]$, $\{[(n\text{-}Bu)_3Sn]_2(C_7HCl_3O_3)\}_n$, $[(Me_3Sn)_2(C_7HCl_3O_3)]_n$, $[(Ph_2Sn)(C_7HCl_3O_3)_2]$, $[(n\text{-}Bu)_2Sn(C_7HCl_3O_3)_2]$, and $[(Me_2Sn)_4(C_7HCl_3O_3)_2(\mu_3\text{-}O)_2(CH_3O)_2]$ have been obtained from 3,5,6-trichlorosalicylic acid and an organotin chloride or organotin oxide [117]. All the complexes were characterized by elemental analysis, FT-IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy. The structural analyses reveal that complex $[(Ph_3Sn)_2(PhSn)_{10}(Sn)_2(\mu_2\text{-}O)_8(\mu_3\text{-}O)_{18}(C_7HCl_3O_3)_2]$ has a novel cage structure, which contains two triphenyltin nuclei, 10 monophenyltin nuclei and two inorganic tin nuclei; complex $[(Me_3Sn)_2(C_7HCl_3O_3)]_n$ has an infinite chain structure and complex $[(Me_2Sn)_4(C_7HCl_3O_3)_2(\mu_3\text{-}O)_2(CH_3O)_2]$ displays a typical ladder structure [118]. New bis-*o*-benzosemiquinonato tin(IV) complexes $(3,6\text{-}SQ)_2SnCl_2$, $(3,6\text{-}SQ)_2SnBr_2$, and $(3,6\text{-}SQ)_2SnPh_2$ (3,6-SQ is radical-anion 3,6-di-*tert*-butyl-*o*-benzosemiquinone) were synthesized by different methods in [119]. The reaction of tin(IV) catecholates $(3,6\text{-}Cat)SnX_2 \cdot 2THF$ (X = Cl, Br) with nitrogen(IV) oxide leads to EPR-active six-coordinated mono-*o*-benzosemiquinonato complexes of $(3,6\text{-}SQ)SnX_2(NO_2) \cdot THF$ type which undergo symmetrization to the corresponding diradical bis-*o*-benzosemiquinonato species $(3,6\text{-}SQ)_2SnX_2$. Diphenyltin(IV) catecholate $(3,6\text{-}Cat)SnPh_2 \cdot THF$ reacts with Br_2, I_2 and NO_2 to give five-coordinated species $(3,6\text{-}SQ)SnPh_2X$ (X = Br, I, NO_2) which transform to bis-(*o*-benzosemiquinonato)diphenyltin(IV) $(3,6\text{-}SQ)_2SnPh_2$. The molecular structures of $(3,6\text{-}SQ)_2SnBr_2$ and $(3,6\text{-}SQ)_2SnPh_2$ were determined by X-ray analysis.

Electronic spectra. Electronic spectral data of the ligands and their metal complexes contain absorption reasons, band assignments and proposed geometry of the complexes. Ligands show strong peaks ~448, 380 and 259 nm. The two strong bands are attributed to the benzene π–π^* and imino π–π^* transitions. These bands are not significantly affected by the chelation, the third band in the spectra of the ligand is assigned to the n–π^* transition. In the metal complexes this band shifted to a longer wavelength with increasing intensity. This shift may be attributed to the donation of lone pairs of electron of nitrogen atoms of the ligands to the metal ions.

IR spectra. Practically all the ligands and metal complexes have been characterized in detail by recording their IR spectra. The free ligands show absorption bands in the range ~1650 cm^{-1} that characterize azomethine (C=N) group [104, 105]. The band due to the thiazole ring (–C=N) was absorbed in the range 1600–1610 cm^{-1}, and the vibrational characteristics of thiazole ring have been found at ~2600 cm^{-1}. The C–S–C group vibrations of thiazole ring in free ligands occur in the range ~705 cm^{-1}. The formation of the Schiff base *o*-vanillidene-2-aminobenzothiazole is noted from the absence of C=O and NH_2 peaks in the spectrum of the ligand [106]. The bands in the region 500–600 cm^{-1} were assigned to ν(Sn–O). Furthermore, there are two kinds of Sn–O–Sn vibrations in the respective spectra of complexes $\{[n\text{-}Bu_2SnOL]_2O\}_2$ and $[n\text{-}BuSn(O)OL]_6$, which is absolutely absent in complex $[n\text{-}Bu_3SnOL]_6$ (L = 2-(9H-carbazol-9-yl) acetic acid [107]. In the triorganotin(IV) derivatives two strong or medium absorptions are always observed in the 500–600 cm^{-1} region. They are due to ν_{as} and ν_s Sn–C stretching vibrations and are consistent with an essentially trigonal pyramidal arrangement of organic groups with a marked deviation from planarity. The appearance of a single Sn–C stretching band at ~550 cm^{-1} in the spectra of trimethyltin(IV) complexes has been observed. A single Sn–C stretching vibration has been also observed in the spectra of the diorganotin(IV) derivatives with a *trans*-octahedral configuration of two alkyl groups. In the spectrum of derivatives, two medium absorptions at 565 and 525 cm^{-1} were found. The bands at 550–560 cm^{-1} can be assigned to the Sn–O bond. The bands at 450–500 cm^{-1} can be assigned to the Sn–N bond. For tin compounds, the bands at 299–305 and 440–460 cm^{-1} can be assigned to the Sn–Cl and Sn–S bonds, respectively.

^1H 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) complexes show absence of signals due to N(2)H in ^1H 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. The ^{13}C NMR spectra also support the structures proposed for the Sn complexes. The signal due to the carbon atom attached to the azomethine nitrogen atom in the ligand appeared at δ 158.2 ppm.

However, in the spectra of the metal complexes, the signal appeared at the lower δ values. This considerable shift in the spectra of metal complexes indicates the coordination of nitrogen to the central metal atom in complexes. Furthermore, the shifting of the ^{13}C resonance, which is attached to the sulfur atom in the spectra of metal complexes compared to the free ligand indicates coordination through sulfur to the metal atom. The new signal due to the methyl group attached to the metal atom in the spectra of metal complexes was also recorded. The methine proton for Salen-Sn and Salen(*t*-Bu)Sn type complexes are located at δ 8.5–8.7 ppm as a single peak. This suggests that the two CH=N protons are equivalent, and further supports the idea of a monomeric solution state structure. It also suggests planarity of the ligand. The equivalence of the methane and *t*-Bu protons and the CH_3 protons of the Me-Ph group indicates a *trans* arrangement of the two alkyl groups on tin. The symmetrical arrangement of the ligand and *trans* arrangement of the alkyl groups on tin suggest an octahedral environment around the central tin atom. The NH_2 protons were located at 2.91 ppm. Coupling (^3J) of the methine proton to the tin atom was observed. The magnitude of the coupling constant was used to determine the tin species present in solution. For the dichloro compounds, a coupling constants of $^3J(^{119}Sn\text{-}/H)$ 37 and 39 Hz, respectively, were observed. This compares well to the value calculated for $SalenSnCl_2$, $^3J(^{119}Sn\text{-}/H)$ 36 Hz. For the alkyl chloro Sn derivatives coupling constants of $^3J(^{119}Sn\text{-}/H)$ 12.6 and 13.2 Hz, respectively, were calculated [120].

^{119}Sn NMR spectra. The most convenient technique used to study organotin(IV) derivatives in solution and in the solid state is ^{119}Sn NMR spectroscopy. The ^{119}Sn nucleus has a spin of 1/2 and a natural abundance of 8.7%; it is about 25.5 times more sensitive than ^{13}C, taking into account the isotopic abundance. The isotope ^{117}Sn is slightly less sensitive (natural abundance 7.7%) and has not been used much. Both of these nuclei have negative magnetogyric ratios, and consequently the nuclear Overhauser enhancements are negative. Some examples of the applications of this method are mentioned later in different sections. ^{119}Sn chemical shifts are influenced by variation in coordination number, bond angles, and nature of substituents at tin. ^{119}Sn NMR is strongly dependent on the coordination number of tin, and an increase in coordination number produces a large upfield shift. The ^{119}Sn 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 up field 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 signals 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 ^1H 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. ^{119}Sn NMR was carried out on ($\delta = -501$ ppm) and ($\delta = -450$ ppm) organotin compounds which have been synthesized in [120]. The chemical shifts are in the range for six-coordinate tin compounds. The values for tin complexes also compare well with other six-coordinate Salen-Sn complexes. These chemical shifts also show that substituents on the phenyl ring of the ligand have no significant effect on the shielding or deshielding of the tin nucleus. The Schiff bases H_2L^x, H_2L^y, and H_2L^z have been prepared from the reaction of 2-amino-4-chlorophenol with acetylacetone, benzoyl acetone, and dibenzoylmethane, respectively [121]. Organotin(IV) complexes $[SnPh_2(L^x)]$, $[SnPh_2(L^y)]$, $[SnPh_2(L^z)]$, and $[SnMe_2(L^z)]$ have been synthesized from the reaction of $SnPh_2Cl_2$ and $SnMe_2Cl_2$ with these Schiff bases. The synthesized complexes have been characterized by elemental analysis and FT-IR, ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. Spectroscopic data suggest the Schiff bases are completely deprotonated and coordinated tridentate to tin via imine nitrogen and phenolic and enolic oxygen atoms; the coordination number of tin is five. Thermal decomposition of the complexes has been studied by thermogravimetric.

^{119}Sn Mössbauer spectra. ^{119}Sn Mössbauer data can usually give information on the more or less covalent nature of the bonds formed by tin with different atoms through determination of the isomer shift values (δ) and also an insight into the probable structure of the complexes, both in the solid state or in frozen solution, by the determination of experimental nuclear quadrupole splittings $|\Delta_{exp}|$. In all the cases, the experimental Mössbauer spectra show a single resonant doublet with full width at half height broader than that of the $Ba^{119}SnO_3$ source (~1 mm s^{-1}) with τ_{av} ~ 90 mm s^{-1}, which is consistent with the occurrence of only one absorbing species. The experimental Mössbauer parameters with calculated Δ according to the point-charge model formalism applied to the idealized tetrahedral structure. The difference between experimental and calculated values does not exceed the limit of tolerance of the method (±0.4 mm s^{-1}), and thus the experimental $|\Delta_{exp}|$ data can be explained satisfactorily by assuming a slightly distorted tetrahedral geometry [110]. The large quadrupole splittings obtained for $(C_4H_9)_2Sn(Pic)_2$ and $(H_2C{=}CH)_2Sn(Pic)_2$ indicate a *trans* arrangement of hydrocarbon groups in these compounds, and the relatively low value for $(C_6H_5)_2Sn(Pic)_2$ reveals a *cis* configuration.

The ^{119}Sn Mössbauer data for the tin(II) compounds prepared, along with previously published data on related heterocyclic tin(II) compounds. All compounds exhibit isomer shift values greater than that of β-tin, evidence generally taken as confirmation of the presence of tin(II). Tin(II) derivatives derived from mercaptoethanol and ethanedithiol exhibit Mössbauer resonances at room temperature, evidence generally considered to indicate strong polymeric lattices which contribute to large recoil-free fraction. The observation of ambient-temperature ^{119}Sn Mössbauer spectra for certain molecular solids does not affect our conclusion which is based upon close analogies with other associated tin(II) solids.

X-ray crystallography. Spectroscopic data and X-ray analysis have shown Salen-Sn (Salen = 2,2'-ethylene-bis(nitrilomethylidene)diphenol) complexes have octahedral (Salen-SnR_2), square pyramidal, and tetrahedral (Salen-Sn) geometries. In each case, the ligand occupies the equatorial coordination sites around the central tin atom. For the new Sn-Salen complexes presented here, the structures consist of a central six coordinate tin atom in a distorted O_h geometry. Chlorine has been passed to the complexes then the Salen(*t*-Bu) ligand occupies the four equatorial positions with the chlorine atoms in the axial positions. The tridentate phensal(*t*-Bu) ligand (phensal(*t*-Bu) = 3,5-di-*tert*-butylsalicylidene(1-aminophenylene-2-amine), occupies three of the equatorial sites. The fourth is occupied by the *n*-butyl group and the axial positions are occupied by chlorine atoms. The distorted octahedral geometry around the tin atom is a result of the strain imposed by the tetradentate ligand and from the constraints imposed by the six membered ring Sn—N—C—C—C—O. This is reflected in the equatorial plane for the large O(1)SnO(2) angle (103.23°) and (101.34°), respectively, and the correspondingly more acute N(1)SnN(2) angle (77.61° and 77.56°, respectively). The distorted geometry can also be seen in the deviation from 180° of the angles O(1)SnN(2) and O(2)SnN(2) (166.35° and 167.10°, 168.39°, and 167.71°, respectively). The distorted octahedral geometry is not reflected in the axial plane. The ClSnCl bond angle for tin complexes is close to the ideal value of 180°. With the slightly more flexible tridentate phensal(*t*-Bu) ligand, the ClSnCl angle of 165° in one tin complex is less than the idealized 180°. However, the geometry around the tin atom is not as distorted as reported for other six-coordinate organotin tetradentate ligand complexes. The bite angles O(1)SnN(1) and O(2)SnN(2) are similar for all the complexes (approximately 90°), but larger than those reported for other six coordinate tin Schiff base compounds. For example, the bite angles for *n*-Bu_2SnVanophen (Vanophen-*N*,*N*'-1,2-phenylene-bis(3-methoxysalicylideneimine)) are 81° and 79°, respectively. The Sn—O bond lengths for all the tin complexes are similar to other tin compounds, a typical Sn—O bond distance in the SnO_4N_2 system being around 202 pm. The Sn—N distances for all the complexes ~217 pm are much shorter than those observed in Sn(IV) systems with Sn ← N donor acceptor bonds ~237 pm. The Sn—N bond lengths for chlorine tin complexes are significantly larger than the Sn—N bond lengths [120].

DFT calculation. Homobimetallic carboxylates with general formulae $(R_3Sn)_2L$ (R = Me, *n*-Bu, Ph; L = acetylene dicarboxylate dianion) have been synthesized by refluxing disodium salt of acetylene dicarboxylic acid with triorganotin chlorides in 1 : 2 (L : M) molar ratio in methanol under reflux [99]. DFT calculations have been performed for structural elucidation and results were compared with semi-empirical data. FT-IR data indicate bidentate chelation of the ligand with tin, and the complexes exhibit five-coordinate geometry in the solid state. Such coordination behavior is also supported by DFT and semi-empirical studies. NMR data confirm four-coordinate geometry in solution.

Biological aspects. Anti-tubercular activity [122] of *p*-acetamidobenzaldehyde thiosemicarbazone in 1946 led to a number of papers concerning pharmacological use Schiff bases of Sn of these compounds due to the wide spectrum of their biological activity [123, 124]. 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. They are mainly used as anticonvulsants, antiprotozoal agents, radio protector, and radiopharmaceuticals. The in vitro antibacterial activities of the Schiff bases and their complexes have been evaluated against Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) and Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria. H_2L^x, H_2L^z, and all complexes exhibited good activities and have potential as drugs [114, 115]. There are also several reports on their anti-leukemic activity in mice [125] as well as on antimicrobial [126] and pesticide effects [127]. Schiff bases show remarkable activity on plant hormones such as the auxins on the root growth. Schiff bases [128] 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 [129, 130]. Thiazole-derived Schiff bases show analgesic and anti-inflammatory activity. Furan semicarbazone metal complexes exhibit significant anthelmintic and analgesic activities. Aryl azo Schiff bases exhibit anticancer activity. Schiff bases of indol-2-carboxaldehyde show inhibitor activities to KB cell lines. Diorganotin(IV) complexes and Schiff bases show antitumor activities in vitro, inhibiting interaction to KB HCT-8 and BEL-7402 tumor cell lines [131, 132].

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REFERENCES

1. Kumar, S., Dhar, D.N., and Saxena, P.N., *J. Sci. Ind. Res.*, 2009, p. 68.
2. Nguyen, T., Sutton, A.D., Brynda, M., et al., *Science,* 2005, vol. 4, p. 844.
3. Xue, L.W., Li, X.W., Zhao, G.Q., and Yang, W.C., *Russ. J. Coord. Chem.*, 2013, vol. 39, p. 872.
4. Noel, J.P., *Nature,* 2010, vol. 468, p. 380.
5. Szczylik, C., Skorski, T., Nicolaides, N.C., et al., *Science,* 1991, vol. 251, p. 562.
6. Balskus, E.P. and Walsh, C.T., *Science*, 2010, vol. 330, p. 1653.
7. Polli, D., Altoe, P., Weingart, O., et al., *Nature,* 2010, vol. 467, p. 440.
8. Hu, N.J., Iwata, S., Cameron, A.D., and Drew, D., *Nature*, 2011, vol. 478, p. 408.
9. Lavallo, V. and Grubbs, R.H., *Science,* 2009, vol. 326, p. 559.
10. Li, N., Lee, B., Liu, R.J., et al., *Science*, 2010, vol. 329, p. 959.
11. Xue, Y.X., Luo, Y.X., and Wu, P., *Science*, 2012, vol. 336, p. 241.
12. Rittle, J. and Green, M.T., *Science*, 2010, vol. 330, p. 933.
13. Ballina, M.R., Olofsson, P.S., Ochani, M., et al., *Science*, 2011, vol. 334, p. 98.
14. Cross, G.A.M., *Nature,* 2010, vol. 464, p. 689.
15. Kumar, U.A. and Chandra, S., *Transition Met. Chem.*, 1993, vol. 18, no. 3, p. 342.
16. Garg, A. and Tandon, J.P., *Transition Met. Chem.*, 1987, vol. 12, p. 212.
17. Fenton, D.E., *Pure Appl. Chem.*, 1986, vol. 58, no. 11, p. 1437.
18. Panda, A., Menon, S.C., Singh, H.B., et al., *Eur. J. Inorg. Chem.*, 2005, vol. 2005, no. 6, p. 1115.
19. Shanker, K., Ashok, M., Reddy, P.M., et al., *Int. J. Chem. Tech. Res.*, 2009, vol. 1, no. 3, p. 777.
20. Collinson, S.R. and Fenton, D.E., *Coord. Chem. Rev.*, 1996, vol. 148, p. 19.
21. Borisova, N.E., Reshetova, M.D., and Ustynyuk, Y.A., *Chem. Rev.*, 2007, vol. 107, p. 46.
22. Schwartsmann, G., Ratain, M.J., Cragg, G.M., et al., *J. Clin. Oncol.*, 2002, vol. 20, p. 47.
23. Neidle, S. and Thurston, D.E., *Nat. Rev. Cancer.*, 2005, vol. 5, p. 285.
24. *Tin Based Antitumor Drugs*, Narayanan, V.L., Nasr, M., Paul, K.D., and Gielen M., Eds., New York: Springer, 1990, p. 200.
25. *Metal-Based Antitumor Drugs*, Crowe, A.J., and Gielen M., Eds., vol. 1, London: Freund, 1988, p. 103.
26. *Metal Based Antitumor Drugs*, Gielen, M., Lelieveld, P., Vos, de D., et al., Eds., vol. 2, Tel Aviv: Freund, 1992, p. 29.
27. Roner, M., Carraher, C., Sabir, T., et al., *Polym. Mater. Sci. Eng.*, 2006, vol. 95, p. 525.
28. Carraher, C., Ashida, Y., and Battin, G., *Polym. Mater. Sci. Eng.,* 2006, vol. 95, p. 556.
29. Carraher, C., Sabir, T., Roner, M., et al., *J. Inorg. Organomet. Polym.,* 2006, vol. 16, p. 249.
30. Höti, N., Zhu, D.-E., Song, Z., et al., *J. Pharmacol. Exp. Ther.*, 2004, vol. 311, p. 22.
31. Chasapis, C.T., Hadjikakou, S.K., Garoufis, A., et al., *Bioinorg. Chem. Appl.,* 2004, vol. 2, p. 43.
32. Tabassum, S. and Pettinari, C., *J. Organomet. Chem.,* 2006, vol. 691, p. 1761.
33. Gielen, M., Tiekink E.R.T., in: *Metallotherapeutic Drags and Metal-Based Diagnostic Agents*, Gielen, M. and Tiekink, E.R.T., Eds., Chichester (England): Wiley, 2005, p. 421.
34. Roner, M., Carraher, C., Roehr, J., and Bassett, K., *J. Polym. Mater.,* 2006, vol. 23, p. 153.
35. Doucette, R., Siegmann-Louda, D., Carraher, C., and Cardoso, A., *Polym. Mater. Sci. Eng.,* 2004, vol. 91, p. 564.
36. Blower, P.J., *Annu. Rep. Prog. Chem. A*, 2004, vol. 100, p. 633.
37. Sriram, D., Yougeeswari, P., Myneedu, M.S., and Saraswat, V., *Bioinorg. Med. Chem. Lett.*, 2006, vol. 16, p. 2127.
38. Abou-Sleiman, P.M., Muqit, M.M.K., and Wood, N.W., *Nat. Rev. Neurosci.*, 2006, vol. 7, p. 207.
39. Ryck, M.D., Keersmakers, M.R., Duytschaever, H., et al., *J. Pharmacol. Exp. Ther.,* 1996, vol. 279, p. 748.
40. Choi, M.M., Kim, E.A., Hahn, H.G., et al., *Toxicology,* 2007, vol. 239, p. 156.
41. Araki, T., Muramatsu, Y., Tanaka, K., et al., *Neurosci. Lett.,* 2001, vol. 312, p. 50.
42. Crim, J.A., Buskrik, H.H., and Petering, H.G., *Cancer Res.*, 1967, vol. 27, p. 1109.
43. Scozzafava, A., Mastrolorenzo, A., and Surpan, C.T., *Exp. Opin. Ther. Patent*, 2001, vol. 11, p. 756.
44. Casini, A., Scozzafava, A., Mastrolorenzo, A., and Surpan, C.T., *Curr. Cancer Drug Target,* 2002, vol. 2, p. 55.
45. Heim, M.E., *Metal Complexes in Chemoterapy*, Weinheim: Verlag Chemie*,* 1993.
46. Hassan, M.U., Chohan, Z.H., and Surpan, C.T., *Main Group Met. Chem.,* 2002, vol. 25, p. 291.
47. Shockravi, A., Sadeghpour, M., and Olyaei, A., *Synth. Commun.,* 2010, vol. 40, p. 2531.
48. Aldridge, W.N., Street, B.W., and Noltes, J.G., *Chem. Biol. Interact.,* 1981, vol. 34, no. 2, p. 223.
49. Anderson, H.H., *Inorg. Chem.,* 1964, vol. 3, p. 912.

50. Armarego, W.L.F. and Chai, C.L.L., *Purification of Laboratory Chemicals*, London (United Kingdom): Butterworth–Heinemann, 2004, p. 6.
51. Attar, K., *Appl. Organomet. Chem.*, 1996, vol. 10, p. 317.
52. Bacchi, A., Carcelli, M., Pelegatti, P., et al., *J. Inorg. Biochem.*, 2005, vol. 99, p. 397.
53. Basu Baul, T.S., *Appl. Organomet. Chem.,* 2007, vol. 22, p. 195.
54. Bauch, T., Bocker, W., Mallek, U., et al., *Strahlenther. Onkol.*, 1999, vol. 175, p. 333.
55. McLaughlin, J.L., Rogers, L.L., and Anderson, J.E., *Drug Inform. J.*, 1998, vol. 32, p. 513.
56. Merk, O. and Speit, G., *Environ. Mol. Mutagen,* 1999, vol. 33, p. 167.
57. Meyer, B.N., Ferrigni, N.R., Putnam, J.E., et al., *Planta Med.,* 1982, vol. 45, p. 31.
58. Micheal, A.S, Thompson, C.G., and Abramovitz, M., *Science,* 1956, vol. 123, p. 464.
59. Miller, J.M., Luo, Y., and Wharf, I., *J. Organomet. Chem.*, 1997, vol. 542, p. 89.
60. Moellering, R., Graybill, J.R., McGowan, J.E., and Corey, L., *Am. J. Infect. Control*, 2007, vol. 35, p. 1.
61. Moller, P., *Clin. Pharmacol. Toxicol.*, 2005, vol. 96, no. 1, p. 1.
62. Jiménez, A.R., Gomez, E., and Hernandez, S., *J. Organomet. Chem.*, 2009, vol. 694, p. 2965.
63. Ng, S.W., Kumar Das, V.G., Holešek, J., et al., *Appl. Organomet. Chem.,* 1997, vol. 11, p. 39.
64. Kersten, P.J., Dagle S., Whittaker, J.W., et al., *J. Bacteriol.*, 1982, vol. 152, no. 3, p. 1154.
65. Jimenez, A.R., Gomez, E., and Hernandez, S., *J. Organomet. Chem.*, 2009, vol. 694, p. 2965.
66. Tsangaris, J.M. and Williams, D.R., *Appl. Organomet. Chem.*, 1992, vol. 6, p. 3.
67. Galbacs, G., Buzas, N., and Haraszti, T., *Talanta*, 2000, vol. 52, no. 6, p. 1061.
68. Hutin, M., Schultz, D., and Nitschke, J.R., *Chimia*, 2008, vol. 62, p. 198.
69. Fiedler, D., Leung, D.H., Bergman, R.G., and Raymond, K.N., *Acc. Chem. Res.*, 2005, vol. 38, p. 351.
70. Schmidbaur, H., Nowak, R., Huber, B., and Muller, G., *Organomet.*, 1987, vol. 6, p. 2266.
71. Cisneros, R.J., Zapf, J.W., and Dunlap, R.B., *J. Biol. Chem.,* 1993, vol. 268, p. 10102.
72. Keyomarsi, K. and Moran, R.G., *J. Biol. Chem.*, 1988, vol. 263, p. 14402.
73. Evans, R.M. and Hakala, M.T., *Cancer Res.*, 1981, vol. 41, p. 3288.
74. Kane, M.A., Roth, E., Raptis G., et al., *Cancer Res.,* 1987, vol. 47, p. 6444.
75. Wright, J.E., Dreyfuss, A., EI-Magharbel, I., et al., *Cancer Res.*, 1989, vol. 49, p. 2592.
76. Peters, G.J., Laurensse, E., Leyva, A., and Pinedo, H.M., *Eur. J. Cancer Clin. Oncol.*, 1987, vol. 23, p. 1869.
77. Mini, E., Trave, F., Rustum, Y.M., and Bertino, J.R., *Pharmacol. Ther.,* 1990, vol. 47, p. 1.
78. Borisova, N.E., Ustynyuk, Y.A., Reshetova, M.D., et al., *Russ. Chem. Bull.,* 2004, vol. 53, no. 2, p. 340.
79. Reddy, P.M., Prasad, A.V.S.S., Reddy, C.K., and Ravinder, V., *Transition Met. Chem.,* 2008, vol. 33, p. 251.
80. Reddy, P.M., Prasad, A.V.S.S., Rohini, R., and Ravinder, V., *Spectrochim. Acta*, *A*, 2008, vol. 70, p. 704.
81. Reddy, P.M., Ho, Y.P., Shanker, K., et al., *Eur. J. Med. Chem.*, 2009, vol. 44, p. 2621.
82. Shanker, K., Rohini, R., Ravinder, V., et al., *Spectrochim. Acta*, *A*, 2009, vol. 73, p. 205.
83. Shanker, K., Rohini, R., Reddy, P.M., and Ravinder, V., *Int. J. Chem. Tech. Res.*, 2009, vol. 1, p. 300.
84. Baul, T.S.B., Masharing, C., Ruisi, G., et al., *J. Orgnomet. Chem.*, 2007, vol. 692, p. 4849.
85. Basu Baul, T.S.B., Paul, A., Pellerito, L., et al., *Invest New Drugs*, 2010, vol. 28, p. 587.
86. Singh, P. and Bhardwaj, A., *J. Med. Chem.*, 2010, vol. 53, p. 3707.
87. Mairesse, N., Devleeschouwer, N., Leclercq, G., and Galand, P., *Biochem. Biophys. Res. Commun.,* 1980, vol. 97, p. 1251.
88. Ruiz, M.C.R. and Rivas, A.L., *Cell Death Differ.,* 1999, vol. 6, p. 271.
89. Ali, M.A., Mirza, A.H., Bakar, H.J.H.A., and Bernhardt P.V., *Polyhedron,* 2011, vol. 30, p. 556.
90. Jimenez, A.R., Gomez, E., and Hernandez, S., *J. Organomet. Chem.*, 2009, vol. 694, p. 2965.
91. Derebe, M.G., Raju, V.J.T., and Retta, N., *Bull. Chem. Soc. Ethiop.*, 2002, vol. 16, no. 1, p. 53.
92. Singh, K., Singh, D.P., Barwa, M.S., et al., *J. Enzyme Inhib. Med. Chem.,* 2006, vol. 21, p. 749.
93. Singh, K., Barwa, M.S., and Tyagi, P., *Eur. J. Med. Chem.,* 2006, vol. 41, p. 141.
94. Mishra, A.P. and Soni, M., *Metal-Based Drugs,* 2008, 847410.
95. Khan, M.I., Baloch, M.K., Ashfaq, M., and Obaidullah, *Appl. Organomet. Chem.*, 2006, vol. 20, p. 463.
96. Labib, L., Khalil, T.E., Iskander, M.F., and Refaat, L.S., *Polyhedron*, 1996, vol. 15, p. 349.
97. Khalil, T.E., Labib, L., Iskander, M.F., and Refaat, L.S., *Polyhedron,* 1994, vol. 13, p. 2569.
98. Ahmad, M.S., Hussain, M., Hanif, M., et al., *Molecules*, 2007, vol. 12, p. 2348.
99. Oztas, N.A., Ehirli, G.Y., Ancin, N., et al., *Spectrochim. Acta, A*, 2009, vol. 72, p. 929.
100. Labisbal, E., Guez, L.R., and Pedrares, A.S., *J. Inorg. Gen. Chem.*, 2005, vol. 631, p. 2107.
101. Obakhidze, N.K., Farfan, N., Romero, M., et al., *J. Organomet. Chem.*, 2010, vol. 695, p. 1189.
102. Li, M.X., Zhang, D., Zhang, L.Z., et al., *J. Organomet. Chem.*, 2011, vol. 696, p. 852.
103. Basu Baul, T.S.B., Basu, S., de Vos, D., and Linden, A., *Invest. New Drugs,* 2009, vol. 27, p. 419.
104. Samanta, B., Chakraborty, J., Dey, D.K., et al., *Struct. Chem.*, 2007, vol. 18, p. 287.
105. Garg, R., Saini, M.K., Fahmi, N., and Singh, R.V., *Indian J. Chem.*, *A*, 2005, vol. 44, p. 2433.
106. Fahmi, N. and Singh R.V., *Indian J. Chem.*, *A*, 1998, vol. 37, p. 1126.
107. Ruan, B., Tian, Y., Zhou, H., et al., *Inorg. Chim. Acta,* 2011, vol. 365, p. 302.

108. Affan, M.A., Salam M.A., Ahmad F.B., et al., *Inorg. Chim. Acta*, 2012, vol. 387, p. 219.
109. Salam, M.A., Affany M.A., Ahmad, A.B., et al., *J. Coord. Chem.*, 2012, vol. 65, p. 1999.
110. Tushar, S.B.B., Paul, A., Pellerito L., et al., *J. Inorg. Biochem.*, 2012, vol. 107, p. 119.
111. Ahmadi, F., Tangestaninejad, S., Moghadam, M., et al., *Polyhedron*, 2012, vol. 32, p. 68.
112. Dubey, R.K., Singh, A.P., and Dwivedi, N., *Phosphorus, Sulfur, and Silicon*, 2012, vol. 187, p. 1045.
113. Tlahuext-Aca, A.T., Medrano, F., Tlahuext, H., et al., *Polyhedron*, 2012, vol. 33, p. 223.
114. Sedaghat, T., Naseh, M., Khavasi, H.R., and Motamedi, H., *Polyhedron*, 2012, vol. 33, p. 435.
115. Hussainy, S., Ali S., Shahzadi, S., et al., *J. Coord. Chem.*, 2012, vol. 65, p. 278.
116. Kubicki, M., Owczarzak, A., Balas, V.I., and Hadjikakou, S.K., *J. Coord. Chem.*, 2012, vol. 65, p. 1107.
117. Aman, R. and Matela, G., *J. Chem.*, 2013, vol. 2013, ID 637290.
118. Wang, Q.F., Ma, C.L., He, G., et al., *Polyhedron*, 2013, vol. 49, p. 177.
119. Ilyakina, E.V., Poddel'sky, A.I., Piskunov, A.V., et al., *Inorg. Chim. Acta*, 2013, vol. 394, p. 282.
120. Yearwood, B., Parkin, S., and Atwood, D.A., *Inorg. Chim. Acta*, 2002, vol. 333 p. 124.
121. Tahereh, S., Marjan, M., and Hossein, M., *J. Coord. Chem.,* 2011, vol. 64, p. 3169.
122. Szorcsik, A., Nagy, L., Deak, A., et al., *J. Organomet. Chem.,* 2004, vol. 689, p. 2762.
123. Domagk, G., Behnisch, R., Mietzsch, F., and Schmidt, H., *Nature*, 1946, vol. 33, p. 315.
124. Beraldo, H., *Quimica Nova*, 2004, vol. 27, p. 461.
125. Beraldo, H. and Gambino, D., *Mini-Rev. Med. Chem.*, 2004, vol. 4, p. 159.
126. Pandeya, S.N. and Dimmock, J.R., *Pharmazie*, 1993, vol. 48, p. 659.
127. Singh, A., Dhakarey, R., and Saxena, G.C., *J. Indian Chem. Soc.*, 1996, vol. 73, p. 339.
128. Anderson, R.J., Cloudsdale, I.S., Lamoreaux, R.J., et al., US Patent 6110869, 2000.
129. Wang, Y., Yu, X., Lu B., et al., *Chem. Abstr.*, 2001, vol. 23, p. 257.
130. Latha, K.P., Vaidya, V.P., and Keshavayya., J.J., *Teach. Res. Chem.*, 2004, vol. 11, p. 39.
131. Phatak, P., Jolly, V.S., and Sharma, K.P., *Orient. J. Chem.*, 2000, vol. 16, p. 493.
132. Yin, D.D, Yan, L., and Shah, L., *Chin. J. Chem.*, 2001, vol. 19, p. 1136.